Electrocatalytic properties of transition metals towards reduction of chlorinated volatile organic compounds （Cl-VOCs）

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过渡金属电极对挥发性有机氯化物的电催化还原研究

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摘要

挥发性有机氯化物（Cl-VOCs）包括氯代甲烷（PCMs）、氯代乙烷（PCEs）、氯代乙烯三类物质，是环境中最常见的一类污染物。然而，由于其自身的毒性，部分物质甚至被推测为环境致癌物，致使它们中的一些物质被包括中国，美国环保署以及欧盟在内的国家和政府机构列为优先控制污染物，在饮用水中严加控制。因此，开展对此类物质的削减技术研究，寻求高效的污染控制技术，具有重要的科学技术意义。本研究在N,N-二甲基甲酰胺溶液中，考察了不同电极材料对挥发性有机氯化物的电催化脱氯活性，探讨了Cl-VOCs的电催化还原脱氯机理，并验证了电催化脱氯技术用于控制该类污染物的技术可行性。乙炔是电催化去除氯代乙烷类物质的主要中间产物，且去除乙烯气体中的乙炔杂质，是聚合物合成工业中一个非常重要的技术环节。在本研究的最后，首次提出并开发了一种新型的催化乙炔加氢技术——电催化乙炔加氢技术。

在N,N-二甲基甲酰胺溶液中，系统考察了Ag，Au，Pd，Pt，Cu，Fe，Ni，Pb，Zn和GC（玻碳电极）对氯代乙烷类物质的电化学还原脱氯活性，其中，GC电极由于其极弱的电催化特性，被选为衡量各金属电极催化效果的基准电极。研究发现各金属电极的催化活性主要取决于金属特性和氯代乙烷类物质的分子结构。Ag，Au和Cu电极表现出最强的催化活性。根据各催化金属电极对氯代乙烷类物质的催化能力，氯代乙烷类物质的脱氯活性顺序表现为：1,1-二氯乙烷 ＜1,1,1-三氯乙烷 ＜1,2-二氯乙烷< 六氯乙烷 ＜ 1,1,1,2-四氯乙烷 ＜1,1,2-三氯乙烷< 1,1,1,2-四氯乙烷。研究表明，氯代乙烷类物质的电子传递遵从同步离解电子传递理论（电子传递和C-Cl键的断裂同时发生），与电极的类型以及PCEs的分子结构无关；氯代乙烷类物质的电化学脱氯反应，其反应活化能与标准自由能的关系符合“Sticky DET”模型，在该模型中引入了离解产生的自由基与氯离子间的相互作用力。

基于对氯代乙烷类物质的循环伏安曲线分析，以及在GC和Ag电极上的1,1,1-三氯乙烷，1,1,1,2-四氯乙烷的电解实验结果表明，氯代乙烷类物质的分子结构决定了电化学还原脱氯机理。其中，偕-氯代乙烷类物质主要遵从顺序脱氯加氢机理，每一个还原步骤脱除一个氯离子，直至完全脱氯产物乙烷生成；邻-氯代乙烷类物质则遵从同时脱除两个氯原子的还原消除脱氯机理，该机理在每一个还原步骤中同时脱除两个氯离子，伴随有（氯）乙烯类产物的生成，其在更负的电位下可进一步还原去除。研究发现，质子供

体的存在与否对还原脱氯过程有着重要的影响。在疏质子条件下，对于偕-氯代乙烷类物质，除了顺序脱氯加氢反应机理外，脱除HCl机理（dehydrochlorination, base promoted α,β-elimination）和卡宾路径在整个还原过程起着非常重要的作用；当强质子供体（醋酸）加入后，顺序脱氯加氢则成为还原过程的主要反应机理。质子供体的存在与否对于邻-氯代乙烷类物质的同时脱除两个氯原子的还原消除脱氯机理影响甚微，其主要对生成的氯代乙烯类物质的后续还原产生影响。

本研究进一步考察了Cu电极对偕-氯代乙烷类物质以及氯代甲烷类物质的催化脱氯特性。研究发现，Cu电极表现出极其优良的电催化活性，与GC电极相比，可显著促使该两类氯代烷烃类物质的还原电位正移。质子供体（醋酸，水）的存在，可进一步活化Cu电极对此两类氯代烷烃类物质的催化脱氯活性，促使其还原电位显著正移，并对反应机理产生影响：进一步阻碍自我加氢反应（self-protonation）、卡宾路径等副反应的发生，促使顺序脱氯加氢成为主要的还原机理；而在疏质子条件下，则存在上述反应的竞争，尤其是卡宾路径，致使碳质量平衡严重降低。通过对顺序恒电位电解及单步恒电位电解的实验结果的比较表明，两种不同的电位施加方式从本质上来说得到了相同的电解产物。唯一比较显著的差异是，由于单步恒电位电解所施加的电位，可以还原电解过程中的所有中间产物，因此中间产物一旦形成可迅速得到去除，不利于中间产物的积累。而对于顺序恒电位电解，通过控制还原电位可以使反应停留在中间反应阶段，这在电化学合成工业上有着重要的意义。

最后，在N,N-二甲基甲酰胺溶液中，考察了不同贵金属和非贵金属电极对乙炔的电化学催化加氢反应。研究表明，乙炔的电化学还原行为与电极的特性以及体系中水的存在与否密切相关。其中Au，Ag，Pd三种金属电极表现出显著的电催化活性。在体系中加入水后，可显著提高各电极上乙炔还原峰的峰强度，并且促使峰电位正移。进一步的电解实验表明，电极材料及溶剂的条件决定了电解乙炔产物的分布。在疏质子条件下，在Cu和Ag电极上得到了较高的乙烯产率，分别为58.75,%，51.81%，但过程中伴随有大量的C4产物生成（大于35%，丁烷、丁烯等）。对于Pt电极的电解实验，其主要产物为C4物质，研究发现78.33%的乙炔转化生成了74.68% 的C4产物。在体系中加入水后，Cu和Ag电极上的乙烯选择产率分别提高到75%和68%以上，并且伴随有极其少量的C4产物生成，分别是Cu 3.14%，Ag 0.27%，可显著抑制自由基聚合反应。由于电解液放电，Pt电极则表现出低的乙炔转化率（34.14%）和高的C4产率（27.18%）的特点。需要指出的是，无论是在疏质子条件下还是加入水后，产物中乙烷的产量甚微，

乙炔的过度加氢反应在电化学乙炔加氢反应中可得到显著遏制。

总之，本研究表明，电化学还原脱氯技术作为一种新型的技术可成功用于挥发性有机氯化物的去除。研究揭示了 Cu 电极对氯代烷烃类物质极其优良的电催化脱氯活性，其催化活性甚至可以与 Ag 电极相比拟。其中，后者被认为是在有机溶剂中具有最强催化脱氯活性的金属催化剂，但 Cu 的价格要远低于 Ag，且来源丰富。此外，本研究首次提出并开发了电催化乙炔加氢技术，希望通过本研究为该技术的发展打开研究之门，并在聚合物合成工业上为乙炔的去除提供一种可供选择的新型技术。

关键词：脱氯； 挥发性有机氯化物； 电催化材料； 还原机理

Abstract

Chlorinated volatile organic compounds (Cl-VOCs), including polychloromethanes (PCMs), polychloroethanes (PCEs) and polychloroethylenes, are among the most ubiquitous pollutants in environment. Some of them have been listed as the priority pollutants by China, U.S.EPA and European Union, and are strictly controlled in drinking water. Therefore, searching for innovative, high efficient remediation technologies for the abatement of Cl-VOCs waste and for the removal of Cl-VOCs from contaminated water and soil sites are significantly important. In this work, electrochemical reductive cleavages of Cl-VOCs were carried out in dimethylformamide (DMF) + 0.1 M tetrapropylammonium tetrafluoroborate ($TPABF_4$) at different cathodic materials under different solvent conditions, to investigate the dechlorination mechanisms of Cl-VOCs, evaluate the electrocatalytic activities of different transition metal electrodes, and further examine the feasibility of this method on the abatement of Cl-VOCs. Finally, an innovative electrochemical hydrogenation technology on the removal of acetylene, which is the main electrolysis intermediate of polychloroethanes, was explored.

Electrochemical reduction of PCEs were investigated in DMF + 0.1 M $TPABF_4$ at Ag, Au, Pd, Pt, Cu, Fe, Ni, Pb, Zn and glassy carbon (GC), the last used as a reference system with negligible catalytic properties. Results indicate electrocatalytic activities of transition metals are strongly dependent on the nature of electrode and chemical structure of PCEs. In any case, Ag, Au and Cu behave the most remarkable catalytic effects toward the reductive cleavage of PCEs. Based on the positive shift values of catalytic electrodes with respect to GC for PCEs reduction, the electrochemical reactivity of all the investigated polychloroethanes follow the order: 1,1-DCA < 1,1,1-TCA < 1,2-DCA < HCA < 1,1,2,2-TeCA < 1,1,2-TCA < 1,1,1,2-TeCA. Electron transfer (ET) coefficients indicate that the first ET to PCEs undergoes concerted dissociative electron transfer (DET) mechanism, regardless of the nature of electrodes and chemical structure of PCEs, where the electron transfer and reductive cleavage of C-Cl bond take place simultaneously. The activation-driving force relationships of the

dechlorination reactions for all investigated PCEs are found to conform to "Sticky DET" model, in which a sizable interaction between the caged fragments is survived.

Based on the voltammetric investigations of PCEs and the electrolysis results of 1,1,1-trichloroethane (1,1,1-TCA) and 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) at GC and Ag electrode in different solvent conditions, respectively, the dechlorination mechanism is found strongly dependent on the structure of PCEs. Geminal PCEs undergo a sequential hydrodechlorination mechanism, in which one chlorine atom is lost with successive hydrogenation occurrence at one reduction step until completely dechlorination product ethane are formed. In contrast, vicinal PCEs follow reductive α,β-elimination mechanism by expelling two chlorine ions at one single step, leading to the corresponding (chloro-)olefin formation, which could be further reduced at more negative potentials. Reductions of PCEs are found very sensitive to the proton availability in the solvent. For geminal PCEs, regardless of the type of electrode, in dry aprotic DMF conditions, apart from sequential hydrodechlorination mechanism, dehydrochlorination (base promoted α,β-elimination) and carbene route play significant roles towards the dechlorination of PCEs process; whereas, sequential hydrodechlorination becomes the primary reduction mechanism in the presence of strong proton donor (acetic acid). In contrast, reductive α,β-elimination mechanism for vicinal PCEs couldn't be suppressed by the presence of proton donor, concomitant with (chloro-)olefin formation.

Electrocatalytic activity of Cu was investigated towards the reductive dechlorination of geminal PCEs and polychloromethanes. It shows that Cu exhibits an excellent catalytic activity for the reduction of these two types of compounds with evident positive shift of reduction potentials with respect to GC. Results indicate the addition of proton donor (HAc, H_2O) has significant effects on the reductive dechlorination process, which could activate the catalytic activity of Cu toward the abatement of C-Cl bond. Besides, the presence of proton donor may also affect the reduction mechanisms of these two types of chlorinated hydrocarbons by suppressing side reactions favoring the sequential hydrodechlorination route. Comparison of two different potential applied manners (sequential and single step potentiostatic electrolysis), indicate essentially the same electrolysis results are obtained toward the reductive cleavage of chlorinated aliphatic hydrocarbons, with the only significant difference that electrolysis intermediates are repulsive to accumulate in the case of single step electrolysis, since the potential applied locate at which all the intermediates are reducible. However, for the stepwise electrolysis, by choosing appropriate working conditions, it can keep the reaction retain at a determined stage, which are very significant in electrosynthesis industry.

Eventually, electrochemical hydrogenation of acetylene was carried out extensively at precious and non-precious electrodes in DMF + 0.1 M $TPABF_4$ in different solvent conditions. It shows the electrochemistry behaviors of acetylene are strongly dependent on the nature of electrode and water availability. Among them, Au, Ag and Pd display remarkable electrocatalytic activity toward the reduction of acetylene. Addition of water could enhance the peak current intensity of acetylene and promote the reduction peak shift to more positive direction. Electrolytic results of acetylene further indicate the product distributions depend on the cathodic materials and solvent conditions. In dry aprotic DMF solvent, high ethylene selectivity was obtained, namely 58.75% for Cu and 51.81% for Ag, whereas, more than 35% C4 hydrocarbons were obtained in the both cases. For Pt electrode, considerable C4 hydrocarbons were produced (74.68%) with 78.33% conversion of acetylene. In the presence of water, more than 75% and 68% ethylene were obtained at Cu and Ag electrode, respectively, concomitant with quite few C4 hydrocarbons formation (3.14% for Cu and 0.27% for Ag), indicating that radical coupling reaction could be effectively suppressed. However, low acetylene (34.14%) was converted at Pt electrode, concomitant with high yield of C4 hydrocarbons (27.18%) due to the discharge of water. It should be noted that trace of ethane were generated in all different solvent conditions, it appears the overhydrogenation of acetylene could be successfully inhibited by using this method.

In general, electrochemical reductive dechlorination technology as a promising approach has been successfully applied on the abatement of Cl-VOCs in this study. Cu is found to exhibit excellent electrocatalytic activities toward the reductive cleavage of C-Cl bond, sometimes it’s even comparable with Ag, the latter is believed to be the most remarkable catalytic electrode for dechlorination of chlorinated compounds in organic solvent, but with much cheaper price. This work provides a significant technical support for the abatement of Cl-VOCs and the electrosynthesis process of (chloro-) hydrocarbons. A novel technology for

acetylene removal has been proposed and explored in this work, we hope it can open a gate for the development of electrochemical acetylene hydrogenation technology through our research, and provide an alternative technology for acetylene removal in the polymer synthetic industry.

Keywords: dechlorination; chlorinated volatile organic compounds (Cl-VOCs); electrocatalytic materials; reduction mechanisms.

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Chapter 1 Introduction

Chlorinated volatile organic compounds (Cl-VOCs), including polychloromethanes (PCMs), polychloroethanes (PCEs) and polychloroethylenes, were introduced into environment media starting from the early of 20th century. They were widely applied in numerous industrial processes and products as useful solvents, such as metal degreasing, dry cleaning, pharmaceuticals, adhesives, refrigerants and so on, which played an essential role in the industrial development over the past several decades [1]. On the other hand, their widespread use make them become the most ubiquitous environment contaminants subsisted in the soils and any kind of fluvial mediums, such as groundwater, rivers, lakes [2,3]. For instance, there are thousands of contaminated sites polluted by chlorinated organic solvents throughout the United States [4]. According to the samples analysis from Beijing-Tianjin-Tangshan area, Yangtze River Delta area and Pearl River Delta area, chlorinated volatile organic compounds are found to be one of the most frequently detected pollutants in the underground water [5]. Among them, carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), perchloroethylene (PCE), trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), 1,2-dichloroethane (1,1-DCA) are the representative examples of this type of compounds and frequently found in contaminated groundwater [6,7]. In general, the inattention and inadequate to proper disposal methods of Cl-VOCs over the past decades result into the current widespread polluted situation. However, due to their toxicity, some of them are even indentified or suspected as human carcinogens, and persistence character in environment, the threat of Cl-VOCs to human being have forced to focus attention from the health authorities. Some of them thus have been listed as the priority controllable pollutants in China, U.S. Environment Protection Agency (EPA) and European Union, and strictly controlled in drinking water [8,9,10]. Therefore, the development of effective destructive abatement technology for removal of Cl-VOSCs from contaminated waters attracts tremendous attentions of worldwide.

1.1 The properties, sources of Cl-VOCs and their harms to human

1.1.1 Chlorinated methanes

Carbon tetrachloride (CT) is a colorless liquid with special sweet smell. It's commonly used as an excellent non-polar solvent in dissolving other non-polar organic compounds in industry, such as fats, oils, lacquers, wax, rubber and resin. It was widely used as fire extinguishers, dry cleaning, degreasing, pesticide, and known as the precursor to refrigerants in the past. According to Chemical and Engineering News [11], production of carbon tetrachloride peaked at 1970s with annual production of 500,000 metric tons in US. At 1987, its global production amounted to 960, 000 tonnes [12]. Whereas, the production of carbon tetrachloride has steeply decreased since 1980s due to environment concerns and the decline demands of chlorofluorocarbons (CFCs). In 1992, the overall production in U.S.-Europe-Japan was estimated at 720,000 tonnes [13]. The main sources of carbon tetrachloride released to environment were primarily from the discharge of chemical manufacturing industry over the past decades, such as the production of chlorofluorocarbons (CFCs), and chlorinated organic solvents. However, research shows that carbon tetrachloride has severe adverse effect to human health, which could degenerate the liver and kidneys, and result into acute central nervous systems effects, including dizziness, headache, depression, confusion and, in severe cases, even respiratory failure, coma, and death [11]. There is epidemiological evidence that links of lymphohematopoietic malignancies to carbon tetrachloride exposure. It readily evaporates and could be persistent in the atmosphere with atmospheric lifetime of 100 years, and contributes to both ozone depletion and climate warming [14]. Carbon tetrachloride is among the most frequently detected volatile organic solvent in groundwater, has been listed one of the 129 priority pollutants by U.S.EPA [9], and also appeared in the blacklist of 68 priority pollutants in water at China [8].

Chloroform (CF) is a common solvent due to its character of relatively unreactive and miscible with most organic liquids in laboratory. It's also widely used as a solvent in pharmaceutical industry, and as an important chemical raw material for producing dyes, pesticides, chlorodifluoromethane (HCFC-22) in industry. Chloroform serves as a source of producing dichlorocarbene applied in organic synthesis industry. Besides, chloroform was once widely used as an anesthetic [15]. Chloroform [16] is mainly produced in U.S., European Union and Japan, the total global annual production capability was 520,000 tonnes in the late 1990s. The production of chloroform was 216, 000 tonnes in U.S. at 1993, and 316, 000 tonnes in European Union at 1997. In China, the production capacity is estimated at 500,000 tonnes per year. Chloroform is mainly used in the synthesis of HCFC-22, and this accounts for around 90-95% of its total use in European Union [16]. The main sources of chloroform emitted to environment were principally through the exhaust gas and wastewater discharge of related industry during production. Chloroform could depress the central nervous system of human. According to the U.S. National Institute for Occupational Safety and Health, it can immediately disserve to human life and health once approximately at 500 ppm. The U.S. National Toxicology Program's eleventh report on carcinogen supposes chloroform to be a human carcinogen, and the IARC classify it a group 2 B designation which indicates CF possibly carcinogenic to human [15]. Chloroform also has been found that mostly associated with hepatocellular carcinoma [15]. A general survey of groundwater quality throughout China, including the region of Beijing-Tianjin area, Yangtze delta area and Pearl River delta area, shows volatile organic compounds are among the most frequently detected contaminants, in particular, chloroform, carbon tetrachloride, perchloroethylene and trichloroethylene [5]. In virtue of its potential carcinogenetic to human, CF has been listed as the priority pollutant by U.S.EPA, China and European Union.

Dichloromethane, also known as methylene chloride, is the main raw material for producing cellulose acetate film, and also used as a solvent in pharmaceutical industry in China. While in U.S., Europe and Japan, methylene chloride is widely used in metal degreasing, varnish stripper, adhesives and pesticide [17]. Taking US as an example, the total production amounts to 147,720 tonnes at 2000; the annual production capacity in China is 55,000 tonnes [17]; the usage in Europe was 150,000 at 1993 [18]. Most of methylene chloride released to environment principally resulted from its use as an end-product by various industries, and home use as varnish stripper and aerosol products. According to the research by U.S.EPA, it has estimated almost 85% production of methylene chloride in U.S. is released to environment, of which 86% as gas form [18]. Toxic Chemical Release Inventory at 1988 indicated that approximately 170, 000 tonnes out of 230, 000 tonnes (total amount at that year in U.S.) was lost to atmosphere; among them, 60, 000 tonnes resulted from methylene chloride production emission and 110,000 came from the consumer products and other sources, such as hazardous waste sites [18]. The total emission of methylene chloride to air in Western Europe at 1991 was estimated at 180,000 tonnes, accounted for 36% of global emission (500,000 tonnes per year) [18]. Moran revealed that methylene chloride is among the most frequently detected pollutants with its concentration close to or even greater than the Maximum Contaminant Levels (MCLs) throughout the survey of more than 5,000 wells all over US between 1985 and 2002 [6]. Methylene chloride is found that can cause the body carbon monoxide poisoning via metabolizing by the body to CO. Acute exposure by inhalation has resulted in optic neuropathy and hepatitis. It presumed to be a carcinogen, which has been proved by the laboratory animals linked to liver, lungs and pancreas cancer [19]. Similar with the previous two chlorinated methanes, methylene chloride also is one of the priority pollutants and strictly controlled by U.S.EPA, China and European Union.

1.1.2 Chlorinated ethanes

Chlorinated ethanes are low molecular weight saturated compounds with analogous molecular structures, containing two carbons in which one to six hydrogen atoms are substituted by chlorine atoms. All of chlorinated ethanes are low boiling point liquids except hexachloroethane; most of them have water solubility with relatively low volatility. In general, both solubility and volatility decrease with the increase of chlorine numbers in their molecule structures.

Chlorinated ethanes are widely used as industrial solvents, degreasing agents and as intermediates in producing plastics, textiles and some other compounds in industry. Many of these compounds still have significant usage presently, such as chloroethane, 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) have all been listed as the most high production volume chemicals list by Organization for Economic Co-operation and Development with production levels greater than 1,000 metric tonnes per year [20]. On the other hand, due to the widely production and usage of these compounds, the chemicals may enter environment through water discharge and accidental spills during their production, storage and secondary processing. Accordingly, chlorinated ethanes have become the widespread and frequently detected groundwater contaminants in North America, Europe and China [5,7,21]. Owing to the poor biodegradation ability, chlorinated ethanes could be persistent surviving in groundwater under natural conditions. The human health impacts by these compounds show circulatory and respiratory failure, neurological disorders as well as damage to skin, liver, heart, kidney, mammalian glands, some of them are even suspected to be carcinogenic to human being [22,23]. On account of the severe effects to human health and environment, 1,2-DCA, 1,1,1-TCA, 1,1,2-TCA, 1,1,2,2-TCA have been listed as the priority controllable pollutants both by U.S. EPA and China, besides, 1,1-DCA and hexachloroethane also appear in the list of U.S. EPA except for the previous four substrates.

1.1.3 Chlorinated ethylenes

Perchloroethylene (PCE) and tetrachloroethylene (TCE), as representatives of chloroethylenes, are synthetic chlorinated hydrocarbons known for their excellent solvent properties and low fire and explosion potential. They have been widely used as effective solvents for waxes, resins, fats, rubbers, oils and paint varnishes by private and public sectors, and also extensively used as dry cleaning and metal degreasing since 1920s [24-26]. Owing to the common occurrence of leaks, spills and their improper disposal at industrial sites, significant amounts of PCE and TCE have been introduced into environment, together with their good water solubility, which have made them among the most popular groundwater contaminants. PCE and TCE have been ranked as the first and third most frequently detected VOCs in groundwater with concentration higher than the Maximum Contaminant Levels (5 ppb) all over America [6]. These two compounds are also among the top 33 priory hazardous substances that possess the most significant threat to human health according to the Department of Health and Human Services at the same time [27]. Exposure to low levels of these substrates in drinking water could cause the risk of carcinogen to human being. Actually, there is epidemiological evidence that relates to the increase rate of esophageal cancer, cervical cancer and non-Hodgkin's lymphoma with exposing to TCE and PCE [28]. Therefore, PCE and TCE have been strictly regulated (lower than 5 ppb) in drinking water by U.S. EPA and Ministry of Environmental Protection of China, and they are among the priority controllable pollutants constituted by the two organizations [8,9].

1.2 Remediation technologies for Cl-VOCs

Numerous non-destructive and destructive methodologies have been widely developed and applied to decompose chlorinated volatile compounds from the contaminated water and soil media over the past decades. Presently used non-destructive technologies for disposal of Cl-VOCs are including air stripping and adsorption method by activated carbon. Although these techniques are very effective in removal chlorinated hydrocarbons from contaminated sites, the nature of chemicals doesn't change; instead, these methods only transfer the contaminants from one phase to another, which will require further addition disposal procedures for the polluted gas to be cleaned and the adsorbent to be regenerated [29,30].

Destructive techniques towards the abatement of Cl-VOCs include thermal incineration, aerobic or anaerobic biodegradations and advanced oxidation processes (AOPs). In thermal incineration technique, it needs an elevated temperature of 1000℃ to destructive chlorinated hydrocarbons due to their relative lower flammability, which evidently increase the processing cost. Besides, owing to the high capital cost and the potential emissions of high toxic byproducts, such as dioxins, furans and phosgene at insufficient high combustion temperature, it restricts the development of this technology [31]. Aerobic and anaerobic microbial conversions of Cl-VOCs to non-toxic hydrocarbons have been studied for the potential application in in-situ treatment over the past decades. Numerous aerobic microorganisms, including but not limited to methanotrophs, propane-oxidizers, ammonia-oxidizers and toluene-oxidizers, have been shown the ability to co-metabolize some certain of Cl-VOCs [32]. Under anaerobic conditions, both metabolic and co-metabolic microorganisms have been reported that could achieve reductive dechlorination process of geminal-chloroethanes in the and sulfate-reducing conditions [33,34]. However, since Cl-VOCs are a species of synthetic hydrocarbons with high toxicity, there are no microorganisms that could rely on them as sole carbon source in environment. Therefore, a major challenge proposed for biodegradation techniques is that it often takes quite long time for the bacteria to acclimate and remove the chlorinated hydrocarbons from contaminant sites due to their toxicity and inhibition effects.

Advanced oxidation processes (AOPs), including ultraviolet, UV/H_2O_2, ozonation, Fenton reaction, photocatalytic oxidation and electrochemical oxidation techniques, have been successfully applied as one of the most promising technologies on the abatement of

Cl-VOCs [35-62].

Photocatalytic oxidation mainly utilizes the generated hydroxyl radical (•OH) resulted from light irradiation of a catalyst, such as titanium oxides (TiO_2), zinc oxide (ZnO), to participate in the reaction with pollutants [35,36]. The destruction of Cl-VOCs by using photocatalytic methods could be performed under ambient temperature and pressure conditions with significant lower cost compared to thermal treatments when the contaminant concentration is low [37]. A number of photocatalytic degradation studies have been carried out in the removal of dichloromethane, chloroform, carbon tetrachloride, and trichloroethylene [37-42]. However, studies found photocatalytic oxidation methods alone may produce chlorinated species [37,41], while a combination of UV with ozone, hydrogen peroxide, Fenton's regent could enhance degradation of these compounds effectively [43,44].

Fenton oxidation is another representative of AOPs. There are two categories of Fenton process, one is the standard Fenton reaction with soluble ferrous ion (Fe^{2+}) as catalyst; the other is so-called Fenton-like process, in which utilizes ferric ion (Fe^{3+}) and iron oxides as the catalysts. Both of them utilize the strong oxidizing hydroxyl radicals (•OH) resulted from the reaction between H_2O_2 and catalyst to decompose the recalcitrant compounds, with the only difference that iron oxides as a catalyst can effectively degrade the organic compounds at circumneutral pH, compared to those standard Fenton reaction performed at acidic conditions [45]. The application of Fenton oxidation process has received widely attention in the removal of chlorinated volatile organic compounds (Cl-VOCs) due to its simple and efficient characters [45-53]. According to the Vilve et. al research, reduction of 1,2-dichloroehtane (1,2-DCA) and TOC from wash water of ion-exchange resin could reach up to 100% and 87% by using classical Fenton reaction, respectively [49]. Tsai et al reported that around 81% trichloroethylene (TCE) could be removed by using Fenton-like reaction, in which 1,000 mg•L^{-1} of H_2O_2 and 10 g• L^{-1} of basic oxygen furnace slag were introduced into the system [45]. Chloroform, trichloroethylene (TCE), perchloroethylene (PCE), and 1,2-dichloroethane (1,2-DCA) all have been treated by Fenton's reagent. Taking 1,2-DCA for instance, where led to 100% degradation of 1,2-DCA with 78% TOC removal [50-52]. 40% of the added trichloroethylene (TCE) DNAPL (dense non-aqueous phase liquid) was oxidized in 1 h with a single application of 3% H_2O_2 to the aquifer sand containing 2.01 g•Kg^{-1} of extractable iron, which indicated the ability of mineral catalyzed Fenton-like reaction to directly oxidize TCE in non-aqueous liquid [53].

These methods, however, are limited by various reasons, for instance, Fenton reaction is limited by the presence of dissolved oxygen, and photocatalytic technique suffers from poor oxidation efficiency in ground water treatment. Besides, the addition of cost chemicals, potential forming of secondary pollutants and requirement of rigorous conditions, such as acidic pH, high temperature, restrict the development of these technologies.

In recent years, electrochemical AOPs, such as anodic oxidation and electro-Fenton process, have also gained much interest in the removal of chlorinated solvents due to their remarkable technical characters. Some researches even revealed electrochemical degradation of organic compounds by using boron-doped diamond (BDD) anode behaves more efficient property than ozonation and Fenton oxidation, concomitant with higher substrate removals and lower cost [54-56]. It has been shown that the effectiveness of electrochemical oxidation of chlorinated aliphatic compounds drastically depends on the anodic materials, in which high oxygen overvoltage electrodes exhibit remarkable performance [57-59]. Among them, BDD electrode was found to give high dissolved organic carbon abatement in the oxidation of 1,2-DCA with much higher current efficiency than stainless steel, Pt, Au, Ebonex, Ti/IrO_2-Ta_2O_5 and PbO_2 anodes [58,59], where almost complete conversion of 1,2-DCA could be obtained at BDD electrode with more than 40% current efficiency at proper applied current density [58]. Chen et. al indicated that the oxidizing specie for abatement of chlorinated solvents was surface-adsorbed hydroxyl radicals resulted from oxidation of H_2O and OH^- at titanium oxide anode [60]. Recently, some united techniques have been developed to enhance the abatement efficiency towards the chlorinated aliphatic hydrocarbons. Some researchers proposed the combination of anodic oxidation and cathodic reduction, simultaneously, and higher removal of chloroethanes (1,2-DCA and 1,1,2,2-TeCA) were observed in the same amount of charge passed with respect to uncoupled process [61]. Electro-Fenton process was carried out for the treatment of chloroethanes by combination a BDD as anode and an air diffusion cathode to be able to generate the H_2O_2 in situ, which could be further react with Fe^{2+} to yield •OH, leading to almost total mineralization of 1,2-DCA and 1,1,2,2-TeCA at 300 mA in 420 min. Comparative treatments without Fe^{2+}

(anodic oxidation) or using Pt anode resulted into a poorer mineralization performance [62].

The electronegative character of chlorines in Cl-VOCs molecule structure indicates reductive dechlorination of chlorinated hydrocarbons is thermodynamically favorable to take place, besides, the reductive dechlorination products are environment benign non-chlorinated hydrocarbons and chlorine ions. Therefore, these promote the prosperous development of reduction techniques towards the abatement of chlorinated hydrocarbons, such as zero valent iron (ZVI)/bimetal catalyst reduction technology, catalytic hydrodechlorination technology and electrochemical reduction technology. Since Gillham and O'Hannesin found metallic iron fillings could be utilized in groundwater remediation [63], the use of ZVI for in situ remediation of groundwater contaminated by Cl-VOCs has received considerable attentions from worldwide [63-68], in which iron serves as electron donor to reductively dechlorinate of Cl-VOCs to their non-chlorinated analogs and chlorine ions. Besides iron, other base metals, such as zinc and magnesium, also have been found to be effective on mediating the reductive dechlorination of chlorinated volatile compounds in aqueous system [69-72]. However, an obvious drawback of zero valent metal remediation technology is the relative slow reaction rates, which necessitate a degradation time of Cl-VOCs over couple of days to achieve dechlorination requirements. In addition, the dissolution and surface passivation problems over active metals bring forward a great challenge to this technology.

For the sake of enhancing dechlorination activity of base metals and prolonging its longevity, second transition metal with high hydrogenation ability, such as Pd, Ni, Ru and Pt, are incorporated to constitute a bimetal system towards the abatement of Cl-VOCs [73-79]. The main mechanism is presumed that a transition metal complex is formed through the interactions between empty orbital of transition metal and the p electrons of chlorines in Cl-VOCs structure or the π electrons from unsaturated compound (M···Cl···R), which could lower the activation energy barrier of dechlorination reaction. The dechlorination process normally involves three reduction steps. Firstly, H_2 is produced accompanying the corrosion of base metals under aqueous conditions; the formed H_2 chemisorbs at the transition metal (Pd) surface, or even inserts to its lattice concomitant with formation a strong reductive substance (PdH_x); eventually, reductive dechlorination is achieved through the hydrogen attached at metal surface continuous attacking with Cl-VOCs molecular, successively. The proposal reduction mechanism of this process is described as follows (taking Pd/Fe bimetal as an instance):

$Fe + 2H^+ \rightarrow Fe^{2+} + H_2$ (1.1)

$Pd + R\text{-}Cl \rightarrow Pd\cdots R\cdots Cl$ (1.2)

$Pd\cdots R\cdots Cl + 2H(Pd) \rightarrow RH + HCl$ (1.3)

Due to the remarkable catalytic characters of bimetal catalyst, such as high reactivity and fast kinetic reaction rate, it has been widely applied on the remediation of Cl-VOCs, including carbon tetrachloride (CT), chloroform (CF), methylene chloride, perchloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE), 1,1-dichloroethane (1,1-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA) with encouraging dechlorination efficiencies [73-79].

However, the prepared bimetals, in particular the nano-sized particles, are readily prone to taking place agglomeration phenomenon due to magnetic interaction. Various modification strategies over particle surface by polymers or surfactants have been developed to overcome the agglomeration problems, while the excessive preparation procedures coupled with the consumption of costly materials severely limit the industrial application of this technology [80,81].

Catalytic reductive hydrodechlorination is another promising novel technology for the treatment of hazardous chlorinated hydrocarbons and pesticides in contaminated groundwater [82-85]. In catalytic hydrodechlorination technique, it is usually comprised of a packed catalyst reactor and a hydrogen source two parts. Based on the reaction conditions, it can be divided into aqueous phase reaction and gas phase reaction. The influent is saturated with hydrogen for an aqueous-phase reaction, and hydrogen gas mixed with Cl-VOCs vapor are fed into the reactor, in which the substrate reacts with hydrogen over catalyst surface achieving hydrodechlorination process [86,87]. Similar with bimetal reductive dechlorination mechanisms, heterogeneous catalysis normally is comprised of three steps, the first is adsorption, followed by reaction at the catalyst surface, and then desorption. Among the three steps, the adsorption between the chlorinated molecular and catalyst could lower C-Cl bond strength of the molecular and promote it easier to be ruptured [86]. Obviously, catalyst plays a significant role during dechlorination process. Palladium is found to be the best hydrodechlorination catalyst among the noble and transition metals, which is capable and has been widely applied on the dechlorination of various types of chlorinated compounds, involving chlorinated methanes, ethanes, ethylenes, and chlorinated aromatics [86].

Catalytic dechlorination of PCE, TCE, 1,2-DCE, cis-DCE, trans-DCE over NiMo/Al_2O_3 catalyst, indicated that a multiple chlorines removal process rather than sequential dechlorination occurrence during the reduction process [88]. A catalytic hydrodechlorination investigation over dichloromethane, chloroform and PCE on Pd/TiO_2 reveals that reactivity order is chloroform > PCE > dichloromethane [89], while significant catalyst deactivation phenomenon was also observed due to chlorine poisoning in this research.

However, the reactivity of catalyst is readily to be deactivated in both gas phase and aqueous phase dechlorination reactions, which behaves a trend that drops rapidly initially and then decreases gradually with the proceeding of research. The deactivation mechanisms till now is not very clear, but it's postulated to attribute to the dechlorination products that occupy the activation sites of catalyst and have poisoning effect on the reaction sites [86], accordingly, regeneration procedures must be taken into account. In addition, as aforementioned, external hydrogen source is required to feed into this system, coupled with noble metals demand in catalyst increase the processing cost of this technology.

Similar with zero valent metals remediation technology, the potential problems of catalytic dechlorination technique include dissolution of metals ions, passivation of catalyst surface, precipitation of metal hydroxides and slow kinetics, which limit the development of this technology. However, these problems could be effectively avoided by using these metals as cathode materials in electrochemical reduction methodology. In contrast to the zero valent metals, which are consumed through providing electrons for hydrodechlorination process, the metal cathode are served as electron donor protected from corrosions by cathodic potentials. Another attractive characteristic of electrochemical reduction technology is that the main reactant is electron, which is a clean reagent produced by choosing appropriate cathode materials without additional of chemicals. Therefore, electrochemical dechlorination of Cl-VOCs is an environment friendly process, by which could realize detoxification of Cl-VOCs through removal chlorines from their structures, concomitant with non-chlorinated hydrocarbons and chlorine ions generation. Besides, the superiority of this technology over others is that could provide controllable reaction rate as well as cathodic protection of metals against passivation, which can prolong the longevity of cathodic materials. Electrochemical dechlorination methods as a new promising technology are attracting more and more attentions on the abatement of chlorinated organic compounds from the worldwide presently.

1.3 Research motivations

Recent investigations reveal that electrochemical reductive dechlorination technology has successively applied on the removal of Cl-VOCs [90-104]. Even though chlorinated solvents are among the most frequently detected contaminants in the groundwater, and possess severe impacts on human health, their concentration levels are normally very low, which result into sluggish reaction rates with poor current efficiencies due to mass limitation control when employ electrochemistry methods. In addition, some other problems were encountered by using electrochemical methods towards the abatement of Cl-VOCs in groundwater: (1) owing to the relative negative reduction potentials of some Cl-VOCs with respect to water electrolysis, hydrogen evolution reaction (HER) readily takes place concomitant with the dechlorination process of chlorinated hydrocarbons, which severely decrease the current efficiency of this process, resulted from the fraction electrolytic current for Cl-VOCs reduction dropping drastically and the activated sites for target substrates reaction being occupied; (2) besides, the bulk production of H_2 during electrolysis could cause the release of chlorinated solvents to atmosphere due to their volatility character; (3) large quantities of metals ions, such as Mg^{2+}, Ca^{2+} etc., exist in the tap water or groundwater, leading to the cathodic deactivation because of their deposition at cathode surface during electrolytic reduction process, besides, inorganic ions, like SO_4^{2-}, NO_3^-, also contribute to the poison of catalyst.

As already stated before, air stripping and adsorption by activated adsorbent are very effective methodologies for Cl-VOCs removal from contaminated sites, while the main disadvantage is the post-disposal of collected hazardous gases and adsorbents. Actually, these toxic compounds could be well extracted into organic solvents by choosing appropriate solvent. Accordingly, the investigation media transfer from aqueous to organic solvent. Electrochemical reduction of Cl-VOCs in organic solvent could be well solved the problems encountered in aqueous conditions. The superiority of this technology is that some Cl-VOCs are hard to reduce in aqueous resulted from the relative negative potential compared to water discharge could be dechlorinated successfully in organic solvent.

Of course, one might dispute the feasibility of conducting dechlorination reaction in organic solvents; however, the wastewater treatment may be not the only situation we face with. Actually, if the issue is to dispose the existing stock of PCEs, which can be served as good solvents themselves, the direct electrochemical dechlorination can be achieved by choosing an appropriate supporting electrolyte or realized in a micro-fluidic system which can prevent the ohmic drops and therefore decrease the burdening of chemical addition.

Chemical reactions in solutions are often drastically affected by the solvents used. Dimethylformamide (DMF) is a good organic solvent with strong Cl-VOCs solubility. It's an aprotic protophilic solvent with high permittivity (ε_r=36.7) and weak electron acceptable ability, which expand the reduction potential window to the negative direction much wider than that in water, therefore, substances are difficult to reduce under aqueous conditions could be reduced in DMF solvent . Due to the aprotic character, DMF has a very weak proton donating and hydrogen bond-donating ability. Besides, most DMF molecular exist as monomers, they are no-structured or only weakly structured and could primely dissolve large organic molecules and ions. DMF is a solvent with strong basicity, so it can readily accept hydrogen ions from solutions, which is very significant for electrochemical hydrogenation process, since we could control both the electron transfer and proton transfer two processes, simultaneously, to further investigate the dechlorination mechanisms more comprehensively [105].

Although electrochemical dechlorination of chlorinated VOCs have been extensively investigated in different organic solutions. Comparison of electrocatalytic activities of different transition metals towards Cl-VOCs reduction and selecting the high remarkable reduction catalysts have not been concluded so far. The comprehensive dechlorination mechanisms of different compounds in Cl-VOCs by electrochemical reduction methods in DMF solution are still not fully addressed. According to our preliminary researches, electrochemical reductive dechlorination of polychloromethanes at GC electrode follows two competitive reaction routes: sequential hydrodechlorination and reductive Cl^- elimination to give carbene route. It's not very clear whether the reduction of other Cl-VOCs at GC, and at other catalytic cathodes conform to the same dechlorination mechanisms or not. Besides, the controversy on reduction of Cl-VOCs through direct reduction of C-Cl bond or indirect reduction by electrogenerated atomic hydrogen in the presence of water is still carrying on. The mechanism of dissociate electron transfer to C-Cl bond of polychloroethanes are also still not fully interpreted. As known, the main obstacle for developing commercially viable electrochemical dechlorination technology is to explore an electrode material that is stable, high catalytic activity as well as low price and high availability. Herein, different cathodic materials were examined towards the abatement of Cl-VOCs. Eventually, electrochemical hydrogenation of the acetylene, which is as the dechlorination intermediate, was carried out at precious and non-precious metals for exploring a novel technology on acetylene removal. We hope to supply several hints on the aforementioned questions through this research, so as to comprehensive understand the dechlorination mechanisms of chlorinated aliphatic hydrocarbons, therefore, providing instructions for the potential application of this technology towards the abatement of Cl-VOCs from contaminated sites both in ground water and soils.

The main objects of this study was to explore the feasibility of electrochemical reductive dechlorination of Cl-VOCs in DMF solution by employing different cathode materials, including inert electrode (GC) and catalytic electrodes, to further search for stable and high efficient cathodic materials. Reduction mechanisms of Cl-VOCs were investigated by combination of voltammetric studies and electrolysis experiments in this research. The effects of cathode materials, molecule structures, proton availability and the potentials applied manners (stepwisely or single step) on electrochemical dechlorination process were also investigated in this research. In the end, the feasibility of electrochemical acetylene hydrogenation was investigated.

1.4 Research scope

The objects were accomplished in virtue of different electrochemistry techniques by carrying out under various working conditions as given below:

- Cyclic voltammetries of Cl-VOCs at different cathodic materials (GC, Au, Ag, Pd, Pt, Cu, Fe, Ni, Pb, Zn) in DMF + 0.1 M $TPABF_4$ in the presence or absence of proton donor

- Electrolytic investigations of polychloroethanes (1,1-DCA, 1,1,1-TCA and 1,1,1,2-TeCA) by using GC rod, Ag or Cu plate in DMF + 0.1 M $TPABF_4$ with or without proton donor addition
- Electrocatalytic properties of Cu electrode towards reductive cleavage of polychloromethanes
- Electrochemical hydrogenation of acetylene, as an intermediate of dechlorination product, was carried out in DMF + 0.1 M $TPABF_4$ containing different amounts of water addition at precious and non-precious metals

The dissertation is divided into seven chapters. The first chapter provides background information on the research topic. Chapter2 is a relevant literature review on electrochemical reductive dechlorination of Cl-VOCs. Chapter3 investigates the electrochemistry behaviors of polychloroethanes at different cathodic materials. Electrocatalytic activity of different metals are ranked based on their catalytic effects with respect to GC, while the distinct dechlorination mechanisms based on the molecule structure of polychloroethanes and the dissociative electron transfer (DET) mechanisms to C-Cl bond are proposed. In chapter4, the reduction pathways, product distributions, and the effects of different potential applied manners (stepwisely or single step) towards the reductive dechlorination of polychloroethanes (1,1-DCA, 1,1,1-TCA and 1,1,1,2-TeCA) at GC, Ag or Cu electrode under different solution mediums (aprotic or with proton donor addition) are explored. Electrocatalytic properties of Cu with respect to GC for the reductive cleavage of polychloromethanes are carried out in chapter5, in which cyclic voltammetry experiments and electrolytic investigations of Cu are conducted, and the reduction mechanisms of polychloromethanes are proposed over there. Chapter6 illustrates a novel technology towards the removal of acetylene which is an intermediate in polychloroethanes reduction process: electrochemical hydrogenation of acetylene in DMF solution. Since the removal of acetylene from ethylene stream is a key step in polymer synthetic industry, this discovery in our research has significant roles both from scientific and industrial point of view, which would open a new gate for acetylene hydrogenation study. Eventually, conclusions and suggestions of this research are summed up in chapter 7.

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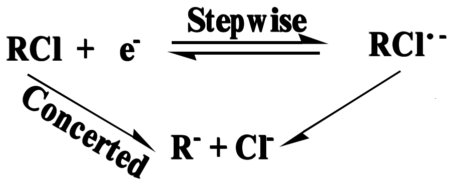
Chapter 2 Literature review

Electrochemical reductive dechlorination methodology as a promising technology, could achieve the reductive detoxification of chlorinated compounds to environment benign non-chlorinated hydrocarbons and chlorine ions. In addition, due to the character of better environment compatibility, controllable reaction kinetics, cathodic protection against catalyst passivation as well as mild working conditions, electrochemical dechlorination technology has attracted numerous attentions and widely used in the removal of chlorinated aliphatic and aromatic compounds from contaminated sites in environment [1-15].

2.1 Electron transfer mechanism to chlorinated aliphatic compounds

Single electron transfer to molecules is often accompanied by other reactions, involving bond formation and/or cleavage. The resulting high-energy intermediates may undergo further electron transfer with the same electron source or sink that initiated the reaction. Among the reactions accompanying electron transfer, bond breaking is a common mode by which a free radical and a leaving group may be produced via single electron transfer to a molecule [16]. Reductive dechlorination of chlorinated hydrocarbons occurring at cathode is recognized as a dissociative electron transfer (DET) process, in which accompanying the electron transfer results into the scission of C-Cl bond [17,18]. According to the sequence of electron transfer and C-Cl bond rupture, there are two possible DET mechanisms for electron transfer to chlorinated compounds, namely stepwise and concerted DET mechanisms. For stepwise DET mechanism, also known as out-sphere electron transfer mechanism, the chlorinated substrate firstly accepts one electron concomitant with a stable π^* anion radical formation, followed by the C-Cl bond rupture, stepwisely; while electron transfer and bond rupture take place at one single step in the concerted DET mechanism, simultaneously [6,16-18], as shown in scheme2.1. Distinguishing the DET mechanisms of chlorinated compounds is very significant for both understanding the reduction mechanisms and determining the rate-limiting step of electrochemical dechlorination process.



Scheme 2.1 DET mechanism of chlorinated compounds

Transfer coefficient is a significant parameter in electrode reaction, representing the efficiency with which electric energy supplied to the electrode is used to overcome the electrode reaction activation energy, it can be used as a diagnostic criterion to distinguish the two different DET mechanisms [6,16]. Normally, if $\alpha << 0.5$, the reaction follows concerted DET mechanism, whereas α 0.5 denotes a stepwise DET mechanism. The peak potential, E_p, varies linearly with log v, as shown in eq.(2.1), which can be used to calculate the transfer coefficient.

(2.1)

Several groups have conducted the investigations of DET mechanisms to chlorinated aliphatic compounds [6,7,18,19]. Polychloromethanes were found to follow concerted dissociative electron transfer mechanisms by using different cathode materials. For instance, carbon tetrachloride accepts one electron from the cathode surface, in concomitant with formation of trichloromethyl radical by eliminating one chlorine ion, simultaneously. This step is recognized as the rate-limiting step of electrochemical reduction of CT. The reduction potential of trichloromethyl radical is significantly positive than that of CT, consequently, the initial reduction of CT is essentially a two-electron transfer reduction process that produces carbanion as intermediate. The fate of trichloromethyl carbanion could undergo different transformation pathways: (1) being protonated by any proton donor present in the solutions with formation of chloroform, which could be successively reduced to methane as the final product following the sequential hydrodechlorination mechanism; (2) reductive Cl^- elimination to generate $:CCl_2$. This species could either undergo a series of stepwise reductions and reductive Cl^- elimination reactions till forming methane as the final electrolytic product or react with water existing in the system to produce CO or formate as the final product. As described in the following reactions [7,18,19].

$$CCl_4 + e^- \rightarrow CCl_3^{\bullet} + Cl^- \qquad (2.2)$$

$$^{\bullet}CCl_3 + e^- \rightarrow CCl_3^- \tag{2.3}$$

$$CCl_3^- + H^+ \rightarrow CHCl_3 \tag{2.4}$$

$$CCl_3^- \rightarrow \mathbf{:}CCl_2 \tag{2.5}$$

$$\mathbf{:}CCl_2 + e^- + H^+ \rightarrow {}^{\bullet}CHCl_2 + e^- \rightarrow CHCl_2^- \rightarrow \mathbf{:}CHCl \rightarrow \cdots \rightarrow CH_4 \tag{2.6}$$

$$\mathbf{:}CCl_2 + H_2O \rightarrow CO + 2Cl^- + 2H^+ \tag{2.7}$$

The reductive dechlorination mechanisms of vicinal-polyhaloroalkanes have been widely explored and found to follow a reductive α,β-elimination mechanism in an overall two-electron transfer step with a corresponding olefin formation. However, there is a controversy on the sequence of double bond formation and chlorine ions elimination. Fry et al [20] presumed the dihalo-elimination of vicinal polyhaloalkanes was a concerted process, in which carbon-halogen bond is partially broken and the double bond is partially formed in a transition state, as described in eq.(2.8). The remarkable ease of dihalides are reduced with respect to those of mono-halides supports the assumption that the reduction must be concerted. For instance, the half wave potential for 1-chloro-2-iodoethane, ethyl iodide and ethyl chloride are namely -0.90 V, -1.60 V and -2.79 V, besides, those of 1,2-diboromoethane, ethyl bromide are -1.52 V and 2.08 V, respectively [21,22]. Whereas, Savéant et al [18] supposed this process involves discrete radical and carbanion intermediate, as described in eq.(2.9). The transfer coefficient values of α,β-polychloroethanes at first wave are in a range between 0.3 and 0.4, which indicates that the first electron transfer and expulsion of the first chlorine ion are concerted process, a second electron transfer immediately results in the formation of carbanion, which is readily preferential to expel β-chlorine ion leading to olefin formation than to be protonated, successively.

$$X{-}H_2C{-}CH_2{-}X + 2\,e^- \longrightarrow \left[X{-}{-}{-}CH_2\overset{=}{=}CH_2{-}{-}X\right]^{2-} \longrightarrow \rangle C{=}C\langle + 2X^- \tag{2.8}$$

$$X{-}H_2C{-}CH_2{-}X \xrightarrow[-X^-]{e^-} X{-}H_2C{-}\dot{C}H_2 \xrightarrow{e^-} X{-}H_2C{-}CH_2^- \xrightarrow[-X^-]{} \rangle C{=}C\langle \tag{2.9}$$

Different with the previous two species of polyhaloroalkanes, a variety of reduction pathways were observed towards the reduction of vicinal-polyhaloroalkenes. Cis-2,3-dichloroacrylnitrile was found to be dechlorinated in a sequential hydrodechlorination way, where 2-chloroacrylnitrile was firstly formed, and then was reduced to acrylonitrile at a more negative potential. However, the reduction of trans-2,3-dichloroacrylnitrile follows a concerted DET mechanism. Propiolonitrile was produced by a $2e^{-}$-$2Cl^{-}$ reaction sequence, and followed by being reduced to acrylonitrile after accepting another two electron transfers [23]. Savéant et al [18] investigated the dechlorination mechanisms of α,β-polychloroethenes at GC electrode. It showed that the reduction mechanisms of α,β-polychloroethenes conform to reductive α,β-elimination path, leading to the corresponding alkynes generation. Based on the diagnostic criterion of dissociative electron transfer process stated above, unlike the case of vicinal-polychloroethanes, the expulsion of the first chlorine ion follows a stepwise electron transfer/C-Cl bond cleavage mechanism.

2.2 Electrochemical kinetics towards dechlorination of Cl-VOCs

A typical electrode reduction reaction is comprised of the following series of steps [24]:

(1) The dissolved species transfer from main body of bulk solution to the electrode surface;

(2) The dissolved species adsorb at the electrode surface by physical or chemical interactions;

(3) Electron transfer from cathode to the adsorbed substrate takes place and the substrate gets reduced;

(4) The reduced substrate desorbs;

(5) The reduced species transfer from the electrode surface to the main body of solution.

An overall electrode reduction process is controlled either by electron transfer limitation or mass transfer limitation, sometimes is controlled by both of them. In the absence of mass transfer limitation, the dependence of reaction rate of multi-electrochemical steps on potentials could be described by the well known Butler-Volmer equation [24]:

(2.10)

where is the net current density due to the electrode reaction ($A \cdot m^{-2}$); represents the exchange current density ($A \cdot m^{-2}$), depending on the reactant concentrations and electrode materials; is the electron transfer coefficient, defined as the fraction of electric energy that is used to overcome the reaction activation energy, mainly depends on the numbers of electron transfer before the rate-limiting step; is the applied cathode potential (V), while stands for equilibration potential of the electrode reaction (V); denotes the electron transfer coefficient of the reverse reaction, whose value equals to 1- ; is Faraday's constant (964850 C/mol); is the gas constant (8.314 $J \cdot K^{-1} \cdot mol^{-1}$); is temperature (K). The first term in brackets represents the rate of forward reduction reaction, whereas the second term in brackets is the rate of reverse oxidation step. As known, electrochemical dechlorination reaction is normally an irreversible process accompanying C-Cl bond rupture, therefore, the backward reaction can be neglected and the Butler-Volmer equation could be rearranged to eq.(2.11):

(2.11)

As known, the electrochemical reaction rate is related to reaction current:

(2.12)

Therefore, the reaction rate could express as:

(2.13)

Eq.(2.13) is considered to be a pseudo-first-order kinetic model, in which is the first order rate constant for electrochemical reduction reaction, is the specific rate constant at equilibrium (i.e. overpotential= 0), n is the number of electron transfers at rate-determining step. The Butler-Volmer equation is only valid in electron transfer controlled reaction, as shown in eq.(2.13), the reaction rate increases exponentially with the decrease of cathodic potentials.

In most cases, first-order kinetics is often encountered in the electrochemical dechlorination of chlorinated aliphatic compounds with respect to reactant concentration. Reductive dechlorination of carbon tetrachloride on rotating Ni electrode was studied by Wang et al [25]. It showed that electron transfer from cathode surface to the adsorbed substrates was the rate-determining step. Complete dechlorination reaction was achieved during electrolysis, in concomitant with methane as the principal reduction product, while the reaction rate was found to conform to the Butler-Volmer equation in the electrochemical dechlorination process.

Electrolytic reduction of CT at different metals consisting Ag, Al, Au, Cu, Fe, Ni, Pd and Zn were carried out by Liu et al [26]. Results indicated the reaction rate towards CT reduction was first order in the bulk liquid phase concentration. Pseudo-first-order rate constants were as a function of cathode material, pH, and applied cathode potential (-1.40 V≤ E≤ -0.40 V, vs. SHE). At all electrodes, reaction rates were found to conform to Butler-Volmer equation, modified to account for mass transfer limitation.

Li and Farrell [1,27] investigated the dechlorination kinetics of CT and TCE by using a 2 mL porous iron flow-through electrode with a cation exchange membrane wrapped around the cathode separating from a platinum wire anode. The CT reduction followed the Butler-Volmer equation combined with a mass transfer limitation. However, the reduction rate of TCE didn't essentially alter with cathode potentials. It implied that the reduction of TCE was not controlled by electron transfer reaction. A linear free energy relationship was developed between dechlorination rate constants and C-Cl bond dissociation enthalpy. The reaction rates for chlorinated ethylenes were orders of magnitude greater than the predicted results based on the relationship between C-Cl bond dissociation enthalpy and kinetic data for chlorinated alkanes, which indicates that these two species follow two different dechlorination mechanisms. Further investigation by adopting a rotating iron electrode implied the rate-determining step of TCE was controlled by chemisorption process [1].

However, in the practical situations, mass transfer limitations sometimes couldn't be neglected, in particular in the case performed under low substrate concentration, of which are often encountered in the laboratory research and groundwater contaminations. The contributions of both electron transfer control and mass transfer limit to the kinetic of electrochemical reduction process could be mathematically described by Levich equation described as follows [28]:

(2.14)

In which is the mass transfer coefficient, or the overall kinetic rate at mass transfer limitation controlled reaction. From Levich equation, kinetic parameters could be determined for a certain dechlorination reaction under both electron transfer and mass transfer controlled.

Liu et al. [28] carried out electrolytic investigations of a series of Cl-VOCs over a porous nickel cathode at the potential range from -0.3 V to -1.40 V. Electrolysis results indicated the transformation of chlorinated hydrocarbons over elapsed time followed first-order reaction kinetics with respect to the target compound throughout the experiment. The dependence of apparent first-order reaction rate constants on cathode potentials conformed to the

Butler-Volmer equation, modified to account for mass transfer limitation to reaction. The reduction kinetics followed the Levich equation over the full experiments of cathode potential range.

2.3 Electrochemical reduction of chlorinated volatile organic compounds (Cl-VOCs)

As stated before, electrode reaction is a quite complex process, involving a series of steps from the dissolved substrates transferring to electrode surface till desorption of reduction products [24], while the change of one step or several steps among them would evidently enhance the extent or even mechanisms of electrode reaction. Accordingly, numerous researches have been conducted for the investigation of various determinant factors on the dechlorination of Cl-VOCs over the past decades, in the sake of better understanding the reduction mechanisms and obtaining high efficient chlorinated hydrocarbons abatement process [1-42].

2.3.1 Cathode materials

Electrode properties and the interaction between cathode and substrates may be among the most determinant factors on the dechlorination reaction rate and efficiency during electrolysis process. The thermodynamics of an electrode reaction is strongly influenced by the nature of electrode materials, which could affect not only on the reaction rate but even on the reaction mechanisms. In electrochemical reductive dechlorination process, cathode not only serves as an electron donor providing electrons and reaction sites for chlorinated substrates, but also can participate in the dechlorination reaction directly. Besides, electrochemical dechlorination reaction normally takes place at more negative potentials, where hydrogen evolution reaction (HER) as a side reaction competes with the dechlorination reaction. Suppression of HER can substantially increase the dechlorination current efficiency [27]. The HER overpotential is strongly dependent on the nature of cathode materials. Therefore, selecting an appropriate cathode material is an extremely significant step in dechlorination process. Different cathode materials have been tested on the dechlorination efficiency over the past decades [26-33].

Liu et al.[26] compared the catalytic activities of different metals towards the reductive cleavage of carbon tetrachloride (CT), including Pd, Au, Ag, Al, Fe, Ni, Cu and Zn. Fast dechlorination rate were obtained at Ni and Cu electrode compared with the others, while the reactivity orders of these metals under the same working conditions exhibited: Ni > Cu > Pd > Fe > Au > Ag > Zn > Al. The current efficiencies of different cathode materials were found to be inversely proportional with their exchange current density for hydrogen evolution, which presented an order of: Zn > Cu > Fe > Ni.

Mishra et al. [29] investigated the reduction of trichloroethylene at boron-doped diamond film cathode (BDD) by using a rotating disk electrode reactor. Results indicated that the rates of TCE dechlorination were determined as function of cathode potential and TCE concentration over a temperature range from 2 to 32 ℃. Whereas, kinetic studies showed reduction rates of TCE at current density of 15 $mA\cdot cm^{-2}$ and concentration below 0.75 mM were first orders with respect to TCE concentration, with surface area normalized rate constants two orders magnitude greater than those for iron electrode.

The reductive cleavage of chloroform and carbon tetrachloride were investigated at Ag, Pd, Cu and GC electrode in CH_3CN + 0.1 M $(C_2H_5)_4NClO_4$ by Isse et al [6]. All three metal cathodes were found to exhibit remarkable catalytic activities for the reduction of CF and CT. The peak potentials recorded at metal electrodes are positively shift by 0.56 - 0.81 V with respect to those performed at non-catalytic electrode (GC). A possible dechlorination mechanism for catalytic metals was proposed, in which involves a bound transition state where an activated complex interacting with metal surface is formed. The catalytic properties of metals were presumed to originate from its affinity for halide ions [30].

Sonoyama et al. [31] compared the electrocatalytic activities of different metal electrodes towards the reductive destruction of dichloromethane, involving Ag, Cu, Pd, Zn, Pb, Co, Sn, Ni, Au and Pt. Results indicated the destruction current efficiency of dichloromethane was largely dependent on nature of materials, among them, Cu behaved the best catalytic activity for the destruction of dichloromethane with the highest current efficiency, while Pd, Zn, Pb and Ag showed moderate activity, whereas, the other electrodes were found hardly to decompose dichloromethane during electrolysis.

Electrochemical dechlorination of perchloroethylene in aqueous was carried out at lead cathode by controlling current density. PCE could be almost totally degraded (lower than 7%

of the initial concentration) at potentials lower than hydrogen evolution reaction onset. However, even though the high overpotential character for lead, 27% of chlorinated byproducts, such as TCE and DCE, were found accumulated in the system. While no ethane and ethylene, or four or six-carbon molecules were detected in the electrolytic products throughout the electrolysis, it indicated that the reduction of PCE didn't follow soluble radical mechanisms [32]. The dechlorination investigations on PCE under similar working conditions were carried out by Liu et al. [28], except the cathode substituted by a porous nickel electrode. Reduction kinetic was first order with respect to PCE throughout the electrolytic experiment, while TCE and *trans*-DCE were the only detected chlorinated intermediates during experiments, both of them were observed transiently under experiment conditions. Complete dechlorination of PCE was achieved at the end of electrolysis study, with ethane, ethylene, *trans*- and *cis*-2-butene, 1-butene, propane, isobutene and hexane as the final products. The formation of four or six-carbon molecules from the reduction of PCE indicated that free radical intermediates were generated during electrolysis, and that the longevity of radicals readily favored the occurrence of polymerization.

The size of catalyst seems also contribute to the electrocatalytic activity towards reduction of chlorinated hydrocarbons. Nano-structured Pd thin film over GC prepared by cyclic voltammetric deposition methods exhibited remarkable electrocatalytic effect for the reductive cleavage of carbon tetrachloride. In the cyclic voltammetry experiment of Pd/GC electrode performed in dilute H_2SO_4 solution, it could display well separated current peaks corresponding to adsorption and desorption of various forms of hydrogen, which is similar in the profile with the one of Pd nano-particles but totally different from that of bulk Pd [33], indicating Pd in nano-sized that exhibits more remarkable catalytic activity than that of bulk Pd.

In general, cathode materials play a significant role in the dechlorination reaction. If consider the application of electrochemical dechlorination technology in the practical wastewater contaminated by Cl-VOCs, the requirement of cathode materials utilized in dechlorination process should satisfy with: (1) fast dechlorination rate; (2) avoidance of severe poisonous intermediates formation; (3) high current efficiency; (4) high stability against catalyst poison and long longevity; (5) availability and low cost-effective of cathode material; (6) environment acceptable.

2.3.2 Cathodic potentials

The potential applied for an electrode reaction, not only controls the thermodynamic feasibility and extent of an electrochemical reaction, but also determines the reaction rate. The relation between applied potential and reaction rate could be seen from the Butler-Volmer equation (2.10), while the reaction rate can be further rearranged as described in eq.(2.13) when the cathodic reaction is an irreversible process; reaction rate increases exponentially with decreasing of cathodic potential under electron transfer reaction controls. When the cathodic potential is sufficiently negative, the reaction becomes mass transfer limitation.

Cathodic potential as significant parameter in dechlorination process was found that can determine the intermediate distributions during electrolysis. TCE, as an intermediate of electrochemical dechlorination of PCE at nickel cathode, was observed peaking at 20% and 10% of the initial PCE concentration with the applied potential at -1.0 V and -1.2 V, respectively. More negative potential apparently minimized the accumulation of potential toxic, chlorine-containing intermediates during electrolytic studies [28].

A silver electrode was used to reduce CT by Criddle and McCart [34]. The experiments further confirmed the hypothesis that the extent of hydrogenolysis is related with the potential applied. At -0.71 V (vs. SHE), 15% of chloroform and other dechlorinated compounds were formed with conversion of CT. whereas, the amount of CF accounted for 6% of CT transformation, concomitant with 75% formate production after shifting the potential to -0.93 V (vs. SHE).

Electrochemical reductive dechlorination of TCE and CF were carried out in a two apartment cell, where Ebonex ceramic sheet plated with platinum (Pt) or palladium (Pd) were used as working electrode, respectively [2]. The transformation of TCE and CF followed pseudo-first order with respect to target concentrations at constant pH and cathode range from -0.3 V to -1.4 V. Area-specific first order rates remained constant at initial concentration of 1.0 μM and 1.0 mM. TCE and CF reduction kinetics were limited by mass transport to the cathode surface when the applied potential shifted to more negative than -1.4 V. The current efficiency for TCE and CF reduction decreased with the cathodic potential shift to negative direction, which was presumed to be the mass transfer limit, but not the reduction of water.

Durante et al. [7,8] conducted the electrolytic investigation of polychloromethanes (PCMs) at both GC and Ag electrode in DMF solution. Cyclic voltammetry of PCMs presented distinct reduction behaviors which were dependent on the species of compounds and nature of cathode materials. The research showed that electrochemical reduction of PCMs could be selectively retained at determined reaction stage by controlling the applied potential conveniently. Since the successive reduction of PCMs required increasing negative potentials, it provides significant information for the synthesis of less chlorinated or non-chlorinated methanes.

Electrochemical reduction rates of TCE at boron-doped diamond (BDD) cathode as functions of cathodic potentials were investigated by Mishra et al. [29]. The data indicated that there were two distinct electron transfer coefficients for TCE reduction at different cathodic potentials. At potential between -0.45 V and -0.95 V, $\alpha = 0.102 \pm 0.006$，whereas, $\alpha = 0.017 \pm 0.003$ at potential negative than -0.95 V. One possible explanation for this may be due to the transfer of rate-determining step at potential more negative than -0.95 V; another possibility was presumed to be that the number of activated sites at BDD surface increase with decreasing of cathodic potential, since the decreasing of cathodic potential not only enhances the reaction rate at each activated site, but also increases the number of reactive sites.

2.3.3 Solvent chemistry

Protonation or hydrogen extraction is required to achieve complete hydrodechlorination reaction for chlorinated compounds. While under aqueous conditions, the source of proton may come from water molecules and hydrogen ions. Therefore, solvent pH may have effect on the dechlorination process. The role of atomic hydrogen towards the dechlorination of chloroethylenes at iron electrode was explored by using Tafel analysis and electrochemical impedance spectroscopy at different pH conditions [35]. Comparison of iron corrosion rates with those for TCE removal showed that TCE reduction was almost exclusively via atomic hydrogen reduction at low pH conditions, while both direct electron transfer and indirect reduction via atomic hydrogen took place at neutral pH conditions. In contrast, PCE reduction followed direct electron transfer over the pH range both at acidic and neutral pH conditions. Besides, the relative differences of reaction rates between TCE and PCE at iron electrode were dependent on the contributions of atomic hydrogen during the reduction process, which were controlled by pH values and chlorinated substrate concentrations in the system.

The present ions in solution were found that may have effects on the dechlorination efficiency by influencing the catalyst activity. As known, chlorine ion and sulfate are common ions in groundwater. The effect of hydrogen ions, chlorine ions and sulfate on the dechlorination efficiency of TCE and CF at Pt- and Pd-modified Ebonex ceramic electrode had been investigated by Chen et al. [2]. Reduction rates of TCE and CF increased with hydrogen ion concentrations at a pH range from 2 to 7. After several repetitive experiments and external addition of chlorine ions into the system, chlorine ion was found that didn't essentially affect the dechlorination activities of Pt- and Pd-coated Ebonex. Whereas, in the presence of sulfate, declining of reaction rates were observed at Pd-coated Ebonex electrode involved in both the TCE and CF sequential reduction experiments. For instance, the half life of CF was 20 min for a newly prepared Pd modified electrode; while its activity for CF reduction was totally lost after five repetitive experiments. However, Pt-coated electrode behaved a resistance character against sulfate poison in the study.

Solvent ORP (Oxidation reduction potential) may also influence on the dechlorination process. Significantly high dechlorination efficiency (up to 99%) of trichloroethylene was achieved by Mao et al. [36], when used iron and foam copper as anode and cathode, respectively. The cast role of Fe anode was found to generate ferrous species in the medium, which could regulate the electrolyte to reducing conditions (low OPR) and favor the occurrence of TCE dechlorination reaction. The main reduction products of TCE were ethylene and ethane, the distributions of which depended on the ORP values as well as the applied current density to the system.

Scialdone et al. [12] investigated the electrochemical reduction behaviors of some chlorinated aliphatic compounds at Ag electrode in aqueous and organic solvents (acetonitrile and DMF), respectively. It was observed that Ag exhibits a remarkable catalytic effect towards the reduction of investigated chlorinated substrates in water medium, evidently higher than those in aprotic solvent, such as in DMF and acetonitrile. The remarkable electrocatalytic effect of Ag in aqueous was attributed to the role of ion solvation which is more facile for the reduction in water than those in aprotic solvents.

Electrochemical reductive cleavages of polychloromethanes were carried out by Isse et al. [7,8], at GC and Ag electrode in DMF solution in the absence and presence of proton donor, respectively. The dechlorination mechanism of polychloromethanes (PCMs) was found dependent on both nature of cathode materials and proton availability in the medium. In pure aprotic solvent, reduction of PCMs follows two competitive reaction pathways: one is sequential hydrodechlorination mechanism, while the other is reductive Cl^- elimination by carbene route. Whereas, sequential hydrodechlorination became the exclusive reaction route if external strong proton donor was added into the solvent. Besides, the presence of proton donor could evidently enhance the production of methane by inhibiting the occurrence of carbene reaction at both GC and Ag electrode.

2.3.4 Fabrication of electrochemical reactor

As known, electrode reaction takes place at the interface of electrode surface and ion conducting medium (electrolyte). The heterogeneous nature of electrochemical reaction implies that this process may suffer from mass transfer limitations and the size of specific electrode area problems. A well designed electrochemical reactor can accelerate the mass transport from the bulk solution to electrode surface, which could further increase the kinetic reaction rate of reaction and reduce the energy consumption during electrolysis process [37,38]. Therefore, the fabrications of electrochemical reactor as a significant parameter for the degrading of target pollutant from system have been extensively studied in recent years [13,37-40].

Packed-bed electrochemical reactors are widely used for commercial practice in the field of metal removing from wastewater and electrowinning. This type of reactor is suitable for situations with low reaction rates and low limiting current densities [38].

A continuous flow reactor with Cu cathode and carbon cloth anode was designed by He et al. [39], to investigate the reductive dechlorination of CT. The reactor was comprised of a foam Cu cathode and a downstream carbon cloth anode framed with a flow-through configuration. A mathematic model was created by combination intrinsic kinetic and mass transfer limit to simulate the reactor performance. The model and experimental results all indicated that CT conversion along the length of cathode surface was evidently affected by solution conductivity. By comparison the CT conversion results in both high solution conductivity (2.7 S•m^{-1}) and low conductivity (0.067 S•m^{-1}), it showed CT conversion was uniform through the whole reactor at high conductivity, while the CT conversion only took place at the last 25% of the cathode at the same potentials for low conductivity solution. Latter, the same group [40] improved the constructions of electrochemical reactor and desired a new novel cylindrical reactor for CT dechlorination, which was comprised of a cylindrical porous Cu cathode with a concentric carbon-cloth anode wrapped around it. The results indicated that the reductive dechlorination of carbon tetrachloride could achieve a high reaction rate, even in low conductivity solutions, 80% of CT conversion were obtained with a residence time of 10 min at -0.40 V (vs. SHE). The model and experiment observations all demonstrated the entire of cathode surface was activated during the reduction of CT under both low (0.06 S•m^{-1}) and high (0.68 S•m^{-1}) solution conductivity conditions.

Sonoyama et al. [13] designed a flow electrolysis reactor with a column type metal-impregnated carbon fiber as cathode (CFE), to investigate the removal of chloroform, PCE, TCE, 1,1,1-TCA, 1,1,2-TCA, dichloromethane and 1,2-DCA from tap water. Results showed that chloroform could be successfully removed from the system, concomitant with methane as the main product when use Ag- and Zn- impregnated CFE electrode. At a flow rate of 1 mL•min^{-1}, the current efficiency towards the abatement of chloroform could almost reach to 100%, even in the solution without supporting electrolyte. Likewise, PCE, TCE, 1,1,1-TCA and 1,1,2-TCA were also removed at Ag impregnated CFE electrode with almost 100% current efficiency, while dichloromethane and 1,2-DCA were recalcitrant to the electrochemical decomposition in this study.

2.3.5 Molecular structure of chlorinated compounds

The dechlorination mechanisms of successive expulsion chlorine ions from chlorinated aliphatic compounds were investigated by different groups [7,18,23,27,41,42], in which cyclic voltammetry as the main tool was used to investigate the reaction kinetics and reduction mechanisms of chlorinated hydrocarbons at different cathodes. Results indicated the removal of chlorine ions from Cl-VOCs is strongly dependent on the molecular structures.

Rondinini et al.[41] revealed that molecular structures play a key role on the electrocatalytic reduction of organic halides at Ag electrode, where an organometallic complex was presumed to form by strong specific interaction between Ag and halide ion.

The ease of dechlorination of polychloromethanes at GC electrode was investigated in DMF solution, as expected, it presented an order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ [7,42]. It should be noted that similar reduction sequence was also observed at Ag electrode except the methyl chloride, which was found more readily reduced than methylene chloride due to the catalyst character of Ag. In contrast to GC, cyclic voltammetry of carbon tetrachloride at Ag validated the lost of methyl chloride by only displaying three successive reduction peaks.

Savéant et al. [18] investigated the reduction mechanisms of chlorinated aliphatic compounds at GC electrode in DMF solution by using cyclic voltammetry methods. For the reduction of polychloromethanes, it presents a sequential hydrodechlorination mechanism. At each chlorine elimination step, the reaction involves an electron transfer concerted with C-Cl bond cleavage, accompanying with the formation of ensuing radical. Followed by an immediate electron transfer to the radical, it takes place at more positive potential with respect to the first electron transfer occurring. The formed carbanion is readily to be protonated by any weak proton donor existing in the medium, concomitant with less chlorinated hydrocarbon formation, which follows the same reduction route till obtaining complete dechlorination product. In the case of α,β-polychloroethanes, likewise, the first step is a concerted dissociated electron transfer and a second electron transfer immediately leads to the formation of carbanion, the same mechanism like polychloromethanes, whereas, the carbanion are more preferential to expel another chlorine ion with corresponding olefin generation than to be protonated to form the hydrogenolysis product. It follows the reductive α,β-elimination mechanism for the reduction of α,β-polychloroethanes. While for the case of α,β-polychloroethylenes, it conforms to reductive α,β-elimination mechanism, too, with the corresponding formation of alkynes. Whereas, different with the one in polychloroethanes, the first electron transfer to α,β-polychloroethylenes follows stepwise mechanism, where electron transfer and C-Cl bond breaking takes place stepwisely.

Li et al. [27] investigated the electrochemical reduction efficiencies of TCE and CT at iron and iron-palladium electrode in dilute aqueous solution, respectively. By comparisons amperometrically measured current efficiencies with those measured in flow-through reactors, together with the weak effects of electrode potential on TCE reaction rates, indicated the principal pathway for TCE dechlorination was indirect reduction, in which atomic hydrogen was involved as reductive reagent, whereas, similar measures indicated the primary reduction route for CT followed direct electron transfer. The following research of this group [1] on the rate constants of TCE and CT dechlorination as function of electrode potential over a temperature range from 2 to 42 ℃, revealed that the rate-limiting step for CT reduction was out-sphere electron transfer step, in contrast to CT, the transfer efficient for TCE was temperature dependent, which indicated the reduction of TCE was controlled by chemical dependent factors and not exclusively by the rate of electron transfer.

Even for Isomers, they may also undergo distinct reductive dechlorination mechanisms in the same reduction conditions. Although the reduction product is the same, cis-2,3-dichloroacrylnitrile was found to be dechlorinated in a sequential hydrodechlorination path to acrylonitrile, whereas the reduction of trans-2,3-dichloroacrylnitrile follows a reductive α,β-elimination process with propiolonitrile as intermediate, followed by reduced to acrylonitrile by accepting another two electron transfer [23].

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Chapter 3 Electrocatalytic properties of transition metals towards reductive dechlorination of polychloroethanes

Abstract

Chlorinated volatile organic compounds (VOCs) such as polychloromethanes and polychloroethanes (PCEs) are among the most ubiquitous pollutants in environment. Reductive electrochemical dechlorination at catalytic cathodes is one of most promising methods for the abatement of these pollutants. In this study, electrochemistry behaviors of several polychloroethanes have been investigated in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at Ag, Au, Pd, Pt, Cu, Fe, Ni, Pb, Zn and glassy carbon (GC). GC is known with its negligible catalytic properties and used as a reference system to evaluate the electrocatalytic activities of transition metals at here. The electrocatalytic activities of all investigated transition metals are remarkably influenced by the nature of electrode material and the chemical molecule structures. Three catalytic ranks are divided based on their catalytic abilities towards polychloroethanes reduction. Ag, Cu, Au exhibit the most powerful electrocatalytic activities, followed by Pd, Pt and Ni electrode, whereas, Fe, Pb and Zn present less significant catalytic effect. The electrochemical activities of all investigated polychloroethanes follow the order: 1,1-DCA < 1,1,1-TCA < 1,2-DCA < HCA < 1,1,2,2-TeCA < 1,1,2-TCA < 1,1,1,2-TeCA. Based on the voltammetric studies of all PCEs, the reduction mechanism is shown to be strongly dependent on the structure of PCEs. Geminal PCEs follows the sequential hydrodechlorination mechanism, in which one chlorine atom is lost with successive hydrogenation occurrence at one reduction step until completely dechlorination product ethane are formed. In contrast, vicinal PCEs undergoes reductive α,β-elimination mechanism by expelling two chlorine ions at one single step, leading to the corresponding (Chloro-)olefin formation, which could be further reduced at more negative potentials.

3.1 Introduction

Groundwater contamination becomes a major worldwide challenge nowadays, which recently attracts tremendous attention of the worldwide. Chlorinated volatile organic compounds (VOCs) are among the most ubiquitous environment pollutants owing to their widespread use as solvents and raw materials in industrial application, and their poor biodegradability [1]. However, these compounds are also among the most toxic, some of them even being suspected as carcinogenic pollutants, and are recalcitrant to the common remediation technologies, leading to long-lasting dangerous to human being. Therefore, some of them have been listed as the priority controllable pollutants by China, U.S. Environment Protection Agency (EPA) and European Union [2,3,4].

Much effort has been devoted to develop efficient abatement techniques for the removal of chlorinated compounds based on physical, chemical, as well as biological methods over the last decades. These include adsorption by activated carbon, air stripping, bio-degradation under aerobic [5,6] or anaerobic conditions [7,8], photocatalytic degradation [7], chemical reductions by zero valent metals or bimetals [10-12], electrochemical anodic oxidation [13,14]. Recently, reductive destruction technology towards the treatment of chlorinated compounds, in particular, the electrochemical reduction methods as a promising approach has attracted numerous attentions on the abatement of chlorinated hydrocarbons, due to its specific characters of better environmental compatibility, controllable reaction kinetics, cathodic polarization against electrode passivation or corrosion, as well as working under mild conditions [14,15].

Electrochemical reduction of chlorinated VOCs has been widely investigated at various electrode materials in different media, including water, aprotic solvents and aqueous solvent mixtures [14-26], not only for the reasons of pollution remediation, but also from the standpoints of reduction mechanisms [18-21] and electrosynthesis [21-24]. These studies have revealed that reductive cleavage of chlorinated hydrocarbons is a quite complicated process influenced by different determinant factors. According to the researches, the nature of cathode materials plays crucial roles on dechlorination efficiency and overall reaction mechanisms of chlorinated compounds [19,20,26,27]. In particular, electrode materials with remarkable catalytic activities are required in order to reduce the high overpotential associated with the dissociative electron transfer to C-Cl bond and thus avoid the occurrence of hydrogen evolution reaction in water. Therefore, extensive studies have already been devoted to this important issue, investigating a number of metals and composite materials modified with metal catalysts [15-31]. Among the various metals investigated, Ag, Cu and Pd have been found to exhibit splendid electrocatalytic activities toward the abatement of chlorinated VOCs, with remarkable positive shifts of peak potentials and high current efficiencies [11, 9,28-31].

The reduction mechanism is also affected by the solvent and proton availability in the reaction medium. According to our own research [20,21], electrochemical dechlorination of poly-chloromethanes takes place through two different reduction routes: sequential hydrodechlorination leading to methane through successive elimination of chlorine ions and being protonated, and a carbene route leading to the same final product. The first mechanism is favored in the presence of strong proton donors, whereas the second one dominates in the dry aprotic solvent, such as DMF. Another dechlorination route involving the direct reduction by atomic hydrogen, produced at the electrode surface by electrolysis of water, has been proposed by Li and Farrell [11,32] for the dechlorination of trichloroethylene (TCE) at iron electrode in aqueous.

Chemical structures are also found to have effect on the dechlorination mechanisms. Rondinini [33] revealed that molecular structures play a key role on the electrocatalytic reduction of organic halides at Ag electrode, where an organometallic complex is presumed to form by strong specific interaction with halide ion. The ease of elimination chlorine ion from polychloroethanes at GC electrode follows the order [20-21,34]: CCl_4 > $CHCl_3$ > CH_2Cl_2 > CH_3Cl. Therefore, four successive reduction waves for carbon tetrachloride reduction appear at GC electrode. The distinct peak locations for polychloromethanes were presumed to stem primarily from the difference in dissociative standard potentials. Farell et al [11] adopted iron as cathode, revealed that the reduction of carbon tetrachloride and tetrachloroethylene (PCE) occurred primarily through direct electron transfers in aqueous solution, while the dechlorination of trichloroethylene took place under the participation of atomic hydrogen by indirect reduction exclusively.

Although various of electrode materials have been investigated for the activation of carbon-halogen bonds, a systematic study of electrocatalytic properties of metal electrodes on the reductive dehalogenation of polychloroethanes (PCEs, $C_2H_{6-x}Cl_x$; x =1-6) is still missing.

A comprehensive electrochemical dechlorination mechanism of PCEs hasn't fully addressed so far. It's known that reduction of polychloromethanes undergoes two different reduction paths dependent on the proton availability in the medium. It's wondering whether polychloroethanes follow the same dechlorination routes like PCMs, due to the analogous but not exactly the same structure or not. In addition, the mechanism of dissociate electron transfer to C-Cl bond of polychloroethanes are also still not fully interpreted. Herein, we hope to supply several hints on the aforementioned questions in this chapter, so as to comprehensive understand the dechlorination mechanisms of chlorinated aliphatic compounds, and provide instructions for the potential application of this technology to control the contaminations by these compounds both in groundwater and soil sites.

3.2 Experimental and methods

3.2.1 Materials and chemicals

Dimethylformamide (DMF) was treated in the presence of anhydrous Na_2CO_4 for several days. After double distillations at lower pressure under N_2 conditions, DMF was then stored in a brown bottle under the protection of Argon. Tetrapropylammonium tetrafluoroborate ($C_{12}H_{28}BF_4N$, $TPABF_4$, Fluka) was recrystallized twice in ethanol and dried in a vacuum oven at 70 ℃ for at least two days. 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), hexachloroethane (HCA), 1,1-dichloroethylene (1,1-DCE), 1,2-dichloroethylene (1,2-DCE), tetrachloroethylene (PCE), chloroethylene were purchased from Sigma-Aldrich and used directly as received.

3.2.2 Experiment instrumentation

Electrochemical measurements were performed on a computer controlled EG&G PARC Model 273 potentiostat/galvanostat. All experiments were conducted at 20 ℃ in a three electrode system with GC, Pd, Ag, Cu, Au, Pt, Fe, Ni, Pb, or Zn disk as working electrode, a Pt wire as counter electrode and Ag/AgCl/ Me_4NCl(sat) in DMF + Acetonitrile (3:1,V/V) solution as reference electrode, respectively. The reference electrode was calibrated at the end of each experiment against the ferricenium/ferrocene couple ($E_{Fc+/Fc}$ = 0.475 V vs SCE in

DMF), which allowed conversion of all potentials to saturated calomelelectrode (SCE) scales. To be noted that all the potential values in this thesis are calibrated to SCE except specialization.

The working electrode in this research were disks from 2 mm diameter metal wires (Pd, Ag, Cu, Au, Pt, Fe, Ni, Pb, Zn. Alfa Aesar ≥ 99.99%) or from a 3 mm diameter GC rod (Tokai, GC-20), which were always polished to a mirror finish with silicon carbide papers by decreasing grain size (Struers, grit: 1000, 2400, 4000); followed by diamond paste (3-, 1-, 0.25-μm particle size). After each polishing step, the electrodes were always cleaned in ethanol in an ultrasonic bath for about 5 min. the electrodes were constructed as previous described [20].

3.2.3 Cyclic voltammetry experiments

Voltammetric experiments were performed in a thermostated undivided cell with 0.1 M $TPABF_4$ as supporting electrolyte and 2 $mmol\cdot L^{-1}$of chlorinated substrate in DMF. The system was operated under Argon flow conditions all through the research. Cyclic voltammograms were recorded at different scan rates at each electrode, respectively.

Electrolytic experiments were carried out in a sealed thermostated divided cell, with Ag/AgCl/ Me_4NCl(sat) as reference electrode, Pt as counter electrode, using Ag plate, or GC plate as working electrode, respectively. During electrolysis process, samples of gas and solution phase were withdrawn from the sealed electrolytic cell for analysis by GC or GC-MS periodically.

3.2.4 Analysis

The electrolysis products in the gas phase were withdrawn by a gas syringe, followed by directly injecting into a HP 6890 system gas chromatograph equipped with a HP Plot Q 30 m ×0.537 mm× 0.40 mm capillary column (Agilent Technologies, USA) and a flame ionization detector (FID). The injector was equipped with a 0.75 mm i.d. liner and was operated in a split mode (15:1). The oven temperature was set at 60 ℃ for 2 min, then increased to 240℃ at a rate of 30℃$\cdot min^{-1}$ and held for 2 min. The injector and the detector were set at 150 and 250 ℃, respectively, and the carrier gas (He) flow was 4.4 $mL\cdot min^{-1}$. Identification and quantification of the products were based on comparison with authentic samples and calibration curves, respectively.

Solution phase products were analyzed by withdrawing 1 μL of sample and subsequently injecting into the column of GC-MS for identification and quantification analysis. The sample analysis were performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector (MS) and a DB-5 ms 30 m×0.25 mm×0.25 mmcapillary column (Agilent Technologies, USA). The oven temperature was set at 32 ℃ and held for 4 min, then increased to 40 ℃ at the rate of 10 ℃·min^{-1} holding for 1 min. Helium with a flow rate of 0.5 mL·min^{-1} was used as a carrier gas. Authentic compounds were used for the identification and quantification of the products based on a calibration curve prepared before electrolysis.

3.3 Results and discussion

3.3.1 Cyclic voltammetries of polychloroethanes

Cyclic voltammetry is the most widely used technology in electrochemical reactions, which has the ability to rapidly provide considerable information on the thermodynamic of redox process and the kinetics of heterogeneous electron transfer reactions and on coupled chemical reactions [35]. Voltammetric reduction experiments of polychloroethanes (PCEs) were carried out at 10 different electrodes in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at scan rates from 0.02 Vs^{-1} to 10 Vs^{-1}, for the sake of obtaining the rapid locations of peak potentials of these electroactive species, and investigating the reaction thermokinetics and mechanisms of theses redox processes.

Representative cyclic voltammograms of all investigated PCEs are shown in Fig. 3.1 for GC and Ag as an example of a catalytic electrode, whereas data on the first peak of all compounds are collected in Table 3.1. All compounds exhibit irreversible reduction peaks on all electrodes, but the number of peaks and their location strongly depend on PCE molecular structure and electrode type, respectively. Regardless the nature of electrode, all reduction peaks of PCEs shift to more negative direction upon raising the scan rate, which confirm the irreversible reduction process.

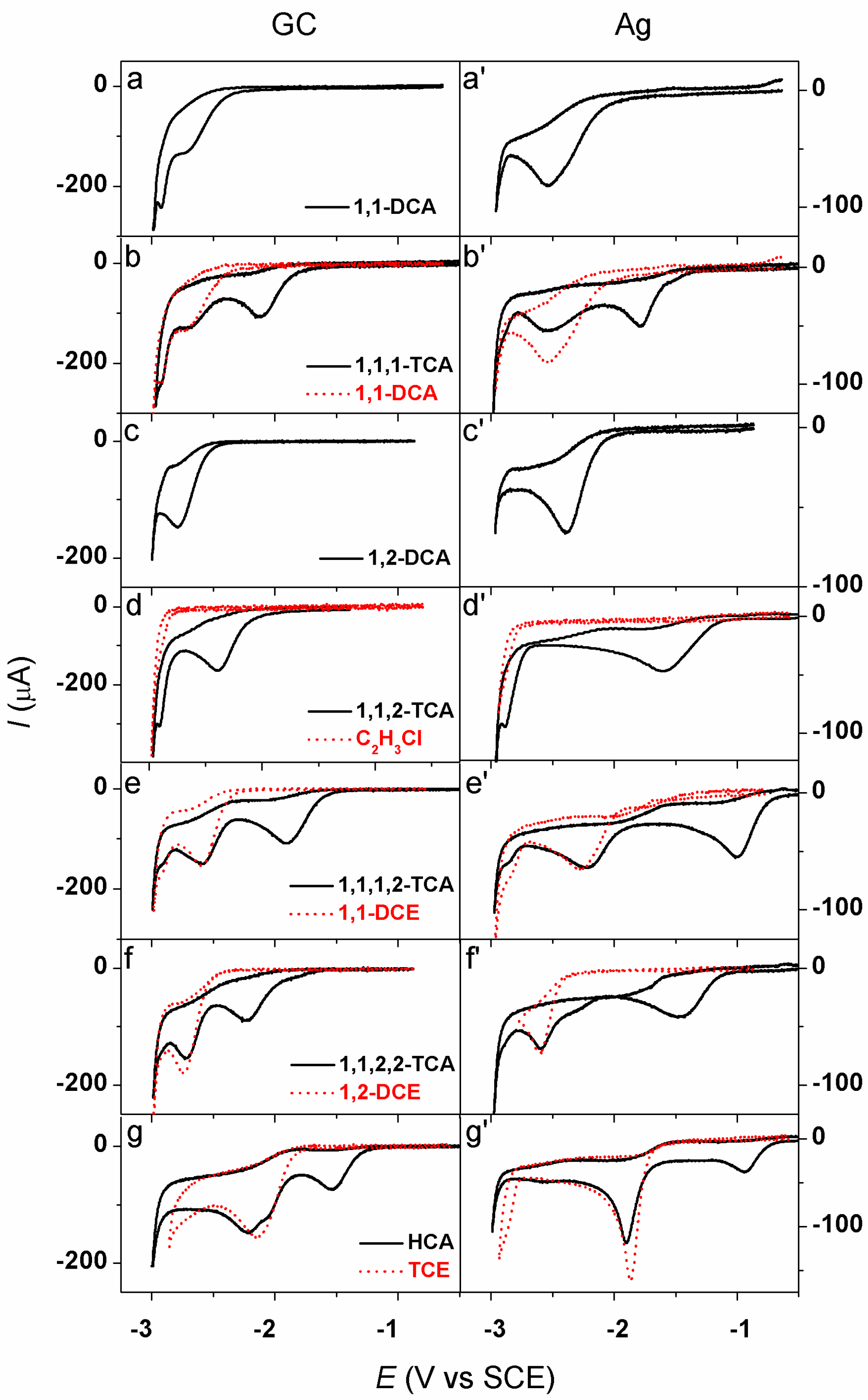


Fig. 3.1. Cyclic voltammetry of polychloroethanes and polychloroethylenes (2 mM) recorded at GC and Ag electrodes in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at $\nu = 0.2$ V·s^{-1}. Substrates in the right-hand side are the same as those indicated in the left-hand side.

It's known that the reductive cleavage of aliphatic chlorides follow a concerted mechanism, in which electron transfer and bond breaking occur in one single step with radical compound and chlorine ion formation. Since the radical formed is often readily reduced by accepting another electron transfer than the parent molecule, accordingly, an overall 2 e^- irreversible reduction process is observed. Based on this reduction mechanism, the reactions underlying the first reduction peak of any PCEs may be written as follows:

$$C_2H_{6-x}Cl_x + e^- \longrightarrow {}^{\bullet}C_2H_{6-x}Cl_{x-1} + Cl^- \qquad (3.1)$$

$$^{\bullet}C_2H_{6-x}Cl_{x-1} + e^- \longrightarrow {}^{-}C_2H_{6-x}Cl_{x-1} \qquad (3.2)$$

Owing to the basic character of carbanion, it could be protonated by any weak acid present in the system following the hydrodechlorination mechanism. Alternatively, it also may lose another chlorine ion attached on the same carbon to give carbene. For vicinal-PCEs, a third possibility may take place, where chlorine ion is eliminated from the adjacent carbon by forming the corresponding olefin. Since different reduction products may be formed, the overall electrochemistry behavior of each PCEs thus depends on the fate of its carbanion $^{-}C_2H_{6-x}Cl_{x-1}$. A first indication of the electrochemical reduction mechanism can be concluded by careful examination of the voltammetric pattern of each PCEs and comparing it with that of the possible reduction product.

Table 3.1. Voltammetric data for the reduction of polychloroethanes (2 mM) in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at different electrodes

electrode		1,1-DCA	1,2-DCA	1,1,1-TCA	1,1,2-TCA	1,1,1,2-TeCA	1,1,2,2-TeCA	HCA
GC	E_p^a	-2.74	-2.79	-2.13	-2.42	-1.91	-2.23	-1.54
	α^b	0.28	0.29	0.32	0.28	0.22	0.28	0.27
	ΔE_p^c	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cu	E_p^a	-2.57	-2.41	-1.87	-1.74	-1.02	-1.51	-0.93
	α^b	0.33	0.32	0.21	0.18	0.38	0.22	0.33
	ΔE_p^c	0.17	0.38	0.26	0.68	0.89	0.72	0.61
Ag	E_p^a	-2.53	-2.39	-1.75	-1.63	-1.0	-1.52	-0.94
	α^b	0.29	0.32	0.21	0.21	0.28	0.23	0.35
	ΔE_p^c	0.21	0.40	0.39	0.79	0.91	0.71	0.60

Au	E_p[a]	-2.50	-2.33	-1.93	-1.67	-1.10	-1.48	-0.96
	α[b]	0.35	0.31	0.14	0.23	0.23	0.20	0.10
	ΔE_p[c]	0.24	0.46	0.20	0.75	0.81	0.75	0.58
Ni	E_p[a]		-2.50	-1.74	-1.93	-1.41	-1.71	-1.15
	α[b]		0.23	0.15	0.11	0.28	0.25	0.12
	ΔE_p[c]		0.29	0.39	0.49	0.50	0.52	0.39
Pd	E_p[a]		-2.35	-1.81	-1.78	-1.12	-1.61	-1.13
	α[b]		0.36	0.17	0.23	0.26	0.25	0.15
	ΔE_p[c]		0.44	0.28	0.64	0.79	0.62	0.41
Pt	E_p[a]		-2.35	-1.78	-1.71	-1.16	-1.46	-1.05
	α[b]		0.27	0.23	0.20	0.26	0.25	0.17
	ΔE_p[c]		0.44	0.35	0.71	0.75	0.77	0.49
Fe	E_p[a]		-2.59	-1.98	-1.92	-1.46	-2.21	-1.26
	α[b]		0.28	0.23	0.21	0.24	0.17	0.11
	ΔE_p[c]		0.20	0.15	0.50	0.45	0.02	0.28
Zn	E_p[a]	-2.72	-2.53	-1.75	-2.08	-2.52	-2.02	-1.78
	α[b]	0.25	0.30	0.19	0.22	0.36	0.21	0.26
	ΔE_p[c]	0.02	0.26	0.38	0.34	0.39	0.21	-0.24
Pb	E_p[a]		-2.46		-2.11	-2.47	-1.77	-0.95
	α[b]		0.29		0.20	0.27	0.17	0.32
	ΔE_p[c]		0.33		0.31	0.44	0.46	0.39

[a] E_p (V vs SCE) measured for the first reduction peak at 0.2 Vs^{-1}.

[b] Electron transfer coefficient, calculated from $\partial E_p/\partial \log v = -1.151RT/F\alpha$.

[c] $\Delta E_p = E_{p1}^{M} - E_{p1}^{GC}$, where E_{p1}^{M} and E_{p1}^{GC} are the potentials of the first reduction peak measured at 0.2 Vs^{-1} at an electrode M and GC, respectively.

1,1-DCA exhibits two irreversible reduction peaks on GC electrode, whereas only one on Ag electrode (Fig. 3.1a and 3.1a′). The two peaks on GC can be attributed to the reduction of 1,1-DCA and chloroethane (CA), respectively. Hydrodechlorination takes place over the reduction of 1,1-DCA, which means that $^{-}C_2H_4Cl$ produced after the first electron transfer is mainly protonated to C_2H_5Cl, and then it is reduced at the second reduction peak. A similar reduction mechanism is reasonably presumed on catalytic electrodes, such as Ag. However, the absence of the second reduction peak in this case could be well explained that the reduction peak (E_p) of CA is more positive than that of 1,1-DCA, leading to the reduction process of CA being concealed correspondingly. Actually, this inversion reduction order on catalytic electrodes has also been observed on the reduction of polychloromethanes, where E_p (CH_3Cl) > E_p (CH_2Cl_2) [20,21].

Fig. 3.1b and 3.1b′ show cyclic voltammetry of 1,1,1-TCA on both GC and Ag. On both electrodes, the voltammetric pattern of 1,1,1-TCA, aside from the first reduction peak, coincides with that of 1,1-DCA, thus clearly showing that the reduction product of 1,1,1-TCA at the first peak is indeed 1,1-DCA, which are further decomposed at more negative potential following sequential hydrodechlorination mechanism till ethane as the final product produced.

Cyclic voltammetries of 1,2-DCA on both GC and Ag are reported in Fig. 3.1c and 3.1c′. In contrast to 1,1-DCA where two irreversible reduction waves appear on GC, only one single peak presents on both electrode. A careful examination of voltammetric responses of 1,2-DCA and CA will allow one to rule out the parent-daughter relationship between them, at least on GC. It’s likely that the leading path of decay for intermediate carbanion $^-CH_2CH_2Cl$ is eliminating the adjacent chlorine ion, resulting into the formation of ethylene.

Fig. 3.1d and 3.1d′ present the cyclic voltammograms of 1,1,2-TCA on GC and Ag, two successive irreversible reduction peaks appear on both electrodes . A carful comparison of these voltammetric responses with those of 1,1-DCA and 1,2-DCA, indicates that neither of these compounds is formed in the electrochemical reduction of 1,1,2-TCA process. Whereas, the second peak on both electrode is located in the region of chloroethylene reduction. It seems that also in this case intermediate carbanion$^-CHClCH_2Cl$ is more prone to eliminating adjacent chlorine ion to give olefin than being protonated to form DCA successively.

The cyclic voltammetric reduction of 1,1,1,2-TeCA and 1,1,2,2-TeCA are reported in Fig. 3.1e(e′) and Fig. 3.1f(f′), separately. It exhibits three and two irreversible reduction waves respectively. Similar examination of the voltammetric patterns of these two substrates lead to the conclusion that neither of them gets reduced to trichloroethane (1,1,1-TCA, 1,1,2-TCA) on GC or any catalytic metal electrode. Apart from the first reduction peak, the voltammetric pattern of 1,1,1,2-TeCA is compatible with that of 1,1-dichloroethylene (1,1-DCE). Likewise, the second peak of 1,1,2,2-TeCA coincides with that of 1,2-dichloroethylene (1,2-DCE). It once again confirms that vicinal-PCEs are readily to eliminate two adjacent chlorine ions after successive accepting two electron transfers, leading to the corresponding olefin formation.

The last one, hexachloroethane (HCA), cyclic voltammograms of which on GC and Ag are shown in fig. 3.1g and 3.1g′, respectively. It's pity that pentachloroethane is unavailable for comparison. However, stepwise hydrodechlorination can be easily ruled out because of the complete absence of characteristic reduction peak of trichloro- and dichloroethanes. By thorough comparison the voltammogram of HCA on GC and Ag with that of tetrachloroethylene (PCE), in particular on Ag, one can easily conclude that PCE is formed by electrochemical reduction of HCA. Two chlorine ions elimination from HCA by accepting two electrons ($2\ Cl^- - 2\ e^-$) is the main reduction mechanism at the first peak regardless of electrode types, which are in accordance with those of the other vicinal-PCEs.

To sum up, the voltammetric analysis of PCEs can divide these species into two classes: (i) geminal-PCEs, which mainly undergo sequential hydrodechlorination mechanism whereby reaction (3.1) and (3.2), followed by protonation, are critically repeated till ethane as the end product obtained; (ii) vicinal-PCEs, which follow the reductive α,β-elimination by losing two Cl^- upon two electron transfers, one at each carbon, to give olefin.

3.3.2 Electron transfer to PCEs

Electron transfer to PCMs and some of PCEs on GC electrode was found to follow concerted mechanism, where ET and bond breaking take place at one single step [20,36]. Herein, we also investigate electron transfer mechanisms to the investigated PCEs on GC and catalytic electrodes, to further unravel the ET to PCEs and examine the difference between non-catalytic and catalytic electrodes. Electron transfer coefficient, α, as an important electrochemical reaction parameter, can be used as a diagnostic criterion to determine ET mechanism. According to the expression of transfer coefficient resulted from the quadratic activation-driving force relationship and from the definition of intrinsic barrier [37]:

(3.3)

(3.4)

In which the bond breaking energy,, is in most cases much larger than the reorganization bond lengths and angles, . Accordingly, the transfer coefficient in the first case is much smaller than the second case, which significantly smaller than 0.5 for concerted dissociative electron transfer, in contrast with stepwise ET. This can be used as an indication to distinguish the two ET mechanisms.

The electron transfer coefficient of the first reduction peak of PCEs can be calculated from equation [19]

$$\frac{\partial E_{\mathrm{p}}}{\partial \log \upsilon} = -\frac{1.151RT}{\alpha F} \tag{3.5}$$

Representative figures of peak potential as function of logarithm scan rate for 1,1,1-TCA on GC and Ag are given in Fig. 3.2. The linearity relationship of peak potential upon raising scan rate confirms the irreversible character for the first reduction process. Electron transfer coefficients of 1,1,1-TCA on GC and Ag, namely are 0.32 and 0.21, which evidently imply that electron transfer to C-Cl bond of 1,1,1-TCA on both electrodes undergo concerted mechanisms. Likewise, all the transfer coefficients of the 7 PCEs at the first reduction peak on the 10 different electrode materials are gathered in Table 3.1. As shown in Table 3.1, all the values are smaller than 0.5, which is in accordance with the assumption that aliphatic chlorides follow concerted ET mechanism, no matter whatever types of electrode. Owing to the character that the split radical is readily reducible with respect to the parent molecule, an overall two-electron irreversible reduction wave is observed in all the reduction processes of PCEs.

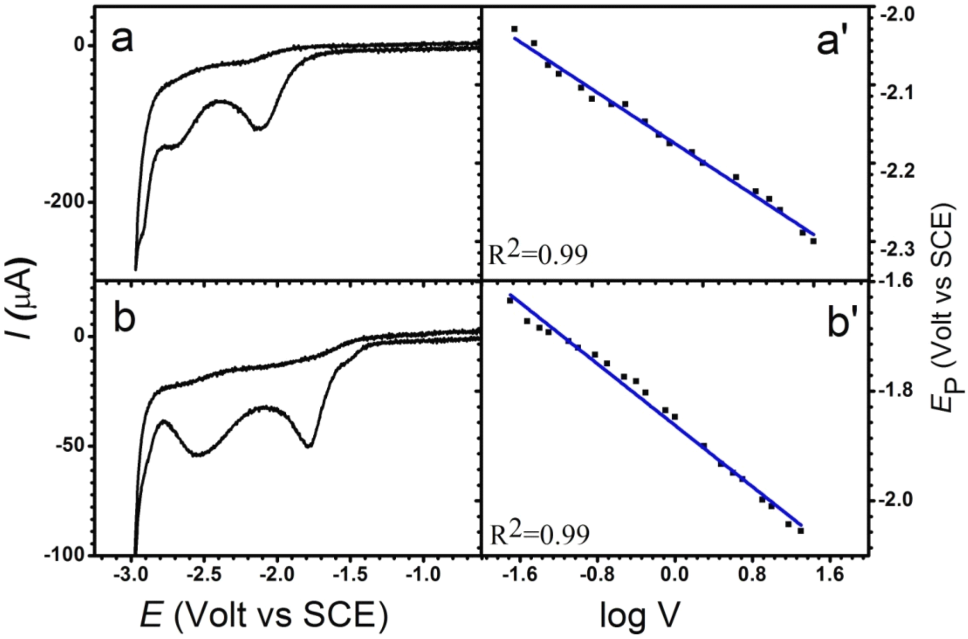


Fig. 3.2 Cyclic voltammetry of 1,1,1-TCA on GC (a) and Ag (b), and their peak potentials as function of logarithm scan rate, (a′) for GC, (b′) for Ag.

However, a close examination of the voltammetric data of PCEs on GC and Ag, we found the numbers of electron exchanged in the first reduction peak were lower than two, by calculating from equation [35,38]:

(3.6)

(3.7)

Besides, if the investigated substrate has more than one reduction waves, one would expect a series of successive equal height reduction peaks, since reduction of each PCEs to the less chlorinated ethanes or ethylenes intermediate require an overall two electron transfers. However, as shown in Fig. 3.1, in most cases, particularly for geminal-PCEs, the peak current of the first peak is higher than those of the successive peaks. All of these indicate that chemical reactions may involve in the electrochemical reduction process.

Some possible chemical reactions involved, which may play significant roles in the overall reduction process, are self-protonation where PCEs act as proton donor and decomposition of intermediate carbanion, $^{-}C_2H_{6-x}Cl_{x-1}$, by eliminating chlorine ion attached on the carbanion. The latter reaction leads to the formation of halocarbenes, which might give rise to other reactions, for instance, electron transfer from the electrode and carbene rearrangement with olefin formation. Taking 1,1,1-TCA as an example to interpret the aforementioned reactions.

$$H_3C\text{-}CCl_3 + e^- \longrightarrow {}^{\bullet}CCl_2\text{-}CH_3 + Cl^- \qquad (3.8)$$

$$^{\bullet}CCl_2\text{-}CH_3 + e^- \longrightarrow {}^{-}CCl_2\text{-}CH_3 \qquad (3.9)$$

$$^{-}CCl_2\text{-}CH_3 + H^+ \longrightarrow CHCl_2\text{-}CH_3 \qquad (3.10)$$

$$^{-}CCl_2\text{-}CH_3 + H_3C\text{-}CCl_3 \longrightarrow CHCl_2\text{-}CH_3 + {}^{-}CH_2\text{-}CCl_3 \qquad (3.11)$$

$$^{-}CH_2\text{-}CCl_3 \longrightarrow CH_2{=}CCl_2 + Cl^- \qquad (3.12)$$

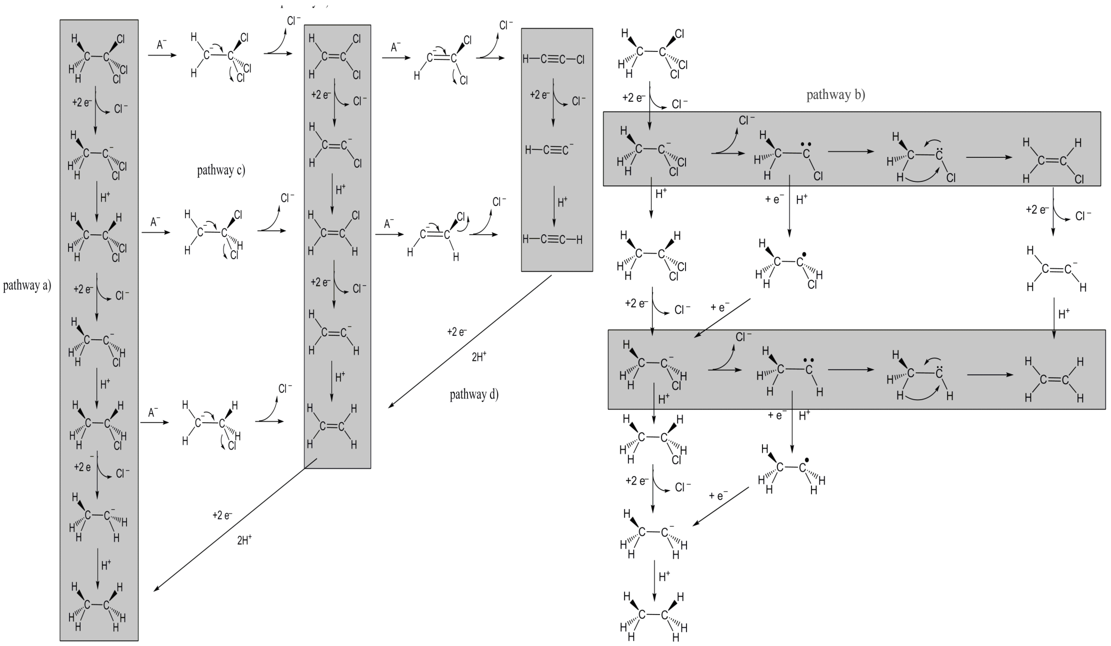
$$^{-}CCl_2\text{-}CH_3 \longrightarrow {:}CCl\text{-}CH_3 + Cl^- \qquad (3.13)$$

$${:}CCl\text{-}CH_3 \longrightarrow CH_2{=}CHCl \qquad (3.14)$$

$${:}CCl\text{-}CH_3 + e^- + H^+ \longrightarrow {}^{\bullet}CHCl\text{-}CH_3 \qquad (3.15)$$

$$^{\bullet}CHCl\text{-}CH_3 + e^- + H^+ \longrightarrow CH_2Cl\text{-}CH_3 \qquad (3.16)$$

As already stated before, the first reduction step of 1,1,1-TCA is a concerted dissociative ET to C-Cl bond yielding Cl^- and $^{\bullet}CCl_2\text{-}CH_3$ which is readily further reduced to $^{-}CCl_2\text{-}CH_3$. The fate of this carbanion is a little complex due to the aprotic character of solvent. In competition with occurring protonation reaction whereby hydrodechlorination product $CHCl_2\text{-}CH_3$ is formed (eq.3.10), $^{-}CCl_2\text{-}CH_3$ also can eliminate another chlorine ion with the reactive carbene ${:}CCl\text{-}CH_3$ formation (eq.3.13), which either give rise to chloroethylene by carbene rearrangement (eq.3.14), or may be reduced and protonated to $CH_2Cl\text{-}CH_3$ (eq.3.15-16), subsequently. In addition, the parent molecule can act as proton donor for its cathodic reduction product, $^{-}CCl_2\text{-}CH_3$, by losing one hydrogen in concomitant with $^{-}CH_2\text{-}CCl_3$ production, which can further give rise to 1,1-DCE through expelling the adjacent chlorine ion (eq.3.11-12). The effect of self-protonation is to subtract part of the starting molecule from electrochemical reduction, which results into the successive un-equal height reduction waves of 1,1,1-TCA, as well as leading to the reduction process less than 2 e^-/molecule. A comprehensive reduction mechanism of 1,1,1-TCA including chemical reactions are described in schem3.1.



Scheme 3.1. Electrochemical reduction mechanism of 1,1,1-trichloroethane.

Where reductive dechlorination of 1,1,1-TCA mainly undergo three competitive decomposition mechanisms, namely are sequential hydrodechlorination (path a)), the carbene route (path b)) and self-protonation (dehydrochlorination) pathway (path c)). The latter two mechanisms are primarily influenced by the proton donor availability in the medium. Actually, when acetic acid is added into the solution, all peaks in the voltammogram are indeed observed considerably increasing in our study, which will be discussed detailedly in the next two chapters. It appears that in the presence of excess acetic acid, protonation of intermediate carbanion is more preferential to self-protonation and carbene route.

As stated above, based on the voltammetric analysis, PCEs can be divided into two distinct species, geminal-PCEs and vicinal-PCEs. The reduction mechanism of 1,1,1-TCA has been discussed before, here we transfer our attention to investigate another type of compound, vicinal-PCEs. 1,1,1,2-TeCA is chosen as a representative of this type of compounds to conduct the comprehensive reduction analysis. Similar with 1,1,1-TCA, the first electron transfer to 1,1,1,2-TeCA triggers concerted dissociative ET mechanism, yielding Cl^- and $^\bullet CCl_2$-CH_2Cl (eq.3.17), the latter is readily reduced to form $^-CCl_2$-CH_2Cl (eq.3.18), whereas, in contrast to the resulting carbanion of 1,1,1-TCA being protonated by any proton donors in the medium, this carbanion is more prone to eliminating adjacent Cl^-, concomitant with 1,1-DCE formation (eq.3.19). According to the investigations on trichloroethylene

(TCE), tetrachloroethylene (PCE) and 1,2-dichloroethylene (1,2-DCE), the first stage of electrochemical reduction of them is under the kinetic control of outersphere ET reaction in case of a stepwise mechanism [36]. It could infer from this finding and thus lead to conclude that 1,1-DCE may follow the same ET transfer mechanism, where the first electron transfer-bond breaking goes through the intermediacy of π* anion radical, and then split to Cl^- and $^{\bullet}CCl{=}CH_2$ which is further reduced to $^{-}CCl{=}CH_2$ (eq.3.22-23). The fate of vinyl chloride carbanion in DMF might either to be protonated with chloroethylene formation (eq.3.24), or continue to expel another Cl^- accompanying with vinyl carbene production (eq.3.25). The formed chloroethylene by protonation reaction could be conversed to ethylene at more negative potential subsequently, while vinyl carbene could give rise to acetylene by carbene rearrangement (eq.3.26), or it may directly react with DMF to give CO [20].

$$Cl_3C\text{-}CClH_2 + e^- \longrightarrow {}^{\bullet}CCl_2\text{-}CClH_2 + Cl^- \tag{3.17}$$

$$^{\bullet}CCl_2\text{-}CClH_2 + e^- \longrightarrow {}^{-}CCl_2\text{-}CClH_2 \tag{3.18}$$

$$^{-}CCl_2\text{-}CClH_2 \longrightarrow CCl_2{=}CH_2 \tag{3.19}$$

$$Cl_3C\text{-}CClH_2 + B^- \longrightarrow {}^{-}CHCl\text{-}CCl_3 \tag{3.20}$$

$$^{-}CHCl\text{-}CCl_3 \longrightarrow CCl_2{=}CClH + Cl^- \tag{3.21}$$

$$CCl_2{=}CH_2 + e^- \longrightarrow {}^{\bullet}CCl{=}CH_2 + Cl^- \tag{3.22}$$

$$^{\bullet}CCl{=}CH_2 + e^- \longrightarrow {}^{-}CCl{=}CH_2 \tag{3.23}$$

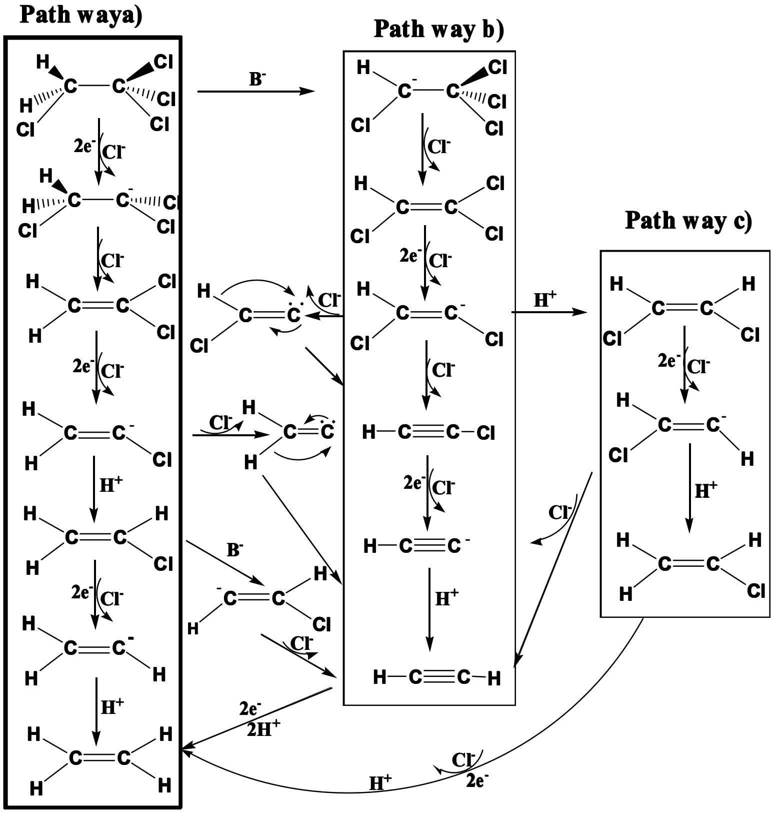
$$^{-}CCl{=}CH_2 + H^+ \longrightarrow CHCl{=}CH_2 \tag{3.24}$$

$$^{-}CCl{=}CH_2 \longrightarrow {:}C{=}CH_2 + Cl^- \tag{3.25}$$

$${:}C{=}CH_2 \longrightarrow CH{\equiv}CH \tag{3.26}$$

$$CHCl{=}CH_2 + 2e^- + H^+ \longrightarrow H_2C{=}CH_2 \tag{3.27}$$

A close examination of voltammograms of vicinal-PCEs, we find that the successive reduction peaks of 1,1,1,2-TeCA on all electrodes decline gradually. It will make sense if one considers the self-protonation reaction of parent molecule. 1,1,1,2-TeCA is partially subtract from formation of 1,1-DCE through participating in self-protonation reactions concomitant with TCE as reaction product (eq.3.20-21), while the further electrochemical reduction product of TCE is chloroacetylene rather than 1,1-DCE [36]; similarly, only fractional transformation of 1,1-DCE into chloroethylene owing to the influence of self-protonation, leading to the decline tendency of the successive reduction waves of 1,1,1,2-TeCA. A comprehensive reduction mechanism of 1,1,1,2-TeCA is presumed and reported in scheme 3.2.



Scheme 3.2. Electrochemical reduction mechanism of 1,1,1,2-tetrachloroethane.

3.3.3 Electrocatalytic activities of transition metals towards PCEs reduction

Since GC is known and widely used as an inert electrode and doesn't exhibit obviously catalytic effect on the electrochemical reduction process [39], therefore, it is used as a reference to measure the catalytic ability of different metal electrodes at here. The electrocatalytic activities of different electrodes were examined by using the positive shift of E_p with respect to GC as a measure of the ability of any electrode material, M, to catalyze ET to $C_2H_{6-x}Cl_x$. Thus, we report in Table 1 this positive shift, which is defined as $\Delta E_p = E_{p1}^{M} - E_{p1}^{GC}$, where E_{p1}^{M} and E_{p1}^{GC} are peak potentials of the first reduction peak of PCEs at M and GC, respectively.

Fig. 3.3 illustrates the catalytic effects of several transition metals towards polychloroethanes reduction. It appears that all the metals possess catalytic properties for the reductive cleavage of PCEs, which are in accordance with the previous researches that noble metals and other transition metals located at group ⅧB have been confirmed to possess excellent catalytic effect toward the electrochemical hydrodehalogenation process [15-33]. However, on the other side, the different values of ΔE_p in Fig. 3.3 and Table 3.1 also indicate the electrocatalytic activities of different metals are strongly dependent on their intrinsic nature and chemical structure of PCEs, in particular the number of Cl atoms in the molecule.

As shown in Fig. 3.1, the least activated PCE is 1,1-DCA. A reduction peak for this compound could be observed only on GC, Cu, Ag, Au and Zn electrodes; on all other electrodes the process occurs beyond the cathodic limit. We are therefore forced to exclude 1,1-DCA from the analysis of the electrocatalytic effect. The ten electrodes examined in this study can be divided into three groups according to their overall electrocatalytic properties. The first group is Cu, Ag and Au (group 11 elements). These metals show very good electrocatalytic activities with average ΔE_p values in the range from 0.28 V to 0.87 V. The second group is Ni, Pd and Pt (group 10 elements); the average ΔE_p values obtained on these metals are in the range from 0.34 V to 0.68 V. The last group Fe, Pb and Zn has discrete electrocatalytic properties, with a maximum ΔE_p not exceeding 0.5 V. In this ranking, when possible, we gathered the metals into groups of the periodic table and considered the overall electrocatalytic property of each group. If single metals are considered there may be some overlaps albeit in general the above general ranking is obeyed. For example, Pt shows slightly better electrocatalytic properties than Cu for some PCEs.

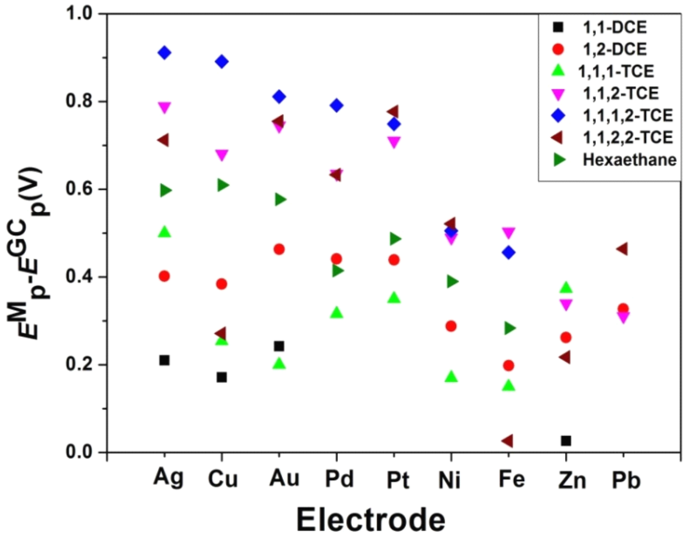


Fig. 3.3 Catalytic activities of transition metals towards polychloroethanes reduction in DMF+ 0.1 M $\mathrm{TPABF_4}$, measured at 0.2 $\mathrm{V{\cdot}s^{-1}}$.

Regarding the effect of molecular structure, a general trend of ΔE_p, based on group 11 and group 10 elements, which show the best and most regular electrocatalytic properties, may be as follows: 1,1-DCA < 1,1,1-TCA < 1,2-DCA < HCA < 1,1,2,2-TeCA < 1,1,2-TCA < 1,1,1,2-TeCA. Some conclusions can be drawn from this trend. First, the electrocatalytic effect increases with increasing number of Cl atoms bound to the same carbon center (compare 1,1-DCA with 1,1,1-TCA or 1,2-DCA with 1,1,2-TCA and 1,1,1,2-TeCA). Both the standard reduction potential E^0 and the intrinsic barrier of the reduction process depend on the C-Cl bond dissociation energy (BDE) which decreases with increasing number of Cl atoms [20]. Second, addition of a Cl atom to the second carbon may or may not be beneficial. The catalytic effect increases on passing from 1,1-DCA to 1,1,2-TCA, but remains essentially the same or even decreases at some electrodes if one compares the latter with 1,1,2,2-TeCA. A similar effect is evident if one compares 1,1,1-TCA with 1,1,1,2-TeCA and HCA. This effect is probably related to the interactions between the metal and the substrate. We have previously proposed for Ag a reduction mechanism starting with adsorbed species and evolving through a bound transition state in which both the C and Cl atoms are involved [19,40]. More recently, the role of adsorption of RCl, $R^\bullet$ and Cl^- has been demonstrated for the electrocatalytic reduction benzyl chloride at Ag [41]. As expected, the presence of one Cl atom at the vicinal carbon produces an activating effect, possibly through decrease of BDE of the breaking bond and/or stabilization of the ensuing radical. We may speculate that the deleterious effect of a second or a third Cl atom on the vicinal carbon arises from increased steric hindrance around the C-Cl bond to be reduced, which weakens the interaction of the substrate with the metal.

3.3.4 Thermodynamics of ET to PCEs

At last, we want to discuss the thermodynamics of reduction of PCEs. Cyclic voltammetry is among the most widely used technique in electrochemistry, which can provide significant information on thermodynamics of electron transfer reactions. In the cyclic voltammetry of PCEs, the current-potential curves are totally irreversible regardless of the scan rates, because of the irreversible character of ET/bond-breaking process. Dissociative electron transfer to PCEs, followed by immediate reduction of $R^\bullet$, accordingly, giving rise to a two-electron reduction wave, which is in line with the observation that there is neither splitting of the two-electron reduction wave, nor the change of numbers apparent electron transfer exchanged. Therefore, the first electron transfer reaction is the rate-determining step, which allows one to derive the kinetic characteristic from the CV, ignoring the second electron transfer step aside from doubling the peak current [36].

The thermodynamics of ET to PCEs may be analyzed by the classical dissociative electron transfer theory [36,37,43], which describes the relationship between activation free energy, $\Delta G^{\neq}$, and standard free energy, according to:

(3.28)

Where is a quadratic function of the free energy reaction; , the intrinsic barrier free energy, is the sum of two contributions, is the bond dissociation energy of C-Cl in PCEs, and stands for the solvent reorganization energy. This theory assumes that the repulsive interaction of the products formed after ET is the same as the dissociative component of the reactant Morse curve. To apply this theory, a series of values of $\Delta G^{\neq}$ and are demanded, which can be calculated from the experimental data of CV. The experiment values of activation free energy at the peak () is obtained from:

(3.29)

In which, is the scan rate and D represents diffusion coefficient (taking the value of 10^{-5} $cm^2 \cdot s^{-1}$ in average), is the transfer coefficient which can be obtained from the peak width (eq.3.7), is collision number at the electrode surface, and M stands for molecule mass. All activation energy data of PCEs on GC (non-catalytic electrode) and Ag (catalytic electrode) are gathered in Table 3.2. It should be pointed that the energies are in electronvolts and potentials are in volts throughout this chapter. While the standard free energy for the reaction leading to complete dissociation of C-Cl bond of PCEs can be acquired by:

(3.30)

In which the values of standard reduction potential, , for reductive cleavage of PCEs can be derived from:

(3.31)

Where, is the bond dissociation energy of starting molecule, is the standard bond dissociation entropy. Considering that these values are calculated in the gas phase, so it's important to note that these standard values should be corrected for the change when pass from gas to solution phase (1 atm and 1 mol/L, respectively), which amounts to decreasing each of the values obtained by *R/F* (ln 22.4), that is, 0.268 mev/ (mol•K), the data of are listed in Table 3.2, for which there are no experiment data, whereas some theoretically values can be found in the literature. Therefore, when available, the theoretical data are used. However, when the theoretical data are not available, we adopt the average value for R-Cl (=38.8 KJ•mol^{-1}, T=298.15 K) reported by Lin et al [44,45]. Experimental bond dissociation energies, , for some PCEs are not available, however, theoretically computed and enthalpies based on quantum chemical calculation method are available for all PCEs [46,47], in which the reliability of this method is confirmed by comparison the theoretical values with those of available experimental data. The standard reduction potential of chlorine in DMF has recently been estimated from thermo-chemical data to be 2.12 V (vs SCE) [43]. Therefore, the standard reduction potentials for PCEs can be calculated from eq.3.31 and listed in Table 3.2.

A series of values for each compound of PCEs can be calculated from eq.3.29 at a wide range of scan rates, while the corresponding at each scan rate can be obtained from eq.3.30, simultaneously. Variations of experimental activation free energy with as function of standard free energy of the reaction for DET to C-Cl bond of PCEs are shown in Fig. 3.4.

The solvent reorganization energies, λ_0, in eq.3.28 are derived from the appropriate relationship:

(3.32)

Where, the corresponding radii of equivalent spheres for PCEs can be obtained from density and molecule mass of PCEs according to:

(3.33)

(3.34)

These radii values of PCEs, together with the solvent reorganization energies calculated from eq.3.32 are listed in Table 3.2. Application of eq.3.28 by using thermochemical data of and leads to acquire the theoretical values of , which can be compared with the experiment values above. The comparison between experimental (red solid circle) and theoretical values (dotted line) as function of standard free energy, , are shown in Fig. 3.4. However, as indicated in the figures, application of the classical dissociative electron transfer model (eq.

3.28), does not give satisfactory fitting of the experimental data. The predicted activation energies are significantly larger than those of experimental ones. A reasonable explanation for this is the radical-ion interaction resulted from the dissociative electron transfer. Actually, for the case of CCl_4, a sizable interaction among the cage fragments were indeed observed, which was shown to be essentially of the charge (Cl^-)-induced dipole ($^\bullet CCl_3$) [36,37]. So it's reasonable to expect that the interaction should also persist in the PCEs. We may therefore take into account of the fragments interaction by using the modified DET model. The "sticky" DET model introduces the interaction of radical-ion, D_p, into the classical DET model, leading to the following activation-driving force relationship:

(3.35)

where D_p not only modifies the driving force of reaction, but also decreases the intrinsic barrier. It' noteworthy that quite small values of D_p could result into strong effect on the intrinsic barrier, for instance, if D_p is 4% of D_{RCl}, a decrease of 20% of the intrinsic barrier follows [37]. Adjusting the value of D_p until obtain the best fit of experiment data. As can be seen in Fig.3.4 , an excellent fit are achieved among all the seven PCEs and the best fitting values of D_p are given in Table 3.2. We also report the intrinsic barrier of PCEs calculated from "Sticky" DET model in the table. As shown in Fig. 3.4, the validity of "Sticky" DET is confirmed by the perfect coincidence of experimental values with the model.

We are thus led to conclude that all the investigated PCEs are compatible to the "Sticky" DET model, where ET to C-Cl bond gives rise to a loose radical-ion complexes, rather than the anion radical product by stepwise mechanism, in addition, a sizable interaction are confirmed surviving in the fragment clusters.

It might be interesting to discuss the dissociative DET mechanism on catalytic electrode. Ag, exhibits the most remarkable electrocatalytic character toward reductive cleavage of PCEs, is chosen as a representative of catalytic metal electrode. The standard potential of PCEs, , depend on the contribution of bond dissociation energies, standard bond dissociation entropies and standard reduction potential of $Cl^\bullet$. None of these parameters is influenced by electrode materials. may decrease owing to the interaction of R-Cl substrate with catalytic electrode, which leads to lower the number of solvent molecules involved. However, for the simplification of DET mechanism, we exclude the variation of caused by the interaction of

Ag electrode. Similar with GC, variation of peak potentials with scan rate is carried out for Ag electrode, by using the parameters listed in Table 3.3. Experimental values of $\Delta G_p^{\neq}$ at variation of peak potentials derived from eq.3.28, and theoretical predictions of $\Delta G_p^{\neq}$ based on the classical DET model and "sticky DET" model, as function of standard free energy are displayed in Fig 3.4(right hand). An excellent agreement of experiment data with the theoretical predictions based on "sticky DET" model are observed from the figures, thus validating the "sticky DET" model for PCEs that is also applicable to catalytic electrode. The interaction energies of radical-ion are calculated and listed in Table 3.3. By comparison the thermodynamic parameters with those on GC electrode, two evident differences will be found, one is the remarkable electrocatalytic character of Ag behaved, in which the reduction potentials of PCEs are positively shifted by 0.21-0.91 V with respect to GC, and the other is the greatly enhancement of interaction energies between the caged fragments of PCEs on Ag electrode compared to GC, the interaction energy differences is varying from 1.73 for 1,1-DCA to 21.00 $KJ\bullet mol^{-1}$ for HCA.

The activation free energy of an electrochemical reaction is determined by two different factors, one is an extrinsic factor, standard free energy of reaction, ; the second is an intrinsic factor, standard activation free energy, also known as intrinsic barrier, which reflects the bond dissociation energy and solvent reorganization energy. Because of the positive shifts of peak potentials on Ag electrode, it leads to a decrease of driving force for PCEs reduction reactions. Whereas, it's not difficult to observe that there are negligible changes on the overall activation free energies,(exp), for the PCEs reduction reactions at the two electrodes. It means the intrinsic barrier must be lowered to compensate a decrease of driving force contribution to . As aforementioned, the composition of intrinsic barrier involves two contributions. One is the solvent reorganization energies, which is supposed to be constant for the reactions occurring on both electrodes. The other is bond dissociation energies. For PCEs, owing to the interaction between the dissociation fragments, D_p, which can result into a significant modification of intrinsic barrier, as shown in "Sticky DET" model. However, in the case of electrocatalytic electrode, except for the interaction of caged fragments, an activated intermediate complex characterizing by strong interaction of chlorinated substrate with Ag surface is formed. Consequently, an obvious increase of interaction energy is observed at Ag electrode than that of at GC. Due to this strong interaction surviving in the transition state, the intrinsic barrier free energy for the electrochemical reactions is evidently lowered with respect to those at non-catalytic electrode. It should be noted that the interaction energy for Ag is not only involved the one taking place on the fragments, but also included this occurring between the substrate and electrode surface. Therefore, if we subtract the interaction value of radical-ion which is presumed to be equivalent for both electrodes from the overall interaction energy, the dispersion could be taken as the electrocatalytic effect of Ag electrode, which plays a significant role on the overall decrease of intrinsic barrier, as shown in the Table 3.3. The decrease of intrinsic barrier results in a decrease of driving force to overcome this barrier, and hence results in a positive shift of peak potentials with respect to GC electrode, which could be well explained the catalytic effects of metal electrodes. In addition, a general increase of interaction energy with chlorine numbers is found for PCEs, which is in accord with the assumption that the interaction is essentially a high affinity of metal for chlorine ions [47].

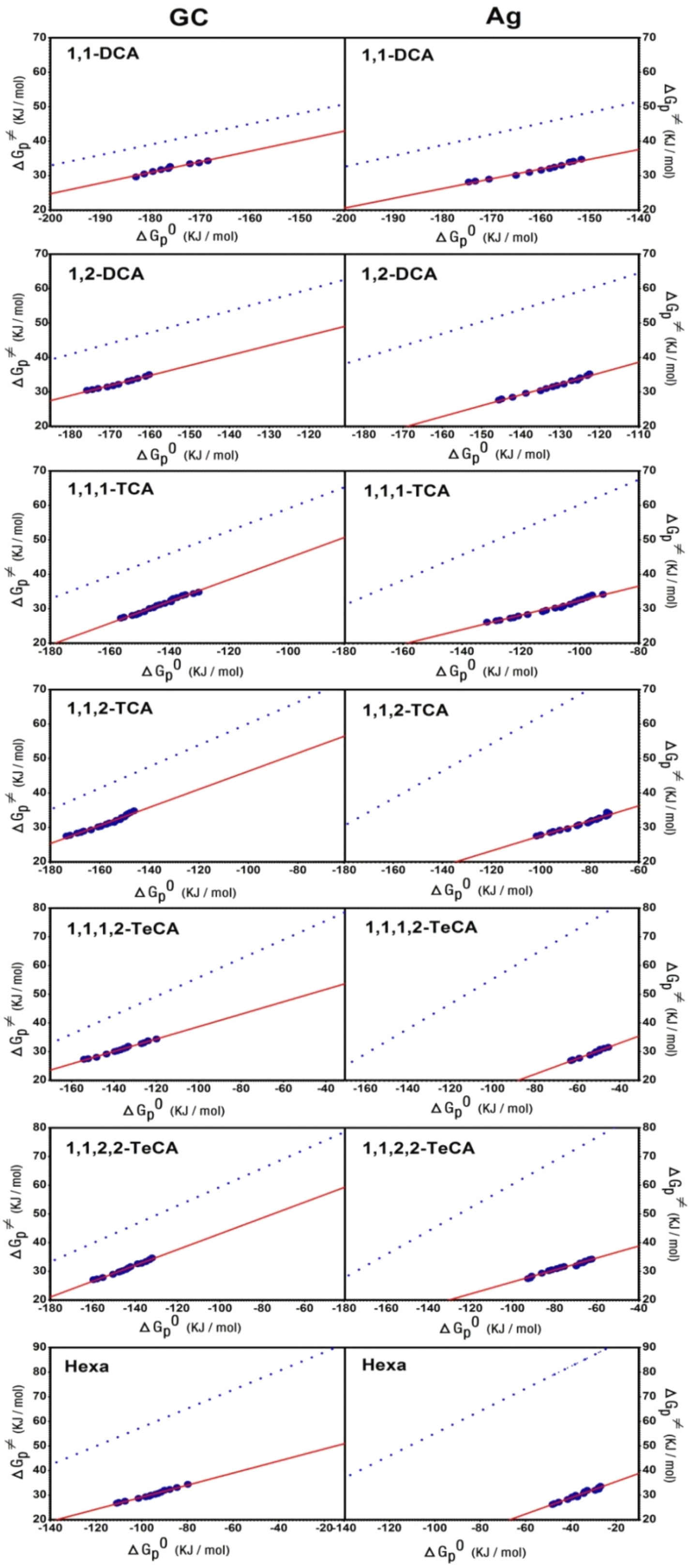


Fig. 3.4 Activation-driving force plots on GC (left hand) and Ag (right hand) electrode for the dissociative ET to PCEs, derived from variation of peak potentials with scan rates. The royal dots are the experimental values calculated by using eq.3.29; the dashed (blue) and solid (red) line represent the predictions by classical and "sticky" DET model, respectively.

Table 3.2 Thermodynamic parameters for analysis of dissociative DET to PCEs on GC electrode in DMF solution

Compounds	D_{RCl}	Z^{el}					a	λ_0	(exp)	(pred)		D_p (GC)
	(KJ•mol^{-1})	(cm/s)	(V vs SCE)	(KJ•mol^{-1})	(V, vs SCE)	(V, vs SCE)	(Å)	(KJ•mol^{-1})	(KJ•mol^{-1})	(KJ•mol^{-1})	(KJ•mol^{-1})	(KJ•mol^{-1})
Cl_2HCCH_3	331.20	6261	-2.744	38.15	2.12	-0.92	2.60	111.52	32.65	40.10	101.33	1.12
$ClHCCH_2Cl$	344.21	6261	-2.790	38.15	2.12	-1.05	2.68	108.04	32.19	44.76	99.32	2.39
Cl_3CCH_3	308.09	5392	-2.125	38.15	2.12	-0.68	2.66	108.71	32.02	46.08	89.24	3.23
Cl_2HCCH_2Cl	318.30	5392	-2.419	33.58	2.12	-0.83	2.71	106.88	32.02	43.49	94.01	2.06
Cl_3CCH_2Cl	293.82	4807	-1.911	38.15	2.12	-0.53	2.68	107.86	31.87	44.84	86.39	2.97
$Cl_2HCCHCl_2$	312.48	4807	-2.233	34.63	2.12	-0.76	2.73	105.90	31.62	45.59	89.39	3.29
Cl_3CCCl_3	298.04	4048	-1.539	36.81	2.12	-0.59	2.70	107.28	31.17	60.62	74.08	12.35

Table 3.3 Thermodynamic parameters for analysis of dissociative DET to PCEs on Ag electrode in DMF solution

Compounds	D_{RCl}	Z^{el}					a	λ_0	(exp)	(pred)		D_p (Ag)	ΔD_p
	(KJ•mol^{-1})	(cm/s)	(V vs SCE)	(KJ•mol^{-1})	(V, vs SCE)	(V, vs SCE)	(Å)	(KJ•mol^{-1})	(KJ•mol^{-1})	(KJ•mol^{-1})		(KJ•mol^{-1})	(KJ•mol^{-1})
											(KJ•mol^{-1})		
Cl_2HCCH_3	331.20	6261	-2.534	38.15	2.12	-0.92	2.60	111.52	32.95	46.51	96.03	2.85	1.73
$ClHCCH_2Cl$	344.21	6261	-2.388	38.15	2.12	-1.05	2.68	108.04	32.26	57.73	87.89	8.69	6.30
Cl_3CCH_3	308.09	5392	-1.750	38.15	2.12	-0.68	2.66	108.71	31.29	58.97	78.79	10.14	6.91
Cl_2HCCH_2Cl	318.30	5392	-1.630	33.58	2.12	-0.83	2.71	106.88	32.26	71.02	73.01	17.93	15.87
Cl_3CCH_2Cl	293.82	4807	-1.000	38.15	2.12	-0.53	2.68	107.86	31.51	79.04	62.74	26.82	23.85
$Cl_2HCCHCl_2$	312.48	4807	-1.482	34.63	2.12	-0.76	2.73	105.90	31.90	72.66	70.80	19.03	15.74
Cl_3CCCl_3	298.04	4048	-0.942	36.81	2.12	-0.59	2.70	107.28	31.34	85.08	59.82	33.35	21.00

3.4 Conclusions

The electrochemical reduction of polychloroethanes (PCEs) have been conducted on different transition metals in DMF + 0.1 M $(C_3H_7)_4NBF_4$. Based on the analysis of voltammetric patterns, PCEs can be divided into two types species, one is the geminal-PCEs, which follow the sequential hydrodechlorination mechanism by eliminating one chlorine ion per two electron transfer at each step; the other is vicinal-PCEs, which undergo a reductive α,β-elimination mechanism, upon two electron transfer losing two chlorine ions, one at each carbon, to give rise to olefin.

The mechanism of electron transfer to C-Cl bond is an important topic in electrochemical reductive cleavage of chlorinated compounds, which can be determined by using electron transfer coefficient as diagnostic criteria. It was found that the single electron transfer to C-Cl bond of PCEs initiates concerted dissociative electron transfer mechanism regardless of electrode types, in which ET and bond breaking take place at one single step. After a close examination of the CV of PCEs at different electrodes, comprehensive reduction mechanisms of 1,1,1-TCA and 1,1,1,2-TeCA, involving sequential hydrodechlorination or reductive α,β-elimination mechanism, self-protonation and carbene route, are proposed subsequently.

The electrocatalytic activities of transition metals towards reductive cleavage of PCEs have been evaluated with respect to GC, the latter used as a reference system. Electrocatalytic activities of different metals are found strongly dependent on the nature of electrode materials and molecule structures. Three ranks are divided based on the electrocatalytic effects of transition metals for the reduction of PCEs, following the order: Ag, Cu, Au > Pd, Pt, Ni >> Fe, Pb, Zn. The molecule structures also play a significant role on the electrocatalytic reduction of PCEs. In general, the electrocatalytic activity increases with increasing number of Cl atoms bound to the same carbon center. Instead, the number of Cl atoms bound to the second C atom has contrasting effects: activation enhancement due to polar effects contrasted by steric hindrance effects on the transition state. Considering the most active electrodes of the series, gives the following order of increasing electrocatalytic reactivity: 1,1-DCA < 1,1,1-TCA < 1,2-DCA < HCA < 1,1,2,2-TeCA < 1,1,2-TCA < 1,1,1,2-TeCA.

According to the voltammetric analysis of peak characteristics of PCEs at both GC and Ag electrodes, it confirms that the first ET to PCEs follows concerted DET mechanisms. A series of activation free energy for PCEs reduction reactions were obtained by analysis the variations of peak potentials with the scan rates. In contrast to the classical DET model, excellent fitting of experiment values were achieved for all PCEs by using the “sticky DET” model, where the interaction between the caged fragments are taken into account. Compared to GC electrode, a significant decrease of intrinsic barrier and driving force were observed at Ag electrode, which were presumably attributed to the effect of interaction energies, that included not only the interactions between the caged fragments but also the strong interactions between chlorinated substrate and Ag electrode. The dispersion between this two interaction energies of Ag and GC could be taken as the electrocatalytic effect of Ag electrode, which played a significant role on the overall decrease of intrinsic barrier. The decrease of intrinsic barrier results in a decrease of driving force to overcome this barrier, and hence results in a positive shift of peak potentials with respect to GC electrode. These could be well explained the catalytic effects of metal electrodes.

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Chapter 4 Electrolytic dechlorination of polychloroethanes (PCEs) on catalytic and non-catalytic electrodes

Abstract

Polychloroethanes (PCEs) are among a class of the most ubiquitous environment pollutants, chlorinated volatile compounds (Cl-VOCs). Searching for an effective approach to abate the pollution of these compounds is strongly desired due to their high toxicity. In this study, electrolytic investigations of several representative PCEs have been carried out in DMF + 0.1 M $TPABF_4$ in different solvent conditions, at non-catalytic (GC) and catalytic (Ag, Cu) electrode, respectively. Voltammetric and further electrolysis results confirm two distinct reduction mechanisms taking place towards the reduction of PCEs, regardless of the nature of electrode materials. Geminal PCEs undergo sequential hydrodechlorination mechanism, in which evolves a series of two electron transfer reduction step by eliminating one chlorine at each step till ultimately ethane formation. Whereas vicinal PCEs conform to reductive α,β-elimination route where two chlorine ions are expelled at one single step with corresponding olefin formation. As a candidate of noble metals, electrocatalytic activities of Cu towards geminal PCEs reduction have been investigated. It shows Cu exhibits an excellent catalytic effect towards geminal PCEs reduction. Addition of HAc can enhance the catalytic nature of Cu for the reductive cleavage of C-Cl bond. Electrolysis of geminal PCEs at Cu electrode in different solvent conditions shows that the reduction mechanisms of geminal PCEs are sensitive to the proton availability. Addition of proton donor may promote hydrodechlorination mechanism by restricting base promoted α,β-elimination reaction and carbene route. Water as a proton donor has double roles in the electrolytic process, one is as proton donor favoring the hydrodechlorination mechanism, the other is to provide bases enhancing the occurrence of base promoted α,β-elimination mechanism. By comparison with using sequential potentiostatic electrolysis, single step potentiostatic electrolysis may effectively suppress side reactions and decrease the accumulation of electrolytic intermediates, leading to the enhancement of C2 hydrocarbons yield.

4.1 Introduction

Polychloroethanes (PCEs) are among a class of the most ubiquitous environmental pollutants, chlorinated organic compounds (Cl-VOCs). Because of their widespread use as solvents and chemical raw materials, together with their character of high volatility and dissolubility in water, which cause them become one of the most commonly detected pollutants in the soil and groundwater of industrial sites [1,2]. However, PCEs also belong to the particularly undesirable compounds in view of their toxicity or even carcinogenic nature. The conventional technologies employed for the treatment of PCEs including air stripping, carbon adsorption, and membrane separation, only transfer the pollutants from one phase to another, but not a real solution for this problem, thus methodologies which can totally degrade the toxic nature of the molecule are held in a great consideration from worldwide.

Due to the electronegative character of chlorine atoms in the chlorinated compounds, reduction appears as a valid disposal methods. Indeed, reduction dechlorination can be successfully achieved by chemical reaction routes, for instance, zero valent metal reduction technology [3], catalytic hydrodechlorination method [4], and also electrochemical dechlorination methods by using both bulk metal [5] and nano-structured catalyst electrodes [6]. Electrochemical technology as a promising approach presents competitive characters over other reductive technologies, such as controllable reaction kinetics, cathodic polarization against electrode passivation or corrosion, as well as working under mild conditions. For the sake of making electrochemical methodologies more attractive from the application point of view, the major issue to be settled is exploring long longevity, high catalytic activity of electrode materials, to reduce the processing cost of wastewater containing chlorinated substrates. Even though noble metals, such as Pd and Pt have been found exhibiting excellent catalytic activities over reductive dechlorination technologies [7-9], the use of them as electrode materials in large scale application, even at low loading, is too costly. Extensive studies have been carried out for searching for remarkable catalytic electrode toward the electrochemical reduction of chlorinated compounds in aqueous [10,11], non-aqueous solvents [8,12-14], and Ag has shown to be one of the most predominant catalysts both in terms of catalytic activity and current efficiency [8,12-14]. In addition, Cu also has recently been found to present excellent catalytic properties for electrochemical reductive dechlorination process, and in some case even resemble with those of on Ag [8,10,15-17]. However, owing to the low price and high availability, it allows Cu to be an excellent candidate electrode in application, and the modification of Cu constructions with high surface area can assure high process efficiency. The electrolytic dechlorination of chlorinated compounds on Cu is now only concentrated under aqueous conditions, and it behaved a general tendency of gradual passivation of electrode [18]. On this regard the direct transfer of electrocatalytic behavior of Cu from aqueous to organic solvent is not straightforward, while in the latter case, the electrocatalytic of Cu has not been fully exploited, in particular for environmental application.

Among PCEs, 1,1,1-TCA is a banned chemical due to its activity in the depletion of ozone and potential carcinogenic character to human being. 1,1,1-TCA is susceptible to a variety of natural abiotic and biotic transformations; whereas the rate of these transformation is often sluggish, and far insufficient to prevent its migration in groundwater, in particular, at the polluted sites where 1,1,1-TCA is always co-contaminant with other common chlorinated solvents, such as tetrachloroethylene (PCE) and trichloroethylene (TCE), and hence restricting the rate of dechlorination by the inhibitory substrate interactions. Common 1,1,1-TCA daughter products include 1,1-dichloroethane (1,1-DCA), vinyl chloride (VC) and chloroethane (CA), all of them have solubility in groundwater and are suspected as carcinogen. 1,1,1,2-TeCA, is widely used as a solvent, herbicides and in the production of wood strains and vanishes. In analogy with 1,1,1-TCA, 1,1,1,2-TeCA is suspected as potential carcinogen [19], and suffering from a low dechlorination rate in the natural conditions. It should be noted that both 1,1,1-TCA and 1,1-DCA have been listed in the priority pollutants by U.S. EPA owing to their toxicity. Accordingly, all of these aspects are driven to check the feasibility of electrochemical methodology towards the reduction of these compounds.

As stated in the previous chapter, the electrochemical reduction mechanisms of PCEs are strongly dependent on the molecule structures. It can be divided into two classes based on the voltammetric analysis, geminal-PCEs and vicinal-PCEs. Besides, the electrocatalytic activities of PCEs are found depending on the nature of electrodes. Ag has shown the best catalytic activity towards PCEs reduction over the other electrodes. Preliminary reduction mechanisms of these two types of compounds have already been proposed over there, while it would be wise and necessary to further support the conclusions driven from the voltammetric analysis by preparative scale electrolysis. Herein, 1,1,1-TCA and 1,1,1,2-TeCA were chosen as representatives of these two types of compounds, to carry out the electrolysis experiments by using GC and Ag electrode as the non-catalytic and catalytic electrode, respectively, for further confirming the reduction mechanisms by following the evolution of intermediates and final products during electrolysis. Cu, as a candidate of noble metals, it would be attractive to examine its applicability in PCEs dechlorination, and thus the electrochemistry behaviors of Cu towards the reduction of geminal-PCEs were investigated in this chapter. Hydrodechlorination process involves both electron and proton transfer two processes, it will be helpful to control both processes. Dimethylformamide (DMF) was chosen as the aprotic solvent, and different types of proton donors (H_2O, HAc) are intentionally added to investigate their influence to the reduction mechanisms of PCEs.

Of course, one might dispute the feasibility of conducting dechlorination reaction in organic solvents; however, the wastewater treatment may be not the only situation we face with. Actually, if the issue is to dispose the existing stock of PCEs, which can be served as good solvents themselves, the direct electrochemical dechlorination can be achieved by choosing an appropriate supporting electrolyte or realized in a micro-fluidic system which can prevent the ohmic drops and therefore decrease the burdening of chemical addition. Besides, because of the high solubility of PCEs in organic solvents, it would be a good solution by combination with adsorption methods, where highly concentrated solution could be prepared, leading to a high current density during electrolysis, by which it means that a great amounts of PCEs may be converted to less dangerous or more valuable products in a reasonable short period of time.

4.2 Experimental and methods

4.2.1 Materials and chemicals

Dimethylformamide (DMF) was treated in the presence of anhydrous Na_2CO_4 for several days. After double distillations at lower pressure under N_2 conditions, DMF was then stored in a brown bottle under the protection of Argon. Tetrapropylammonium tetrafluoroborate ($C_{12}H_{28}BF_4N$, $TPABF_4$, Fluka) was recrystallized twice in ethanol and dried in a vacuum oven at 70 ℃ for at least two days. 1,1-dichloroethane (1,1-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), 1,1-dichloroethylene (1,1-DCEy), 1,2-dichloroethylene (1,2-DCEy), trichloroethylene (TCE), chloroethylene (VC) were purchased from Sigma-Aldrich company and used directly as received.

4.2.2 Experimental instrumentations

Electrochemical measurements were performed on a computer controlled EG&G PARC Model 273 potentiostat/galvanostat. All experiments were conducted at 20 ℃ in a three electrode system with GC, Ag or Cu disk as working electrode, a Pt wire as counter electrode and Ag/AgCl/ Me_4NCl(sat) in DMF + Acetonitrile (3:1,V/V) solution as reference electrode, respectively. The reference electrode was calibrated at the end of each experiment against the ferricenium/ferrocene couple ($E_{Fc+/Fc}$ = 0.475 V vs SCE in DMF), which allowed conversion of all potentials to saturated calomel electrode (SCE) scales. To be noted that all the potential values in this thesis are calibrated to SCE except specialization.

The working electrode in this research were disks from 2 mm diameter metal wires (Ag, Cu, Alfa Aesar ≥ 99.99%) or from a 3 mm diameter GC rod (Tokai, GC-20), which were always polished to a mirror finish with silicon carbide papers by decreasing grain size (Struers, grit: 1000, 2400, 4000); followed by diamond paste (3-, 1-, 0.25-μm particle size). After each polishing step, the electrodes were always cleaned in ethanol in an ultrasonic bath for about 5 min. the electrodes were constructed as previous described [12].

4.2.3 Cyclic voltammetry and electrolysis

Voltammetric experiments were performed in a thermostated undivided tank cell containing 0.1 M tetrapropylammonium tetrafluoroborate ($TPABF_4$) as supporting electrolyte and 2 $mM\cdot L^{-1}$of chlorinated substrate in DMF solution.

Electrolytic experiments were carried out in a sealed thermostated divided tank cell, with $Ag/AgCl/Cl^-$ as reference electrode, Pt as counter electrode, by using Ag plate, Cu plate or GC plate as working electrode, respectively. During the electrolysis, the samples of gas and solution phase were withdrawn from a septum cap of the cell for products analysis by GC or GC-MS periodically.

4.2.4 Analysis

The electrolytic products in the gas phase were withdrawn by a gas syringe, followed by directly injecting into a HP 6890 system gas chromatograph equipped with a HP Plot Q 30 m

×0.537 mm× 0.40 mm capillary column (Agilent Technologies, USA) and a flame ionization detector (FID). The injector was equipped with a 0.75 mm i.d. liner and was operated in a split mode (15:1). The oven temperature was set at 60 ℃ for 2 min, then increased to 240℃ at a rate of 30℃·min^{-1} and held for 2 min. The injector and the detector were set at 150 and 250 ℃, respectively, and the carrier gas (He) flow was 4.4 mL·min^{-1}. Identification and quantification of the products were based on comparison with authentic samples and calibration curves, respectively.

Solution phase products were analyzed by withdrawing 1 μL of sample and subsequently injecting into the column of GC-MS for identification and quantification analysis. The sample analysis were performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector (MS) and a DB-5 ms 30 m×0.25 mm×0.25 mm capillary column (Agilent Technologies, USA). The oven temperature was set at 32 ℃ and held for 4 min, then increased to 40 ℃ at the rate of 10 ℃·min^{-1} holding for 1 min. Helium with a flow rate of 0.5 mL·min^{-1} was used as a carrier gas. Authentic compounds were used for the identification and quantification of the products based on a calibration curve prepared before electrolysis.

4.3 Results and discussion

4.3.1 Electrolysis of 1,1,1-TCA

4.3.1.1 Electrolysis results of 1,1,1-TCA

For further support the mechanistic conclusions driven from the voltammetric data in the previous chapter, in particular the distinction between geminal and vicinal PCEs, 1,1,1-trichloroethane (1,1,1-TCA) and 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), chosen as representatives of the two types of PCEs, were studied by electrolysis. On each compound a set of experiments was performed on GC and Ag cathodes in DMF in the absence and presence of acetic acid (HAc), used as a proton donor. The working electrodes were chosen in order to gain information on both non-catalytic and highly catalytic materials. All experiments were carried out under potentiostatic conditions, in which the applied potential, E_{app}, was shifted during electrolysis so that stepwise dechlorination could be achieved. For example, if the substrate exhibits three reduction peaks, the electrolysis was performed at three E_{app} values corresponding to the observed three peaks. The first step of the electrolysis was always performed at an applied potential located after the first peak but well before the second one. Then as a rule E_{app} was shifted to the successive step potentials (say, after the second peak, then after the third and so on), each time changing the potential when the current decreased to ca 5% of its initial value. During electrolysis, samples were withdrawn both from the solution and gas phases and analyzed by GC-MS and GC, respectively.

The electrolysis results of 1,1,1-TCA performed both in the absence and presence of HAc are summarized in Table 4.1, in which the numbers in the first column stand for the experiments, whereas the letters indicate different steps within the same electrolysis. Figs. 4.1 and 4.2 show the concentration profiles of the substrate and its main reduction products together with the voltammetric responses recorded at the beginning of the experiment and at the end of each electrolysis step. The concentration profiles are plotted as n/n_{PCE}^{0} vs charge, where n and n_{PCE}^{0} are the observed quantity of any substrate and the initial amount of PCE, respectively. On GC the principal reduction products at the end of the first stage of electrolysis (E_{app} = -2.26 V) were 1,1-DCA (53.1%), 1,1-DCE (8.0%) and chloroacetylene (12.2%). This corresponds to 96.5% conversion of 1,1,1-TCA with a charge consumption of 1.40 e^{-}/molecule. At the second stage, when E_{app} was shifted to -2.81 V, complete conversion of 1,1-DCA occurred after a further charge consumption of 1.96 e^{-}/molecule. The principal products at the end of this stage were chloroethane (8.2%), acetylene (21.4%), ethylene (8.1%) and ethane (20.1%). When in the last step E_{app} was shifted to -2.94 V, complete dechlorination was achieved with an overall charge consumption of 5.44 e^{-}/molecule. Analysis of the products shows that at the end of the electrolysis 1,1,1-TCA was converted to ethylene (20.7%) and ethane (30.6%). In addition to these products the presence of C4 hydrocarbons, which, however, were not quantified, was observed.

A full picture of the above described electrolysis can be observed in Fig. 4.1c, which reports the trends of all intermediate products as a function of consumed charge. 1,1-DCA, 1,1-DCE, chloroacetylene, chloroethane and acetylene were found to accumulate and then decrease during electrolysis. These intermediates reach maximum yields at different stages of the electrolysis, but completely disappear at the end. The maximum yields (n/n_{PCE}^{0}) are

51.2% (1,1-DCA), 20.2% (1,1-DCE), 16.2% (C_2H_5Cl), 12.2% (C_2HCl) and 19.4% (C_2H_2). It is worth noting that the yields of ethane and ethylene increase simultaneously, indicating that C_2H_6 does not arise from reduction of C_2H_4 in our reaction conditions.

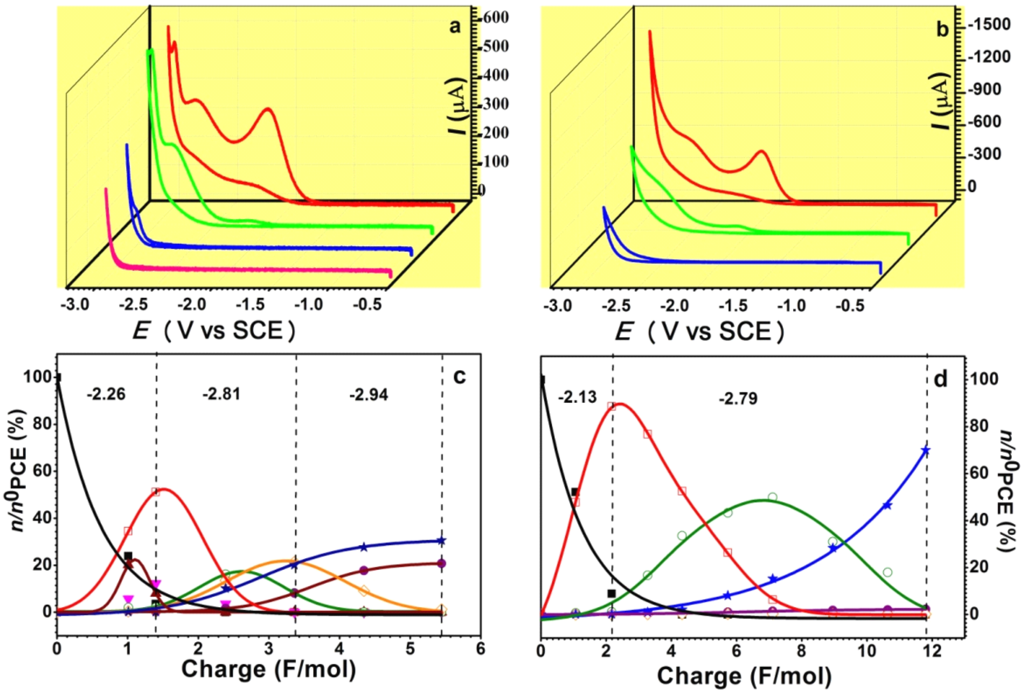


Fig. 4.1 Electrolysis of 10 mM 1,1,1-TCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on GC in the absence (a, c) and presence (b, d) of 100 mM acetic acid. (a,b) cyclic voltammogrms recoded before electrolysis and at the end of each step; (c, d) concentration profiles: (■) 1,1,1-TCA; (□) 1,1-DCA; (▲) 1,1-DCE; (▼) C_2HCl; (○) C_2H_5Cl; (◇) C_2H_2; (●) C_2H_4; (★) C_2H_6. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

Table 4.1 (entry 2) and Fig. 4.1 b,d also report electrolysis of 1,1,1-TCA performed in the presence of HAc. In this case, only two reduction peaks can be observed, the third being covered by a reduction wave due to HAc. Therefore, the electrolysis was carried out at -2.13 V and -2.79 V in two steps. At the end of the first step, which consumed 2.2 e^-/molecule, only 1,1-DCA (98%) and trace amounts of chloroethane (1.3%) were obtained. Further reduction at -2.79 V completely converted 1,1-DCA to ethane (70%), ethylene (2.3%) and C4 hydrocarbons (not quantified). Note that at the potential of the second step also acetic acid can be reduced. Indeed, the charge consumed in this last step considerably exceeds that required for the stoichiometric conversion of 1,1-DCA and the remaining 1,1,1-TCA to dechlorinated products because of the contribution of the acid reduction.

Similar results were obtained from the electrolysis of 1,1,1-TCA at Ag. As shown in Fig. 4.2a, 1,1,1-TCA shows two reduction peaks at Ag. Therefore, the electrolysis was carried out at -1.88 V and -2.88 V in two successive steps. Complete conversion of the starting substrate was achieved in the first step, which consumed 2.17 e^-/molecule. The products of this step were 1,1-DCA (26.4%), C_2H_5Cl (5.5%), C_2HCl (3.4%), C_2H_2 (43.0%), C_2H_6 (8.4%) and some C4 compounds. In the second step, the charge consumption increased to 6.50 e^-/molecule and all chlorinated compounds were converted to hydrocarbons. Thus, the final products of the electrolysis were C_2H_4 (19.4%), C_2H_2 (8.2%), C_2H_6 (29.3%) and some C4 compounds.

Fig. 4.2c shows the concentration variations of all species involved in the reduction of 1,1,1-TCA on Ag in DMF without added proton donors. The trends are quite similar to those observed on GC in the same electrolysis conditions. 1,1-DCA, 1,1-DCE, C_2HCl, C_2H_5Cl and C_2H_2 are intermediates with concentration trends passing through a maximum during the electrolysis, whereas C2 hydrocarbons are formed as the final products. The principal difference between the two electrodes is that less 1,1-DCA is accumulated during electrolysis at Ag than at GC. On the other hand, more C2 hydrocarbons are formed at Ag than at GC in the initial stages of the electrolysis. This implies the existence of some differences in the reduction mechanisms at the two electrodes. In particular, completely dechlorinated compounds such as C_2H_2 and C_2H_6 are formed at the catalytic Ag electrode at a potential where neither 1,1-DCA nor chloroethane are reducible. This seems to be typical character of Ag, as similar findings have been previously observed for the reduction of polychloromethanes at Ag in similar reaction conditions [13].

Table 4.1. Electrolysis of 1,1,1-TCA at GC and Ag electrodes in the absence and presence of a proton donor.[a]

Entry	Cathode	HA	E_{app}[b]	n (F/mol)	1,1,1-TCA (%)[c]	1,1-DCA (%)[d]	CA (%)[d]	1,1-DCE (%)	C_2HCl (%)	C_2H_4 (%)[d]	C_2H_2 (%)[d]	C_2H_6 (%)[d]
1a	GC		-2.26	1.01	23.9	46.8	2.6	26.5	7.5	0.3	0.4	0.1
1a’			-2.26[e]	1.40	3.5	53.1	2.1	8.0	12.2	0.2	0.6	0.1
1b			-2.81	3.36	0	0	8.2	0	0	8.1	21.4	20.1
1c			-2.94	5.44	0	0	0	0	0	20.7	1.3	30.6
2a	GC	CH_3CO_2H	-2.13	1.10	52.1	99.8	0.2	0	0	0	0	0.2
2a’			-2.13	2.17	8.9	98	1.3	0	0	0.1	0	0.2
2b			-2.79	11.80	0	0	0	0	0	2.3	0.2	70.0
3a	Ag		-1.88	1.04	22.7	27.7	3.1	43.8	7.4	0.1	13.7	3.1
3a’			-1.88	2.17	0	26.4	5.5	0	3.4	0.1	43.0	8.4
3b			-2.88	6.51	0	0	0	0	0	19.4	8.2	29.3
4a	Ag	CH_3CO_2H	-1.41	2.28	37.5	34.1	2.4	0	0	1.1	0	19.36
4a’			-1.41	4.00	1.0	34.8	3.5	0	0	0.9	0	258.6
4b			-1.99	7.22	0	15.7	7.0	0	0	1.0	0	35.95
4c			-2.69	11.41	0	0	0	0	0	2.2	2.9	60.29

[a] Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [1,1,1-TCA] = 10 mM; [CH_3CO_2H] = 100 mM. [b] E_{app} = applied potential in V vs SCE. [c] Remaining substrate. [d] Yield calculated with respect to converted 1,1,1-TCA. [e] Also 8.3% of 1,1-DCE and 12.6% of chloroacetylene were found.

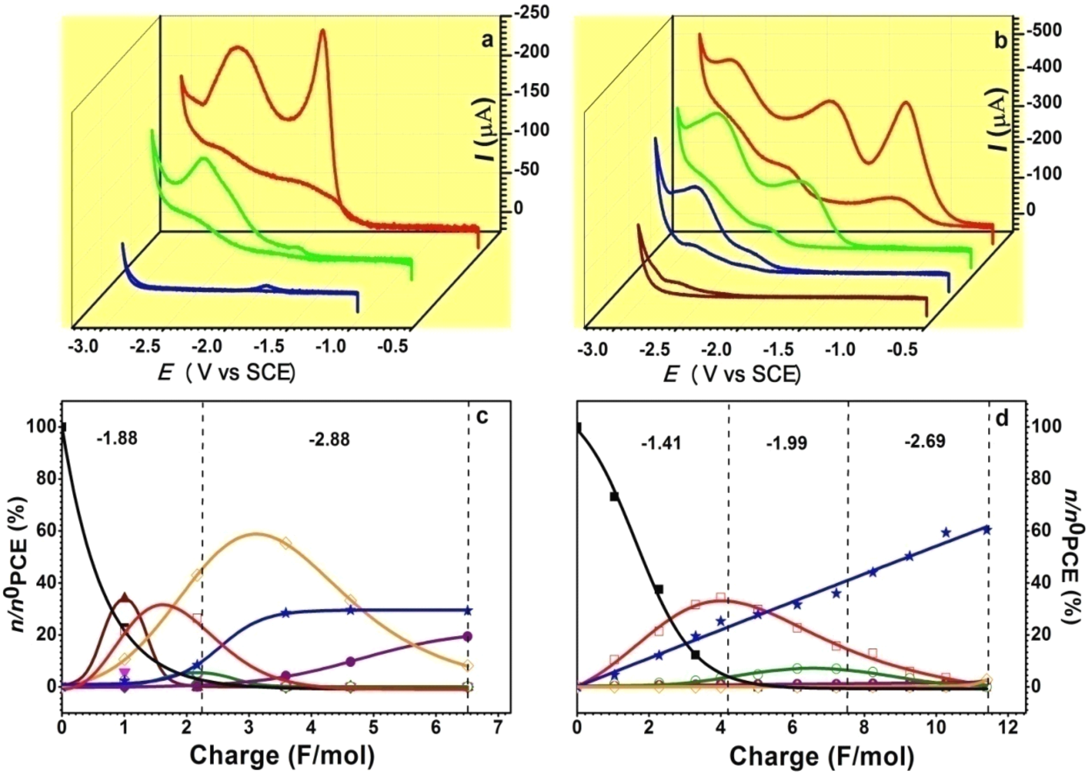


Fig. 4.2. Electrolysis of 10 mM 1,1,1-TCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Ag in the absence (a, c) and presence (b, d) of 100 mM acetic acid. (a,b) cyclic voltammogrms of 1,1,1-TCA recoded before electrolysis and at the end of each step; (c, d) concentration profiles (■) 1,1,1-TCA; (□) 1,1-DCA; (▲) 1,1-DCE; (○) C_2H_5Cl; (◇) C_2H_2; (●) C_2H_4; (★) C_2H_6. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

As in the case of GC, the process became less complicated when the electrolysis on Ag was repeated in the presence of HAc. Fig. 4.2b shows cyclic voltammetry of 1,1,1-TCA on Ag in DMF containing acetic acid. Besides the original two peaks of 1,1,1-TCA, which are shifted to more positive potentials, a third peak mainly due to the reduction of the acid is observed at ca -2.7 V. As usual the stepwise electrolysis was performed selecting E_{app} values corresponding to each of the observed voltammetric peaks. The results are reported in Table 4.1 (entry 4). At E_{app} = -1.41 V, 99% of 1,1,1-TCA was converted to 1,1-DCA (34.8%), C_2H_5Cl (3.5%), C_2H_6 (23.0%) together with some C4 compounds; the charge consumption was 4.0 e^-/molecule. Further electrolysis at -1.99 V consumed 3.2 e^-/molecule with total and partial conversion of 1,1,1-TCA and 1,1-DCA, respectively. The products at the end of this step were 1,1-DCA (15.7%), C_2H_5Cl (7.0%), C_2H_4 (1.0%), C_2H_6 (32.5%) together with increased amount of C4 compounds. Finally when E_{app} was shifted to -2.69 V, all chlorinated compounds were dechlorinated and the yields of the final products rose to 2.9% for C_2H_2, 2.2% for C_2H_4 and 54.4% for C_2H_6. Trends of the product yields of this electrolysis are reported in Fig. 4.2d. The main intermediates in this case are 1,1-DCA and chloroethane. Overall, the electrolysis leads to the formation of ethane but the charge consumption (11.4 e^-/molecule) is quite high due to reduction of the added acid.

4.3.1.2 Reduction mechanism of 1,1,1-trichloroethane

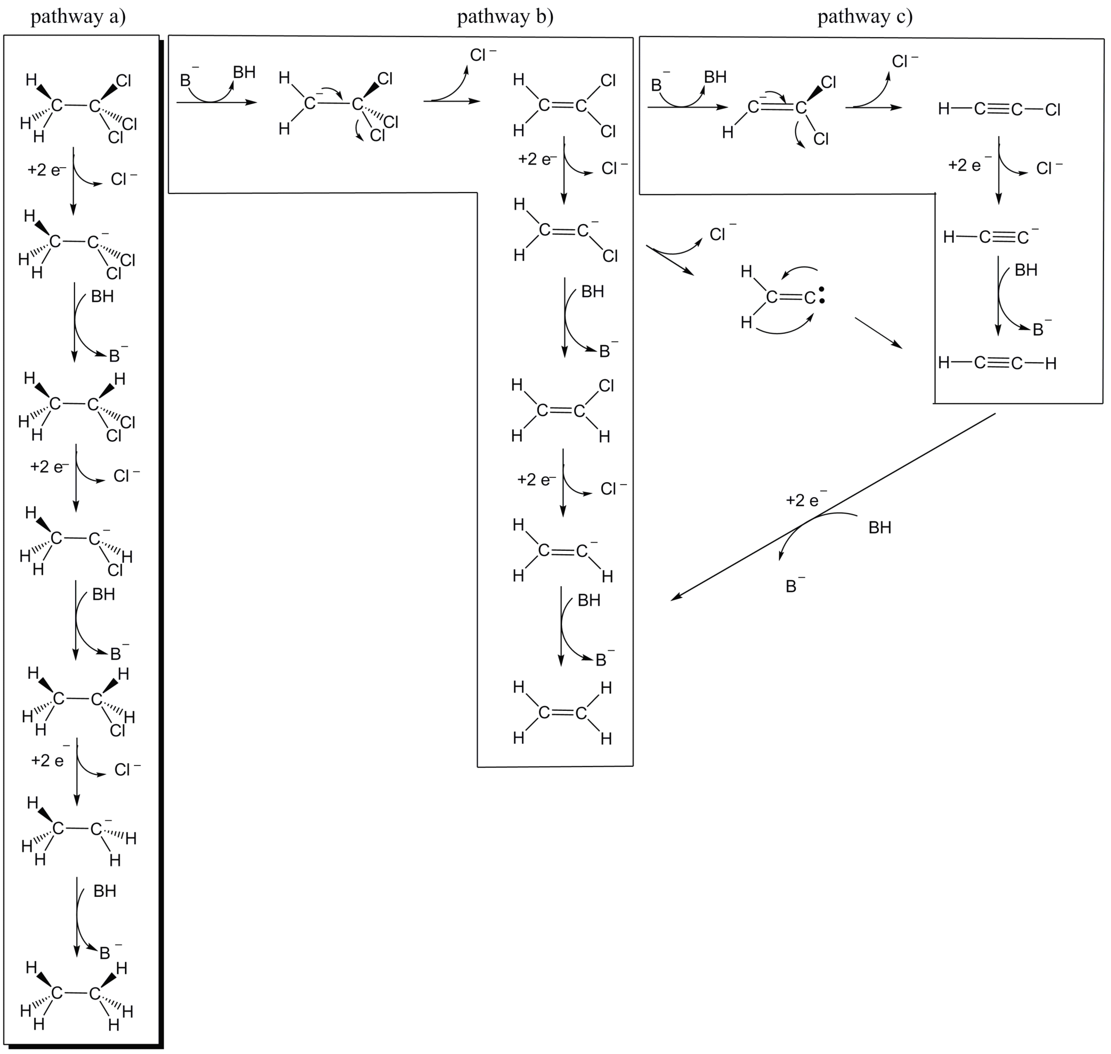
The principal reduction product of 1,1,1-TCA is 1,1-DCA both in the absence and presence of a good proton donor, regardless of the nature of the electrode material, provided that an E_{app} value corresponding to the first reduction peak is imposed. This is a clear indication that a hydrodehalogenation mechanism prevails for this geminal PCE, as predicted by the voltammetric analysis in the previous chapter. It is also clear from both voltammetric and electrolysis results that further reduction of 1,1-DCA at the appropriate potential produces less chlorinated products according to the same reaction mechanism of its precursor. In all experiments the principal product at the end of the electrolysis was always ethane with yields even as high as 70% in some case. However, some products and intermediates that are not compatible with stepwise hydrodechlorination were observed in different phases of the electrolyses. In addition, if no acid is added, the charge consumption in the first step on GC is significantly less than the $2e^-$/molecule stoichiometry required by hydrodehalogenation of 1,1,1-TCA to 1,1-DCA. An overall reaction mechanism including reaction pathways for all important products and intermediates is illustrated in Scheme 4.1.

Pathway (a) illustrates stepwise hydrodechlorination up to ethane. Each step involves two electron transfers (Eqs (4.1) and (4.2)), removal of one Cl atom and protonation of the ensuing carbanion (Eq (4.3)) by the strongest proton donor, BH, in solution.

$$CH_3CCl_3 + e^- \longrightarrow {}^{\bullet}CH_3CCl_2 + Cl^- \tag{4.1}$$

$$^{\bullet}CH_3CCl_2 + e^- \longrightarrow {}^{-}CH_3CCl_2 \tag{4.2}$$

$$^{-}CH_3CCl_2 + BH \longrightarrow CH_3CHCl_2 + B^- \tag{4.3}$$



Scheme 4.1. Electrochemical reduction mechanism of 1,1,1-trichloroethane

In the absence of purposefully added acids, BH might be the residual water in the solvent, the background electrolyte or the PCE itself. The possible involvement of CH_3CCl_3 in protonation reactions opens a new reaction route in which the starting molecule is converted into products without reduction (pathway (b)). In this pathway, CH_3CCl_3 reacts with a generalized base B^- (Eq. (4.4)), which might be the conjugate base arising from reaction (4.3) (e.g., OH^-) or electrogenerated $CH_3CCl_2^-$.

$$CH_3CCl_3 + B^- \longrightarrow {}^-CH_2CCl_3 + BH \qquad (4.4)$$

The base ${}^-CH_2CCl_3$ generated in reaction (4.4) can undergo Cl^- elimination to give 1,1-dichloroethylene, CH_2CCl_2. The presence of reaction (4.4) and the successive elimination explains the formation of 1,1-DCE during electrolysis at the first reduction peak. This mechanistic proposal is also confirmed by two other observations. First, exhaustive reduction of 1,1,1-TCA consumes less than 2e$^-$/molecule because a fraction of the starting substrate does not undergo reduction. Second, when the electrolysis was repeated in the presence of acetic acid, no 1,1-DCE was formed while the charge consumption increased to ca 2e$^-$/molecule.

To further check the role of reaction (4.4) in the electrode process, a blank experiment was performed by mixing equimolar amounts (10 mM) of 1,1,1-TCA and tetrabutylammonium hydroxide. Analysis of the solution and gas phases after few minutes has shown that 52% of 1,1,1-TCA has been converted into 1,1-DCE (45%) and chloroacetylene (41%), the latter arising from deprotonation of CH_2CCl_2, followed by Cl$^-$ elimination (eq. 4.5 and 4.6). It is to be stressed that although both CH_3CCl_3 and CH_2CCl_2 are very weak C-H acids and reactions (4.4) and (4.5) are probably far shifted to the left, the deprotonation reactions proceed thanks to the following irreversible Cl$^-$ eliminations leading to stable products.

$$CH_2CCl_2 + B^- \longrightarrow {}^-CHCCl_2 + BH \tag{4.5}$$

$${}^-CHCCl_2 \longrightarrow CHCCl + Cl^- \tag{4.6}$$

Reaction pathway (b) is important in all electrolyses performed in the absence of added acids. During electrolysis in the first step, 1,1-DCE arising from base promoted α,β-elimination of 1,1,1-TCA can further follow reductive α,β-elimination to give chloroacetylene (pathway (c)). In addition, 1,1-DCE and CHCCl can undergo reductions in later stages of the electrolysis when E_{app} is shifted to the appropriate potentials. In fact, 1,1-DCE shows reduction peaks at -2.60 V and -2.25 at GC and Ag, respectively (Fig.3.1e,e′). Although we did not measure the reduction potential of CHCCl, we assume it to be reducible in the same region. As shown in Scheme 4.1, reduction of both products according to a sequential hydrodechlorination pathway leads to dechlorinated products, ethylene and acetylene. For reasons that will become clear in the following sections, we added in Scheme 4.1 another possible reaction route in which 1,1-DCE is reduced to acetylene.

A last point to be considered is conversion of unsaturated hydrocarbons to ethane. We checked the reduction of C_2H_4 and C_2H_2 on GC and Ag, but observed a reduction peak at very negative potentials only for acetylene. This means that during electrolysis while C_2H_4 is not converted to C_2H_6, acetylene is effectively reduced to ethylene. This is confirmed by the yield trends shown in Figs. 4.1c-d, which show that in the last stages of electrolysis the yield of C_2H_4 increases at the detriment of that of C_2H_2.

The above proposed mechanism is based on the intermediates and products analysis during electrolyses, does not consider coupling reactions leading to C4 hydrocarbons. Although these compounds were found among the electrolysis products they were not analyzed accurately. Therefore, we refrained from commenting and speculating on their formation.

4.3.2. Electrolysis of 1,1,1,2-tetrachloroethane

4.3.2.1 Electrolysis results of 1,1,1,2-TeCA

As a representative example of vicinal PCEs electrolysis experiments were performed on 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA) in conditions similar to those used for 1,1,1-TCA. The results obtained on GC both in the absence and presence of acetic acid are reported in Table 4.2 (entries 1 and 2), whereas the concentration profiles of the starting substrate as well as its reduction products, together with the cyclic voltammograms recorded before electrolysis and at the end of each step, are illustrated in Fig. 4.2. In line with the voltammetric response recorded in the absence of HAc, the electrolysis was carried out in three steps at -2.08 V, -2.72 V and -2.95 V. At the end of the first step, which consumed 1.81 e^-/molecule, 93.2% of 1,1,1,2-TeCA was converted to 1,1-DCE (66.6%), C_2H_2 (5.6%), C_2HCl (3.2%) and C_2H_3Cl (0.9%). Further electrolysis at -2.72 V resulted in almost complete conversion of both 1,1,1,2-TeCA and 1,1-DCE to C_2HCl (5.7%), C_2H_3Cl (3.8%), C_2H_2 (66%) and C_2H_4 (3.9%). The charge consumed in this step was 1.91 e^-/molecule. After shifting E_{app} to -2.95 V, all chlorinated compounds were dechlorinated and acetylene was in part converted to ethylene. The products observed at the end of the electrolysis were C_2H_2 (22.4%) and C_2H_4 (39.5%) and C4 compounds.

When the electrolysis was repeated in the presence of HAc, essentially the same results were observed with the only significant difference that more charge was consumed due to the contribution of the acid reduction (Table 4.2, entry 2). In this case E_{app} values for the three steps were chosen as -2.01 V, -2.61 V and -2.93 V. The principal products at the end of the first step, in which 92.9% of 1,1,1,2-TeCA was converted, were 1,1-DCE (77.9%) and C_2H_2

(1.3%). In the second step, all remaining 1,1,1,2-TeCA and most of the 1,1-DCE generated in the first step were converted to C_2H_3Cl (11.9%), C_2H_4 (2.2%) and C_2H_2 (71.8%). When E_{app} was shifted to -2.93 V in the last step, complete dechlorination of C_2H_3Cl occurred together with some conversion of C_2H_2 to C_2H_4. Thus, the final products were C_2H_2 (60.9%), C_2H_4 (29.9%), C_2H_6 (3.4%) and trace amounts of C4 compounds.

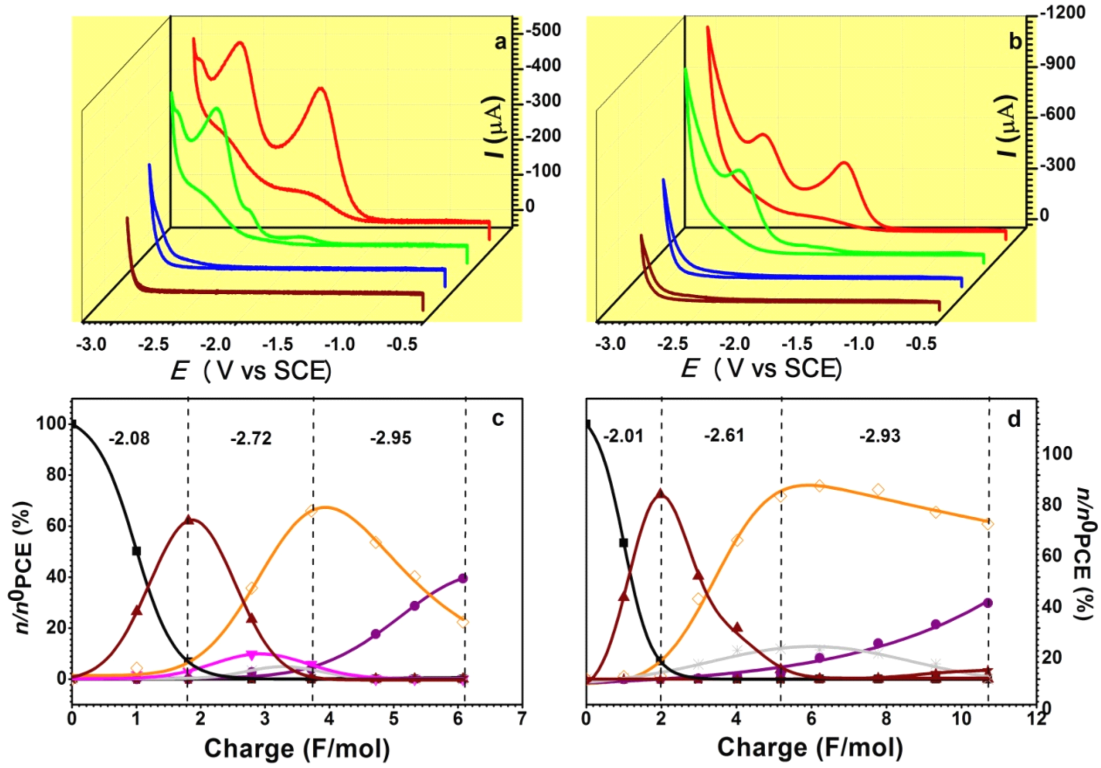


Fig. 4.3. Electrolysis of 10 mM 1,1,1,2-TeCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on GC in the absence (a, c) and presence (b, d) of 100 mM acetic acid. (a,b) cyclic voltammogrms of 1,1,1,2-TeCA recoded before electrolysis and at the end of each step; (c, d) concentration profiles: : **(■)** 1,1,1,2-TeCA; (▲) 1,1-DCE; (▼) C_2HCl; (◇) C_2H_2; (✳) C_2H_3Cl; (●) C_2H_4. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed**.**

The electrolyses on Ag have shown results in general agreement with those obtained on GC, but at less negative potentials. The data are reported in Table 4.2 (entries 3 and 4), whereas the cyclic voltammograms and concentration trends are illustrated in Fig. 4.3. The electrolysis without added acid was performed at -1.59 V, -2.41 V and -2.87 V. In the first step, 94.9% of 1,1,1,2-TeCA was converted mainly to 1,1-DCE (70.5%) and C_2H_2 (6.8%). Further reduction at the second step resulted in complete dechlorination of both 1,1,1,2-TeCA and 1,1-DCE and production of more C_2H_2 (88.2%) together with small amounts of C_2H_3Cl (3.3%) and C_2H_4 (3.8%). At the end of electrolysis after the third step, complete dechlorination of the starting 1,1,1,2-TeCA and its chlorinated intermediates were achieved, the principal reduction products being C_2H_2 (76.4%) and C_2H_4 (14.9%).

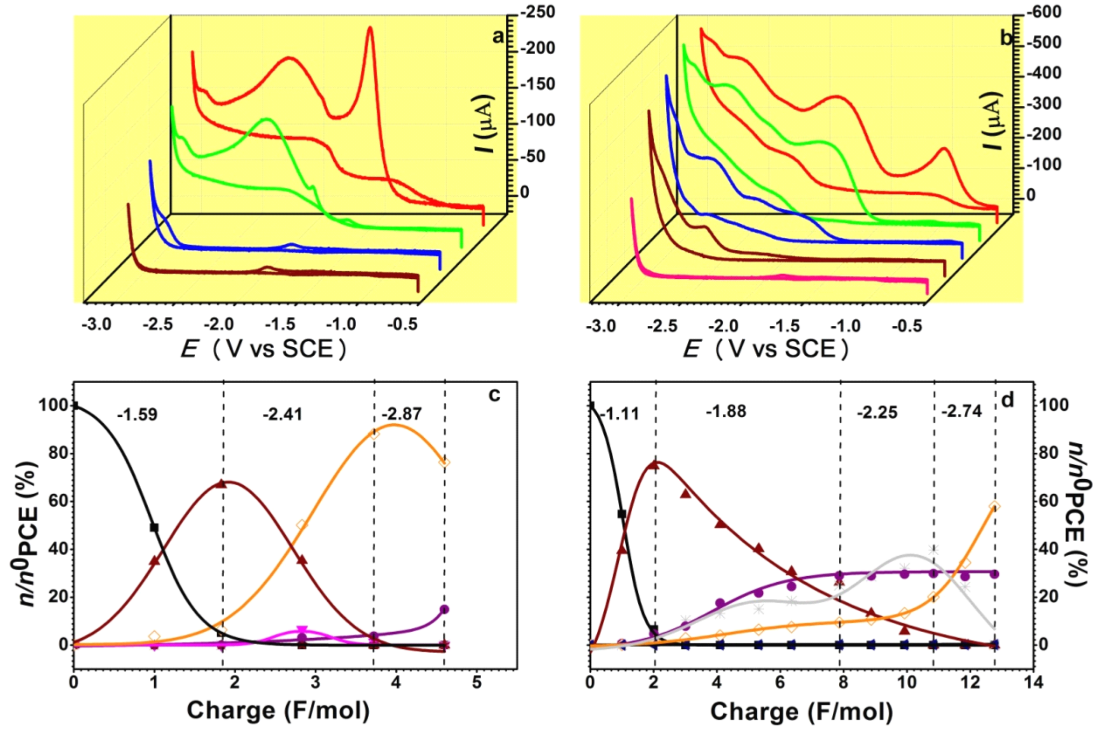


Fig. 4.4. Electrolysis of 10 mM 1,1,1,2-TeCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Ag in the absence (a, c) and presence (b, d) of 100 mM acetic acid. (a,b) cyclic voltammogrms of 1,1,1,2-TeCA recoded before electrolysis and at the end of each step; (c, d) concentration profiles: (■) 1,1,1,2-TeCA; (▲) 1,1-DCE; (▼) C_2HCl; (◇) C_2H_2; (∗) C_2H_3Cl; (●) C_2H_4. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

As shown in Fig. 4.3b, the reduction peaks of 1,1,1,2-TeCA on Ag are shifted to more positive potentials when HAc is added to the solution. This kind of cathodic shift has been observed also for 1,1,1-TCA as well as for other systems reported in the literature [12,20]. In general, the presence of acids enhances the catalytic activity of Ag toward reduction of carbon-halogen bonds possibly because of increased rate of regeneration of active sites on the electrode surface [21]. The electrolysis of 1,1,1,2-TeCA on Ag was performed at -1.11 V, -1.88 V, -2.25 V and -2.74 V. As usual 93.5% of the starting 1,1,1,2-TeCA was converted in the first step to 1,1-DCE (80.0%) and C_2H_3Cl (3.0%) together with C_2H_2 (1.9%) and C_2H_4 (5.0%). In the second and third steps 1,1-DCE is further reduced to C_2H_3Cl, which increased up to 39.7%, and the unsaturated hydrocarbons C_2H_2 and C_2H_4. When E_{app} was finally shifted to the last step value, C_2H_3Cl was completely dechlorinated and the final products of the electrolysis became C_2H_2 (29.6%) and C_2H_4 (58.0%) and some C4 hydrocarbons.

Table 4.2. Electrolysis of 1,1,1,2-TeCA at GC and Ag electrodes in the absence and presence of HAc.[a]

Entry	Cathode	HA	E_{app}[b]	n (F/mol)	1,1,1,2-TeCA (%)[c]	1,1-DCE (%)[d]	CE (%)[d]	C_2H_4 (%)[d]	C_2H_2 (%)[d]	C_2H_6 (%)[d]
1a	GC		-2.08	1.81	6.8	66.6	0.9	0.0	5.6	0
1b			-2.72	3.72	0	0.5	3.8	3.9	66.0	0.1
1c			-2.95	6.08	0	0	0	39.5	22.4	0.4
2a	GC	CH_3CO_2H	-2.01	1.97	7.1	77.9	0.4	0.0	1.3	0
2b			-2.61	5.18	0	3.8	11.9	2.2	71.8	0.0
2c			-2.93	10.70	0	0	0	29.9	60.9	3.4
3a	Ag		-1.59	1.83	5.1	70.5	0	0.0	6.7	0
3b			-2.41	3.72	0	0	3.3	3.8	88.2	0.1
3c			-2.87	4.60	0	0	0	14.9	76.4	0.2
4a	Ag	CH_3CO_2H	-1.11	2.01	6.5	80.0	3.0	5.0	1.9	0.1
4b			-1.88	7.87	0	26.1	24.9	29.0	9.4	0.2
4c			-2.25	10.84	0	0	39.7	29.9	20.1	0.2
4d			-2.74	12.77	0	0	0	29.6	58.0	0.2

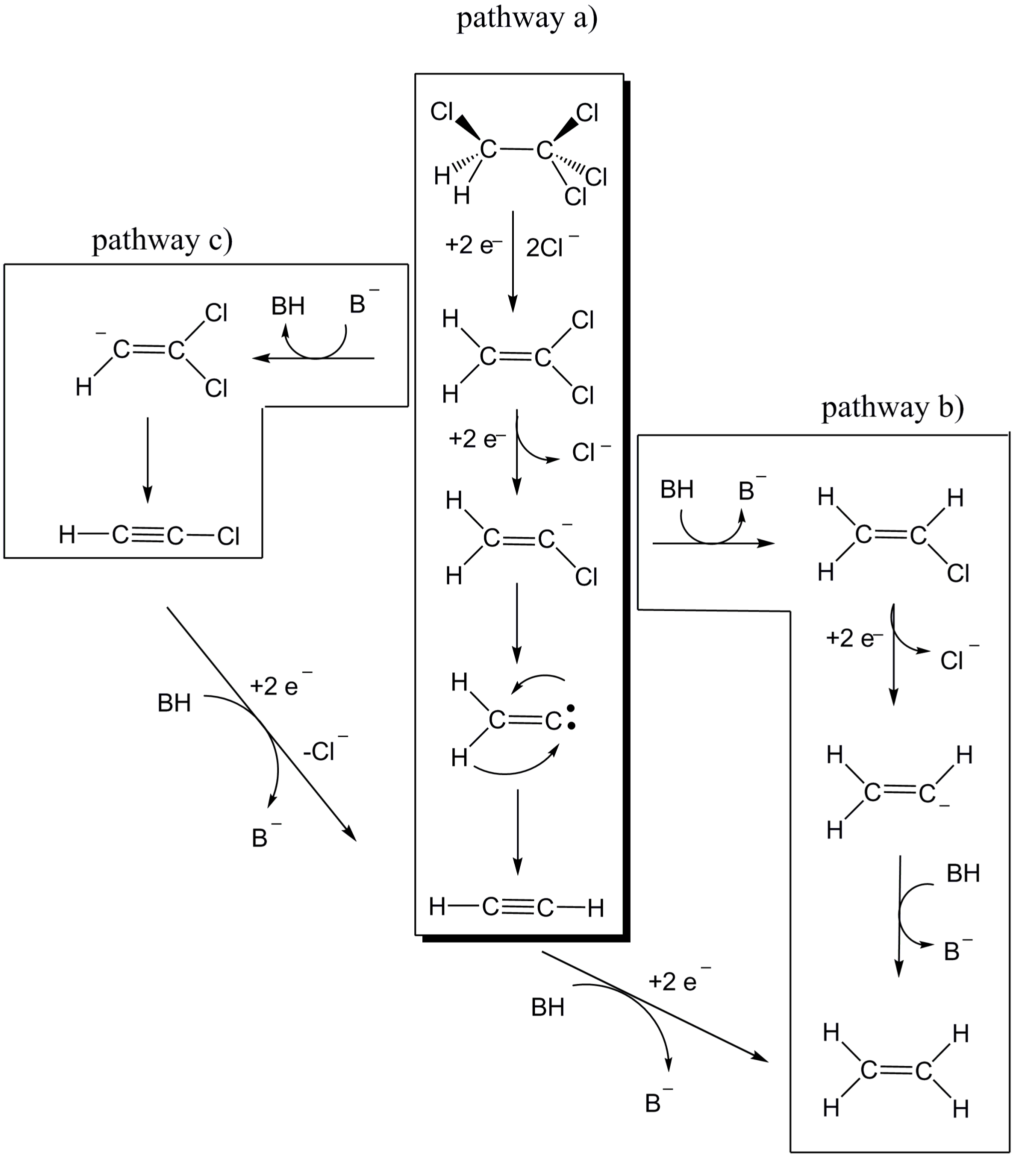
[a]Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [1,1,1,2-TeCA] = 10 mM; [CH_3CO_2H] = 100 mM. [b]E_{app} = applied potential in V vs SCE. [c]Remaining substrate. [d]Yield calculated with respect to converted 1,1,1,2-TeCA.

4.3.2.2 Reduction mechanism of 1,1,1,2-TeCA

Although there are some variations of minor importance, depending on electrode type and proton availability in the medium, the electrolysis results clearly show that reduction of 1,1,1,2-TeCA yields 1,1-DCE as the principal product. Further reduction of the latter gives mainly C_2H_2, which is ultimately reduced to C_2H_4. As shown by the concentration profiles reported in Figs. 4.3 and 4.4, the principal intermediates of the process are 1,1-DCE and C_2H_2. A plausible reaction mechanism showing the passage from 1,1,1,2-TeCA to 1,1-DCE to C_2H_2 and ultimately to C_2H_4 based on the electrolysis products is reported in Scheme 4.2. The first step is the easiest to explain. It is an α,β-elimination reaction triggered by electron transfer to the carbon-chlorine bond. α , β -elimination of haloalkanes promoted by strong bases is a well-known method of synthesis of olefins. It is important to note that this elimination reaction could not be suppressed by a good proton donor, indicating that expulsion of Cl^- from $ClCHCCl_2^-$ is much faster than protonation of the carbanion.

The passage from 1,1-DCE to C_2H_2 is less straightforward. $2e^-$ reduction of 1,1-DCE gives the carbanion $CH_2{=}CCl^-$, which can undergo either protanation to yield $CH_2{=}CHCl$ or Cl^- elimination to give a carbene **:**$C{=}CH_2$ that further rearranges to acetylene. 1,2-hydrogen migration in **:**$C{=}CH_2$ is reported to be the prototype rearrangement of vinylidenes [22,23]. Indeed, **:**$C{=}CH_2$ is an unstable isomer of acetylene and its conversion to the latter is a very fast reaction. For example, the energy barrier for this rearrangement reaction in the gas phase is 4-8 kJ mol^{-1} [24]. The principal reaction route in the absence of a good proton donor is pathway (a) (Scheme 4.2). Pathway (c) requires the presence of a strong base such as OH^- and is thus subordinated to pathway (b). When a good proton donor was added to the solution, the yield of chloroethylene increased while that of chloroacetylene dropped to zero (Figs. 4.3 and 4.4). As expected, the rate of protonation of $CH_2{=}CCl^-$ is enhanced by the presence of HAc. However, Ac^- is not so strong a base as to remove a proton from $Cl_2C{=}CH_2$ and hence pathway (c) is suppressed.

In the last step at very negative potentials, C_2H_2 is reduced to C_2H_4. This is a $2e^-$ process probably occurring in a sequence of electron transfer and proton transfer reactions, typical of the electrochemical reduction of unsaturated organic compounds. Further reduction of C_2H_4 to C_2H_6 was not observed as the process requires potentials beyond the cathodic limit of the electrolyte.



Scheme 4.2. Electrochemical reduction mechanism of 1,1,1,2-tetrachloroethane

4.3.3 Electrocatalytic dechlorination of geminal PCEs on Cu electrode

4.3.3.1 Cyclic voltammetry of geminal PCEs

The cyclic voltammetry of 1,1,1-TCA and 1,1-DCA were carried out in DMF + 0.1 M $TPABF_4$ on Cu and GC electrodes, the latter of which was chosen as a reference. Actually, the voltammetric data of these two electrodes towards geminal PCEs reduction have shown in the previous chapter, we present their voltammograms for further elucidation at here, as shown in Fig. 4.5. In analogy with Ag electrode, two successive irreversible reduction peaks of 1,1,1-TCA appear at Cu electrode. A careful examination of the reduction peaks of 1,1,1-TCA and 1,1-DCA will allow one conclude that the second reduction peak of 1,1,1-TCA coincides with that of 1,1-DCA, thus clearly indicating that the electrochemical reduction of 1,1,1-TCA yields 1,1-DCA. Only one single reduction peak of 1,1-DCA is observed on Cu electrode, it's reasonable to assume that the reduction peak of CA as the dechlorination product of 1,1-DCA is more positive than that of 1,1-DCA, similar like the case of that occurring at Ag. In particular, a close examination of the current intensities of the two reduction peaks at 1,1,1-TCA, one will find that the second peak (34.79 μA) is a little higher than the first one (27.20 μA). Since reduction of each polychloroethanes to its less chlorinated products by sequential hydrodechlorination, one would expect a series of almost equal height peaks, whereas, the invertion observed at here indicates that the second reduction peak of 1,1,1-TCA may be comprised of two reduction processes, one for 1,1-DCA and the other for its reduction product, CA. Overall reduction of geminal PCEs on Cu electrode are supposed to undergo sequential hydrodechlorination mechanism, the same as GC and Ag electrode. As reported in Table 3.1, the transfer efficient of 1,1-DCA and 1,1,1-TCA at Cu are 0.33, 0.21, respectively, implying converted dissociative electron transfer taking place during the electrochemical reduction processes. In addition, it should be stressed that Cu exhibits a good electrocatalytic activity towards 1,1-DCA and 1,1,1-TCA reduction, it promotes a positive shift of their first peak potential by 170 mV and 260 mV with respect to those of on GC electrode, respectively, in comparison, 210 mV and 390 mV are presented on Ag.

As aforementioned, proton availability in the system significantly effect on the product distributions arising from different reaction routes of the starting substrates, in particular for 1,1,1-TCA, during the electrolysis on both GC and Ag electrode. The effect of proton towards the voltammetric reduction of geminal PCEs was investigated by intentionally addition of strong proton donor, acetic acid, into the system. As shown in Fig. 4.5, the voltammetric behaviors of geminal PCEs are very sensitive to the presence of acid in the solution. Addition of one equivalent of acetic acid to a solution containing 1,1,1-TCA increases all the reduction peaks on both of GC and Cu electrode. Besides, a remarkable shift of the first reduction peak of 1,1,1-TCA was observed on Cu, while the second one doesn't alter appreciably. As well as GC behaves the same behavior, even though not as obvious as Cu. Further addition of acetic acid enhances all the reduction peaks at the two electrodes, whereas, the peak potentials appear keep constant. Further addition of HAc beyond 4 equivalents doesn't significantly modify the voltammetric patterns. Similarly, addition of HAc into solution containing

1,1-DCA leads to the increase of all the peak intensities. In contrast to 1,1,1-TCA, slightly effect on the peak potential of 1,1-DCA at Cu electrode after HAc addition.

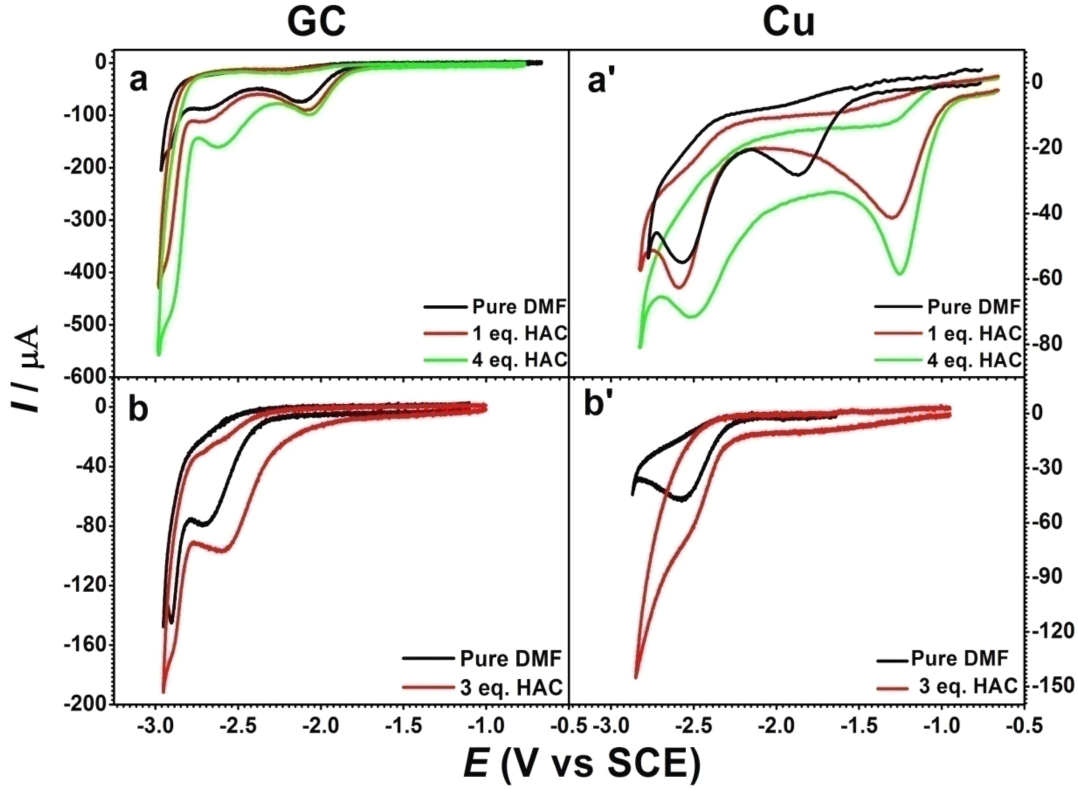


Fig. 4.5 Cyclic voltammetry of 2 mM geminal PCEs, 1,1,1-TCA (Upside) and 1,1-DCA (downside) in the absence/presence of HAc, recorded on GC and Cu electrodes in DMF + 0.1 M $(C_3H_7)_4NBF_4$ at $\nu = 0.2\ V{\cdot}s^{-1}$. Substrates in the right-hand side are the same as those indicated in the left-hand side.

Owing to the aprotic character of system, substrates, involving the starting molecule and its reduction products, may be converted by base promoted α,β-elimination and other chemical reactions without reduction, leading to a series of un-equal height peaks, which can be effectively suppressed in the presence of good proton donor. This assumption is confirmed by the cyclic voltammetry reduction experiments, that addition of excess HAc into the system enhances all the successive reduction peaks to almost the same height, as shown in Fig. 4.5. Interestingly, the presence of acetic acid in the solution activates the catalytic nature of Cu towards the reductive cleavage of geminal PCEs to different extent. The catalytic effect of Cu towards 1,1,1-TCA reduction, defined as $\triangle E_p^{cat} = E_p^{Cu} - E_p^{GC}$, which has been clarified before, induces a great promotion of reduction potentials with respect to GC from 260 mV in the absence of HAc to 820 mV when four equivalents HAc are added. Whereas, it appears the catalytic effect of Cu for 1,1-DCA reduction is a little lower. The enhancement of catalytic effect of Cu towards reduction of geminal PCEs in the presence of HAc is in accord with the one of reduction of 1,1,1,2-TeCA at Ag electrode. Actually, the catalytic effect of proton donor for chlorinated compounds reduction has already been reported before [12]. In general, the presence of HAc enhances the catalytic activity of metal electrode toward reduction of carbon-halogen bonds possibly because of increased rate of regeneration of active sites at the electrode surface [21].

4.3.3.2 Electrolysis of 1,1,1-TCA on Cu

Although the voltammetric investigations have provided convincing evidences for the catalytic effect of Cu as a candidate of noble metals and for the reduction mechanisms of geminal PCEs, it's wise to conduct preparative electrolysis studies to further confirm its performance from the practical application point of view. Since fouling problem of electrodes is common encountered in the electrochemical reaction processes, it's necessary to check whether the electrocatalytic activity of Cu is still retained all over the whole electrolysis experiment. In addition, it will further support the mechanisms proposed by voltammetric analysis through tracking the evolution of electrolytic intermediates.

As aforementioned, proton availability has a significant impact on the dechlorination routes. At here, for the purpose of comparison, two different types proton donor were introduced into the solution to investigate their effects towards the reduction mechanisms, one is acetic acid, as a strong proton donor, has been widely used in the protonation process [12,13,25], the other is water. The consideration of using water is mainly because it can be served as a weak proton donor with respect to HAc, and it will be interesting to compare this difference in the electrochemical reduction process. Besides, as known, water is a commonly solvent, which is always concomitant with organic solvent as an impurity, therefore, it's important to examine its influence for the dechlorination process in DMF solution. A concentration of 0.1 M HAc was added, to make certain that the amount of which is far more excessive with respect to chlorinated substrate. While for water, one thing need to be noted is to avoid the superposition of water discharge with the reduction process of substrates. Preliminary CV experiments indicates addition of water also has catalytic effect towards C-Cl bond reduction at Cu electrode, that the reduction potentials of geminal PCEs shift to the positive direction with water addition, and complete reduction waves of geminal PCEs can be obtained till 1 M H_2O addition. So a concentration of 1 M H_2O was chosen to add into the solution in our following researches.

The same electrolysis procedures were followed at Cu electrode like those of embarking on GC and Ag electrode of that the applied potentials, E_{app}, were chosen based on the reduction peaks and shifted stepwisely during electrolysis. Samples from the gas and solution phases were periodically withdrawn and analyzed by the GC and GC-MS during electrolysis experiments.

The electrolysis results of 1,1,1-TCA on Cu electrode performed in the absence and presence of proton donor were collected and reported in Table 4.3, where the symbols represent the same signification like before, that the number stands for the experiments, while the letter represents the different steps in the same experiment. The concentration profiles of 1,1,1-TCA as well as its main reduction intermediates and products, together with the cyclic voltammetry recorded before and after each electrolysis step were given in Fig. 4.6.

As shown in Fig. 4.6a, two reduction peaks of 1,1,1-TCA are observed at Cu, therefore, the electrolysis were carried out in two successive steps, namely at -2.26 V and -2.77 V. Complete conversion of 1,1,1-TCA was achieved at the first electrolysis step, which corresponds to 1.82 e^{-}/molecule charge consumptions, while the principal products at the end of this step were 1,1-DCA (64.82%), chloroacetylene (0.77%), ethylene (0.11%), acetylene (9.76%) and ethane (0.25%). Further electrolysis at -2.77 V consumed another 1.84 e-/molecule with all the chlorinated intermediates totally dechlorinated to hydrocarbons. The final products of electrolysis were ethylene (2.19%), acetylene (14.45%), ethane (15.04%) and small amounts of C4 hydrocarbons.

Fig 4.6d shows the concentration variations of all the species involved in the reduction of 1,1,1-TCA at Cu electrode in the absence of any proton donor. Essentially the same electrolysis intermediates were obtained with those detected on GC and Ag electrode, that 1,1-DCA, 1,1-DCE, CA and chloroacetylene as the principal intermediates were produced and passed their maximum values during electrolysis, with C2 hydrocarbons as the final products. The principal difference between the two catalytic electrodes is concentrated on the electrocatalytic activities towards C-Cl bond rupture. More positive potential was imposed towards 1,1,1,-TCA reduction at the first peak on Ag electrode than that of on Cu (-1.88 V vs -2.26 V), in which less 1,1-DCA was accumulated at the end of first electrolysis stage of Ag electrode. In addition, more C2 hydrocarbons were produced at Ag electrode than at Cu in the initial stage of electrolysis. It appears that Cu behaves quite similar properties with those on non-catalytic electrode, GC. However, a close examination will allow one find that starting from the second step, the applied potential on Cu was less negative than those of on Ag and GC, namely were -2.77 V, -2.88 V and -2.94 V at the second electrolysis stage. Eventually the final products formed at Cu electrode, ethylene (2.19%), acetylene (14.45%), ethane (15.04%), were lower than those produced on Ag electrode, which implies some variations in the reduction mechanisms occurring at the two catalytic electrodes. The poor yield of C2 hydrocarbons and mass balance will lead one to conclude that neither sequential hydrodechlorination nor reductive α,β-elimination are the main reduction mechanism, whereas some other side reactions may involve in the electrochemical reduction process. Owing to the aprotic character of DMF solution, we may assume that carbene, formed arising from eq.(4.7-4.9) , participates into the reduction process reacting with DMF solvent to give rise to CO [12,12,26,27]. However, the discussion of the fate of carbene species is out of our research scope. Actually, the involvement of carbene reaction towards chlorinated hydrocarbons reduction reaction has already been reported recently [11,12,27].

$$CH_3CHCl_2 + e^- \longrightarrow {}^{\bullet}CClH\text{-}CH_3 + Cl^- \tag{4.7}$$

$${}^{\bullet}CClH\text{-}CH_3 + e^- \longrightarrow {}^{-}CClH\text{-}CH_3 \tag{4.8}$$

$${}^{-}CClH\text{-}CH_3 \longrightarrow {:}CH\text{-}CH_3 + Cl^- \tag{4.9}$$

$${:}CH\text{-}CH_3 \longrightarrow CH_2{=}CH_2 \tag{4.10}$$

Table 4.3 (Entry 2) and Fig. 4.6(b,e) present the electrolysis results of 1,1,1-TCA at Cu electrode in the presence of 0.1 M HAc. As shown in Fig. 4.6b, except for the reduction waves of 1,1,1-TCA, a series of reduction peaks owing to the reduction of acetic acid, superposed with those of 1,1,1-TCA, are observed on Cu electrode. Three electrolysis steps were carried out by selecting different E_{app} values based on the comprehensive consideration both from the voltammetric responses and reduction potentials of 1,1,1-TCA on Cu. At the end of the first electrolysis step, E_{app}= -1.48 V, 86.83% of 1,1,1-TCA was converted to

80.79% 1,1-DCA, 0.38% ethylene and 2.81% ethane, together with some of C4 hydrocarbons, which corresponds to 2.00 e^-/molecule charge consumptions. Further electrolysis at -1.77 V by another 4.02 e^-/molecule consumption could achieve a total conversion of 1,1,1-TCA with 82.30% 1,1-DCA, 0.58% ethylene and 3.96% ethane as well as some C4 hydrocarbons formation. It should be noted here that the excess charge consumed (6.02 e^-/molecule) than stoichiometry conversion of 1,1,1-TCA indicates the occurrence of acetic acid reduction during these two electrolysis stages. Once the applied potential was switched to -2.53 V, 1,1-DCA started to be reduced, in concomitant with the yield of the final products rising to 1.27% CA, 3.51% ethylene, 68.49% ethane, together with the increase of C4 hydrocarbons.

Concentration profiles of the electrolysis products are reported in Fig. 4.6e. The principal reduction intermediate of 1,1,1-TCA in the presence of HAc is 1,1-DCA, together with the high yield of ethane (68.49%) as the final product, clearly indicating that sequential hydrodechlorination mechanism exclusively prevails the whole reduction process. Addition of a good proton donor can successively inhibit the occurrence of base promoted α,β-elimination and carbene reactions. Whereas, the formation of ethylene (3.51%) implies that side reactions also take place during electrolysis, accompanying with the detriment of acetic acid reduction, ethylene may be produced resulting from path b) as sketched in scheme 4.1, or may be formed from eq.4.10 by carbene rearrangement reaction. A close comparison of the electrolysis results at Cu electrode with that of on Ag, one will observe that essentially the same results are obtained with each other, whereas, the significant differences are the accumulation of 1,1-DCA on Cu electrode at the initial electrolysis steps and the corresponding charge consumption required, for instance, 82.30% 1,1-DCA was produced at Cu electrode after 6.02 e^-/molecule charge consumption, while the maximum values of 1,1-DCA reached to 34.8% when consumed 4.00 e^-/molecule charge during electrolysis on Ag. Besides, similar findings are observed like the one in the absence of acetic acid, that significant C2 hydrocarbons are produced at Ag electrode than at Cu electrode in the initial of electrolysis stages. Surprisingly, the dechlorinated compounds such as ethylene and ethane were formed at a applied potential where neither 1,1-DCA nor CA are reducible, which reveals the strong electrocatalytic activity of catalytic electrode (both Ag and Cu), while on the other hand, Ag presents a dominant catalytic effect over Cu.

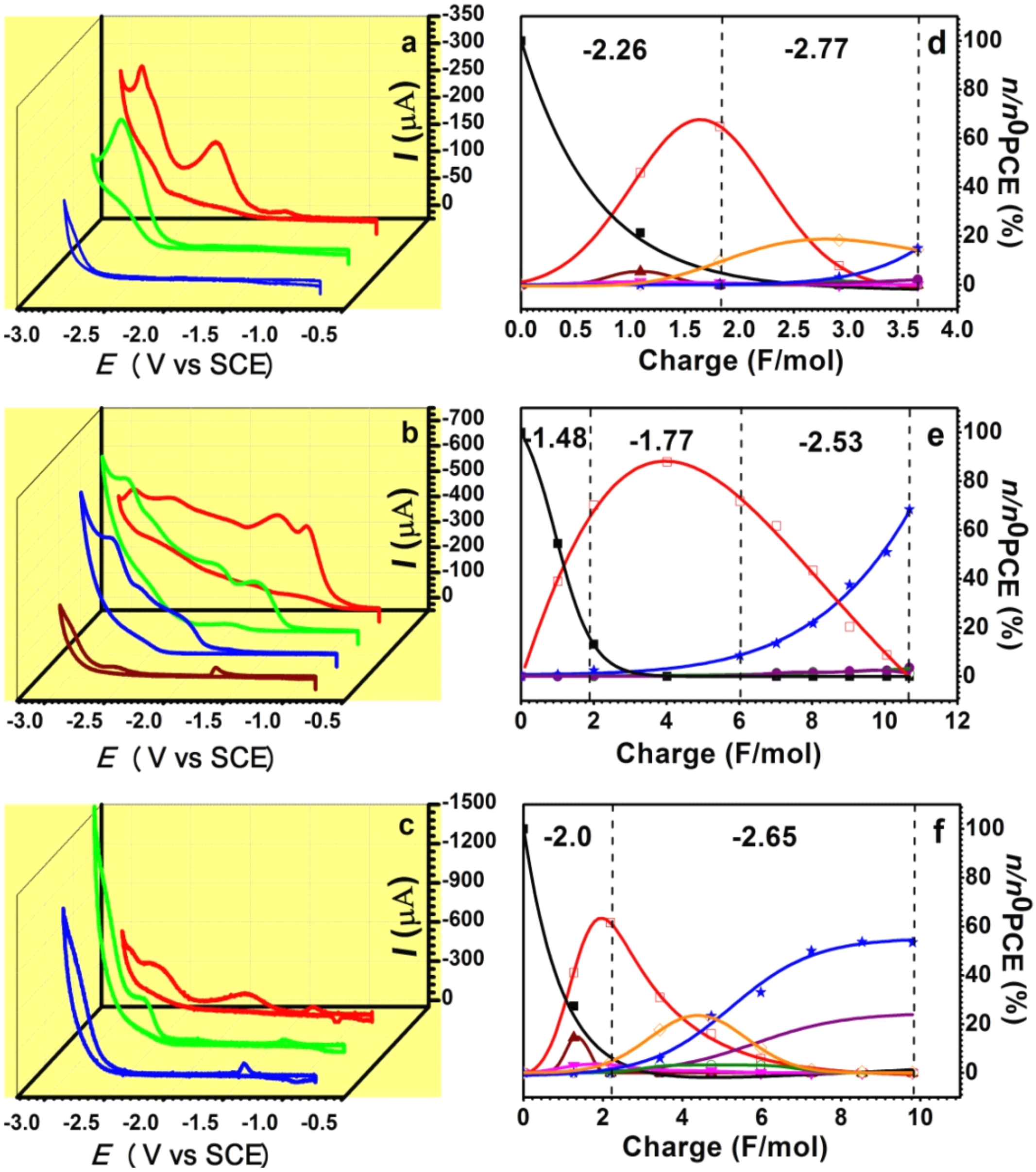


Fig. 4.6. Electrolysis of 10 mM 1,1,1-TCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 1.0 M water (c, f). (a,b,c) cyclic voltammogrms of 1,1,1-TCA recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (■) 1,1,1-TCA; (□) 1,1-DCA; (▲) 1,1-DCE; (○) C_2H_5Cl; (◇) C_2H_2; (●) C_2H_4; (★) C_2H_6. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

The process becomes less complicated when the electrolysis performed in the presence of 1 M H_2O. Fig 4.6c shows the cyclic voltammetry of 1,1,1-TCA at Cu electrode in DMF containing water. Two clearly successive reduction peaks give a hint that the electrolysis can be divided into two separated steps. As usual the E_{app} values for the two steps were chosen based on the observed voltammetric peaks at -2.0 V, -2.65 V, respectively. The electrolysis results are given in Table 4.3 (Entry 3). The principal products at the end of the first electrolysis step, in which consumed 2.19 e^-/molecule with complete conversion of 1,1,1-TCA, were 61.61% 1,1-DCA, 3.39% chloroacetylene, 0.10% ethylene, 4.40% acetylene, 0.16% ethane, together with some trace of C4 hydrocarbons. Further electrolysis at -2.65 V resulted in complete dechlorination of all the less chlorinated intermediates, and the final products became 24.08% ethylene, 0.21% acetylene, 53.27% ethane, and with some C4 hydrocarbons at the last electrolysis stage. The concentration variations of all the species formed in the reduction process of 1,1,1-TCA on Cu are presented in Fig. 4.6f. 1,1-DCA, 1,1-DCE, CA, chloroacetylene and acetylene were accumulated and thus disappeared with the charge passed during electrolysis, eventually ethylene and ethane were as the principal electrolysis products. Because of the different types of proton donors, several evident distinctions are observed in the electrolysis reduction of 1,1,1-TCA by using HAc and H_2O as proton donors, respectively. Owing to the contribution of acetic acid reduction, it takes more charge to complete transformation all the starting substrate from the solution containing HAc than that of containing H_2O (6.02 e^-/molecule vs 2.19 e^-/molecule), in which high yield of dechlorinated products, 1,1-DCA was obtained in the presence of HAc. 1,1-DCE, chloroacetylene and acetylene as intermediates have been produced during electrolysis performed in the presence of H_2O, whereas these compounds were never observed throughout the electrolysis in the presence of HAc. In addition, besides ethane, 24.08% ethylene as principal products was formed at the end of electrolysis experiment conducted with water addition. These imply the existence of some differences in the reduction mechanisms under different types of proton donor additions. As aforementioned, addition of HAc into the solvent leads to sequential hydrodechlorination exclusively prevail the whole reduction process of 1,1,1-TCA. The formed unsaturated chlorinated intermediates, such as 1,1-DCE, chloroacetylene, acetylene, clearly indicates that base promoted α,β-elimination, as a side reaction, playing a significant roles towards 1,1,1-TCA reduction in the presence of H_2O. As stated before, base promoted α,β-elimination reaction can be promoted by the presence of bases in the solution. Water can be used as a proton donor to protonate the carbanion intermediates formed during electrolysis, in concomitant with hydroxide ion (OH^-)

generation. On the other hand, water as a reactant, can participate in the electrochemical reaction, in particular at a more negative potential, electrolysis of H_2O can give rise to OH^-, subsequently, the generated OH^- is readily to react with 1,1,1-TCA together with its less chlorinated hydrocarbons products favoring the base promoted α,β-elimination route occurrence, concomitant with the unsaturated compounds formation. Therefore, water plays a double roles in the electrolysis of 1,1,1-TCA process.

All the above electrolysis experiments were carried out in different steps by shifting the applied potential stepwisely, to remove the formed less chlorinated intermediates one by one. It will be interesting to investigate the single step potentiostatic electrolysis towards 1,1,1-TCA reduction at Cu electrode, to check whether the applied potentials have substantial influence on the intermediates formatoin and product distributions during electrolysis. The electrolysis of 1,1,1-TCA at Cu electrode, were perfomed in the DMF solvent without any proton donor addition, in the presence of 0.1 M HAc, and containing 1.0 M H_2O, respectively, with the applied potential fixed at -2.78 V, -2.61 V and -2.30 V, correspondingly. Talbe 4.3 (Entry 4,5,6) reports the electrolysis results of 1,1,1-TCA performed under different solvent conditions, and the concentration profiles of 1,1,1-TCA together with its reducton products during the electrolysis process are shown in Fig. 4.7.

A close examination of the electrolysis resutls between working under single step petentiostatic electrolysis and those of working under stepwise elecctrolysis conditions, one will lead a conculution that there are ensential the same electrolysis intermediates formed, of which follow the consistent trend that firstly accumulate and then disapper during electrolysis, besides the principal products at the end of electrolysis are identical with each other. However, owing to the applied potential located at which all the intermediates can be reduced, the less dechlorinated products are thus repulsive to accumulate during single step potentiostatic electrolysis, as shown in the Table 4.3. Accordingly, the final products, such as ethylene and ethane, begin to produce start from the initial stages of electrolysis, and increase constantly all over the whole electrolysis. Overall the final products are ensential the same, regardless of the modes of potentiostatic electrolysis.

However, in the presence of H_2O, the principal products apperar to change when switching the applied potential from stepwise to single potentiostatic step, where ethane

(53.27%) is the main product in the first case, while the principal product becomes to ethylene (64.28%) in the latter case. In addition, lower charge consumption was observed when electrolysis of 1,1,1-TCA is carried out by single potentiostatic step (6.73 e^{-}/molecule) than that of performed by stepwise one (9.80 e^{-}/molecule). These imply that different reduction mechanisms may take place due to the influence of applied potential. As clarified above, water plays two different roles in the electrolytic reduction of 1,1,1-TCA at Cu electrode. Hydrodechlorination are dominated over the base promoted α,β-elimination route among the reducion mechanisms by conducting sequential potentiostatic electrolysis, in which water is mainly served as a pronton donor, whereas, the high yield of ethylene in the case of single step potentiostatic electrolysis, indicates that base promoted α,β-elimination turns to the primary reduction mechanism instead of sequential hydrodechlorination. In the base promoted α,β-elimination mechanism, certain amounts of bases must be generated during the electrolysis, since no intentionaly bases are added into the solution. Compared to carbanion intermediates, we presume these bases are mainly OH^{-}, which are produced partilly arising from the protonation reaction of water, and partially resulting from the electrolysis of water. Because the formed carbanion intermediates are readily to be prontonated in the prescence of water, besides, the high yield of ethylene in the presence of 0.1 M water (entry6a,16.98%) than the absence (entry4a, 0.25%) at the initial electrolysis stage also support this assumption. Thses observations also confirm that the relative negative potential imposed appears in favor of the electrolysis of water.

Another evident difference between the two distinct potentiostatic electrolysis methods, is the yield of final electrolysis products, C2 hydrocarbons, highly enhancement when transfer the potentiostatic electrolysis from stepwise one to single step. It seems that either hydrodechlorination or base promoted α,β-elimination reaction routes, or even both reduciton mechanisms are promoted when applying the more negative potential directly instead of shifting the potentials gradually till the last peak during electrolysis of 1,1,1-TCA. Therefore, we can suppose that side reactions involved the formed intermediates, such as radical, carbanion or carbene species, can be effectively suppressed when applying such a negative potential directly, leading to the enhancement of C2 hydrocarbons formaiton by either the sequential hydrodechlorination mechanism or base promoted α,β-elimination mechanism.

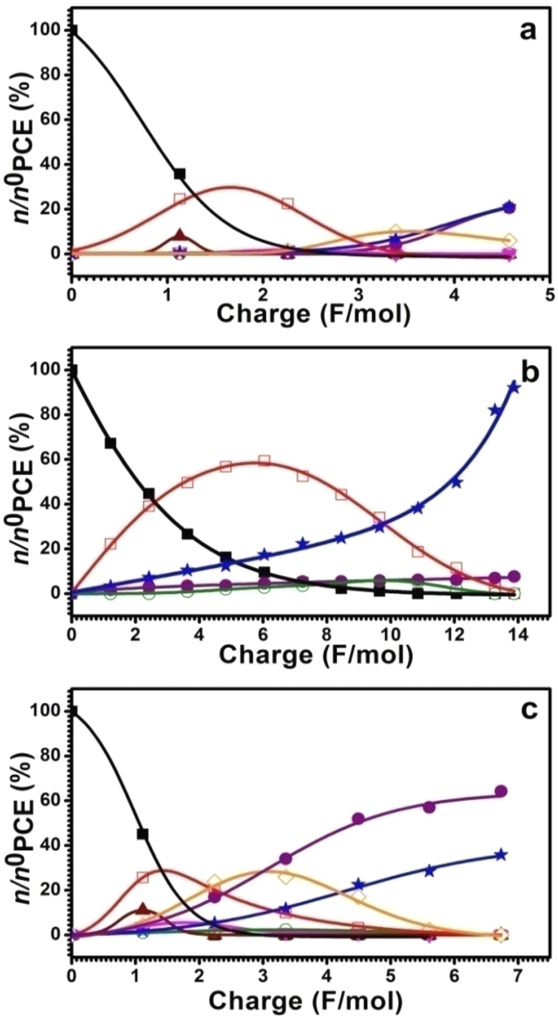


Fig. 4.7. Electrolysis results of 10 mM 1,1,1-TCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Cu in the absence (a), in the presence of 100 mM acetic acid (b), or in the presence (c) 1.0 M water. (■) 1,1,1-TCA; (□) 1,1-DCA; (▲) 1,1-DCE; (○) C_2H_5Cl; (◇) C_2H_2; (●) C_2H_4; (★) C_2H_6. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

From the pratical application point of view, the electrolysis results of 1,1,1-TCA at Cu convince the feasibility of single step potentiostatic electrolysis technology, in which complete dechlorination of all the species involved can be achieved wih high current density. Besdies, it also conveys a message that environment benign hydrocarbons could be obtained with higher yields by choosing an appropriate proton donor. Of course, owing to the reduction of the added proton donor, the charge consuption required for the total complete of chlorinated species are a little higher compared to those in the absence of proton donor, however, it should be noted that the addition of HAc/H_2O could activate the catalytic nature of catalytic electrodes (Ag, Cu) towards the reductive cleavage of C-Cl bond, and it also can promote the yield of usefull hydrocarbons.

Table 4.3. Electrolysis of 1,1,1-TCA at Cu electrode in the absence and presence of different proton donors [a]

Entry	Cathode	HA	E_{app}[b]	n (F/mol)	1,1,1-TCA (%)[c]	1,1-DCA (%)[d]	CA (%)[d]	1,1-DCE (%)	C2HCl (%)	C_2H_4 (%)[d]	C_2H_2 (%)[d]	C_2H_6 (%)[d]
1a	Cu		-2.26	1.09	21.28	58.37	0	6.96	1.49	0	0.07	0.02
1a’			-2.26	1.82	0	64.82	0	0	0.77	0.11	9.76	0.25
1b			-2.77	3.64	0	0	0	0	0	2.19	14.45	15.04
2a	Cu	CH_3CO_2H	-1.48	2.00	13.17	80.79	0	0	0	0.38	0	2.81
2b			-1.77	6.02	0	82.30	0	0	0	0.58	0	3.96
2c			-2.53	10.68	0	2.56	1.27	0	0	3.51	0	68.49
3a	Cu	H_2O	-2.0	1.26	27.36	56.58	0	19.93	4.02	0	0.71	0.14
3a’			-2.0	2.19	0	61.61	0	0	3.39	0.10	4.40	0.16
3b			-2.65	9.80	0	0	0	0	0	24.08	0.21	53.27
4a	Cu		-2.78	2.26	0	22.46	0.55	0	1.84	0.25	1.57	1.07
4b			-2.78	4.57	0	0	0	0	0	20.66	5.94	21.03
5a	Cu	CH_3CO_2H	-2.61	2.42	44.78	70.77	0	0	0	5.44	0	13.12
5b			-2.61	13.88	0	0	0	0	0	7.67	0	92.04
6a	Cu	H_2O	-2.65	2.24	20.03	20.08	1.87	0	4.58	16.98	23.73	5.33
6b			-2.65	6.73	0	0	0	0	0	64.28	0	35.83

[a] Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [1,1,1-TCA] = 10 mM; $[CH_3CO_2H]$ = 100 mM. [b] E_{app} = applied potential in V vs SCE. [c] Remaining substrate. [d] Yield calculated with respect to converted 1,1,1-TCA.

Table 4.4. Electrolysis of 1,1-DCA at Cu electrode in the absence and presence of different proton donors.[a]

Entry	Cathode	HA	E_{app}[b]	n (F/mol)	1,1-DCA (%)[c]	CA (%)[d]	C2H3Cl (%)	C_2H_4 (%)[d]	C_2H_2 (%)[d]	C_2H_6 (%)[d]
1a	Cu		-2.80	1.36	30.3	1.58	0.24	3.03	35.20	17.76
1b			-2.80	2.74	0	0	0	3.90	18.46	27.14
2a	Cu	CH_3CO_2H	-2.62	4.20	68.47	8.90	0	2.07	0	25.43
2b			-2.62	12.13	0	0	0	6.74	0	87.41
3a	Cu	H_2O	-2.7	2.70	19.17	5.75	1.10	0.78	14.01	37.51
3b			-2.7	6.78	0	0	0	7.28	4.78	75.26

[a] Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [1,1-DCA] = 10 mM; [CH_3CO_2H] = 100 mM. [b] E_{app} = applied potential in V vs SCE. [c] Remaining substrate. [d] Yield calculated with respect to converted 1,1-DCA.

4.3.3.2 Electrolysis of 1,1-DCA on Cu

For the sake of further check the applicability of electrocatalytic dechlorination technology by using Cu electrode, and provide more evidences for the reduction mechanisms of geminal PCEs proposed in the previous section. Electrolysis experiments of 1,1-DCA were carried out at Cu electrode in the conditions similar to those used for 1,1,1-TCA, such as in DMF solvent without any proton donor addition, in DMF solution containing 0.1 M HAc, and in the presence of 1.0 M H_2O of the DMF solution, respectively.

Voltammetric studies have revealed that only one reduction peak appears towards the reduction of 1,1-DCA at Cu electrode in DMF solvent. Fig 4.8(a-c) show the cyclic voltammetry of 1,1-DCA in different solvent conditions. Except in the case of 0.1 M HAc presence, voltammograms recorded in DMF solution without any proton donor addition (Fig. 4.8a) and containing 1.0 M H_2O (Fig. 4.8c) further confirm this observation. Whereas, the reduction peak of 1,1-DCA at Cu electrode is superposed due to the reduction of acetic acid, which can well explain the distinct electrochemistry behavior of Cu in the presence of HAc with the others. Therefore, the applied potentials, E_{app}, towards 1,1-DCA electrolysis in different conditions were fixed at the last peak, namely -2.80 V for the case without any proton donor addition, -2.62 V for the one in the presence of 0.1 M HAc, and -2.70 V when 1.0 M H_2O was added. The electrolysis results in all cases are reported in Table 4.4, and the concentration variations involved all the species in the electrolysis reduction of 1,1-DCA are shown in Fig 4.8d-f, respectively.

Table 4.4 (entry 1) and Fig 4.8(a,d) report the electrolysis results of 1,1-DCA performed in the absence of any proton donor. At the end of electrolysis experiment, which consumed 2.74 e^-/molecule, complete dechlorination of 1,1-DCA together with its reduction intermediates were achieved, accompanying the formation of 3.90% ethylene, 18.46% acetylene and 27.14% ethane as the final products. In general, the electrolysis results of 1,1-DCA at Cu electrode present similar trend with those of 1,1,1-TCA performed both under stepwise (Table 4.3, entry1) and single step potentiostatic electrolysis(Table 4.3, entry4), where CA and chloroethylene as intermediates were also produced with the conversion of 1,1-DCA, and C2 hydrocarbons were the principal products, as shown in Fig 4.6d and Fig 4.7a. The production of ethane and unsaturated C2 hydrocarbons indicate that sequential hydrodechlorination and base promoted α,β-elimination mechanism take place during the electrolysis, simultaneously, besides, the low mass balance at the end of electrolysis implies carbene species were also involved in the reduction process. These are in accord with the one in the electrolysis of 1,1,1-TCA.

Electrolysis results of 1,1-DCA performed in the presence of 0.1 M HAc are given in Table 4.4 (entry2), and the concentration profiles are shown in Fig 4.8e. The principal products were 6.74% ethylene and 87.41% ethane at the end of electrolysis experiment, which corresponds to consume 12.13 e^-/molecule charge. As have already stated, the excessive high charge consumption is mainly due to the reduction of acetic acid. Similar with the electrolysis of 1,1,1-TCA in the presence of HAc (Table 4.3, entry2 and entry5), the electrolysis products of 1,1-DCA clearly indicate sequential hydrodechlorination prevails the reduction mechanisms. Whereas, the low yield of ethylene implies that base promoted α,β-elimination, even not so evidently, still takes place during electrolysis.

Finally, let's discuss the electrolysis of 1,1-DCA in DMF solution with 1.0 M H_2O addition, the electrolysis results and the concentration variations of 1,1-DCA together with its reduction intermediates are reported in Table 4.4 (entry3) and Fig 4.8f, respectively. After 6.78 e^-/molecule charge consumption, the electrolysis products became 7.28% ethylene, 4.78% acetylene and 75.26% ethane at the end of experiment. A close comparison of the electrolysis results of 1,1-DCA in the presence of water with those of 1,1,1-TCA (Table 4.3, entry3 and entry6), one will find that the electrolysis products are essential the same with that of 1,1,1-TCA performed under stepwise potentiostatic electrolysis, in which hydrodechlorination are the principal reduction mechanism with ethane as the final product, and 1,1-DCA as a main intermediate was accumulated in that case. However, the electrolysis results are different from the one 1,1,1-TCA performed under single step potentiostatic electrolysis, where ethylene is the principal product. On the other hand, it confirms electrolysis of 1,1-DCA in the presence of water mainly undergoes sequential hydrodechlorination mechanism, while the reduction of 1,1,1-TCA under single step potentiostatic electrolysis can restrict the formation of 1,1-DCA and is more in favor of following base promoted α,β-elimination route. Besides, it also indicates the production of ethylene, which is as the principal product in the electrolysis of 1,1,1-TCA (Table 4.3, entry6), is not primarily arising from the conversion of 1,1-DCA, but resulting from the starting substrate(sheme4.1 path b) and path c)).

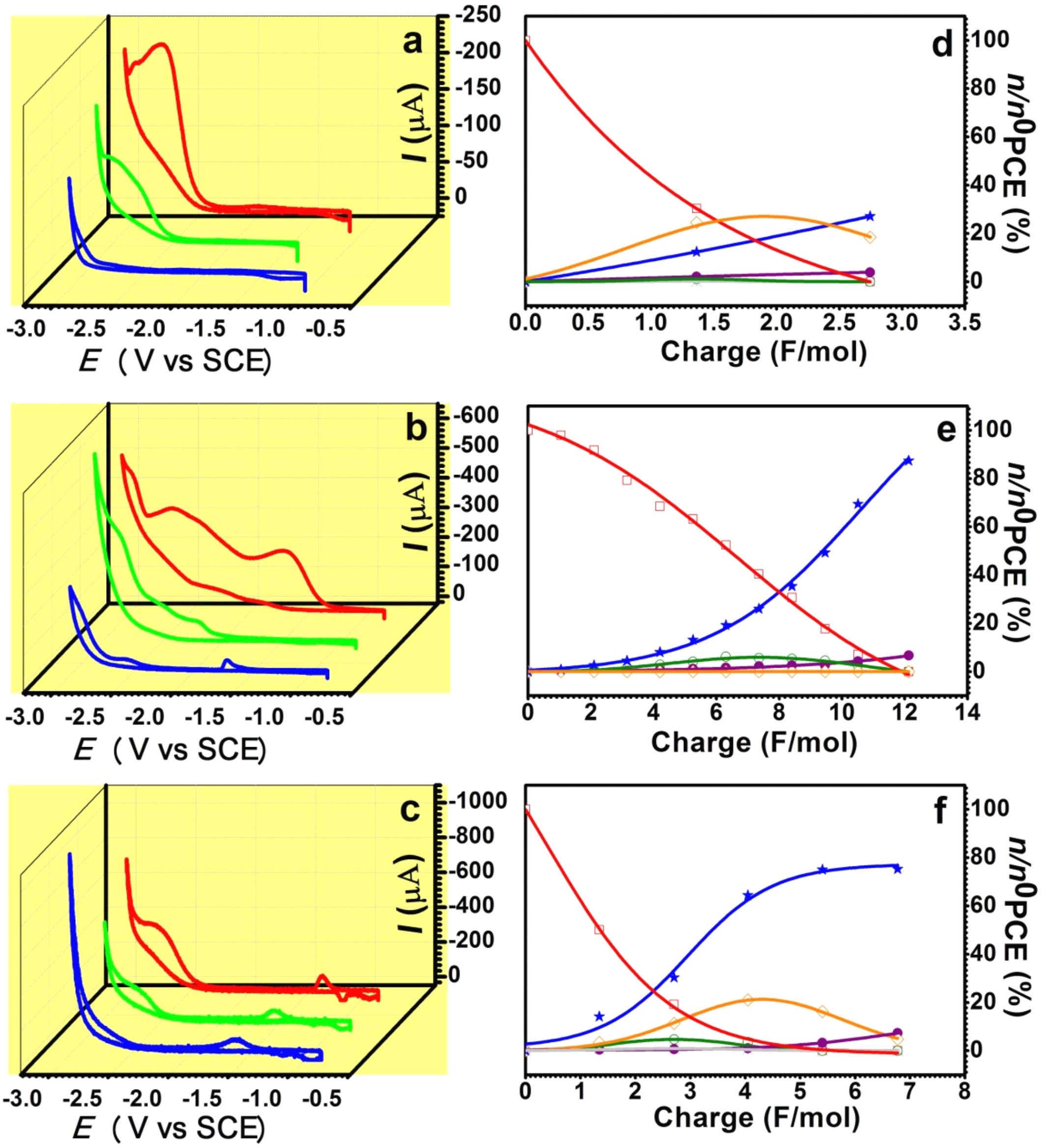


Fig. 4.8. Electrolysis of 10 mM 1,1-DCA in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 1.0 M water (c, f). (a,b,c) cyclic voltammogrms of 1, 1-DCA recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (□) 1,1-DCA; (▲) 1,1-DCE; (○) C_2H_5Cl; (✳) C_2H_3Cl; (◇) C_2H_2; (●) C_2H_4; (★) C_2H_6. The inserted numbers indicate E_{app}, whereas the vertical lines indicate when it was changed.

4.4 Conclusions

Electrolytic investigations of some representative PCEs have been carried out in DMF solution in the absence and presence of different proton donors (HAc, H_2O), at non-catalytic (GC) and catalytic (Ag, Cu) electrode, respectively. Based on the voltammetric analysis and the further electrolysis results, it confirms that the reductive cleavage of PCEs follow two distinct reduction mechanisms regardless of the nature of electrode materials. For geminal PCEs, it mainly undergoes sequential hydrodechlorination mechanism, where evolves a series of 2 e^- reduction steps each involving an elimination of chlorine ion and a subsequent protonation till ultimately ethane formation. Proton donor plays a significant role in this step. Addition of HAc into the solution containing chlorinated substrate can promote the hydrodechlorination mechanism with high yield of ethane, by restricting the occurrence of base promoted α,β-elimination and the formation of carbene species, which have been validated that are readily taken place in the aprotic medium. In contrast to geminal PCEs, vicinal PCEs are found to conform to reductive α,β-elimination mechanism, in which two chlorine ions are expelled by receiving two electron transfers, in concomitant with the corresponding olefin generation which are further reduced at more negative potential. It's interesting to find that, different with geminal PCEs, reductive α,β-elimination mechanism of vicinal PCEs is less influenced by proton donor addition.

Electrocatalytic activities of Cu towards geminal PCEs reduction were also investigated by cyclic voltammetry experiments in this research. It shows Cu exhibits excellent catalytic effect in activating C-Cl bond of geminal PCEs, which can evidently promote the positive shift of reduction potentials of geminal PCEs with respect to GC electrode, namely by 170 mv and 260 mv shift for 1,1-DCA and 1,1,1-TCA, respectively. Acetic acid could further activate the activity of Cu for the reduction of geminal PCE. The reductive cleavage of C-Cl bond seems become readily to take place after HAc addition, in particular for 1,1,1-TCA, whose first reduction peak potential is positive shifted by 820 mv when 4 equivalents HAc were added into the solution. We suppose that the presence of HAc enhances the catalytic activity of Cu electrode toward reduction of carbon-halogen bonds possibly because of increased rate of regeneration of active sites on the electrode surface.

Electrolysis of geminal PCEs at Cu electrode in different solvent conditions have been carried out, to further check the feasibility of complete dechlorination by using Cu electrode, and investigate the different influence parameters towards dechlorination process. The type of proton donors towards the effect of reduction mechanism and product distributions for geminal PCEs has been examined, in which HAc as a strong proton donor and H_2O as a weak proton donor were chosen. The electrolysis results reveal that addition of proton donor promotes the hydrodechlorination mechanism by restricting the formation of carbene species, accompanying with high yield of ethane, in particular for the case in the presence of HAc, in which 68.49% ethane was produced at the end of electrolysis. The addition of water plays double roles in the electrolysis process, one is as proton donor, the other is to provide bases which can facilitate the base promoted α,β-elimination reaction route. Single step potentiostatic electrolysis of 1,1,1-TCA at Cu were performed to validate the applicability of this technology and check whether it has influence on the product distributions compared to the stepwise electrolysis. It is found that complete dechlorination of the starting substrate could be achieved in different solvent conditions with high current intensity by using single step potentiostatic electrolysis. In general, the electrolysis products are essential the same regardless of the modes of potentiostatic electrolysis. One exception is the electrolysis of 1,1,1-TCA in the presence of water where the principal product change from ethane (53.27%) to ethylene (64.28%) when switching the potentiostatic electrolysis from stepwise step to single step, indicating different reduction mechanisms taking place during the electrolysis process. Owing to the potential applied in the single step potentiostatic electrolysis located at which all the reduction products can be reduced, therefore, less intermediates were found accumulated, and the final products, such as ethylene, ethane, are detected start from the initial electrolysis step and increase constantly during electrolysis. Besides, more C2 hydrocarbons were produced at the end of electrolysis when using single step potentiostatic electrolysis; it seems that side reaction can be effectively suppressed at more negative potential, leading to the enhancement of C2 hydrocarbons.

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Chapter 5 Electrocatalytic dechlorination of polychloromethanes (PCMs) on Cu electrode

Abstract

Polychloromethanes are another class of the most ubiquitous environment pollutants, chlorinated volatile compounds (Cl-VOCs). Electrocatalytic dechlorination of chlorinated hydrocarbons has been confirmed as one of the most promising methodologies for the abatement of these compounds. Cu, as a candidate of noble metal electrodes, has been found exhibiting good catalytic activity for the reduction of PCEs. In this study, the electrocatalytic properties of Cu towards the reduction of PCMs were investigated in different solvent conditions at Cu and GC electrode, the latter used as reference for evaluating the catalytic effect of Cu. It shows that Cu displays an excellent catalytic activity for the reduction of PCMs. The addition of proton donor, such as HAc and H_2O, could promote the catalytic effect of Cu for the reductive cleavage of C-Cl bond with a significant positive shift of reduction potentials of PCMs. Based on the voltammetric analysis of PCMs and further electrolysis of CT and CF at Cu in different solvent conditions, reduction of PCMs is shown that not only strongly depends on the proton availability, but also depends on the proton type. In the absence of proton donor, reduction of PCMs mainly undergoes carbene reaction routes with a severe loss of mass balance. Addition of proton into the solution may enhance the yield of hydrocarbons by favoring sequential hydrodechlorination mechanism during electrolysis. Strong proton donor, such as HAc, can considerably increase the yield of CH_4 by restricting side reactions. H_2O is found not only acting as a proton donor; it also dominates OH^- with the detriment of proton donors, which can result into some other side reactions during electrolysis. Essential the same electrolysis products were obtained regardless of the modes of sequential potentiostatic electrolysis, with the only significant difference that electrolysis intermediates were repulsive to accumulate by using single step electrolysis compared to those performed under sequential one. Eventually, the similarities and differences towards the reduction of PCMs and geminal PCEs were investigated.

5.1 Introduction

Chlorinated volatile organic compounds (Cl-VOCs), including polychloromethanes (PCMs), polychloroethanes (PCEs), polychloroethylenes, are among the most frequently encountered contaminants in soils and any kind of fluvial mediums, such as groundwater, rivers, lakes [1], due to their widespread use in industrial and commercial application as solvents, metal degreasing, dry cleaning and pesticides. In general, the inattention and inadequate to proper disposal methods of Cl-VOCs over the past decades result into the current widespread polluted situation. On the other hand, because of their toxicity, some of them are even suspected as human carcinogens, and persistence in environment, which have forced to focus attention from the health authorities. Therefore, some of them are priority controllable pollutants in China, U.S.EPA and European Union, and strictly controlled in drinking water [2-4].

A number of physical, biochemical and chemical methods have been developed to remediate the contamination mediums polluted by Cl-VOCs with limited success. The conventional methods employed for removal of these compounds include adsorption, air stripping technologies; they are very rapid and effective to remove the contaminations from polluted sites. However, these technologies only transfer the pollutants from one phase to another and it requires a further disposal procedure after that. Incineration of gas- and liquid-phase Cl-VOCs may produce dioxins and furans, which are even more poisonous than the starting substrates, therefore this methods is also discouraged [5]. The degradation of Cl-VOCs by biological methods shows the deficiencies of less tolerant of bacteria to the toxicity of chlorinated species, slow reaction rate and even producing more severe intermediates than the precursor [5]. The advanced oxidation technologies, known as Fenton oxidation [6,7], photochemistry oxidation [8,9], electrochemical oxidation technology [10,11], etc, have been employed to abate the contamination of refractory Cl-VOCs in environment. However, the strong reactive intermediates formed during oxidation process, such as radical species, may produce undesired byproducts due to their unselective oxidation properties. Besides, the addition of chemical substances and high energy consumptions increase the processing cost of these technologies.

Because of the electronegative character of chlorinated substituent, heavily chlorinated compounds are readily to be reduced as electron acceptors in redox reactions. Therefore, zerovalent metal technology has received considerable attentions in the remediation of contaminated groundwater by chlorinated compounds [12-15]. Whereas the potential disadvantages of this methods includes the release of metal ions into the environment, deterioration of process kinetics due to metal corrosion and surface passivation by formation oxides or hydroxides. Electrochemical reduction technology, as a promising approach, has attracted numerous attentions and investigations for the abatement of Cl-VOCs, owing to the specific character of better environment compatibility, controllable reaction kinetics, cathodic polarization against metal surface passivation or corrosion, as well as working under mild conditions [16,17]. Previous studies have shown that electrochemical dechlorination of Cl-VOCs can be successively performed both in the non-aqueous solutions [18-20] and aqueous solutions [21-23]. However, due to the relative low solubility of Cl-VOCs in water, besides the rather negative reduction potentials required for complete dechlorination of Cl-VOCs where electrolysis of water may take place, which result into the sluggish reaction rates with poor current efficiencies during electrolysis. These problems can be solved by choosing an appropriate organic solvent, such as, DMF, since it has a strong solubility for Cl-VOCs and can provide a rather wide potential window to prevent the discharge of electrolyte. Therefore, electrochemical dechlorination of chlorinated compounds is attractive applied to the destruction of existing stocks of banned chlorinated solvents or those produced as intermediates during industrial process; in addition, it also can be applied to the treatment of contaminated soils and groundwater by combination with physical methods.

Charge transfer rates for electrochemical reactions are a function of electrode material as well as overpotential [5,24]. The main obstacle for developing commercially viable electrochemical dechlorination technology is to explore an electrode material that is stable, high catalytic activity as well as low price and high availability. Extensive investigations have been carried out for the dechlorination of chlorinated compounds on various electrode materials. Ag, Pt, Pd and other noble metals exhibit excellent catalytic activities towards C-Cl bond dissociation [22,25], whereas, the costly price of these materials limit the large scale applications. Cu, as a common metal, has been found displaying good catalytic effect towards chlorinated compounds reduction [17,25,26], and can be used as a cathode to achieve dechlorination of carbon tetrachloride with obtaining useful hydrocarbons [17]. However, the previous dechlorination studies of Cu are mainly concentrated in aqueous, its electrocatalytic activity in organic solvent has seldom exploited. Actually, in the previous chapter, we have already revealed the excellent electrocatalytic activities of Cu towards geminal PCEs reduction in DMF solvent, and an exhaustive dechlorination of geminal PCEs can be achieved during electrolysis by using Cu electrode. Herein, we switch to investigate another type of Cl-VOCs, PCMs, to check the electrocatalytic properties of Cu towards PCMs reduction, and try to reveal the dechlorination mechanisms of PCMs on Cu electrode. The feasibility of electrolysis of PCMs by using Cu electrode was evaluated, to demonstrate whether the exhaustive dechlorination of PCMs can be obtained like geminal PCEs.

As already stated in the previous chapter, hydrodechlorination mechanism involves electron and proton transfer two processes, and the dechlorination reduction mechanisms are very sensitive to proton availability. Therefore, it’s helpful to be able to control both processes. Herein, we still use DMF as an aprotic solvent to conduct the dechlorination studies of PCMs. Acetic acid and water, as two different types of proton donors, were intentionally added to the solution containing PCMs to investigate their effect on dechlorination mechanisms and product distributions during electrolysis of PCMs.

5.2 Experimental and methods

5.2.1 Materials and chemicals

Dimethylformamide (DMF) was treated in the presence of anhydrous Na_2CO_4 for several days. After double distillations at lower pressure under N_2 conditions, DMF was then stored in a brown bottle under the protection of Argon. Tetrapropylammonium tetrafluoroborate ($C_{12}H_{28}BF_4N$, $TPABF_4$, Fluka) was recrystallized twice in ethanol and dried in a vacuum oven at 70 ℃ for at least two days. Carbon tetrachloride (CT), Chloroform (CF), dichloromethane and chloromethane were purchased from Sigma-Aldrich and used directly as received.

5.2.2 Experiment instrumentation

Electrochemical measurements were performed on a computer controlled EG&G PARC

Model 273 potentiostat/galvanostat. All experiments were conducted at 25 ℃ in a three electrode system with GC, Ag or Cu disk as working electrode, a Pt wire as counter electrode and Ag/AgCl/ Me_4NCl(sat) in DMF + Acetonitrile (3:1,V/V) solution as reference electrode, respectively. The reference electrode was calibrated at the end of each experiment against the ferricenium/ferrocene couple ($E_{Fc+/Fc}$ = 0.475 V vs SCE in DMF), which allowed conversion of all potentials to saturated calomelelectrode (SCE) scales. To be noted that all the potential values in this thesis are calibrated to SCE except specialization.

The working electrode in this research were disks from 2 mm diameter metal wires (Ag, Cu, Alfa Aesar ≥ 99.99%) or from a 3 mm diameter GC rod (Tokai, GC-20), which were always polished to a mirror finish with silicon carbide papers by decreasing grain size (Struers, grit: 1000, 2400, 4000); followed by diamond paste (3-, 1-, 0.25-µm particle size). After each polishing step, the electrodes were always cleaned in ethanol in an ultrasonic bath for about 5 min. the electrodes were constructed as previous described [19].

5.2.3 Cyclic voltammetry and electrolysis experiments

Voltammetric experiments were performed in a thermostated undivided tank cell with 0.1 M $TPABF_4$ as supporting electrolyte, and 2 mmol·$L^{-1}$of chlorinated substrate in DMF. The system was operated under Argon flow conditions all through the research. Cyclic voltammograms were recorded at different scan rates at GC and Cu electrode, respectively.

Electrolytic experiments were carried out in a sealed thermostated divided tank cell, with Ag/AgCl/ Me_4NCl(sat) as reference electrode, Pt as counter electrode, adopting Cu plate, or GC plate as working electrode, respectively. During electrolytic process, samples of gas and solution phase were withdrawn from the sealed reaction cell for analysis by GC or GC-MS periodically.

5.2.4 Analysis

The electrolytic products in the gas phase were withdrawn by a gas syringe, followed by directly injecting into a HP 6890 system gas chromatograph equipped with a HP Plot Q 30 m ×0.537 mm× 0.40 mm capillary column (Agilent Technologies, USA) and a flame ionization detector (FID). The injector was equipped with a 0.75 mm i.d. liner and was operated in a split mode (15:1). The oven temperature was set at 60 ℃ for 2 min, then increased to 240

℃ at a rate of 30 ℃·min^{-1} and held for 2 min. The injector and the detector were set at 150 and 250 ℃, respectively, and the carrier gas (He) flow was 4.4 mL·min^{-1}. Identification and quantification of the products were based on comparison with authentic samples and calibration curves, respectively.

Solution phase products were analyzed by withdrawing 1 μL of sample and subsequently injecting into the column of GC-MS for identification and quantification analysis. The sample analysis were performed on a HP 6890 gas chromatograph equipped with a HP 5973 mass selective detector (MS) and a DB-5 ms 30 m×0.25 mm×0.25 mmcapillary column (Agilent Technologies, USA). The oven temperature was set at 32 ℃ and held for 4 min, then increased to 40 ℃ at the rate of 10 ℃·min^{-1} holding for 1 min. Helium with a flow rate of 0.5 mL·min^{-1} was used as a carrier gas. Authentic compounds were used for the identification and quantification of the products based on a calibration curve prepared before electrolysis.

5.3 Results and discussion

5.3.1 Cyclic voltammetry of polychloromethanes

Voltammetric experiments of polychloromethanes (PCMs) were carried out at GC and Cu electrode in DMF + 0.1 M $TPABF_4$ at the scan rate range from 0.02 V•s^{-1} to 10 V•s^{-1}, in which GC is used as a inert electrode to evaluate the electrocatalytic activity of Cu. Fig. 5.1 illustrates the cyclic voltammograms of CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl recorded on GC and Cu electrode. As shown, a number of irreversible reduction peaks appear on the two electrodes, whereas the numbers of peaks and their potentials are strongly dependent on the structure of molecule and the nature of electrode.

In general, the numbers of reduction peaks present on GC electrode are in accord with the chlorines attaching on the PCMs molecule, for instance, CCl_4 exhibits four reduction waves, whereas $CHCl_3$, CH_2Cl_2 and CH_3Cl present three, two, one reduction peaks, respectively. A close examination of the voltammograms of PCMs, one will find that the second reduction peak of CH_2Cl_2 coincide with that of CH_3Cl, thus indicating that CH_3Cl is indeed the reduction product of CH_2Cl_2. As expected along the same lines, the cyclic voltammogram of chloroform shows three successive reduction peaks, the last two of which are in accord with the reduction of CH_2Cl_2, CH_3Cl, respectively. Besides, the last three reduction peaks of CCl_4 correspond to the first reduction step of $CHCl_3$, CH_2Cl_2 and CH_3Cl, respectively, these are identical with the previous investigations [19,20]. Therefore, an overall sequential hydrodechlorination mechanism for PCMs is proposed, where evolves through a series of two electron transfer reduction steps, in concomitant with eliminating one chlorine ion and being protonated subsequently at one single step, ultimately leading to methane formation. Reduction of PCMs, denoted as CH_nCl_{4-n} (n=1-3), conform to the following reaction sequences:

$$CH_nCl_{4-n} + e^- \longrightarrow {}^\bullet CH_nCl_{3-n} + Cl^- \qquad (5.1)$$

$$^\bullet CH_nCl_{3-n} + e^- \longrightarrow {}^- CH_nCl_{3-n} \qquad (5.2)$$

$$^- CH_nCl_{3-n} + HA \longrightarrow CH_{n+1}Cl_{3-n} + A^- \qquad (5.3)$$

In which HA stands for any proton donor existed in the medium, the first electron transfer is the rate determining step where ET and cleavage of C-Cl bond take place in a concerted mechanism. The formed radical in the first step is readily reduced with respect to the starting substrate, which is in line with the observation that never splitting of two electron-reduction peaks are encountered upon raising the scan rate. The transfer coefficient, α, for the first ET rate determining step, can be calculated from [25,27]:

(5.4)

All the values of transfer coefficient obtained for PCMs at GC are reported in Table 5.1, which are all smaller than 0.5, further confirm the assumption that ET and C-Cl bond cleavage of PCMs conform to the concerted mechanism.

However, if reduction of PCMs strictly undergoes the sequential hydrodechlorination mechanism, one would expect to observe a series of two electron reduction waves with almost equal height. Obviously, this is not our case. There are a number of successive un-equal height peaks toward the reduction of PCMs on GC electrode, in particular for CCl_4, where four irreversible reduction peaks come up in the cyclic voltammogram, whereas the current intensities of them decrease sharply starting from the first one. Actually, this phenomenon has already been reported by the previous research [19,28], which is also similar with the one observed on the reduction of PCEs reported in our last two chapters. This implies except for sequential hydrodechlorination, some other reaction routes also play significant roles towards the reduction of PCMs, which we will discuss later.

Now let's switch our eyes to the reduction of PCMs by using Cu as working electrode. As shown in Fig. 5.1, in contrast to GC electrode, three, two and one irreversible reduction peaks are observed in the voltammetric reductions of CCl_4, $CHCl_3$, CH_2Cl_2, respectively. In general, each compound of PCMs lacks one reduction peak on Cu compared to that of on GC electrode. It appears that distinct reduction mechanism may occur on the two different electrodes. Actually, similar observations have already been found towards the reduction of PCMs at Ag electrode, where one peak is lost in the reduction of CCl_4, $CHCl_3$, CH_2Cl_2, whereas sequential hydrodechlorination mechanism still prevail the whole reduction process of PCMs, the missing peak is due to the reduction potential (E_p) of CH_3Cl is more positive than that of CH_2Cl_2, leading to the overlap of the two reduction processes. It's reasonable to presume that the same situation takes place on the Cu electrode, and further CV experiments confirm this idea, as displayed in Fig. 5.1, E_p (CH_3Cl) > E_p (CH_2Cl_2).

A close comparison of the voltammograms of PCMs at Cu electrode in Fig.5.1 clearly shows that the last peak of both CCl_4 and $CHCl_3$ coincide with that of CH_2Cl_2, indicating that the reduction of both compounds at Cu electrode give rise to CH_2Cl_2 during reduction process. Whereas, there is no common place for the other peaks between CCl_4 and $CHCl_3$, in particular, the first reduction peak in the voltammogram of $CHCl_3$ is totally different with the second of CCl_4 in view of the potential locations and shapes; therefore assignment of $CHCl_3$ as the reduction product of CCl_4 is not straightforward. Herein, the sequential hydrodechlorination mechanism of PCMs on Cu is not as evident as on GC electrode. However, it should be noted that if reduction of CCl_4 at the first peak indeed produce $CHCl_3$, the reduction of the latter would be overlapped by the second reduction peak of CCl_4, in other words, the second reduction peak of CCl_4 may be comprised of several reduction processes, partially arising from reduction of $CHCl_3$, partially resulting from some other reaction routes of CCl_4, for instance carbene routes [19], whatever, all the reduction processes in the second step lead to the formation of CH_2Cl_2. Besides, similar like the reduction of PCMs at GC electrode, a series of un-equal height reduction peaks appear in the voltammograms of $CHCl_3$ and CCl_4, in particular for CCl_4, the current intensity of the last peak is far lower than the first peak, which means that only partially CCl_4 is converted to CH_2Cl_2. All of these indicate that except for the sequential hydrodechlorination leading to the less chlorinated intermediates, side reaction may play significant roles during electrochemical reduction of PCMs at Cu electrode.

Some possible chemical reactions, which may take place due to the aprotic character of the medium, include self-protonation and carbene route by Cl^- elimination from the intermediate of polychloromethyl carbanions. For instance, reduction of $CHCl_3$ gives rise to $^-CHCl_2$ after two electron transfers, as shown in eq.(5.1-5.2), whereas the fate of latter may be involved in three competition reactions, the first one is to expel another chlorine ion by carbene route (eq.5.5), another is to undergo the self-protonation reaction, in which $^-CHCl_2$ is protonated by the starting substrate (eq.5.6), the last one is to be protonated by any proton donor in the solution other than the parent molecule (reaction 5.3)

$$^-CHCl_2 \longrightarrow :CHCl + Cl^- \qquad (5.5)$$

$$^-CHCl_2 + CHCl_3 \longrightarrow CHCl_2 + {}^-CCl_3 \qquad (5.6)$$

The possible involved chemical reactions, in particular the incorporation of carbene species, result into the complexity of electrochemical reduction process, which consist of several electron transfer processes. This can well explain that the electrodes exhibit odd electrochemistry behaviors in some cases. Besides, it shows that proton availability has a significant effect in the electrochemical reduction process.

Sequential hydrodechlorination is recognized involving electron and proton transfer two processes. Since proton transfer is another significant aspect towards the reduction of PCMs, herein two different types of proton donor were intentionally introduced into the solution containing PCMs, to check their influence on the whole reduction process. The variations of cyclic voltammograms of PCMs recorded on GC and Cu electrode in the presence of HAc or H_2O are depicted in Fig. 5.2, in which the presence of HAc are kept excessive, and further addition of HAc do not evidently modify the CV shapes of PCMs any more, whereas, the addition amount of H_2O for PCMs are fixed at 0.6 M, since further addition of water will cover the reduction peaks of PCMs due to the discharge of water.

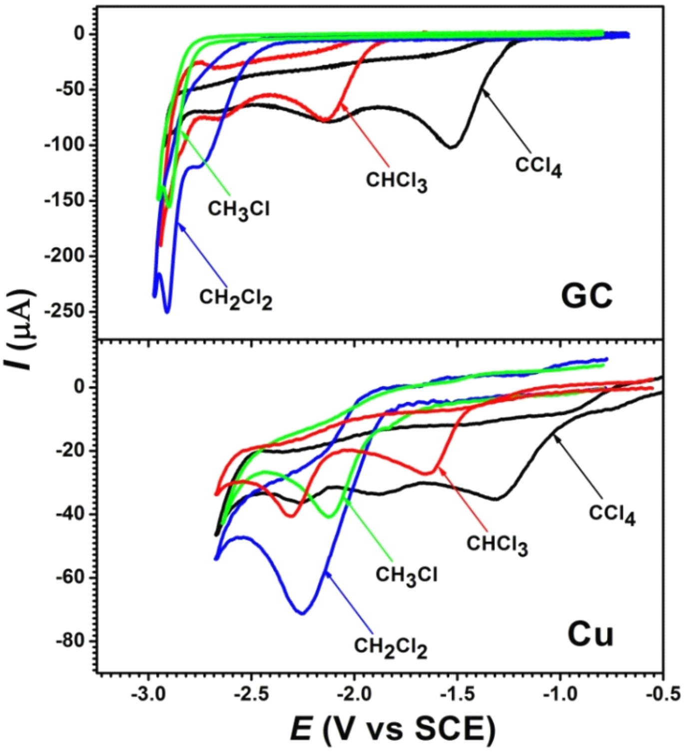
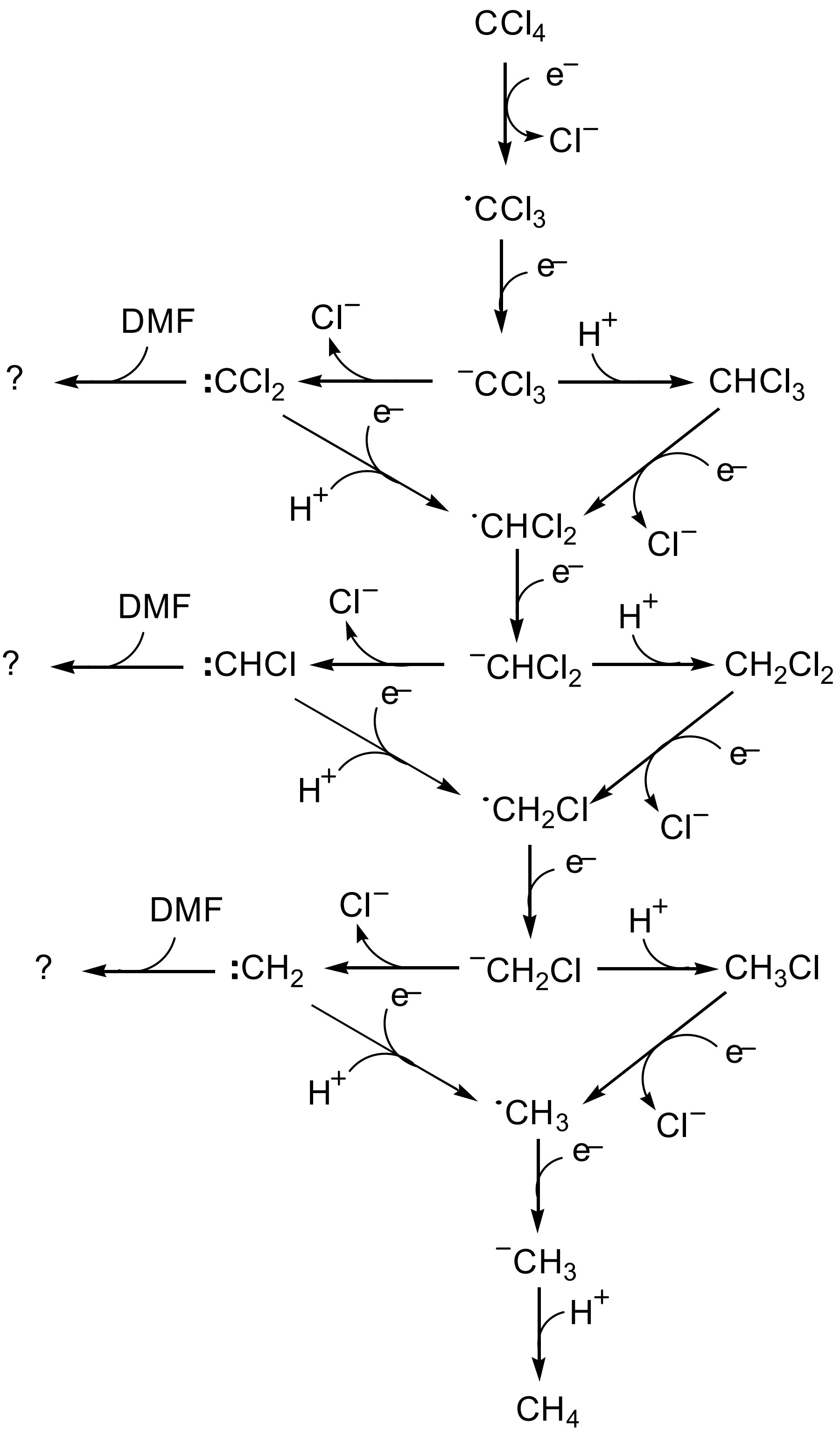


Fig. 5.1 Cyclic voltammetries of 2 mM polychloromethanes (PCMs) in DMF + 0.1 M $TPABF_4$, recorded on GC and Cu electrode at 0.2 $V \cdot s^{-1}$, respectively.

As shown in Fig. 5.2 (solid red line), cyclic voltammograms of PCMs are very sensitive to the presence of HAc. Two evident changes are observed after HAc addition, one is the increase of current intensities of all the reduction peaks on both GC and Cu electrodes, which become almost the same height as expected, the other is the obvious positive shift of reduction potentials of PCMs at Cu electrode, whereas it doesn't appreciably modify the potentials on GC electrode. The reduction processes of PCMs on GC electrode appear to become more simplified in the presence of HAc, the enhancement of the subsequent peaks of PCMs to almost the same height with the first one indicate that chemical reactions can be successfully suppressed, and sequential hydrodechlorination mechanism exclusively dominate the whole reduction processes of PCMs. It should be stressed that, at Cu electrode, the second reduction peak of CCl_4 now matches perfectly with the first of $CHCl_3$ in the presence of HAc, and the last peak of $CHCl_3$ and CCl_4 coincides with the reduction of CH_2Cl_2 as usual, as shown in Fig. 5.2. Besides, similar with GC electrode, the following reduction peaks of PCMs become almost equal height with the first one after HAc addition. All these indicate that reduction of PCMs mainly undergo sequential hydrodechlorination mechanism at Cu electrode, which is in line with the one occurring at GC electrode.

The voltammetric patterns of PCMs in the presence of 0.6 M H_2O is shown in Fig. 5.2 (solid blue line). In general, addition of H_2O into the solution doesn't significantly increase the following peak current intensities of PCMs at GC electrode, except for the last peak, which is assigned to be the reduction of CH_3Cl, whereas the sharply enhancement of CH_3Cl is presumed mainly due to the discharge of electrolyte rather than the contribution of protonation. On the other hand, all the peak intensities of PCMs at Cu electrode increased considerably in the presence of water, except for the first peak of $CHCl_3$, whereas the latter is found stretched a lot after water addition. However, the overall peak intensities increased, for all the reduction peaks of PCMS, are lower in the presence of H_2O than those in the presence of HAc at the two electrodes, even though the amounts of H_2O added is much greater than HAc, which indicates that H_2O is a weak proton donor with respect to HAc in the system. Likewise the previous two cases, reduction of PCMs in the presence of H_2O is presumed that primarily follow sequential hydrodechlorination mechanism. Based on the voltammetric analysis of PCMs in different solvent conditions, a plausible reduction mechanism of PCMs was proposed, which is in accordance with our previus research [19]:



Scheme 5.1. Electrochemical reduction mechanism of polychloromethanes

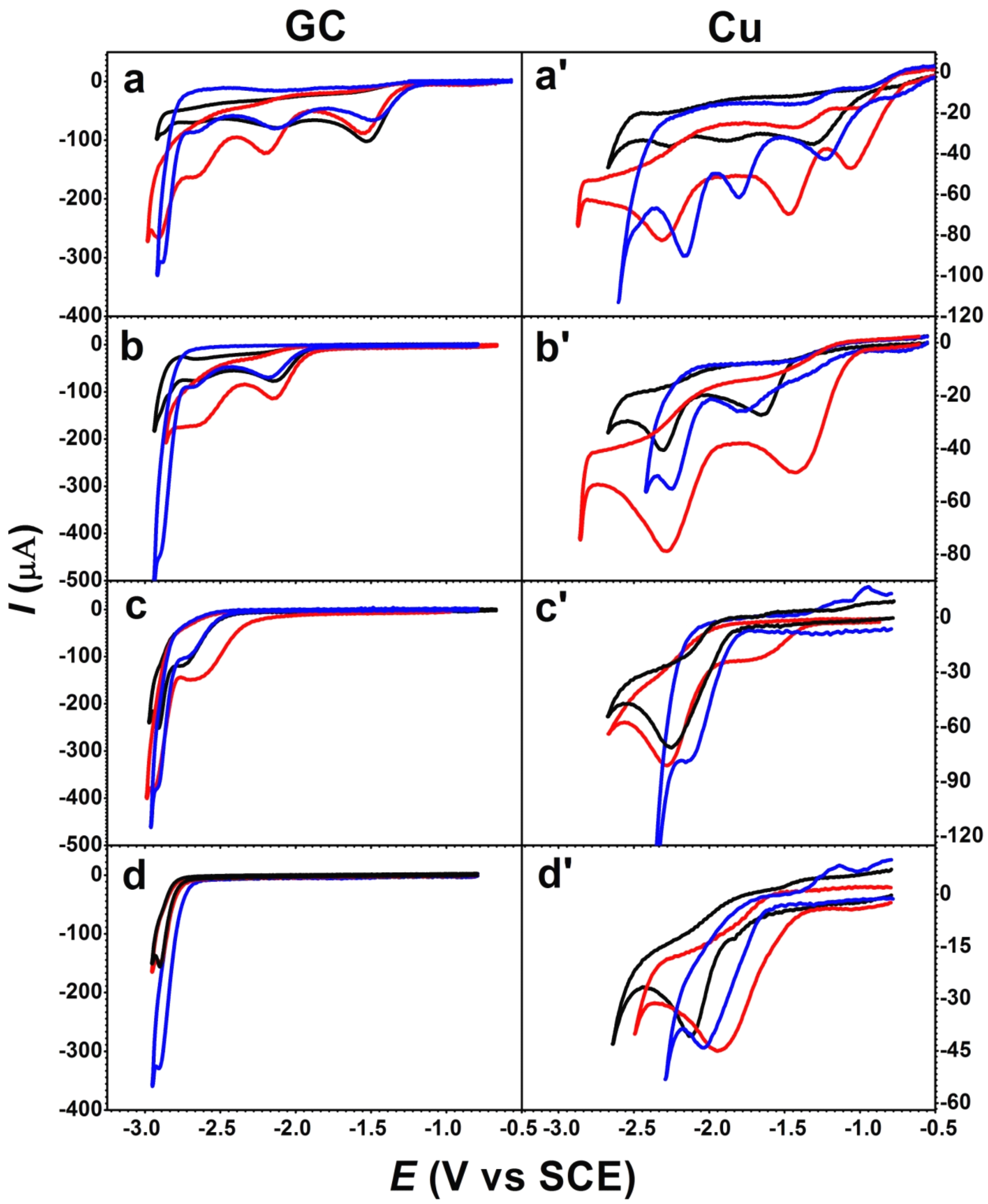


Fig. 5.2 Cyclic voltammetries of 2 mM polychloromethanes (PCMs) in DMF + 0.1 M $TPABF_4$ in the absence (solid dark line), in the presence of excess HAc (solid red line) or the presence of 0.6 M H_2O (solid blue line), recorded on GC (left) and Cu (right) electrode at 0.2 V•s^{-1}, respectively, wherein a) CCl_4; b) $CHCl_3$; c) CH_2Cl_2; d) CH_3Cl.

Finally, let's focus on the electrocatalytic activities of Cu towards reduction of PCMs with respect to GC electrode. The catalytic effects of Cu for PCMs reduction, $\triangle E_p^{cat}$, defined as the differences between the first reduction peak potentials recorded at Cu and GC, are all gathered in Table 5.1. As shown in Table 5.1, Cu exhibits a remarkable electrocatalytic property for the reduction of PCMs in the absence of proton donor, which induces a positive shift range from 216 mv for CCl_4 to 743 mv for CH_3Cl. The presence of HAc in the solution appears significantly activate the catalytic effect of Cu towards the reduction of C-Cl bonds, which result into an even higher positive shift of reduction potentials from 435 mv for CH_2Cl_2 to 934 mv for CH_3Cl, leading to the cleavage of C-Cl bond becoming more readily. In the presence of HAc, the enhancement of positive shift of reduction potentials for PCMs is in accord with those observed on the reduction of geminal PCEs at Cu, where HAc also exhibits an evident catalytic property for the reductive cleavage of C-Cl bond. Addition of H_2O into the solution containing PCMs also bring about the reduction peak potentials of PCMs shifting to the positive direction, where the shifts vary from 299 mv for CCl_4 to 840 mv for CH_3Cl. In general, the presence of proton donor enhances the catalytic activity of Cu towards the reduction of PCMs, whereas HAc exhibits a little stronger catalytic effect than H_2O. We presume it's mainly due to the active sites at electrode surface are frequently regenerated after proton donor addition.

Even though rather clear reduction mechanisms of PCMs have been summarized through the voltammetric analysis, it's wise to carry out electrolysis experiments, for the sake of further support the reduction mechanisms by tracking the evolution of electrolytic intermediates, and check the applicability of Cu electrode in electrolysis removal of PCMs. Herein, CCl_4 and $CHCl_3$ are chosen as the representative of PCMs, to conduct the electrolytic investigations in different solvent conditions, such as in DMF solvent without any proton donor addition, in the presence of 0.1 M HAc, and in the presence of 0.5 M H_2O, respectively.

Table 5.1 Voltammetric data for the reduction of PCMs (2 mM) in DMF + 0.1 M $TPABF_4$, recorded at Cu electrode, in different solvent conditions

Substance	GC					Cu					$\Delta E_p^{Cat\ e}$		
	E_p^a (V)	α^b	$E_p^{c(HAc)}$ (V)	α^b	$E_p^{d\ (H_2O)}$ (V)	E_p^a (V)	α^c	$E_p^{c(HAc)}$ (V)	α^b	$E_p^{d(H_2O)}$ (V)	ΔE_p^{Cat} (V)	$\Delta E_p^{Cat(HAc)}$ (V)	$\Delta E_p^{Cat(H_2O)}$ (V)
CCl_4	-1.529	0.35	-1.554	0.31	-1.480	-1.313	0.15	-1.058	0.67	-1.230	216	471	299
$CHCl_3$	-2.168	0.37	-2.146	0.30	-2.180	-1.653	0.18	-1.420	0.47	-1.780	515	748	388
CH_2Cl_2	-2.726	0.41	-2.684	0.68	-2.719	-2.255	0.20	-2.291	0.23	-2.132	471	435	594
CH_3Cl	-2.870		-2.906		-2.909	-2.127	0.22	-1.936	0.24	-2.030	743	934	840

[a] E_p (V vs SCE) measured at the first reduction peak at 0.2 $V \cdot s^{-1}$;

[b] Electron transfer coefficient, calculated from $\partial E_p/\partial \log \nu = -1.151RT/F\alpha$.

[c] results are recorded in the excess of 1 equivalent HAc addition;

[d] results are recorded in the presence of 0.6 M H_2O;

[e] $\Delta E_p^{cat} = \Delta E_{p,\ Cu} - \Delta E_{p,\ GC}$.

5.3.2 Electrolysis of carbon tetrachloride

For further confirm the reduction mechanisms of PCMs proposed based on voltammetric analysis in previous section, it would be better to be able to control the formation of electrolysis intermediates selectively. Herein, sequential potentiostatic electrolysis methods were used during the reduction of CT, in which the applied potentials, E_{app}, were chosen according to the reduction peaks of CT in the voltammogram that locate at the end of the desired reduction peak but well separated from the subsequent reduction process. The applied potential, E_{app}, was shifted when the current decreased to ca 5% of its initial value at each step, so that step wise dechlorination process could be achieved during electrolysis. HAc and H_2O, two different types of proton donor, were intentionally added into the DMF solvent, for the purpose of further investigating the effect of proton donor and its type on the reduction processes of CT. Samples, from the solution and gas phases, were withdrawn periodically and analyzed timely by GC-MS and GC during electrolysis. The electrolysis results of CT at Cu electrode performed in the absence and presence of HAc/H_2O are reported in Table 5.2, in which the numbers in the first column represents the experiments, while the letters behind them stands for the electrolysis steps in the same electrolysis. Concentration profiles of CT and its main electrolysis intermediates, together with the cyclic voltammetries recorded at Cu before and after each electrolysis step, for the electrolysis of CT in different conditions are shown in Fig. 5.3. The concentration profiles n/n^0_{CT} are plotted as function of charge, where n and n^0_{CT} denote the amount of any substrate detected in the experiments and the initial amount of CT, respectively.

Table 5.2(entry1) and Fig. 5.3(a,d) reports the electrolysis results of CT at Cu electrode in the absence of proton donor. As shown in Fig 5.3a, three irreversible reduction peaks appear in the voltammetric reduction of CT at Cu, therefore the electrolysis was carried out in three successive steps, where the applied potential, E_{app}, were imposed at -1.60 V, -2.04 V and -2.79 V, respectively. Upon the conversion of CT during electrolysis, CF, DCM and CM as intermediates were accumulated successively, and all the less chlorinated species were dechlorinated once the final step was embarked on. CF reached to its maximum value, 28.79%, with 82.06% CT conversion at the end of the first electrolysis step, which corresponds to 1.68 e-/molecule charge consumed, besides, 2.27% DCM and 0.13% CM were also detected in this step. Further electrolysis at -2.04 V, complete conversion of CT and CF transformed from the first step to 3.57% DCM, 0.56% CM, and 2.09% CH_4 together with 0.62% C2 hydrocarbons, after another 2.03 e^- /molecule charge consumption, in which the production of DCM came to the head even though its accumulation was indeed not so obviously, as presented in Fig. 5.3d. When the applied potential shifted to -2.79 V, all the chlorinated intermediates were subsequent removed, in concomitant with 4.95% CH_4 and 0.82% C2 hydrocarbons as the final products.

In general, the less chlorinated intermediates, CF, DCM and CM, formed during the electrolysis of CT, present a sharply decrease trend, which is in line with the voltammetric analysis that only partial conversion of the starting substrate to the following hydrodechlorination products. A close examination of the electrolysis results also shows that the loss of mass balance started from the first electrolysis step, whereas the mass balance in the last step only became to 5.77%. Besides, CH_4 had already been detected in the first two electrolysis steps, where the applied potentials were neither reducible for DCM nor for CM. Surprisingly, the overall charge consumption for the removal of CT was 4.73 e^-/molecule, which is far less than the stoichiometric value, 8 e^-/molecule, corresponding to the hydrodechlorination mechanism. All of these indicate that except for hydrodechlorination, some other reduction mechanisms may play a significant role towards the reduction of CT during electrolysis. As clarified in the previous section, side reactions, involved the strong active intermediates formed during reduction process, such as carbene and radical species, must be taken into account in the whole reduction mechanism. In addition, self-protonation also couldn't be neglected due to the aprotic character of DMF solvent, as shown in equation (5.6) and scheme 5.1. It should be noted that none of chlorinated C2 hydrocarbons were found through the electrolysis of CT process, even though some C2 hydrocarbons were produced but with trace amounts (lower than 1%), which indicated that dimerization reactions arising from radicals could be ignored during the electrolysis process. The chlorinated carbene species, produced during electrolysis, may undergo successive protonation and chlorine ions elimination till methane formation, as sketched in scheme 5.1, and they also can readily react with DMF solvent following hydrolysis to give rise to CO

[19,29,30], while the latter case was presumed prevailing the whole reduction mechanism. Actually, similar observations have been reported on the electrolysis of PCMs by using GC and Ag electrodes [31].

For further revealing the reduction mechanism of CT, electrolysis experiments were carried out in the presence of 0.1 M HAc at Cu electrode, and the electrolysis results are reported in Table 5.2 (entry 2) and Fig. 5.3e. Fig. 5.3b shows the cyclic voltammetry of CT at Cu in the presence of 0.1 M HAc, besides the three reduction peaks of CT, which are shifted to more positive direction after HAc addition, a fourth peak mainly due to the reduction of HAc is observed at the end of the voltammogram. Likewise, the electrolysis was divided into three steps according to the location of reduction peaks, namely -1.25 V, -1.77 V and -2.39 V. At the first step, in which consumed 2.53 e^{-}/molecule, 77.44% CF, 5.37% DCM, 0.25% CH_4 and together with trace amounts of C2 hydrocarbon (0.04%) were produced with the conversion of 96.05% CT. After another 1.97 e^{-}/molecule charge consumption, the yield of DCM reached to the maximum value, 77.95%, at the second electrolysis step, where 0.18% CM, 1.46% CH_4 and 0.16% C2 hydrocarbons were concomitant formed together with 2.09% CF remained in the solution. When the applied potential, E_{app}, was shifted to -2.39 V, the final product of CH_4 began to increase steeply. At the end of electrolysis, in which the overall charge consumed 11.74 e^{-}/molecule, the principal products were 70.03% CH_4 and some C2 hydrocarbons (lower than 1%) with 9.65% DCM residual in the solution.

The reduction process of CT appears to become simplified after HAc addition. The electrolysis of CT at Cu electrode in the presence of HAc clearly shows CF is the main reduction intermediates, which is further reduced to give rise to DCM at more negative potential, and the latter is ultimately reduced to yield CH_4 as the final product with the shifting of potential. It should be stressed that the loss of accumulation of CM is due to its reduction potential (E_{p}) is more positive than that of DCM, which is in accord with the voltammetric analysis. Therefore, sequential hydrodechlorination mechanism exclusively prevail the whole reduction mechanisms towards the electrolysis of CT in the presence of HAc. The chlorinated methyl carbanions, $^{-}CH_xCl_{3-x}$ (x=1-3), formed during electrolysis, is readily to be protonated in the presence of HAc, instead of elimination one more chlorine ion with carbene species formation. However, the detection of CH_4 from the beginning of electrolysis steps, besides, the low amounts of C2 hydrocarbons formation indicate side reactions also inevitably take place during electrolysis.

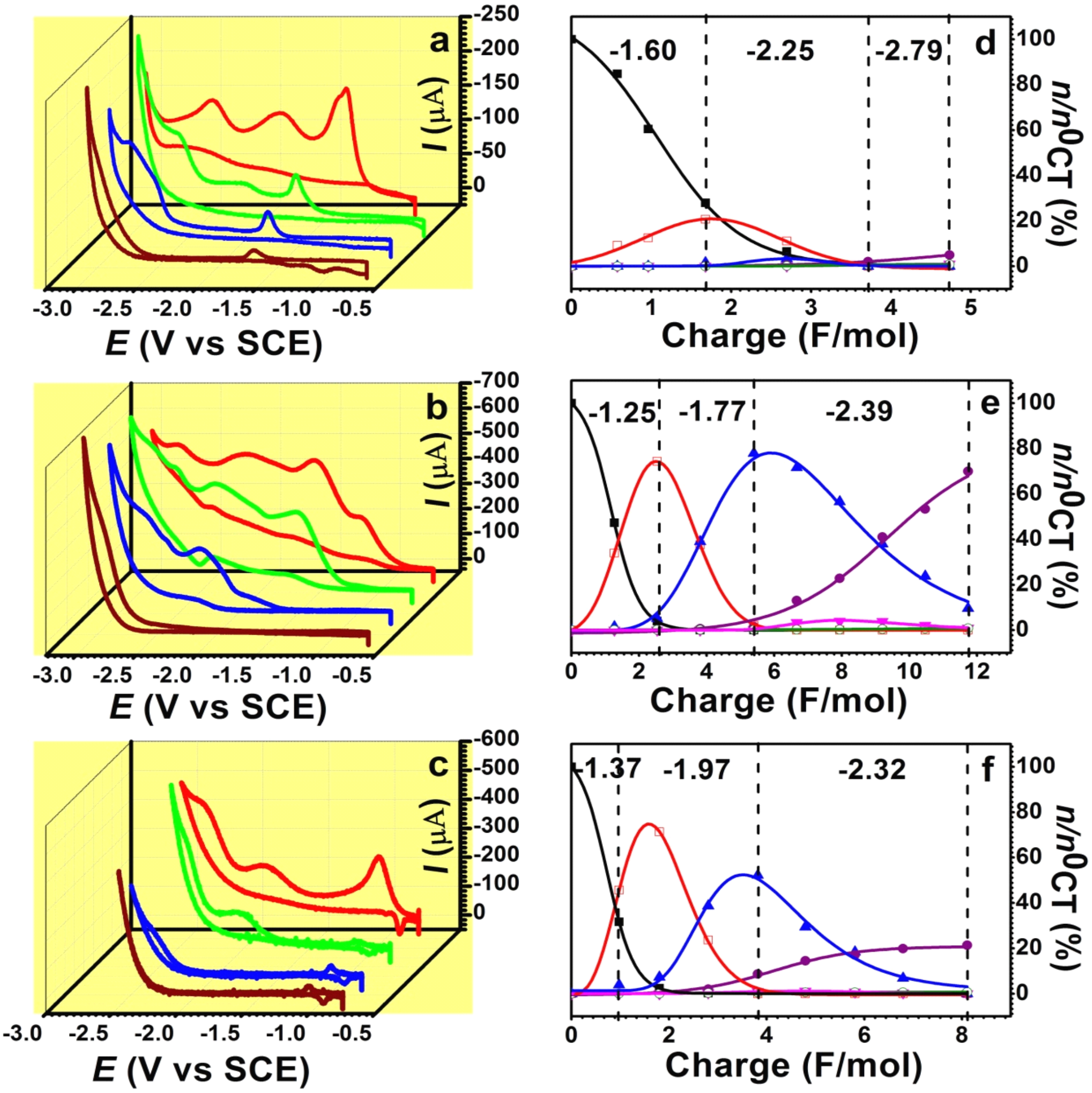


Fig. 5.3. Stepwise controlled-potential electrolyses of 10 mM CT in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 0.5 M water (c, f). (a,b,c) cyclic voltammogrms of CT recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (■) CT; (□) CF; (▲) DCM; (▼) CM; (●) CH_4; (○) C2 hydrocarbons. The inserted numbers denote the value of E_{app}, whereas the vertical lines indicate when it was changed.

H_2O, as a weak proton donor, were intentionally added into the solution containing CT, to perform the electrolysis experiments at Cu electrode, so that investigating the proton effect towards the reduction process of CT. The electrolysis results during electrolysis are gathered in Table 5.3 (entry3), and the concentration profiles of CT and its principal intermediates are presented in Fig. 5.3f. Voltammetric reduction of CT at Cu electrode in the presence of 0.5 M H_2O displays three successive reduction waves, as shown in Fig. 5.3c, as usual the electrolysis was performed at -1.37 V, -1.97 V and -2.32 V, respectively. At end of the first step, 97.62% of CT was mainly converted to 73.00% CF, 7.50% DCM, 0.11% CH_4 and some trace of C2 hydrocarbons (0.03%), which corresponded to 1.80 e^-/molecule charge consumption. Further electrolysis at -1.97 V, resulted in complete conversion of CT and CF to 52.24% DCM, 8.67% CH_4 together with small amounts of CM (0.96%) and C2 hydrocarbons (0.54%) production. Eventually, the principal products became 21.36% CH_4 and 0.67% C2 hydrocarbons at the end of electrolysis. The overall charge consumed 8.11 e^-/molecule in the whole reduction process of CT.

A close comparison of the electrolysis results between the presence of 0.1 M HAc (Table 5.2, entry2) and the presence of 0.5 M H_2O (Table 5.2, entry3), one will find the electrolysis products are essential the same for the two different solvent conditions at the first electrolysis step, where even the accumulation amounts of CF are comparable in the two distinct cases. Whereas, the difference became evidently starting from the second step, in which the production of DCM at the second step and the yield of CH_4 at the last step were lower in the presence of H_2O than that of presence of HAc, in particular the amounts of CH_4 at the end of electrolysis (70.03% vs 21.36%), which indicates that different reduction mechanisms of CT may occur in the two different conditions. As already stated in the previous section, the first electron transfer to PCMs, CH_nCl_{4-n} (n= 0-3), results into the cleavage of C-Cl bond concomitant with $^{\bullet}CH_nCl_{3-n}$ formation, while the latter is more readily reduced to $^{-}CH_nCl_{3-n}$ after accepting another electron transfer. Actually the fate of $^{-}CH_nCl_{3-n}$ in the successive reduction processes determines the whole reduction mechanisms of PCMs. $^{-}CH_nCl_{3-n}$, including $^{-}CCl_3$, $^{-}CHCl_2$ and $^{-}CH_2Cl$, all of them are strong bases compared to OH^-, showing an order as follows: $OH^- < {}^{-}CCl_3 < {}^{-}CHCl_2 < {}^{-}CH_2Cl$. According to the theory of hard and soft acids and bases, the strong bases are readily to react with the strong acids, and vice versa. $^{-}CCl_3$ as a relative weaker base compared to the other two carbanions, which was produced at the first electrolysis step, is inclined to be protonated by any proton donors in the solution with CF formation. Therefore, the amounts of CF formed at the first step were similar with the two distinct proton donor additions. Whereas, with the formation of $^{-}CHCl_2$

and $^{-}CH_2Cl$ in the further reduction processes, in particular the yield of $^{-}CH_2Cl$, the subsequent protonation reactions are in competed with the Cl^{-} elimination by carbene route. Since due to the strong base characters, $^{-}CHCl_2$ and $^{-}CH_2Cl$ are prone to reacting with strong acids, such as HAc, while H_2O behaves as a weak acid. Accordingly, in the presence of HAc, the fate of $^{-}CH_nCl_{3-n}$ is to be protonated by favoring the sequential hydrodechlorination. While the addition of H_2O results into $^{-}CH_nCl_{3-n}$ undergoing two competitive reaction routes, one is sequential hydrodechlorination, the other is carbene route. The produced carbene species rapidly react with the DMF solvent leading the loss of mass balance during the electrolysis. Besides, the continuous accumulation of OH^{-} with the detriment of proton in H_2O, in particular at the last steps of electrolysis, thus don't benefit for the sequential hydrodechlorination mechanism. Accordingly, the presence of H_2O couldn't avoid the competition reaction of carbene routes due to its weak acid character.

In general, the presence of proton donors has catalytic effect towards the reduction of CT that promotes its reduction potentials shifting to more positive direction, and enhances the yield of hydrodechlorination products. The reduction mechanisms of CT are dependent on the types of proton donor, wherein HAc as a strong proton donor, is more favoring sequential hydrodechlorination; H_2O, can play a role as a proton donor, but can't avoid the competition reaction of carbene routes due to its weak acid character.

Table 5.2. Electrolysis of CT at Cu electrode in the absence and presence of different proton donors.[a]

Entry	Cathode	HA	E_{app}[b]	n (F/mol)	CT (%)[c]	CF (%)[d]	DCM (%)[d]	CM (%)[d]	CH_4 (%)[d]	C2 (%)[d]
1a	Cu		-1.60	1.68	27.94	28.79	2.27	0	0.13	0
1b			-2.25	3.71	0	0	3.57	0.56	2.09	0.62
1c			-2.79	4.73	0	0	0	0	4.95	0.82
2a	Cu	CH_3CO_2H	-1.25	2.53	3.95	77.44	5.37	0	0.25	0.04
2b			-1.77	5.40	0	2.09	77.95	0.18	1.46	0.16
2c			-2.39	11.74	0	0	9.65	0	70.03	0.86
3a	Cu	H_2O	-1.37	1.80	2.38	73.00	7.50	0	0.11	0.03
3b			-1.97	3.82	0	0	52.24	0.96	8.67	0.54
3c			-2.32	8.11	0	0	0	0	21.36	0.67
4a	Cu		-2.65	2.00	36.20	17.42	4.25	0.07	5.05	0.24
4b			-2.65	4.50	0	0	0	0.21	9.62	0.85
5a	Cu	CH_3CO_2H	-2.37	3.08	17.46	45.63	39.16	0.91	11.85	0.27
5b			-2.37	10.24	0	0	0	1.79	62.56	2.05
6a	Cu	H_2O	-2.45	2.01	17.21	28.31	32.27	2.00	6.51	0.28
6b			-2.45	8.11	0	0	0	0	36.74	0.33

[a]Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [CT] = 10 mM; $[CH_3CO_2H]$ = 100 mM,$[H_2O]$ = 0.5 M. [b]E_{app} = applied potential in V vs SCE. [c]Remaining substrate. [d]Yield calculated with respect to converted CT.

As stated before, all of the aforementioned electrolysis experiments on CT were carried out under sequential potentiostatic conditions, for the sake of investigation the reduction mechanisms of CT by tracking the electrolysis intermediates. It will be interesting to check the performance of Cu towards the electrolysis of CT by using single step potentiostatic methods, to further investigate its influence on the product distributions. Since single step potentiostatic electrolysis is easier to handle from the practical application point of view, and it also can shorten the processing time because of high current intensity during electrolysis. Electrolysis experiments of CT at Cu electrode were performed in the absence of proton donor, in the presence of 0.1 M HAc and in the presence of 0.5 M H_2O three conditions, respectively, with the applied penitential, E_{app}, fixed at -2.65 V, -2.37 V and -2.45 V, correspondingly. All the electrolysis results of CT at Cu performed in different conditions are gathered in Table 5.2 (entry4-6), whereas the concentration profiles of CT and its main reduction intermediates together with the voltammetric responses recorded at Cu electrode before and after each electrolysis step are shown in Fig. 5.4 (a-f).

Cu exhibits a stable catalytic effect towards the reduction of CT in the three different conditions, where complete dechlorination of the starting substrates and its chlorinated intermediates can be achieved, as shown in Fig 5.4 (d-f). A close comparison of the electrolysis results performed under single step potentiostatic electrolysis (Table 5.2, entry4-6) with those of working under sequential potentiostatic conditions (Table 5.2, entry1-3) correspondingly, will allow one conclude that there are essential the same electrolysis products during electrolysis, where the formed intermediates present a similar trend that firstly increase and then disappear with the charge consumed. Besides, the overall charges consumed in the same solvent conditions between the two different modes of potentiostatic electrolysis are almost the same. However, in contrast to those working under sequential potentiostatic conditions, owing to the applied potential by single step potentiostatic electrolysis methods located at which all the electrolysis intermediates are reducible, the less chlorinated hydrocarbons formed were thus repulsive to accumulate and were reduced simultaneously during electrolysis. It should be stressed that the yield of CH_4 started from the beginning of electrolysis and increased steadily in all different solvent conditions during single step potentiostatic electrolysis.

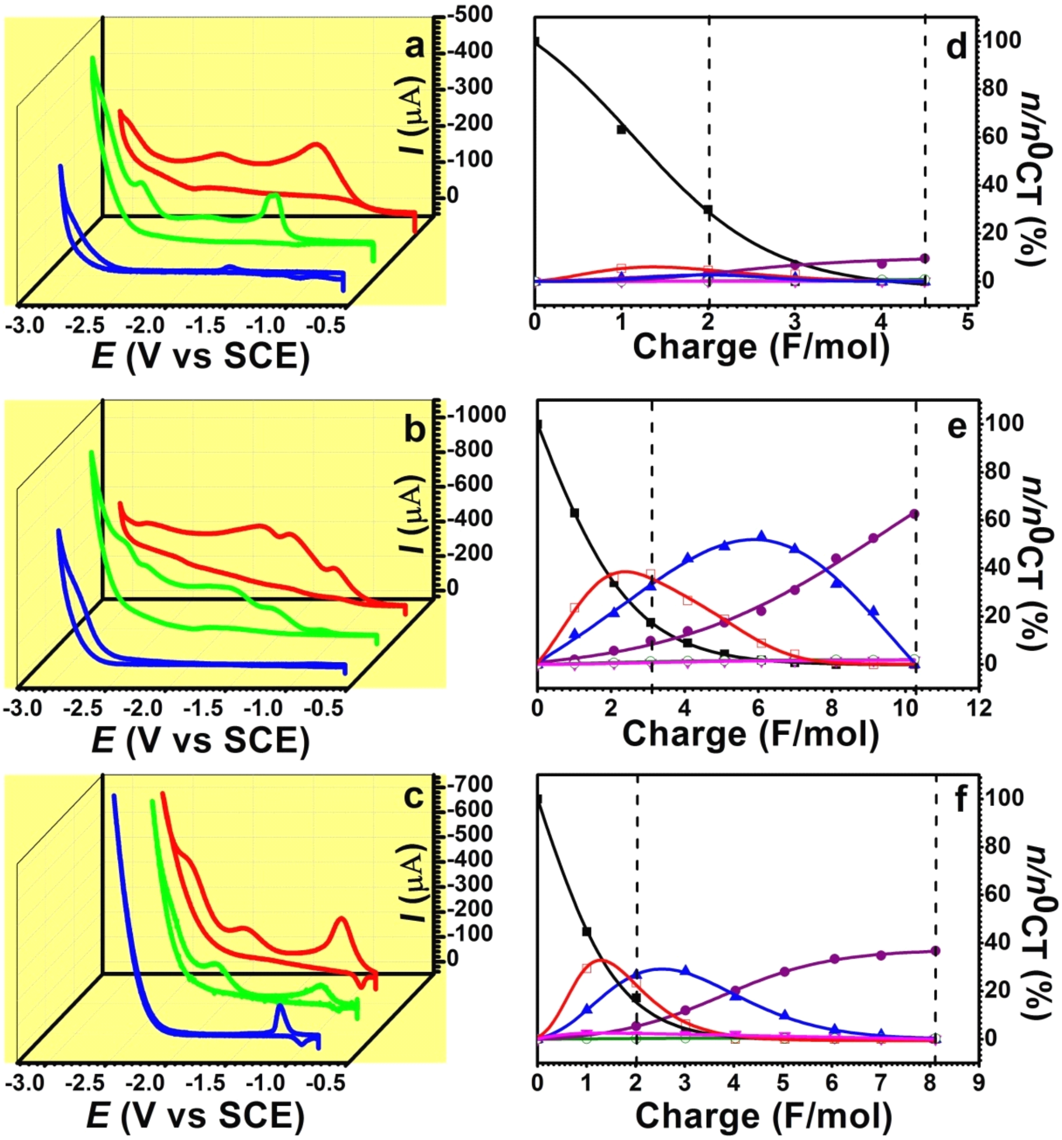


Fig. 5.4. Single step controlled-potential electrolyses of 10 mM CT in DMF + 0.1 M $(C_3H_7)_4NBF_4$ by single step electrolysis at Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 0.5 M water (c, f). (a,b,c) cyclic voltammogrms of CT recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (■) CT; (□) CF; (▲) DCM; (▼) CM; (●) CH_4; (○) C2 hydrocarbons. The inserted vertical lines represents the electrolysis steps during electrolysis.

5.3.3 Electrolysis of chloroform

As another representative of PCMs electrolysis experiments were carried out on the reduction of CF at Cu electrode in the conditions similar to those used in the electrolysis of CT, that worked in DMF solution without any proton donor addition, in the DMF solution

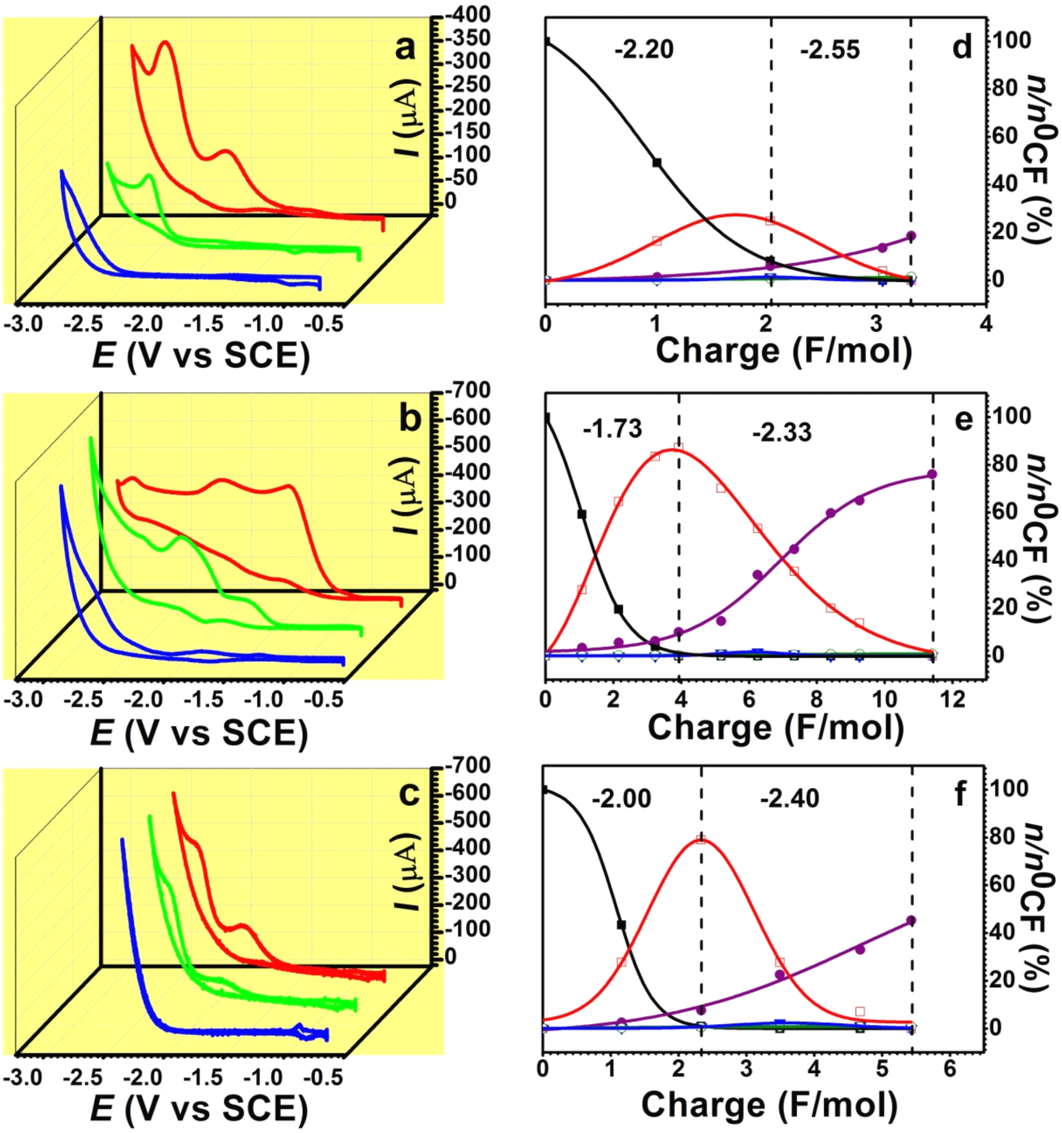


Fig. 5.5. Electrolysis of 10 mM CF in DMF + 0.1 M $(C_3H_7)_4NBF_4$ on Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 0.5 M water (c, f). (a,b,c) cyclic voltammogrms of CF recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (■) CF; (□) DCM; (▼) CM; (●) CH_4; (○) C2 hydrocarbons. The inserted numbers denote the value of E_{app}, whereas the vertical lines indicate when it was changed.

containing 0.1 M HAc, and in the presence of 0.5 M H_2O addition of DMF solvent, respectively. For the sake of evaluating the performance of Cu electrode towards the removal of CF, and further providing more evidences for completing the whole reduction mechanisms of PCMs by using potentiostatic electrolysis methods. The electrolysis results of CF at Cu in different conditions are gathered in Table 5.3 (entry 1-3), whereas the concentration profiles of CF and its main reduction intermediates formed during electrolysis together with the cyclic voltammetries recorded at Cu before and after each electrolysis step are shown in Fig. 5.5 (a-f), respectively.

Table 5.3 (entry1) and Fig. 5.5 (a,d) report the electrolysis results of CF performed in the absence of any proton donor. Voltammetric response in Fig 5.5a displays two reduction waves for the reduction of CF; therefore, the electrolysis was carried out in two steps at -2.20 V and -2.55 V, respectively. At the end of the first step, which consumed 2.04 e^-/molecule charge, 91.93% of CF was converted to 27.08% DCM, 1.38% CM, 6.50% CH_4 and some traces of C2 hydrocarbons (0.77%). Further electrolysis at -2.55 V in the second step, resulted into complete dechlorination of all the chlorinated species with 18.62% CH4 and 1.45% C2 hydrocarbons as the final products. The overall charge consumed 3.32 e^-/molecule for the removal of CF, which is lower than the theoretical value of 6 e^-/molecule based on the sequential hydrodechlorination mechanism. This observation is in line with that of the reduction of CT performed in the same conditions, where it consumed 4.73 e^-/molecule charge while the theoretical value is 8 e^-/molecule. Besides, similar with the case of CT, severe loss of mass balances were observed from the beginning of electrolysis, and only around 20% mass balance was obtained at the end of electrolysis, which is a little better than that of CT (5.77%). All of these further confirm that some other side reactions played significant roles during electrolysis of PCMs. In agreement with the reduction of CT, carbene species may be formed and involved in the reduction process, the reaction of which with DMF solvent is the main cause of the loss of mass balance. Likewise, it should be noted that the self-protonation of CF couldn't be suppressed due to the aprotic character of the system.

The process became less complicated when the electrolysis was repeated in the presence of 0.1 M HAc. As shown in Fig. 5.5b, three irreversible reduction peaks appear for the reduction of CF, while the last of them was suspected to be the reduction peak of acetic acid. Accordingly, the electrolysis was fixed at -1.73 V and -2.33 V according to the first two reduction peaks, respectively. The electrolysis results are reported in Table 5.3 (entry2) and Fig.5.5e. DCM was found to accumulate in the first electrolysis step, in which 88.16% DCM, 4.98% CH_4 together with some trace of C2 hydrocarbons (0.18%) were produced with the complete conversion of CF. Further electrolysis at -2.33 V leads to complete removal of all the chlorinated species with 76.03% CH_4 and 0.85% C2 hydrocarbons as the final product. The electrolysis of CF in the presence of HAc yielded DCM, and the latter was further reduced to CH_4 clearly indicates that sequential hydrodechlorination dominate the whole reduction mechanisms due to the strong acid character of HAc. While the loss of mass balance also implied some other side reaction also take place during the electrolysis process. It should be stressed that the overall charge consumption in the presence of HAc takes 11.40 e^-/molecule, which is greater than the stoichiometric value of 8 e^-/molecule due to the coinstantaneous reduction of HAc.

Electrolysis of CF in the presence of 0.5 M H_2O was carried out, subsequently. According to the cyclic voltammetry in Fig 5.5c, the E_{app} values for the electrolysis of CF were chosen at -2.0 V and -2.40 V, respectively, and the electrolysis results are reported in Table 5.3 (entry3) and Fig5.5f. Essentially the same electrolysis results were observed in comparison with those performed in presence of HAc, with the only significant difference that less DCM and CH_4 were generated in the first case. At the first electrolysis step, the maximum accumulation of DCM was 79.05% with respect to 99% conversion of CF. When the electrolysis was shifted to the last step, the main products became 45.35% CH_4 and 0.83% C2 hydrocarbons. It was obvious that sequential hydrodechlorination was the principal reduction mechanism at the beginning of electrolysis, whereas with the proceeding of electrolysis, bases, such as carbanions and OH^-, accumulated gradually with the detriment of proton donors, which favored the other side reactions, in particular carbene routes, resulting into the loss of mass balance in the following reduction process. This is in accord with the reduction of CT performed in the same condition, where severe loss of mass balance was also observed after the first electrolysis step.

Table 5.2. Electrolysis of CF at Cu electrode in the absence and presence of different proton donors.[a]

Entry	Cathode	HA	E_{app}[b]	n	CF	DCM	CM	CH_4	C2
				(F/mol)	(%)[c]	(%)[d]	(%)[d]	(%)[d]	(%)[d]
1a	Cu		-2.20	2.04	8.07	27.08	1.38	6.50	0.77
1b			-2.55	3.32	0	0	0	18.62	1.45
2a	Cu	CH_3CO_2H	-1.73	3.92	0	88.16	0	4.98	0.18
2b			-2.33	11.40	0	0	0	76.03	0.85
3a	Cu	H_2O	-2.00	2.33	1.00	79.05	0.75	7.66	0.55
3b			-2.40	5.43	0	0	0	45.35	0.83
4a	Cu		-2.69	2.00	17.69	12.09	0.19	7.29	0.34
4b			-2.69	3.53	0	0	0.33	15.95	0.72
5a	Cu	CH_3CO_2H	-2.42	3.66	10.73	83.06	2.91	13.35	0.18
5b			-2.42	12.15	0	0	0	84.85	0.78
6a	Cu	H_2O	-2.45	2.35	4.83	63.79	2.70	9.26	0.34
6b			-2.45	7.07	0	0	0	48.02	0.48

[a] Solvent: DMF +0.1 M $(C_3H_7)_4NBF_4$; [CF] = 10 mM; [CH_3CO_2H] = 100 mM,[H_2O] = 0.5 M. [b] E_{app} = applied potential in V vs SCE. [c] Remaining substrate. [d] Yield calculated with respect to converted CF.

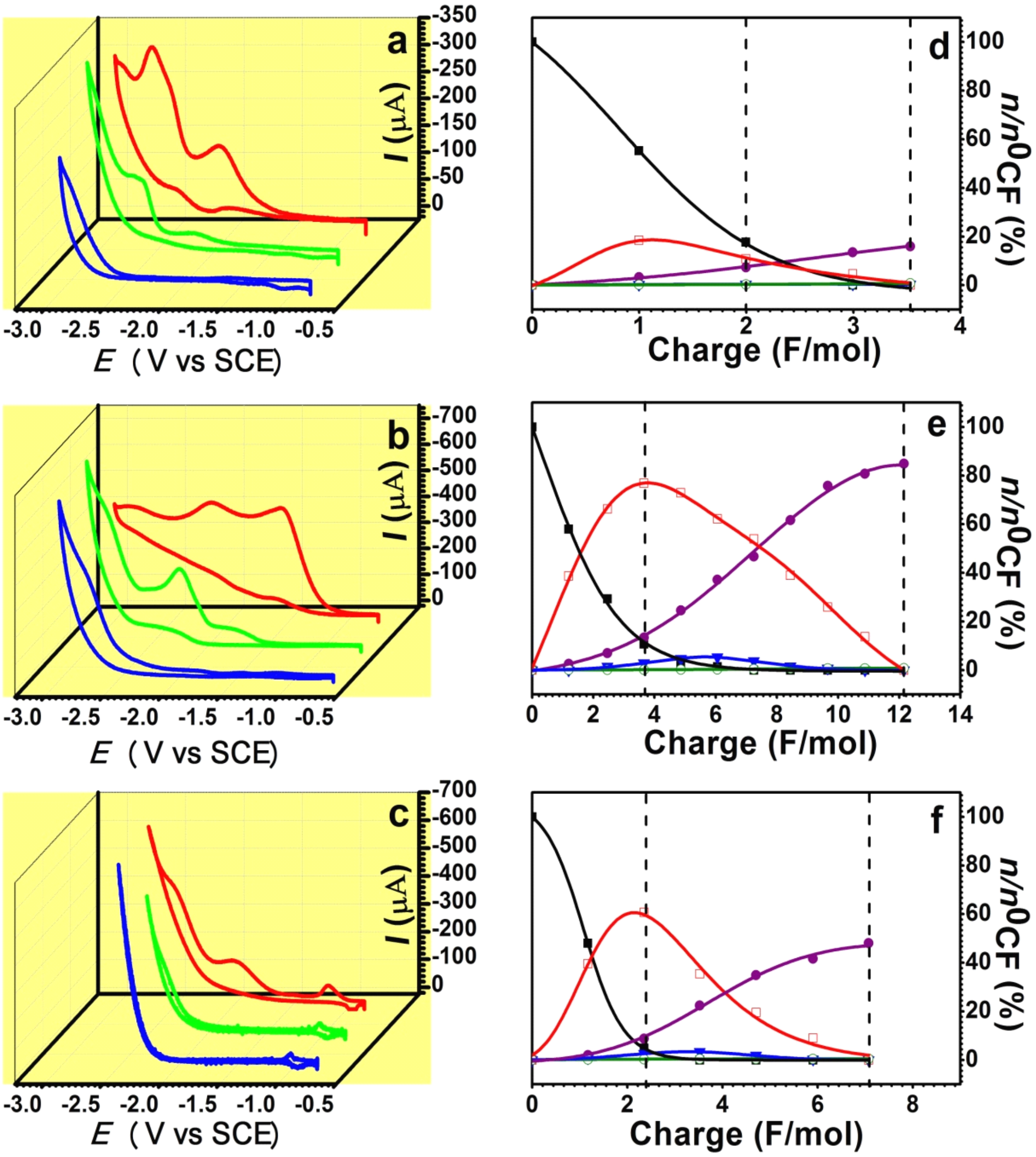


Fig. 5.6. Electrolysis of 10 mM CF in DMF + 0.1 M $(C_3H_7)_4NBF_4$ by single step electrolysis at Cu in the absence (a, d), in the presence (b, e) of 100 mM acetic acid, or in the presence 0.5 M water (c, f). (a,b,c) cyclic voltammogrms of CT recoded before electrolysis and at the end of each step; (d, e, f) concentration profiles (■) CF; (□) DCM; (▼) CM; (●) CH_4; (○) C2 hydrocarbons. The inserted vertical lines represent the electrolysis step.

Finally, we'd like to investigate whether the different potentiostatic electrolysis modes have substantial influences on the intermediates formation and product distributions during electrolysis. Similar with the electrolysis of CT, single step potentiostatic electrolysis of CF was embarked on in different solvent conditions, namely in the DMF solvent without any proton donor addition, in the presence of 0.1 M HAc and containing 0.5 M H_2O, respectively, with the applied potential, E_{app}, fixed at -2.69 V, -2.42 V and -2.45 V, correspondingly. The electrolysis results of CF in different conditions are gathered in Table 5.3 (entry4-6) and Fig. 5.6.

When the electrolysis experiments were repeated by single step potentiostatic electrolysis methods, actually the same electrolysis intermediates were obtained with those performed in the same conditions by sequential potentiostatic electrolysis methods, and all of them present a general trend that firstly increase to the maximum and then disappear with the charge consumed. The principal electrolysis products, performed by single step electrolysis in different solvent conditions, were 15.95% CH_4 and 0.72% C2 hydrocarbons in the absence of proton donor addition, 84.85% CH_4 and 0.78% C2 hydrocarbons for the case containing 0.1 M HAc in the solution, 48.02% CH_4 and 0.48% C2 hydrocarbons with 0.5 M H_2O addition, respectively, the values of which are comparable with those conducted by stepwise electrolysis methods, namely 18.62% CH_4 and 1.45% C2 hydrocarbons, 76.03% CH_4 and 0.85% C2 hydrocarbons, 45.35% CH_4 and 0.83% C2 hydrocarbons in the corresponding three distinct solvent conditions. These observations clearly show that essential the same electrolysis results were obtained in the same conditions, indicating that electrolysis of CF undergo the same reduction mechanisms regardless of the modes of potentiostatic electrolysis. However, in contrast to the results performed by stepwise electrolysis methods, in general, less chlorinated species formed by single electrolysis methods were found repulsive to accumulate due to the applied potential, E_{app}, locating at which all the intermediates could be reduced, and CH_4 increased constantly during electrolysis, as shown in Fig. 5.6(d-f).

It should be noted that a close comparison of the voltammetric responses of CF in Fig. 5.5a and Fig. 5.6a with that of reporting in Fig. 5.2b', one will find that the first reduction peak potential of CF in the electrolysis experiments was shifted by more than 400 mv to the negative direction compared to voltammetric experiment. While the presence of proton donor, in particular HAc, promote the reduction peaks shift to the positive direction but not as positive as the one the voltammetric cases. It appears that some passivation of Cu took place due to the high concentration of CF, resulting into a high energy barrier to overcome towards the cleavage of C-Cl bond in CF. However, luckily, complete dechlorination of CF together with its intermediates could be achieved, no matter this passivation problem, as shown Table

5.3 and Fig. 5.5-5.6.

5.3.4 Reduction of PCMs and geminal PCEs at Cu

PCMs and geminal PCEs, possessing similar structures, belong to the same class of homologue. It will be interesting to investigate whether they have similar reduction mechanisms at Cu electrode because of the analogical configurations. Herein, electrochemistry behaviors of Cu for the reduction of these two classes of compounds, together with their electrolysis results performed in different solvent conditions were examined, in order to clarify their similarities and differences on the reduction process.

Cu has been confirmed that exhibits excellent catalytic effect towards the reduction of both PCMs and geminal PCEs. As shown in Table 5.1, it promotes a positive shift of the first reduction peak potential of PCMs from 216 mv for CCl4 to 743 mv for CH3Cl. whereas a positive shift of 170 mv and 260 mv was observed for the reduction of 1,1,-DCA and 1,1,1-TCA (Table 3.1), respectively. It appears that Cu displays more remarkable catalytic activity for the cleavage of C-Cl in PCMs than those for geminal PCEs. Fig. 4.5 shows that voltammetric reductions of 1,1,1-TCA and 1,1-DCA at Cu give rise to two and one irreversible reduction peaks, respectively, which are in line with those observed on the reduction of CF and DCM, as shown in Fig. 5.2. Sequential hydrodechlorination was found to be the main reduction mechanism towards the reduction of both types of compounds, namely electrolysis of 1,1,1-TCA yields 1,1,-DCA, likewise, DCM is the reduction product of CF. while the loss of reduction peak for CA and CM mainly results from the same reason that the catalytic effect of Cu result into E_p (CA) > E_p (1,1-DCA) and E_p (CM) > E_p (DCM). Besides, successive two reduction peaks with un-equal height are observed at Cu for the reduction of 1,1,1-TCA and CF, indicate that some other chemical reactions may involve in their reduction processes. Self-protonation reactions couldn’t be excluded from the reduction mechanisms of PCMs and geminal PCEs owing to the aprotic character of DMF solvent. In addition, chlorinated carbanions, formed in the reduction of these two classes of compounds, can undergo Cl^- elimination by carbene routes. However, due to the special structure of geminal PCEs that is composed of two carbons in the molecule, some specific reactions, such as reductive α,β-elimination, and carbene rearrangement reactions, can take place during electrochemical reactions, which are distinct with the reduction of PCMs. A last comment should be stressed that the electrochemistry behaviors of Cu towards the reduction of these two types of compounds are very sensitive to the proton availability in the medium. Addition of HAc into the solution containing 1,1,1-TCA and CF, respectively, results into the successive reduction peaks of these two substrates all becoming almost the same height, implying that the presence of HAc could favor sequential hydrodechlorination dominant over other reaction routes. HAc has been found to exhibit excellent catalytic effect for the reductive cleavage of C-Cl bond in PCMs and geminal PCEs, for instance, it induces a great positive shift of reduction peaks from 260 mv in the absence of HAc to 820 mv for 1,1,1-TCA, and from 515 mv to 748 mv for CF. Surprisingly, addition of HAc doesn't promote an obvious positive shift of reduction potential for 1,1-DCA and DCM except the increase of peak intensities. We presume it may be affected by the simultaneous reduction of CA and CM involved in the respective reduction process.

Electrolysis results of geminal PCEs and PCMs are reported in Table 4.3-4.4 and Table 5.2-5.3, respectively. Further investigations by sequential potentiostatic electrolysis confirm the reduction mechanisms proposed in the voltammetric analysis. In the absence of proton donor, both sequential hydrodechlorination and self-protonation reactions take place during the electrolysis of these two classes of compounds, whereas the severe loss of mass balance indicates carbene species also are involved in the reduction processes. The detection of unsaturated carbons, such as acetylene and ethylene, implies that reductive α,β-elimination occurs for the electrolysis of geminal PCEs because of its specific structure. In the presence of H_2O, water has double roles for the reduction of geminal PCEs and PCMs. One can act as proton donor favoring the sequential hydrodechlorination. The other is that it can produce OH^-, which can enhance the bases promoted reductive α,β-elimination routes for geminal PCEs, leading to unsaturated hydrocarbons formation. While the continuous accumulation of OH^- with the detriment of proton donors don't benefit for the protonation reactions of PCMs, it facilitates chlorinated carbanions to undergo carbene routes by elimination of Cl-. Whereas, when the electrolysis were repeated in the presence of HAc, the reduction process of geminal PCEs and PCMs became less complicated, sequential hydrodechlorination exclusively turn into the principal reduction mechanism for the reduction of these two classes of compounds.

In general, the yield of electrolysis products could be enhanced by using single step potentiostatic electrolysis compared to those performed by sequential one, which indicates that single electrolysis could suppress the side reactions. There was one exception of that electrolysis of 1,1,1-TCA in the presence of H_2O by single step electrolysis, where reduction mechanism turn to reductive α,β-elimination from sequential hydrodechlorination, which was presumed to attribute to the accumulated OH- arising from donation of water.

Therefore, owing to the similar structure of these two classes of compounds, there are common places on their reduction process. Whereas some specific reactions may take place due to the special configurations of geminal PCEs.

5.4 Conclusions

Electrocatalytic dechlorination of PCMs was investigated at Cu electrode in the different solvent conditions. Cu exhibits an excellent catalytic effect for the reductive cleavage of C-Cl bond in PCMs with respect to GC; it induces a great positive shift of reduction peak potentials from 216 mv for CCl_4 to 743 mv for CH_3Cl. The addition of proton donors, such as HAc and H_2O, has a promotion for the reduction potentials of PCMs shifting to more positive direction, in particular in the presence of HAc, with a positive shift by 471 mv for CCl_4 to 934 mv for CH_3Cl. These possibly result from the increased generation rates of activation sites at the metal surface after proton addition, besides, the strong solvent ability of HAc and H_2O to solvate Cl^- also enhance the cleavage rate of PCMs. Reduction of PCMs at GC electrode clearly shows a sequential hydrodechlorination mechanism, whereas owing to the possible involved chemical reactions, results into the electrochemistry behaviors of PCMs at Cu electrode becoming more complicated. Reduction of PCMs was found very sensitive to the proton availability in the system. The addition of proton donor could advance the sequential hydrodechlorination to dominate over other reaction routes.

Further electrolysis of PCMs in different solvent conditions were carried out at Cu electrode. Reduction mechanisms of PCMs together with the product distributions were found not only dependent on the proton availability but also dependent on the proton types. Electrolysis results of CF and CT in the absence of any proton donor additions, in particular the latter, showed a severe loss of mass balance during electrolysis, indicating that except the sequential hydrodechlorination mechanism some other reactions, such as carbene reactions, may involve in the reduction process. This is in line with the assumptions proposed in the voltammetric section. Addition of proton donors into the solution, on one side, it can activate the catalytic effect of Cu towards the reductive cleavage of PCMs that promote their reduction potentials shifting to more positive direction, besides, it can enhance the yield of hydrodechlorination products during electrolysis. HAc, as a strong proton donor, can promote reduction of PCMs mainly undergoing sequential hydrodechlorination mechanism, with high yield of CH_4 as the final electrolysis products (more than 70% in most cases). H_2O plays double roles for the reduction of PCMs. As a proton donor, albeit it can favor the protonation reactions, the continuous accumulation of OH^- with the detriment of proton donors, in particular at the last steps of electrolysis, thus don't benefit for the sequential hydrodechlorination mechanism. Accordingly, the presence of H_2O couldn't avoid the competition reaction of carbene routes due to its weak acid character.

A comparison of electrolysis results of PCMs performed by single step potentiostatic electrolysis methods with those carried out under sequential potentiostatic electrolysis conditions, it clearly shows essential the same electrolysis products were obtained regardless of the modes of applied potentials. All of them present an overall trend that firstly increase and thus then disappear with the proceeding of electrolysis. However, the only significant difference, among the two distinct modes of potential application, is that the electrolysis intermediates were repulsive to accumulate in the case of single step electrolysis, since the potential imposed located at which all the chlorinated species are reducible.

Eventually, the similarities and differences towards the reduction of PCMs and geminal PCEs at Cu were investigated. Due to the similar structure of these two classes of compounds, there are some common places on their reduction process. Cu exhibits an excellent electrocatalytic activity for the reductive cleavage of these two types of compounds. The presence of proton donor could enhance the catalytic effect of Cu that leads to the reduction potentials of PCMs and geminal PCEs shifting to even more positive direction. Except for sequential hydrodechlorination, some other reaction mechanisms, such as self-protonation reaction, carbene routes, were involved in the reduction processes because of the aprotic character of DMF solvent. The proton availability and the proton type have significant effect on the reduction mechanisms of these two classes of compounds. Strong proton donor facilitate the sequential hydrodechlorination mechanisms, while the addition of water can not only used as a proton donor, it also dominates OH- during electrolysis process, which may result into some other side reactions. However, owing to the different configurations in molecules result into that some diversity in their reduction process. A close comparison of the catalytic effect of Cu for the reduction of these two classes of compounds will allow one conclude that Cu displays more remarkable catalytic activity for the reductive cleavage of PCMs than those of geminal PCEs. In addition, as a result of the specific structure of geminal PCEs, some typical reaction may take place during electrolysis, for instance, bases promoted reductive α,β-elimination reaction, and carbene rearrangement reaction via hydrogen migration once carbene species formed may occur in the reduction process.

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Chapter 6 Eletrochemical partial hydrogenation of acetylene at precious and non-precious metal electrodes

Abstract

Removal acetylene from ethylene streams is a key process in polymer synthetic industry. A new technology of acetylene hydrogenation has been explored in this research. Electrochemical hydrogenation of acetylene has been carried out in DMF+ 0.1 M $TPABF_4$ at different metal electrodes and glassy carbon (GC) in the absence and presence of water, the latter used as reference for evaluating the catalytic effect of metals. Voltammetric studies show that the electrochemistry behaviors of acetylene depend on the nature of metals and proton availability in the medium. Au, Ag and Pd exhibit remarkable electrocatalytic activities towards acetylene reduction, in which the reduction peak potential shifts to more positive direction stepwisely with water addition. Electrolysis of acetylene in the absence of H_2O indicates that high ethylene selectivity together with considerable C4 hydrocarbons formation were obtained at Cu and Ag electrode, whereas C4 hydrocarbons became the principal product on Pt electrode. However, addition of H_2O in the solution can evidently enhance ethylene selectivity by effectively restricting dimerization reactions during electrolysis. Ethylene selectivity is found dependent on the intrinsic character of electrodes, wherein, Cu presents the highest ethylene selectivity than Ag and Pt electrode in our study. Electrocatalytic hydrogenation of acetylene in the presence of H_2O can give rise to more than 75% ethylene selectivity, trace of ethane production (0.25%) and low C4 compounds yield by using Cu electrode during electrolysis.

6.1. Introduction

Ethylene is an important raw material in polymers synthetic industry. The production of ethylene in industry mainly uses steam cracking methods, in which always accompanies less amounts of acetylene generation as by products. However, the formed acetylene can severely poison the catalysts in the downstream of polymerization processes [1-2]. Therefore, removal of trace acetylene from ethylene streams is a key step for obtaining commercially valuable polymers in industry, and numerous approaches toward acetylene removal have been explored over the last decades, wherein, catalytic hydrogenation of acetylene to ethylene over modified precious metals is the most commonly used technology in industry presently.

Over the past decades, most researches were concentrated on searching for high efficient and extra-ordinary catalysts toward acetylene hydrogenation. Among them, Au, Pd, Pt, Cu, Ni and other transition metals have been found exhibiting prominent catalytic effect in this process [3-7]. Nevertheless, due to the overhydrogenation problems, second metals and organic ligand are incorporated for lessening the activities of catalysts, sometimes even with continuous feeding of CO to compete with ethylene for occupying the activated sites at metal surface, in order to obtain high ethylene selectivity in the reduction of acetylene process[4,8-13]. In view of the expense of costly catalysts, recent investigations switch to seek for alternative catalysts instead of precious metals, such as Ni-Zn alloys, Cu-Ni-Fe alloys, Cu-Al alloys [1,10,13], all of them present remarkable catalytic effect and high ethylene selectivity towards acetylene hydrogenation. Sometimes the ethylene selectivity even could reach to 80% during catalytic hydrogenation process. However, Pd based materials are still the principal catalysts used in acetylene removal industrially and experimentally by far, which greatly increase the processing cost; in addition, rigorous operation conditions, such as high temperature to activate the catalyst, external H_2 and even with CO incorporation feeding into the stream to enhance ethylene selectivity, are always required by using catalytic hydrogenation technology; the problems of over-hydrogenation and catalyst poison resulted from oligomerization to hydrocarbons (green oil), are the main drawbacks of catalytic acetylene hydrogenation and present great challenges to this technology. Therefore, searching for an alternative technology with competitive property and superiority over catalytic hydrogenation technology is significant and strongly demanded in industry.

Owing to the characters of electrochemical hydrogenation methods that works under mild condition, easier operation, controllable reaction kinetics, against catalyst poison and without external H_2 addition, it has been widely applied and advanced on the hydrogenation of halogenated organics, [14-19], nitriles [20], benzene [21], olefins and ketones [22,23] over the past decades. In particular, electrochemical hydrogenation of halogenated organics, could achieve detoxification of these compounds by complete dehalogenation successfully, which attracts the worldwide attentions presently.

Because of the unsaturated character and high positive free energy of formation, acetylene is readily converted to hydrogenation products by addition reaction. Dimethylformamide (DMF) has high acetylene solubility, which is widely used as an excellent solvent to transport acetylene and remove acetylene from ethylene streams in industry [24]. According to our previous researches [16,18], electrochemical hydrodechlorination of volatile chlorinated organic compounds could be successfully achieved in DMF solution, while it could be evidently enhanced in the virtue of proton donor, such as acetic acid, water. So we are wondering whether electrochemical hydrogenation of acetylene can be achieved under the same working conditions. It's new but a significant topic, since if partial hydrogenation could be carried out by electrochemical reduction technology, it can overcome the drawbacks of catalytic acetylene hydrogenation technology, which will make it become a very competitive and promising approach by combination with DMF extraction methods in polymer synthetic industry.

Actually, partial hydrogenation of acetylene by electrochemical reduction methods has been indeed discovered in our research, as reported in chapter4, where acetylene as an intermediate of volatile polychloroethanes could be further reduced to ethylene in the following reduction process. However, based on the purpose of research and complex reduction mechanisms, we didn't conduct further investigation of acetylene reduction over there. As already stated, since acetylene hydrogenation is a key step in polymer industry, further research on acetylene hydrogenation by electrochemical method is strongly demanded to examine the feasibility of this technology.

As already known, precious metals and other transition metals exhibit remarkable catalytic properties towards both catalytic hydrogenation and electrochemical hydrogenation process, besides, according to the previous researches, acetylene normally achieves hydrogenation process in the gas phase. Therefore, the electrochemistry behaviors of acetylene at different electrode materials in solution phase are still blank, and the feasibility together with the reduction mechanisms of electrochemical hydrogenation of acetylene are wondering. To the best of our knowledge, the concept of electrochemical hydrogenation of acetylene is the first time proposed, and no related reports have been published before. Herein, we try to address some of the aforementioned questions to know better of this process and provide some instructions for the potential industry application of this technology. We hope it can open a new gate for the investigation of acetylene hydrogenation through our research.

6.2. Experimental and Methods

6.2.1. Materials and chemicals

Dimethylformamide (DMF) was treated in the presence of anhydrous Na_2CO_4 for one week and stirred discontinuously during this period. After double distillations at lower pressure under N_2 conditions, DMF was stored in a brown bottle under the protection of Argon. Tetrapropylammonium tetrafluoroborate ($C_{12}H_{28}BF_4N$, TPABF4, Fluka) was recrystallized twice in ethanol and dried in a vacuum oven at 70 ℃ for at least two days. Acetylene (Industrial purity), mix gas standard (Ethylene,2.43%; Acetylene, 2.27%; ethane 2.28%; 2-Butene 0.796%; 1,3-Butadiene 1.55%; Butane 1.15%.) preserved in nitrogen were used directly as received.

6.2.2. Experimental instrumentation

Electrochemical measurements were performed on a computer controlled EG&G PARC Model 273 potentiostat/galvanostat. All experiments were carried out at 25 ℃ in a three electrode system with GC, Pd, Ag, Cu, Au, Pt or Ni disk as working electrode, Pt as counter electrode, and Ag/AgCl/ Me_4NCl(sat) in DMF + Acetonitrile (3:1,V/V) solution as reference electrode, respectively. The reference electrode was calibrated at the end of each experiment against ferricenium/ferrocene couple ($E_{Fc+/Fc}$ = 0.475 V vs SCE in DMF), which allowed conversion of all potentials to saturated calomelelectrode (SCE) scales. To be noted that all the potential values in this paper were calibrated to SCE except specialization.

A 3 mm diameter GC rod (Tokai, GC-20) and 2 mm diameter metal wires (Pd, Ag, Cu, Au, Pt, Ni, Alfa Aesar, ≥ 99.99%) were used as working electrode in this research, respectively. Prior to each experiment, the cathode surfaces were polished to a mirror finish with silicon carbide papers by decreasing grain size (Struers, grit: 1000, 2500, 4000), followed by diamond paste (3-, 1-, 0.25-μm particle size). After each polishing step, the electrodes were always cleaned in ethanol in an ultrasonic bath for about 5 min.

6.2.3. Cyclic voltammetry experiments and electrolysis

Voltammetric experiments were performed in a sealed thermostated of undivided cell with 0.1 M $TPABF_4$ as supporting electrolyte, and determined amount of acetylene dissolving into 20 mL DMF, where a three electrode system was adopted as stated before. Cyclic voltammograms were recorded at each electrode, respectively. Electrolytic experiments were carried out in a sealed thermostated of divided cell with Pt as counter electrode, Ag/AgCl/ Me_4NCl(sat) as reference electrode, and using Ag, Cu or Pt plate as working electrode, respectively. During electrolysis, samples of gas for analysis by GC were periodically withdrawn with a syringe through a septum cap of the cell, each point was analyzed twice.

6.2.4. Analysis

Gas phase electrolysis products were withdrawn with a syringe, followed by directly injecting into a HP 6890 system GC equipped with a HP Plot Q 30 m ×0.537 mm× 0.40 mm capillary column (Agilent Technologies, USA) and a flame ionization detector (FID). The injector was equipped with a 0.75 mm i.d. liner and was operated in a split mode (15:1). The oven temperature was set at 60℃ for 2 min, then increased to 240℃ at a rate of 30 $℃\cdot min^{-1}$ and held for 2 min. The injector and the detector were set at 150 and 250℃, respectively, with a carrier gas (He) flow at 4.4 $mL\cdot min^{-1}$. Identification and quantification of the products were based on comparison with authentic samples and calibration curves, respectively. The procedures of creating calibration curves were operated as follows: firstly, certain amounts of gas was withdrawn from the tank of mix gas standard and dissolved into the sealed electrolytic cell containing 20 mL DMF, which was the same setting like the electrolysis experiments. Secondly, determined volume of gas was withdrawn from the headspace of the cell by gas syringe when the system kept equability under continuous stirring conditions, followed by directly injecting into GC for analysis, each point was analyzed for three times. For keeping the same pressure of this system, the same volume of argon was injected into the cell before each withdrawn procedure. Repeat the above two procedures for six times, except the amounts of gas withdrawn from the mix gas standard tank were different each time. Eventually, calibration curves of different gas were created based on the analysis of chromatographic data.

All chromatographic data were acquired and analyzed with validated HP Chestation software.

6.3. Results and discussion

6.3.1. Cyclic voltammetry of acetylene at different electrodes

Voltammetric experiments of acetylene were carried out at 7 different electrodes (GC, Ag, Au, Pd, Cu, Ni, Pt) in DMF + 0.1 M TPABF$_4$ at the scan rate from 0.05 v·s^{-1} to 5 v·s^{-1}, where water as a proton donor was intentionally introduced into the system stepwisely, to observe the effects on acetylene reduction. The voltammograms at different electrodes are reported in Fig.6.1. Reduction of acetylene is found strongly dependent on the nature of electrodes and water availability in the system.

As shown in Fig.6.1, cyclic voltammetries of acetylene at different electrodes present distinct electrochemistry behaviors in the absence of water. Ag and Au electrode present an incomplete reduction peak for the reduction of acetylene; whereas, a broad reduction shoulder appears at Pd, Cu, GC three electrodes; neither reduction peaks nor shoulders are observed in the voltammetric reduction of acetylene at Ni and Pt electrode. Considering the potential ability of water as hydrogen donor, it may facilitate the acetylene hydrogenation process. Therefore, determined amounts of water were thus intentionally introduced into the system stepwisely, to observe the changes of electro-reduction behaviors for acetylene. As shown in Fig. 6.1, with the increase of water addition, an irreversible reduction peak emerges out and becomes complete at Au, Ag, Pd and GC electrode gradually, in concomitant with the peak potential shifting to more positive direction, simultaneously. This reduction peak is presumed to be the reduction of acetylene. In contrast to the above four electrodes, there is no any reduction peaks throughout the whole voltammetric reduction of acetylene at Ni, Pt and Cu electrode, except a wide shoulder comes out at Cu. In addition, another significant feature, delivered from the voltammograms, is that the peak intensity of acetylene at Au, Ag, Pd and GC electrode exhibit a general trend that increases firstly and then decline successively with water addition. Owing to the discharge of electrolyte, narrowed potential widow was obtained gradually with the increase of water addition, for instance, in comparison of the potential window at Au electrode before and after 360 equilibrant water addition, it shortens by 1.02 V. Whereas, a clearly irreversible peak could still be observed at Au, Ag, GC and Pd electrode even after 360 eq. water addition.

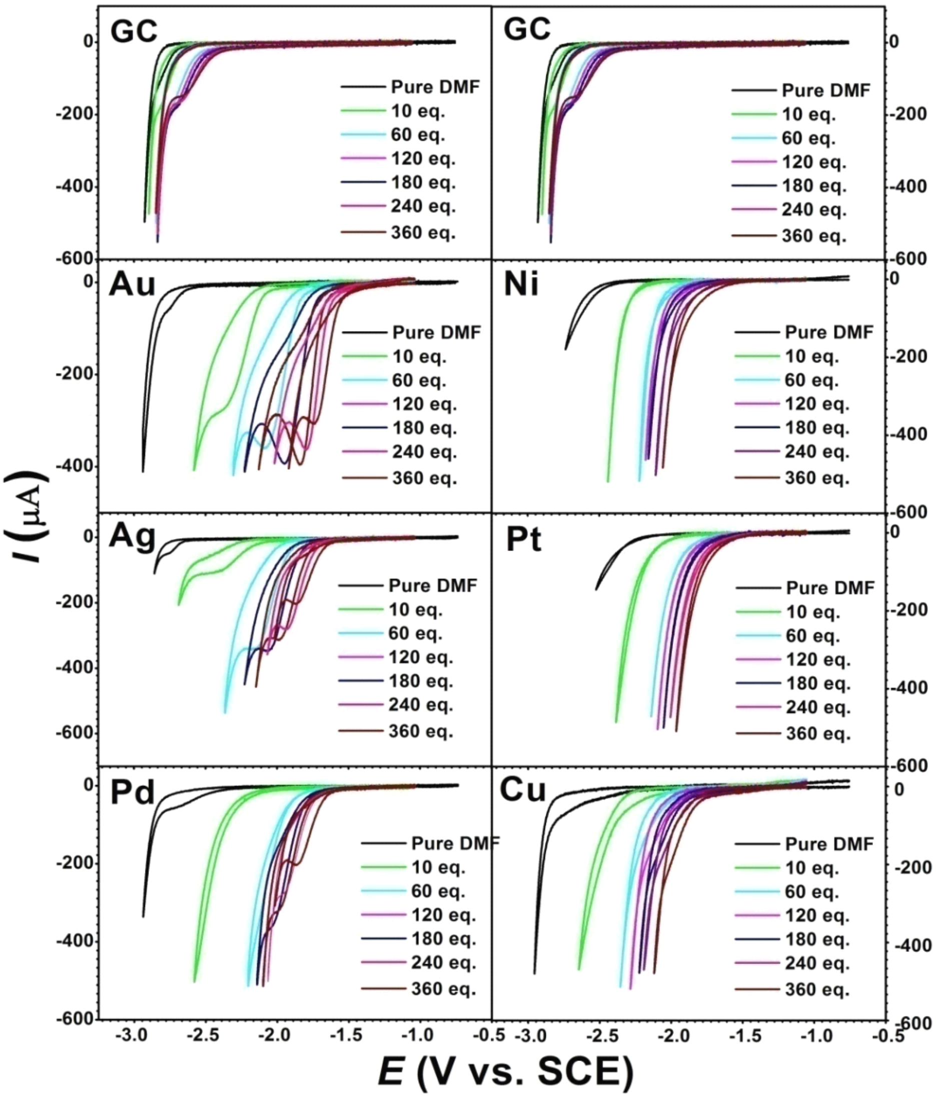

Fig. 6.1. Cyclic voltammetries of acetylene (0.76 mmol, total amounts in the cell) at different electrodes in DMF + 0.1 M 0.1 M $TPABF_4$ recorded at 0.2 $v \cdot s^{-1}$ in the absence and presence of different amounts of water addition.

GC is known and widely used as an inert electrode, which doesn't exhibit obviously catalytic effect towards electrochemical reduction process [25], and thus used as a reference to measure the catalytic activities of different metals at here. As clarified before [18], catalytic effects of different metals, ΔE^{M}, can be evaluated by calculating the peak potential differences of metals with respect to GC recorded at 0.2 $V \cdot s^{-1}$, $\Delta E^{M} = E_{P}^{M} - E_{P}^{GC}$. The voltammetric data at different electrodes, for the reduction of acetylene performed in DMF solutions in the presence different amounts of water, together with the values of catalytic effects at each metal electrode are gathered in Table 6.1. The results in Fig.6.1 and Table

6.1clearly show that the electrochemistry behavior of acetylene and the catalytic effects towards acetylene reduction at different electrode are strong dependent on the nature of electrode materials and water availability in the medium. Wherein, Au exhibits the best electrocatalytic activity with a positive shift of reduction potential, ΔE^{Au}, by 937 mv after 360 eq. water additions. A complete irreversible reduction peak was clearly observed at Au in a rather broad water addition scope. Followed by Ag, it also presents an excellent catalytic effect with a ΔE^{Ag} value at 811 mv after 360 eq. water additions. Similar with Au, an obvious reduction peak appears at Ag in a wide water addition range. Pd also shows a good catalytic character towards acetylene reduction, even though a little lower than Au and Ag, a ΔE^{Pd} value of 777 mv was found after 360 eq. water additions. However, slightly different with Au and Ag, GC and Pd begin to present an irreversible reduction peak only in the presence of high amounts of water (say 60 eq. for GC and 120 eq. for Pd, respectively) and become complete gradually with continuous water additions. Surprisingly, no clear reduction peak but a shoulder appears at Cu electrode throughout the voltammetric experiment, since it is recognized as an alternative catalyst of noble metals that exhibits remarkable catalytic effect towards electrochemical hydrodechlorination of chloride organics, as we have stated in the last two chapters. We presume some passivation may take place at Cu surface, which results into the electrochemistry behavior of acetylene being concealed, and this would be specialized discussed in the following electrolysis section. No reduction responses emerge out at Pt and Ni electrode throughout the whole voltammetric experiment.

Table 6.1. Voltammetric data for acetylene reduction (0.76 mMol) in DMF +0.1 M $\mathrm{TPABF_4}$ on different electrodes in the absence and presence of different amounts of water addition, measured at 0.2 $\mathrm{v \cdot s^{-1}}$

Amounts of water	GC V vs SCE	J^{d} mA•cm^{-2}	Au V vs SCE	J^{d} mA•cm^{-2}	ΔE_p^{e} V	Ag V vs SCE	J mA•cm^{-2}	ΔE_p^{e} V	Pd V vs SCE	J mA•cm^{-2}	ΔE_p^{e} V
0^{a}	--^{c}	--	--^{c}	--	--	-2.750	--	--	--	--	--
10 eq.^{b}	--	--	-2.408	-9.00	--	-2.426	-3.50	--	--	--	--
60 eq.	--	--	-2.084	-11.42	--	-2.156	-8.47	--	--	--	--
120 eq.	--	--	-1.951	-12.53	--	-2.070	-10.94	--	-2.057	-11.62	--
180 eq.	-2.717	-2.57	-1.835	-12.58	0.882	-1.990	-10.02	0.727	-2.006	-10.37	0.711
240 eq.	-2.697	-2.36	-1.798	-11.50	0.899	-1.934	-8.95	0.763	-1.962	-8.89	0.735
360 eq.	-2.679	-2.14	-1.742	-9.79	0.937	-1.868	-6.48	0.811	-1.902	-7.46	0.777

$^{a.}$ no water addition; ^{b} eq. corresond to the equilibrate amounts of acetylene; ^{c} -- denotes no reduction peak obeserved; ^{d} represent current density, j, mA•cm^{-2}; ^{e} $\Delta E_p = E_p^{M} - E_p^{GC}$

As already known, precious metals and other transition metals located at group ⅧB possess excellent catalytic properties towards acetylene hydrogenation, could rapidly interact with acetylene spreading to their surface by chemisorptions in catalytic hydrogenation process [5,10,27]. We presume this chemisorption also survive in the solution phase, which may lead to form an activated metal-organic complex as a transition state, thus induces acetylene more susceptible to be reduced by decreasing the over-potential associated with acetylene reduction and facilitates the hydrogenation reaction occurrence. Obviously, the over-potential is related to the activation energy barrier of the formation of organometallic complex and depends on the intrinsic character of electrodes, which results into the diversities of electrochemistry behaviors and catalytic activities of different electrodes towards acetylene reduction. In addition, due to the splendid catalytic properties of these metals towards the electrochemical hydrogenation processes, the presence of water could advance the formation of atomic hydrogen layer through water electrolysis, covering around their surface and even intercalating hydrogen into their lattice, by which could achieve hydrogenation process through continuous attacking the acetylene molecule spreading to their surface, subsequently [19]. It should be noted that the role of water plays, except as a proton donor, it also can be used to update the catalytic sites at metal surface [28], and further promote hydrogenation reaction occurrence continuously. However, on the other side, the concentration of acetylene in the solution became diluted with the continuous of water addition, resulting into the peak intensity weakened gradually. These can well explain the positive shift of peak potential and the general trend of peak current intensity that increase firstly and then decrease subsequently with water addition.

According to the catalytic acetylene hydrogenation mechanism at transition metals [1-10], that acetylene could be readily adsorbed at the metal surface via the interaction of triple bond; besides, H_2 could be dissociated into atomic hydrogen over metal surface due to the intrinsic properties of transition metals, and an activated atomic hydrogen layer is formed and further covers over the whole metal surface by spillover effect of hydrogen [8,10,15], which could stimulate the hydrogenation reaction occurrence by continuous attacking the adsorbed acetylene. Based on the catalytic acetylene hydrogenation mechanism, a similar but not the same owing to the distinct working condition, electrochemical hydrogenation of acetylene mechanism is proposed that mainly involves the following steps described as 6.1-6.7:

$$\mathrm{HC{\equiv}CH} + \mathrm{M} \rightleftharpoons (\mathrm{HC{\equiv}CH})_{ads}\,\mathrm{M} \tag{6.1}$$

$$(\mathrm{HC{\equiv}CH})_{ads}\,\mathrm{M} + e^- + \mathrm{H}^+ \rightleftharpoons (\mathrm{H_2C{=}\dot{C}H})_{ads}\,\mathrm{M} \tag{6.2}$$

$$(\mathrm{H_2C{=}\dot{C}H})_{ads}\,\mathrm{M} + e^- \rightleftharpoons (\mathrm{H_2C{=}\bar{C}H})_{ads}\,\mathrm{M} \tag{6.3}$$

$$(\mathrm{H_2C{=}\bar{C}H})_{ads}\,\mathrm{M} + \mathrm{H}^+ \rightleftharpoons (\mathrm{H_2C{=}CH_2})_{ads}\,\mathrm{M} \tag{6.4}$$

$$\mathrm{H_2O} + e^- \rightleftharpoons (\mathrm{H})_{ads} + \mathrm{OH}^- \tag{6.5}$$

$$(\mathrm{H_2C{=}\dot{C}H})_{ads}\,\mathrm{M} + \mathrm{H} \rightleftharpoons (\mathrm{H_2C{=}CH_2})_{ads}\,\mathrm{M} \tag{6.6}$$

$$(\mathrm{H_2C{=}CH_2})_{ads}\,\mathrm{M} \rightleftharpoons \mathrm{H_2C{=}CH_2} + \mathrm{M} \tag{6.7}$$

Scheme6.1. The proposal mechanisms of electrochemical acetylene hydrogenation

Firstly, acetylene diffused from the main body of solution phase promptly interacts with metal surface by chemisorptions; secondly, the adsorbed acetylene accepts electrons from cathode, and then take place electrophilic addition reaction by combination with hydrogen ion existing in the system with ethylene radical generation, in which concomitant with the transformation of carbon-carbon bond from π bond to a new σ bond, and this step is speculated to be the rate determining step of acetylene hydrogenation process; ethylene radical is readily to be reduced once formed by receiving another electron transfer accompanying with ethylene carbanion formation, subsequently; the carbanion could be protonated by any proton donor in the medium giving rise to ethylene in succession; eventually, ethylene gas desorbs from metal surface to the headspace of system. By the way, it should be noted that, in the presence of water, atomic hydrogen, resulted from the electrolysis of water, may participate in the hydrogenation reaction with ethylene formation directly, as described in eq.6.6.

Ethylene, as an unsaturated reduction product, has a potential reaction possibility to further form ethane by over-hydrogenation reaction at here. However, this is an undesired process and should be strictly avoided from the industrial application point of view. According to the previous researches on catalytic hydrogenation of acetylene [1,5,10], Au, Ag and Cu based catalysts could achieve higher ethylene selectivity because of their supernal thermodynamic factor, which is defined as the binding energy difference between triple bond and double bond at the metal surface [10], it can accelerate the prompt adsorption of acetylene and the rapid desorption of ethylene at the metal surface, accordingly, restrict over-hydrogenation reaction occurrence. Besides, in term of the TPD results [5], ethylene doesn’t stick to at the Au surface in a detectable amount; Ag existing in the Pd-Ag catalyst could effectively prevent the generation of sub-surface H, by which can result into the formation of over-hydrogenation product ethane [8]. Owing to the spillover effect of hydrogen and the potential formation of hydrides at Pd and Ni electrode (PdH_x, NiH_x), which could activate the undesired pathway with over-hydrogenation product generation in the catalytic acetylene hydrogenation process [10]. Even though numerous researches have revealed high alkene selectivity could be obtained by catalytic hydrogenation of acetylene over Cu catalysts [10,13,29], due to the lower H_2 dissociation ability and lower hydrogen spillover effect at Cu surface, undesired oligomerization products are often produced simultaneously, which also could result into the catalyst poison subsequently. However, as a distinctive technology with totally different working conditions, the feasibility of whether electrochemical hydrogenation of acetylene could be achieved is desired to know; when uses the same metal as electrode, whether electrochemical hydrogenation of acetylene exhibits analogous product distributions like those performed by catalytic hydrogenation methods or not are wondering. As shown in Fig.6.1, Au, Ag, Pd, all present remarkable electrocatalytic activity towards acetylene reduction; Cu as an alternative catalyst of noble metals exhibits a shoulder over there; Pt is known as its strong interaction ability with hydrogen, whereas, no reduction peak is observed at Pt electrode. Based on the comprehensive consideration of expense, exploration reduction mechanism of electrochemical acetylene hydrogenation and searching for high efficient catalyst, Ag, Cu, and Pt were chosen as working electrodes at here, electrolysis of acetylene in different solvent conditions were carried out for further validating the feasibility of this technology.

6.3.2 Electrochemical hydrogenation of acetylene

To further check the applicability of electrochemical reduction methods towards acetylene hydrogenation, electrolysis experiments of acetylene were carried out in different solvent conditions at Ag, Cu and Pt electrode, respectively. All experiments were conducted under potentiostatic electrolysis conditions, in which the applied potential, E_{app}, located at the end of the reduction peak/shoulder but well seperated from the discharge of electrolyte. H_2O, as a proton donor, were intentionally added into the DMF solution, to investigate the effects on the product distributions during electrolysis. Samples of gas phase were withdrawn periodically and analyzed timely by GC during experiments. Electrolysis results of acetylene at the three electrodes in different solvent conditions were gathered in Table 6.2, whereas the concentration profiles of acetylene and its main electrolysis products together with the cyclic voltammetries recorded before and after each electrolysis step are illustrated in Fig. 6.2 - 6.3, respectively.

As shown in Fig.6.2(a-c), an incomplete reduction peak of acetylene with peak potential locating at near the electrolyte discharge region is observed at both Cu and Ag electrode in the absence of water, whereas there is no any reduction repsonses in the voltammogram of Pt electrode. Electrolysis of acetylene were embarked on in DMF solution at Cu, Ag and Pt electrode respectively, where the imposed potentials were thus determined based on the voltammograms of each electrode prior to the dischcarge of electrolyte. Electrolysis results of acetylene at the three electrodes were gathered in Table 6.2 (entry1-3), whereas the concentration profiles of acetylene and its electrolysis products together with the variations of cyclic voltammetry recorded before and after each electrolysis step are illustrated in Fig. 6.2, respectively. At the end of electrolysis, which consumed 2.79 e-/molecule, 58.75% ethylene, 0.54% ethane, 0.14% 1-butene and 36.72% 1,3-butadiene were produced with the conversion of 96.61% acetylene at Cu electrode. For Ag electrode, 92.73% of acetylene were mainly converted to 51.81% ethylene, 1.02% ethane, 0.21% 2-butene and 35.12% 1,3-butadiene at the end of electrolysis experiments, which corresponds to 3.28 e-/molecule charge consumption. It appears that the variations of acetylene and its main electrolysis intermediates at Cu and Ag electrode present quite analogous trends with each other. High ethylene selectivity were obtained both at Cu and Ag electrode, and very low amounts of ethane (lower than 1.5%) resulted from over-hydrogenation reaction were detected in both cases. Besides, massive of C4 hydrocarbons were evidently produced over the two electrodes at the end of electrolysis, namely 36.86% for Cu and 35.33% for Ag. However, in contrast to Cu and Ag, very low ethylene selectivey (1.77%) with 78.33% conversion of acetyleen were obtained at Pt electrode, in concomitant with 74.68% C4 hydrocarbons formed at the end of electrolysis experiments (Table 6.2, entry3).

The high yield of ethylene at both Cu and Ag electrode shows that electrochemical hydrogenation of acetylene indeed could be achieved during electrolysis, and the low amounts of ethane formed indicates that overhydrogenation seems could be effectively suppressed in this process. This is in accordance with the results that performed by catalytic hydrogenation methods, where both Cu and Ag exhibit high ethylene selectivity and could further effectively restrict ethane production [1,8,10,13,33]. Actually, trace of ethane were also observed during electrolysis at Pt electrode, it seems that over-hydrogenation reaction could be prejudiced restricted by electro-reduction methods at here. As already known, the hydrogenation reaction of acetylene is a continuous process [5,34-35], as: $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$, in which the selectivity of hydrogenation products depend on their adsorption ability at metal surface, defined as thermodynamic selectivity. Therefore, a good catalyst for acetylene partial hydrogenation must possess a characteristic of high acetylene adsorption ability and high ethylene desorption ability simultaneously. Triple bond compounds are found exhibiting strong chemisorptions ability with Ag, Au, Cu and other transition metals compared to double bond [1,10]. It's reasonable to assume that the same trend also retain in the solution phase. In addition, acetylene has much better solubility in DMF than ethylene, which could readily distribute to the metal surface and occupy more activated sites by competitive adsorption with ethylene, whereas ethylene is prone to desorption once formed and diffusing to the headspace of system. Besides, electrochemical hydrogenation of ethylene may take place at even more negative potential in the system, which is concealed by the discharge of electrolyte. That's why overhydrogenation reaction could be evidently restricted by using electrochemical hydrogenation methods at here.

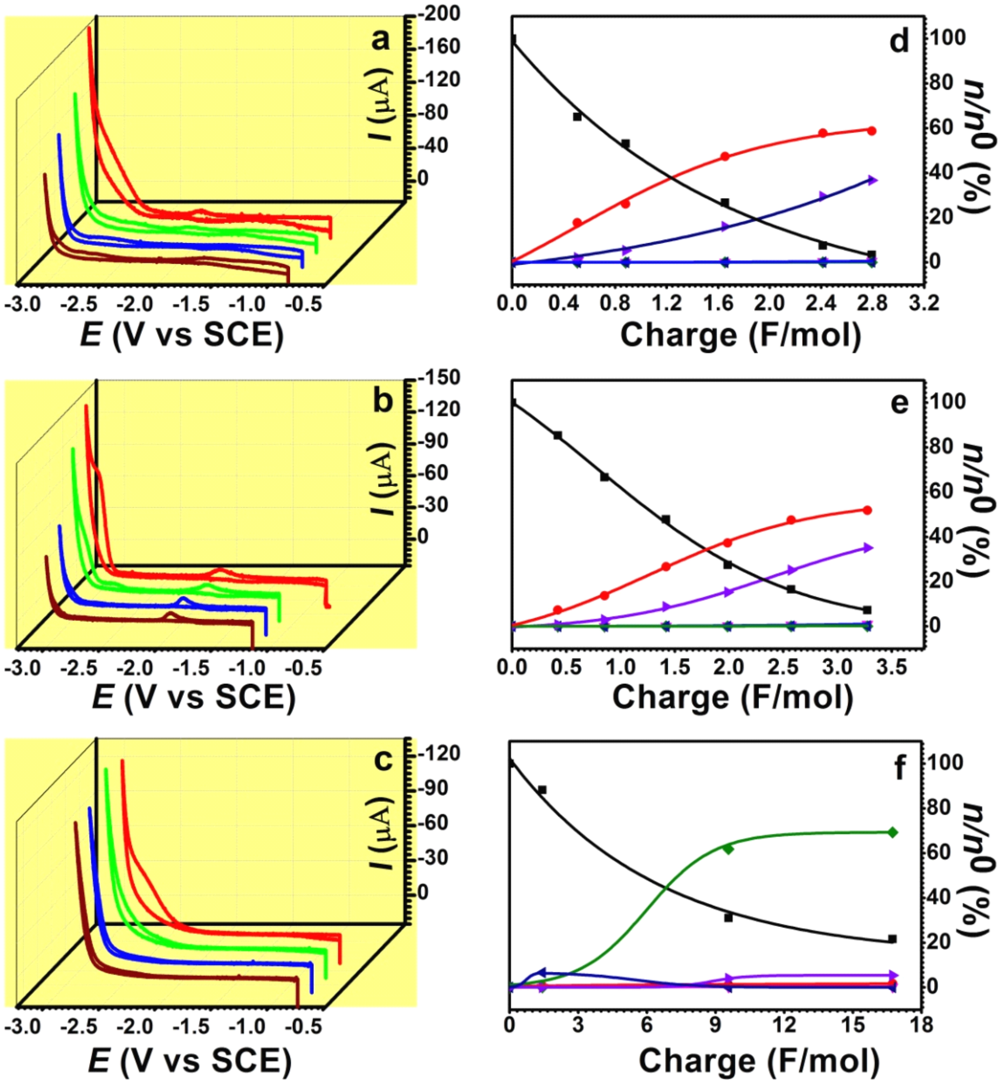

Fig. 6.2. Electrolysis of acetylene in DMF + 0.1 M $TPABF_4$ at Cu (a, d), Ag (b, e) and Pt (c, f) electrode in the absence of 1 M water addition. (a,b, c) show the cyclic voltammograms of acetylene recorded at Cu, Ag and Pt electrode during preparative electrolysis with the charge consumption, respectively; (d, e, f) represent the concentration variations of acetylene and its intermediates in gas phase during electrolysis. (■) acetylene; (●) ethylene; (▼) ethane; (◆) butane; ( ) 1,3-butandiene; ( ) 2-butene

A very interesting phenomen would be discovered, if one takes account of the mass balances of the two electrolysis investigations at Cu and Ag electrode, which present a general trend of firstly decrease and then incarease during the electrolysis of acetylene. As aforementioned before, the metals located at group ⅧB could rapidly interact with acetylene spreading to their surface by chemisorptions [5,10,27]. According to the adsorption theory of acetylene at different metals [30-32], a complex electron transfer process may take place between the acetylene molecule and metal surface, where not only electrons from the occupied orbital of acetylene molecule transfer to the empty d orbital of metals, but also electrons from d orbital of metals can transfer to the anti-bonding orbital of bond in acetylene molecule, thus an transition organometallic complex could be formed at the metal surface. The formed organometallic complex could decrease the activation energy barrier of ethylene formation simultaneously, followed by desorption of hydrogenation products produced at metal surface. In addition, due to the main reaction sites at metal surface immersed into solution phase, it would take time for the formed intermediates, such as C4 hydrocarbons and ethylene, desorbs and distribute to the headspace reaching to equilibrium between solution and gas phases. With the electrolysis proceeding, all the electrolysis products of acetylene were produced and equilibrium between solution and gas phases was reached, gradually. These could be used to explain the changes of mass balance during electrolysis of acetylene at Ag and Cu electrode.

In analogous with catalytic hydrogenation of acetylene, undesired C4 hydrocarbons, which are as the unavoidable by-products of that process, were also discovered and accounted for more than 35% of the total acetylene conversion in the electrolysis studies at Cu and Ag electrode, while 74.68% C4 hydrocarbons as the principal electrolysis product were produced at Pt electrode. Actually, the formation mechanisms of oligomers over catalytic hydrogenation technology are still not very clear, and most researches consider 1,3-butadiene as their precursor [24]. While a close examination of the electrolysis results will find that the main oligomers produced at Cu and Ag electrode was 1,3-butadiene, whereas butane was the principal products at Pt electrode. The formation of C4 hydrocarbons indicates that dimerization reaction, resulted from the radical character of intermediates, took place during electrolysis. Whereas, owing to the strong intrinsic hydrogen interaction ability of Pt, it can promote the further hydrogenation of unsaturated compounds with butane as the final electrolysis product. On the other hand, these formed oligomers may deposit on the metal surface and cover the catalytic sites, which can further cause the catalysts poison and shorten its life cycle, have extremely serious effects on the practical application in industry [10-12], so it’s desired to find a route to avoid or at least evidently control the formation of oligomers if consider the application prospect of electrochemical hydrogenation methods.

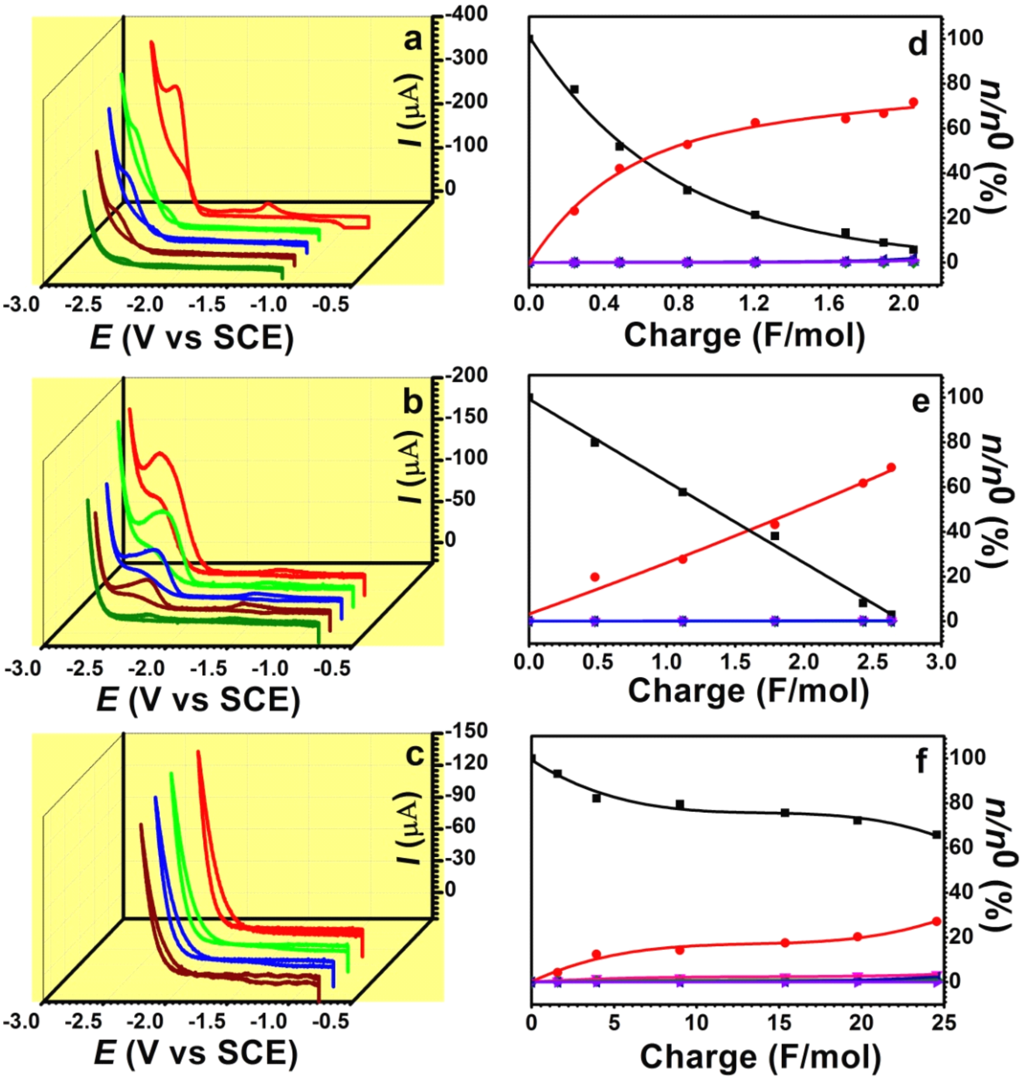

Fig. 6.3. Electrolysis of acetylene in DMF + 0.1 M TPABF$_4$ at Cu (a, d), Ag (b, e) and Pt (c, f) electrode in the presence of 1 M water addition. (a,b, c) show the cyclic voltammograms of acetylene recorded at Cu, Ag and Pt electrode during preparative electrolysis with the charge consumption, respectively; (d, e, f) reprsent the concentration variations of acetylene and its intermediates in gas phase during electrolysis. (■) acetylene; (●) ethylene; (▼) ethane; (◆) butane; ( ) 1,3-butandiene; ( ) 2-butene

It's not difficult to understand that the formation of C4 compounds is primarily attributed to the extensive digemerization reaction due to the low proton availability in the medium, albeit the intrinsical character of metals can also activate the olimerization pathway leading to oligomers formation[10]. Therefore, proton availability in the medium may have an important effect on the product distributions, which can alter the electrolysis product distributions by restricting oligomers formation and favoring the hydrogenation reaction of acetylene. As known, water can be served as a proton donor, which could be reduced to atomic hydrogen covering around the metal surface, and further promote the hydrogenation reaction by continuous attacking the acetylene molecule. Besides, the addition of water can frequently update the active sites at metal surface [28]. Actually, the effect of water on the electrochemical reduction of acetylene has already shown in the voltammetric experiments, it appears the presence of water could promote the hydrogenation of acetylene. However, whether an electrochemical hydrogenation of acetylene process in the presence of water with lower oligomers production and high ethylene selectivity could be achieved is desired to know.

As already stated in the previous section, cyclic voltammetry of acetylene at different electrodes can retain their shapes in a broad water addition scope, herein, 1 M water addition was chosen as an exemplification to carry out the electrolytic investigations. The applied potentials were determined based on the reduction peaks of acetylene at Cu and Ag electrode, while the applied potential at Pt electrode was determined based on the voltammogram before bulk electrolyte discharge occurrence. The electrolysis results of acetylene at Cu, Ag and Pt electrode in DMF solution containing 1 M water are reported in Table 6.2 (entry4-6). The variations of all species involved in the electrolysis of acetylene at the three electrodes in the presence of water, together with the changes of voltammograms recorded at Cu/Ag/Pt before and after each electrolysis step are displayed in Fig.6.3 (a-f), respectively. Compared to the results in the absence of water, higher ethylene selectivity were obtained at Cu and Ag electrode, more than 75% and 68% ethylene selectivity were obtained at Cu and Ag electrode, respectively; likewise, very trace of ethane were produced (lower than 0.3%) in both cases, and another stirring discovery is that quite few C4 hydrocarbons (3.14% for Cu and 0.27% for Ag, respectively) were formed during electrolysis, as shown in Fig.6.3 (d-f). However, in contrast to the previous two electrodes, low acetylene conversion (34.14%) were achieved even after 24.56 e-/molecule charge consumed at Pt electrode, accompanying with 27.18% ethylene and 3.44% ethane formation. Similar with the other two electrodes, low C4 hydrocarbons (3.04%) were produced at Pt electrode.

Scheme 6.2 The sketched reduction mechanisms of electrochemical acetylene hydrogenation

According to the electrolysis results, it appears that the mechanism of electrochemical hydrogenation of acetylene in the presence of water is different with that in the absence of water, since water as a reactant can participate in the reduction process directly, as described in eq.(6.5-6.6). Atomic hydrogen may be formed through water electrolysis, which could be chemisorbed at the activated sites of transition metal surface and form a hydrogen layer. As aforementioned before, acetylene also has a strong chemisorption with the metal surface via triple bond. The two active species may thus have competitions on occupying the activated sites at metal surface, which might result into influences on the product distributions subsequently. Actually, some researchers have indeed observed the interaction between acetylene and metal surface that could be changed by the effect of hydrogen layer, leading to produce various adsorption intermediates at different temperatures in the catalytic hydrogenation methods [36]. Likewise, in contrast to the studies performed in the absence of water with low proton availability in the system, the formed atomic hydrogen layer in the presence of water, covering around the metal surface, is readily to continuously attack the acetylene molecule with high yield of ethylene formation. Negligible over-hydrogenation products were formed in the DMF solution containing water, which is in accord with the results that carried out in the absence of water. The reasons have been clarified before, besides, the strong metal-hydrogen bond formed during electrolysis in the presence of water is also facile for restricting further hydrogenation of ethylene. A very exciting discovery is that, in contrast to the results that in the absence of water, quite few C4 hydrocarbons were produced after water addition, which is presumed to be that the formed hydrogen layer at the metal surface could prevent the radical dimerization occurrence by reacting with the generated radical timely. A sketched reduction mechanism of reduction of acetylene is illustrated in Fig.6.4. A last comment is on the mass balance during electrolysis. In contrast to the experiments performed in the absence of water, where the mass balances exhibit a general trend that firstly decrease and then increase with the proceeding of electrolysis at Cu and Ag electrode, the mass balances in the presence of water decrease constantly throughout the electrolysis. This implies that the activated organometallic complex and radical reaction at the metal surface may have been impacted by the role of hydrogen layer. In general, the electrochemical hydrogenation mechanism of acetylene is strongly dependent on the water availability, whereby the formed atomic hydrogen may have influence on the electrolysis product distributions during electrolysis. In any case, the low yield of overhydrogenation product and oligomers makes electrochemical hydrogenation technology have a great superiority over catalytic hydrogenation methods.

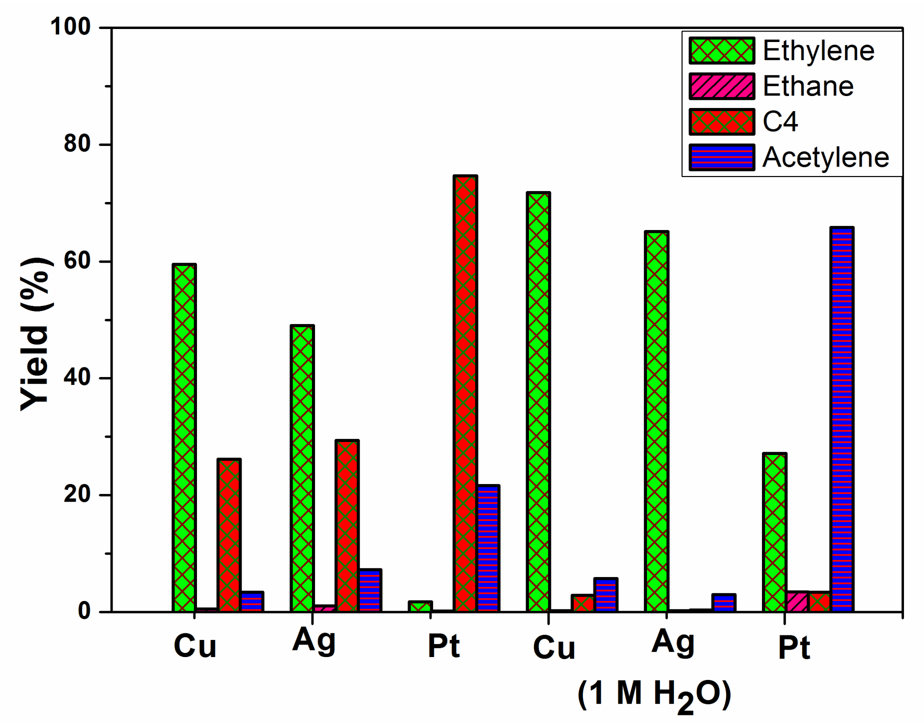

Fig. 6.5 The product distributions of electrochemical hydrogenation of acetylene on Cu, Ag and Pt electrode in the absence and presence of 1 M water addition, respectively.

Table 6.2. Electrolytic results of acetylene in DMF + 0.1 M $TPABF_4$ in the absence and presence of 1 M H_2O at Cu, Ag and Pt electrode, respectively.

Electrode/ conditions	Main Product	E_{app}[a] V	n[b] F/mol	Acetylene %	Ethylene[c] %	Ethane[c] %	Butane[c] %	2-Butene[c] %	1,3-Butadiene[c] %	Total[d] %
Cu Pure DMF	Ethylene, C4 compounds	-2.85	0.51	65.10 (0.42 mMol)[e]	17.70	0	0	0	2.09	84.89
		-2.97	1.65	26.71	47.37	0.13	0	0	16.01	90.22
		-2.97	2.79	3.39	58.75	0.54	0	0.14	36.72	99.54
Ag Pure DMF	Ethylene, C4 compounds	-2.90	0.85	66.64 (0.40 mMol)[e]	13.68	0.07	0	0	2.91	83.30
		-2.90	1.99	27.46	37.29	0.31	0	0.06	15.27	80.40
		-2.90	3.28	7.27	51.81	1.02	0	0.21	35.12	95.43
Pt Pure DMF	C4 compounds	-2.69	1.43	88.24 (0.20 mMol)[e]	0.69	0.10	0	6.65	0	95.67
		-2.84	9.57	31.02	1.18	0.19	61.85	0	3.94	98,18
		-2.84	16.73	21.67	1.77	0.20	69.31	0	5.36	98.32
Cu (1 M H_2O)[f]	Ethylene	-2.42	0.50	77.42 (0.44 mMol)[e]	22.24	0.05	0	0	0.19	99.90
		-2.60	3.47	13.45	67.85	0.18	0	0	0.99	82.46
		-2.47	4.22	5.74	75.83	0.25	0	0	3.14	84.95
Ag (1 M H_2O)[f]	Ethylene	-2.50	0.48	79.81 (0.33 mMol)[e]	19.70	0.03	0	0	0	99.54
		-2.50	1.79	38.10	43.20	0.14	0	0	0.13	81.57
		-2.50	2.64	2.98	68.79	0.27	0	0	0.25	72.28
Pt (1 M H_2O)[f]	Ethylene	-1.92	1.57	93.19 (0.48 mMol)[e]	4.34	066	0.17	0.02	0.01	98.39
		-2.02	8.99	79.63	14.29	1.96	1.56	0.10	0.04	96.82
		-2.02	24.56	65.86	27.18	3.44	1.02	2.32	0	99.86

[a] Applied potential vs. SCE.; [b] Charge consumption per molecule of acetylene; [c] Product yield= 100×(moles of product/moles of starting acetylene);

[d] Mass balance with respect to starting acetylene; [e] Starting moles of acetylene; [f] in the presence of 1 M•L^{-1} H_2O.

A close comparison of the electrolysis results over the three electrodes, one will find Cu appears to exhibit the highest ethylene selectivity than Ag and Pt electrode in all cases both in the presence and absence of water, as shown in Table 6.2 and Fig.6.5. Followed by Ag, it also shows an excellent ability towards promotion of acetylene hydrogenation. While Pt presents a strong hydrogenation ability, which could promote butane formation in the absence of water and enhance the yield of ethane in the presence of water, respectively, albeit with lower current efficiencies in these processes resulted from the discharge of electrolyte. These observations indicate that the electrolysis of acetylene also strongly depends on the nature of electrode materials, which are in line with the discoveries observed in the voltammetric experiment. As already stated before, the thermodynamic factors of acetylene to metals, such as the thermodynamic selectivity, the activation energy barrier of organometallic formation may result into the diversities of ethylene selectivity at different electrodes during electrolysis. It's pity that we couldn't get these values at Cu and Ag electrode in our system to make a correlation with selectivity. However, we still could find some hints from the previous researches and based on our current results. According to the findings of catalytic acetylene hydrogenation, Cu is intrinsically favor the partial acetylene hydrogenation because of its high thermodynamic factor, and often used as a base hydrogenation metal accompanying with high ethylene selectivity[10]. While Ag is often used as an additive substrate, incorporated into the catalyst to enhance ethylene selectivity, mainly resulted from impeding the occurrence of over-hydrogenation reaction by preventing the formation of sub-surface H at its surface [8-9]. To the best of our knowledge, it's never used as a base metal for catalytic acetylene hydrogenation, since Ag has been found possessing an inhibition effect on catalytic acetylene hydrogenation activity [8,33]. Whereas, Pt is known as its strong interaction ability with hydrogen, it's facile for catalytic hydrogenation reaction. These are overall in agreement with the results we got by using the electrochemical reduction methods, but as a distinct technology that works in totally different conditions, some inconsistent places may occur, for instance, Ag as a base metal presents high ethylene selectivity compare to catalytic hydrogenation of acetylene, even though a little lower than Cu.

Eventually, we'd like to frankly discuss some abnormal phenomenon during electrolysis. Some passivation of electrode had been encountered during electrolysis of acetylene. For Ag, the current decreased rapidly when the electrolysis was carried out in the presence of water, albeit high concentration of acetylene existed in the solution. Actually, this may coincide with the previous researches that Ag has an inhibition effect on acetylene hydrogenation activity over catalytic hydrogenation technology [8,33]. In analogous with Ag, Cu also behaved some abnormal behavior during research, one intuitive instance is that no clear reduction peak appears at Cu electrode throughout the whole voltammetric experiments, and repetitive experiment validated the same observation, as shown in Fig. 6.1, whereas an obvious irreversible reduction peak emerged out in Fig.6.3a after 1 M water addition. Actually, a reddish layer covering around Cu surface was found at the end of experiments, which is speculated that acetylene is very readily to interact with active Cu, leading to Cu passivated by forming an organo-copper complex, concomitant with the reduction behavior of acetylene being concealed. Another example is the variations of voltammogram during electrolysis performed in the absence of water at Cu electrode, as shown in Fig.6.2a, where the reduction peak shifted gradually with the electrolysis proceeding. In summary, the main cause of passivation is speculated to be the high coverage of acetylene layer at metal surface that further hinders electron transfers during reduction process, leading to the electrochemistry behavior being concealed in the voltammetric experiment and a decrease of current during electrolysis; another possibility is that some oligomers may generate during electrolysis, which could result into the poison of catalyst. While with the electrolysis proceeding, some activated sites of the metal surface are regenerated due to the decrease of acetylene concentration and desorption of products deposited on the metal surface, which could facilitate the recovery of electrode activity.

6.4. Conclusion

The electrochemical hydrogenation of acetylene had been carried out extensively at different electrodes in DMF + 0.1 M TPABF$_4$ in the absence and presence of water. It shows that the electrochemistry behaviors of acetylene are strongly dependent on the nature of electrode materials and water availability in the system. In any case, Au, Ag, and Pd display remarkable catalytic activities towards the reduction of acetylene. The addition of water could enhance the peak intensity of acetylene and promote the reduction peak shifting to more positive direction.

Electrolysis of acetylene at Cu and Ag electrode could achieve high ethylene selectivity in DMF + 0.1 M $TPABF_4$ in the absence of water, namely 58.75% for Cu and 51.81% for Ag, whereas, considerable C4 hydrocarbons, more than 35% in both cases, were produced in the reduction processes. For Pt electrode, the principal product was C4 hydrocarbons, in which 74.68% C4 hydrocarbons was produced with the conversion of 78.33% acetylene. The production of C4 hydrocarbons severely affect on the ethylene selectivity and catalyst activity. The presence of water can evidently enhance the ethylene selectivity during electrochemical hydrogenation of acetylene. More than 75% and 68% ethylene were obtained at Cu and Ag electrode, respectively. Similar with the result that in the absence of water, very trace of ethane produced (lower than 0.3%) in both cases, and a very stirring discovery is that quite few C4 compounds (3.14% for Cu and 0.27% for Ag) were formed during electrolysis of acetylene. However, owing to the discharge of electrolyte, low acetylene (34.14%) was converted at Pt electrode with high yield of C4 hydrocarbons (27.18%). The presence of water is presumed that could hinder the radical coupling reaction, in which an atomic hydrogen layer may be formed around the metal surface that promote acetylene hydrogenation occurrence by prompt reacting with the formed radical intermediates timely. It appears that water plays double roles in the reduction of acetylene. On one side, it can participate into the acetylene hydrogenation reaction directly either as a proton donor or forming an atomic hydrogen layer resulted from the water electrolysis. Besides, it also can be used to frequently regenerate the activated sites at metal surface. In general, the electrochemical hydrogenation of acetylene is strongly dependent on the nature of electrode materials and water availability in the medium.

It should be stressed that, owing to the potential passivation problems of the electrodes, searching for high stable and catalytic electrodes still leave ample room for improvement of this approach. However, electrochemical hydrogenation of acetylene technology, particularly in the presence of water, has characters of high ethylene selectivity, low yield of byproducts, higher current efficiency, operating under mild conditions and needless of external H_2 addition, which makes this technology have a strong vitality and superiority over other technologies. It could be applied to the acetylene removal in the polymer synthetic industry by combination with solvent extraction technology. Even though only preliminary investigations on electrochemical hydrogenation of acetylene were carried out in our research, there are still lots of unknown parts to be solved, we hope it can open a gate for the development of this technology through our research, and provide an alternative technology for acetylene removal in the polymer synthetic industry.

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Chapter 7 Conclusions and suggestions

7.1 Conclusions

Chlorinated volatile organic compounds (Cl-VOCs), involving polychloromethanes (PCMs), polychloroethanes (PCEs) and polychloroethylenes, are among the most ubiquitous environment pollutants in the soils and any kind of fluvial mediums, such as groundwater, rivers, lakes. However, owing to their toxicity, some of them even are suspected as human carcinogens, persistence character in environment, which have forced to find an efficient abatement technology for removal of them from the health authorities. In this study, electrocatalytic dechlorinations of Cl-VOCs were carried out over different transition metals in DMF + 0.1 M $TPABF_4$ in different solvent conditions. The electrocatalytic activities of different transition metals towards the reduction of Cl-VOCs were evaluated with respect to GC, the latter used as a reference system. Electrochemical reduction mechanisms of Cl-VOCs were investigated by combination of voltammetric analysis and electrolysis experiments. The feasibility of electrochemical dechlorination of Cl-VOCs was examined by using non-catalytic electrode (GC) and catalytic (Ag, Cu) electrodes. Eventually, electrochemical hydrogenation of acetylene, as an intermediate of electrolysis of PCEs, was carried out to validate the applicability of this method, for the sake of opening a new gate of investigation on the removal of acetylene in the polymer synthetic industry. The principal conclusions in our research are as follows:

1). the reduction mechanisms of PCEs are strongly dependent on the structure of PCEs. Geminal PCEs mainly undergo sequential hydrodechlorination mechanism, in which one chlorine ion is lost after accepting two electron transfers at one single step till ultimately ethane formation. Whereas, reduction of vicinal PCEs primarily conform to reductive α,β-elimination mechanism, upon two electron transfers eliminating two chlorine ions, one at each carbon, to give rise to olefin. Based on the values of electron transfer coefficient, it indicates the first electron transfer to C-Cl bond of PCEs follows concerted dissociative electron transfer mechanism (DET), in which the electron transfer and the cleavage of C-Cl bond take place simultaneously.

2). the electrocatalytic activities of different transition metals towards the reduction of PCEs are strongly dependent on the nature of electrode materials and molecule structure of PCEs. Ranking the electrode materials according to the electrocatalytic effects for the reduction of PCEs, the following order is found: Ag, Cu, Au > Pd, Pt, Ni >> Fe, Pb, Zn. The molecule structures also play a significant role on the electrocatalytic reduction of PCEs. In general, the electrocatalytic activity increases with increasing numbers of chlorine atoms bound to the same carbon. Whereas, addition of chlorine atoms to another carbon has contracting effects: activation enhancement due to polar effects contrasted by steric hindrance effects on the transition state. Considering the most active electrodes of the series, gives the following order of increasing electrocatalytic reactivity: 1,1-DCA < 1,1,1-TCA < 1,2-DCA < HCA < 1,1,2,2-TeCA < 1,1,2-TCA < 1,1,1,2-TeCA.

3). in contrast to the classical DET model, the activation-driving force relationship for all investigated PCEs are compatible to “sticky DET” model, where a sizable interaction survives in the cage fragments (radical-ion) resulting into an evidently decrease of intrinsic barrier for the reduction process. Compared to GC, a significant decrease of intrinsic barrier and driving force is found at Ag electrode, it mainly attributes to the interactions among the radical-ion dipole and the strong interactions between chlorinated species and Ag surface in the transition state, the latter are presumed to be the cause of the electrocatalytic effect at Ag electrode, which could be quantified by the difference between the two interaction energies of Ag and GC.

4). further electrolysis of PCEs at GC and Ag electrode confirms that reductive cleavage of PCEs follow two distinct reduction mechanisms regardless of electrode materials. Complete reduction mechanisms of electrolysis PCEs are proposed based on the electrolysis results, where 1,1,1-TCA and 1,1,1,2-TeCA were chosen as representatives of PCEs, respectively. Addition of HAc into DMF solution containing 1,1,1-TCA could promote the sequential hydrodechlorination mechanism with high yield of ethane by restricting side reactions, whereas, it has less effect on the reduction mechanism of 1,1,1,2-TeCA which mainly undergoes reductive α,β-elimination routes with the corresponding olefin formation, the latter is further reduced at more negative potential.

5). Cu exhibits an excellent electrocatalytic activity towards the reduction of geminal PCEs, with a positive shift of 170 mv for 1,1-DCA and 260 mv for 1,1,1-TCA with respect to GC electrode, respectively. This value could further increase to 820 mv for 1,1,1-TCA after excess HAc addition, indicating the presence of HAc can enhance the catalytic activity of Cu for reductive cleavage of C-Cl bond.

6). Complete dechlorination of geminal PCEs could be achieved at Cu electrode performed in different solvent conditions, further validating the feasibility of electrocatalytic dechlorination methods by using Cu electrode. Reduction of geminal PCEs is strongly dependent on the proton availability and proton type in the medium. Addition of proton donor could enhance the sequential hydrogenation mechanism by restricting side reactions, such as base promoted α,β-elimination and carbene routes, in particular addition of HAc. Whereas, the presence of water, beside used as a proton donor, it can donate bases during electrolysis promoting the occurrence of base promoted α,β-elimination mechanism. Essentially the same electrolysis results of geminal PCEs are obtained no matter the modes of potentiostatic electrolysis applied by stepwise or single step one. It appears the side reactions could be effectively suppressed with high yield of C2 hydrocarbons when embark on the single step electrolysis.

7) The electrocatalytic activity of Cu was further investigated towards the reduction of another class of Cl-VOCs, PCMs. Likewise, Cu displays remarkable catalytic effect towards the reductive cleavage of PCMs, and it induces a considerable positive shift of peak potentials from 216 mv for CCl_4 to 743 mv for CH_3Cl with respect to GC. The addition of proton donor appears to activate the electrocatalytic activity of Cu with obvious positive shift of reduction potentials, resulting into the cleavage of C-Cl bond more readily to occur, possibly because the addition of proton donors increase the regeneration rates of activated sites at Cu surface, besides, the strong solvation ability of proton donor to Cl^- also promote the cleavage rate of PCMs. It's found that the presence of proton donor could enhance the peak intensities of PCMs and promote the occurrence of sequential hydrodechlorination mechanism.

8) Further electrolysis of PCMs at Cu electrode indicates carbene species, produced by eliminating one more chlorine ion from the chlorinated methyl-carbanions, may involve in

the reduction process of PCMs resulting into a severe loss of mass balance. On the other side, the presence of proton donor could evidently enhance the yield of hydrocarbons by restricting the possible chemical reactions, and favor the reduction of PCMs mainly undergoing sequential hydrodechlorination mechanism. Water plays double roles in the reduction process. It can be used as proton donor and base donor simultaneously. Continuous accumulation of bases mainly resulted from the detriment of proton donors and electrolysis of water, take place with the electrolysis proceeding, thus benefit for carbene routes rather than sequential hydrodechlorination mechanism. Essentially the same electrolysis results are obtained at Cu electrode regardless the modes of potential applied, with the only significant difference that the electrolysis intermediates are repulsive to accumulate by using single step potentiostatic electrolysis compared to stepwise electrolysis.

9) Owing to the similar structure of geminal PCEs and PCMs, there are some common places in the reduction of these two types of compounds at Cu electrode. As aforementioned, Cu exhibits remarkable catalytic effect towards the reduction of these two classes of compounds; the addition of proton donor could activate the catalytic effect of Cu for the reductive cleavage of C-Cl bond. The reduction of these two types of compounds are all strongly depends on the proton availability and proton types. In the presence of proton donor, they mainly conform to sequential hydrodechlorination mechanism, whereas, some other side reactions, such as self-protonation and carbene routes, are involved in the absence of proton donor. Due to the different configurations in the molecules result into some diversities in the reduction processes. Cu displays more remarkable electrocatalytic effect towards the reduction of PCMs than geminal PCEs. Some specific reactions may take place during the electrolysis of geminal PCEs because of their special structure, for instance bases promoted α,β-elimination reaction, and carbene rearrangement reaction via hydrogen migration.

10) Electrochemical reduction behaviors of acetylene at different electrodes are strongly dependent on the nature of electrode materials and water availability. Au, Ag, Pd exhibits excellent catalytic effect for the reduction of acetylene. The addition of water could enhance the peak intensity of acetylene and promote the reduction peak shifting to more positive direction.

11) A novel technology of acetylene hydrogenation has been explored. Electrochemical

hydrogenation of acetylene could be successfully achieved at Cu and Ag electrode both in the absence and presence of water. In general, the reduction of acetylene is sensitive to the nature of electrode material and water availability in the medium. In the absence of water, considerable of C4 hydrocarbons (more than 35%) were produced at Cu and Ag electrode because of the radical coupling reaction. High ethylene selectivity was obtained in the presence of water, namely 75.83% for Cu and 68.79% for Ag, respectively, possibly because of the formed atomic hydrogen layer resulted from the electrolysis of water that promotes the acetylene hydrogenation by promptly reacting with the radical intermediates. Whereas, electrolysis of acetylene at Pt electrode resulted into significant C4 hydrocarbons formation in the absence of water and low conversion of acetylene due to the discharge of electrolyte in the presence of water.

In general, electrochemical reduction of Cl-VOCs is found strongly dependent on the nature of electrode materials, proton availability and the molecule structures. Ag exhibits the most remarkable catalytic activity towards the reduction of Cl-VOCs, whereas, Cu is also found displaying a very excellent catalytic effect over the reduction processes. In any case, complete dechlorination of Cl-VOCs can be achieved at non-catalytic (GC) and catalytic (Ag, Cu) electrode in our system. Since the expense of Cu is far more less than that of Ag, besides, because of the specific character of better environment compatibility, controllable reaction kinetics, cathodic polarization against metal surface passivation or corrosion, as well as working under mild conditions, which makes the electrocatalytic reduction methods become a promising approach in the removal of Cl-VOCs. As an electrolysis intermediate of PCEs, acetylene has been successfully converted to ethylene by using electrochemical hydrogenation methods at both Ag and Cu electrode. As known, the removal of acetylene from ethylene stream is a key step in polymer synthetic industry. In this work, the concept of electrochemical hydrogenation of acetylene is proposed for the first time, and no related reports published till now, we hope it can open a new gate for the investigation of acetylene/alkynes removal through our work, and provide an alternative technology for acetylene/alkynes removal in the polymer synthetic industry

7.2 Suggestions

The reduction mechanisms of PCEs and PCMs have been investigated in this research, and further electrolysis experiments have validated the feasibility of electrocatalytic dechlorination technology on the abatement of these compounds. However, as another group of Cl-VOCs, polychloroethylenes were not included in this research, albeit some voltammetric experiments were involved for clarifying the reduction mechanisms of PCEs. The complete reduction mechanism of Cl-VOCs are still blank, the electron transfer mechanisms to the C-Cl bond in polychloroethylenes are undiscovered. It will be interesting to investigate the electrocatalytic effect of different electrodes towards the reduction of polychloroethylenes and try to reveal the essence. Of course, it’s wondering whether a complete dechlorination of polychloroethylenes could be achieved， in particular by using Cu electrode, because of its low expense.

Although we have revealed the reduction mechanisms of PCEs and PCMs by combination of voltammetric analysis and potentiostatic electrolysis experiments, the interface behavior between the investigated substrates and metal electrode surface has never been mentioned. We presume that a transition state as a form of organo-metallic complex due to the interaction between metal and chlorinated species may exist in the reduction process; it will be useful to track the variations of adsorption energy between the metal and chlorinated substrates, and track the evolvement of intermediates by using Surface Enhanced Raman Spectroscopy and other scanning probe techniques, for further unravel the reduction process of Cl-VOCs.

In this research, we only concentrated on the investigation at the electrocatalytic activity of base transition metals without any modifications at their surface. As already known, the modification of electrode by incorporation of other catalysts, in particular in nano-sized, could evidently enhance its catalytic activity towards the reductive cleavage of C-Cl bond. Therefore, there still leave ample room for exploring high stable and efficient catalytic electrodes in the electrocatalytic dechlorination technique.

The dechlorination process for Cl-VOCs in this study was mainly carried out in a batch electrolytic cell. It will be interesting to conduct this research in a continuous electrolytic cell from the industrial application point of view, to further check its feasibility and provide consult information for the future application. Besides, the kinetics of electrocatalytic dechlorination of Cl-VOCs were not discussed at here due to the purpose of research, and it will be useful to validate the superiority of this technology by providing kinetic information, and further understand the rate-determining steps of reduction process.

Electrochemical hydrogenation of acetylene is a new methodology for the conversion of acetylene, and preliminary investigations were conducted in this research. This technique still leaves ample room for improvement, such as on the reduction mechanisms of acetylene hydrogenation process, searching for high electrocatalytic electrode to overcome the possible passivation problems and so on.

攻读博士学位期间取得的研究成果

一、已发表（包括已接受待发表）的论文，以及已投稿、或已成文打算投稿、或拟成文投稿的论文情况（只填写与学位论文内容相关的部分）：

序号	作者（仅注明第几作者）	题　　目	发表或投稿刊物名称、级别	发表的卷期、年月、页码	相当于学位论文的哪一部分（章、节）	被索引收录情况
1	第一	Electrocatalytic properties of transition metals towards reductive dechlorination of polychloroethanes	Electrochimica Acta	2012	第三、四章	SCI
2	第二	Electrocatalytic Dechlorination of Volatile Organic Compounds at Copper cathode: Part I Polychloromethanes	Applied Catalysis B-Environment	Submitted	第五章	SCI
3	第二	Dechlorination of Volatile Organic Compounds at Copper cathode: Part II Polychloroethanes	Applied Catalysis B-Environment	submitted	第四章	SCI
4	第一	Electrochemical partial hydrogenation of acetylene at precious and non-precious electrodes.	Chemical Communication	submitted	第六章	SCI

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二、与学位内容相关的其它成果（包括专利、著作、获奖项目等）

参加的会议：

1. Armando Gennaro (Oral presentation), **Binbin. Huang**(导师第一作者), Christian. Durante, Isee. A. Abdirisak. Electrocatalytic dechlorination of volatile polychloroethanes on various metal electrodes. The 61st Annual Meeting of the International Society of Electrochemistry. 26 September to 1 October, 2010, Nice, France.

2. Armando Gennaro (Oral presentation), **Binbin. Huang**(导师第一作者), Christian. Durante, Isee. A. Abdirisak. XXIII CONGRESSO NAZIONALE DELLA SOCIETA' CHIMICA ITALIANA.2010.
3. Christian. Durante, **Binbin. Huang**, Isee. A. Abdirisak, Armando Gennaro. Electrocatalytic Activation of Alkyl halides at copper electrodes. XXIV CONGRESSO NAZIONALE DELLA SOCIETA' CHIMICA ITALIANA.2011.
4. 黄彬彬(口头报告)，A. Gennaro，韦朝海. 过渡金属电极对氯代乙烷类物质的电催化还原脱氯研究. 中国化学会第28届年会(电化学分会), 2012, 四川成都.
5. 黄彬彬(口头报告)，A. Gennaro，韦朝海. 过渡金属电极对挥发性有机氯化物的电催化还原脱氯研究. 中国化学会第28届年会(环境化学分会), 2012, 四川成都.

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