COMMUNICATION

Nitrogen-containing organic products from the treatment of liquid toluene with plasma-activated N₂ gas

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Abstract

This proof-of-principle study explored the possibility to form nitrogen-containing organic products via exposure of liquid toluene to a flow of molecular nitrogen, at room temperature and atmospheric pressure, activated by dielectric barrier discharges. N-containing organic compounds indeed formed under these conditions, including benzonitrile, a high-value chemical that is industrially synthesized from toluene under demanding conditions. Toluene-derived higher hydrocarbons, as well as oxygen-containing derivatives, were also detected, the latter due to efficient reactions of residual oxygen in the system. A mechanistic description of the observed chemistry is provided, together with guidelines for increasing the selectivity for C–N forming reactions and the development of this approach into a novel synthetic approach for high-value organic N-containing chemicals.
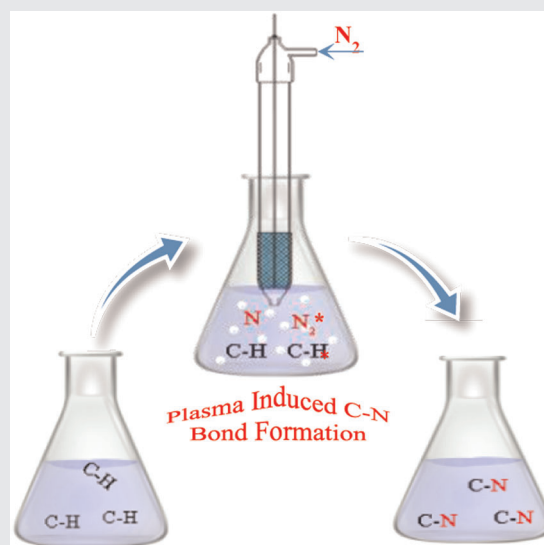
KEYWORDS
benzonitrile, C–N bond, dielectric barrier discharge, N atoms, nonthermal plasma

1 | INTRODUCTION

Since Miller's pioneering studies on the origin of life, showing that amino acids are produced from electric discharges in $CH_4/NH_3/H_2O/H_2$ atmospheres,[1] the possibility to use plasma as a tool to achieve the synthesis of organic compounds has been intriguing and challenging chemists.[2] One process that has been extensively investigated since then is the oxidation of organic compounds by nonthermal plasma in air or in oxygen-containing gases, with fundamental research in this area being motivated by the interest in developing novel advanced oxidation processes (AOPs) to treat polluted air[3] and water.[4] These studies have provided a deep insight into the discharge-generated reactive species (electrons, molecular excited states, atoms, radicals, ions[5,6]), which are responsible for the initial attack on the organic pollutants, and into the resulting degradation intermediates and final products. As the aim of such treatments is the complete mineralization of all organic carbon into CO_2,[7] it is not surprising that discharges and conditions are optimized, so as to achieve as harsh an environment as possible in terms of type and concentration of strong oxidizing reactive species.

A more refined use of plasma is to be envisioned if one wants to master its high potential to promote and achieve the synthesis of valuable chemicals and materials. This goal is indeed being successfully pursued in material science and technology, specifically for the synthesis of nanoparticles.[8] Likewise important and promising in view of possible scaling up is, presently, the very active field of research on plasma-activated conversion of CO_2 into syngas or other high-value feedstock like methanol.[9,10] Similar to the AOP mentioned above, in this case also, the reaction has high energy requirements, which can be met by plasma-based technologies.

Along these lines of development, our attention was drawn to the possibility of using plasma to perform the synthesis of high-value nitrogen-containing organic chemicals, which are difficult and costly to prepare by traditional procedures. One such case is benzonitrile, an important chemical in the industry of dyes, herbicides, agrochemicals, pharmaceuticals, and more, as well as a most versatile reaction intermediate for transformation into many other functional groups. Benzonitrile is synthesized from toluene via the ammoxidation reaction, a process requiring ammonia, a toxic reagent, and high temperatures/costly catalysts.[11] Alternative approaches include electrochemical strategies for C–H functionalization and C–N bond formation[12] and palladium-catalyzed cyanation of aryl halides.[13]

Activation and use of molecular nitrogen as a cheap and safe N source to form useful chemicals beyond ammonia has long been and continues to be one of chemists' most challenging tasks.[14] Electric discharges in nitrogen at room temperature and atmospheric pressure are indeed a powerful tool toward this goal, as they produce molecular excitation, ionization, and dissociation. The reactions of vaporized toluene in a dielectric barrier discharge (DBD) in pure nitrogen have been analyzed and discussed in fundamental studies on the degradation pathways of this organic pollutant in plasma-based remediation processes.[15–17] Several toluene-derived N-containing organic reaction intermediates were observed in these studies, including benzonitrile, methyl pyridines, methyl benzonitriles, as well as HCN and low volatility, high mass polymerization products.[15–17] To the best of authors' knowledge, there are, however, no reports in the literature about plasma treatment of liquid toluene. Based on these observations, we decided to investigate the possibility to synthesize benzonitrile and other valuable C–N-containing organic chemicals from liquid toluene using a DBD in N_2 at room temperature and atmospheric pressure to generate reactive nitrogen species and inject them into the liquid. We report here and discuss preliminary results obtained with a very simple setup in which DBD-activated N_2 was bubbled through liquid toluene, showing that C–N bond formation was indeed achieved in these experiments, which produced benzonitrile and a few other N-containing organic products. The findings of this proof-of-principle study are analyzed and critically evaluated with reference to available literature data and rationalized into a mechanistic scheme. They provide hints for improvements of the design of experimental setup and conditions, so as to limit competing reactions leading to larger hydrocarbons and O-containing organic byproducts.

2 | EXPERIMENTAL SECTION

2.1 | Materials

Toluene was purchased from VWR Chemicals BDH (99.5% purity). 2-Methylpyridine, ethylbenzene, benzaldehyde, phenol, benzonitrile, benzyl alcohol, benzylamine, and benzyl nitrile used as analytical standards were likewise commercial samples of ≥99% purity. The following high-purity gases were supplied by Air Liquide, with impurities as specified in parentheses: argon ($H_2O < 0.5$ ppm, $H_2 < 0.1$ ppm, $O_2 < 0.5$ ppm, $CO_2 < 0.5$ ppm, $CO < 0.1$ ppm, total hydrocarbon content < 0.1 ppm); nitrogen ($H_2O < 3$ ppm, $O_2 < 2$ ppm, $C_nH_m < 0.5$ ppm).
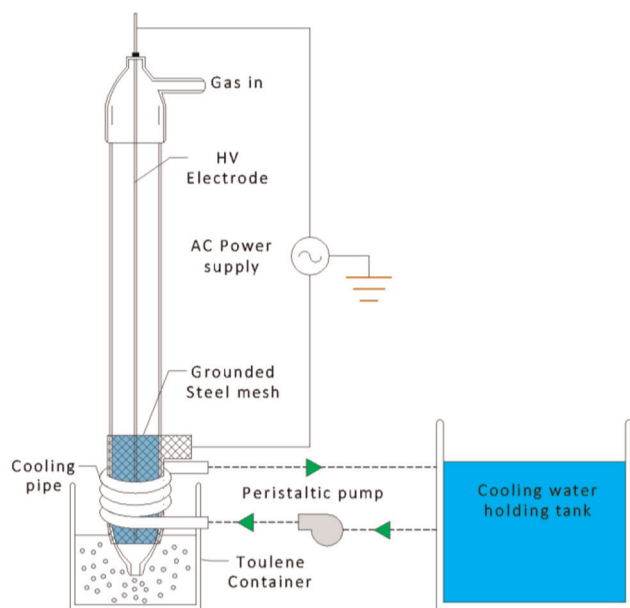
FIGURE 1 Schematic diagram of the experimental setup used to treat liquid toluene with dielectric barrier discharge

2.2 | Plasma reactor

A tubular DBD reactor was developed and used to treat liquid toluene. It consisted of a 90-mm-long Pyrex tube with an external diameter of 9 mm and an internal diameter of 7 mm. One end of the tube was fitted with an air-tight cover made of Pyrex and provided with gas inlet and high-voltage electrode ports, whereas the other end of the tube was narrowed down to an internal diameter of 2 mm. The high-voltage electrode was made of a stainless steel wire (1 mm in diameter), whereas the ground electrode was made of a stainless steel wire mesh with 1-mm-wide uniformly distributed square openings. The mesh was wrapped around the Pyrex tube, covering a total length of 35 mm, as shown in Figure 1. The plasma was created approximately 2–3 mm above the toluene surface; however, the narrowed tip of the glass tube was extended and dipped inside the liquid to a depth of almost 3 mm, as shown in the schematics of Figure 1. In this way, only the effluent gas coming from the discharge and carrying the active nitrogen species was bubbled inside the toluene. Thus, for a flow rate of 100 ml/min, the gas residence time inside the plasma zone (i.e., 35 mm wide) was approximately 0.81 s, whereas it took 0.06 s for the plasma-activated gas to contact liquid toluene after passing through the 3-mm-long narrowed end of the glass tube. The DBD plasma in filamentary mode was ignited at an input power of 10 W using an AC high-voltage power supply (Nadir s.r.l) provided with adjustable frequency (10−30 kHz) and voltage (0−15 kV) knobs. To avoid heating of the reactor

and hence to minimize evaporation of toluene, the reactor was cooled using a peristaltic pump (Masterflex series 77200-12; Cole-Parmer) to circulate ice-cooled water through a 1-mm-diameter plastic pipe wound as a spiral around the grounded electrode, as shown in Figure 1. The gas flow through the reactor was controlled, within the 15–100 ml/min range, using mass flow controllers (16 series; Alicat Scientific). Before starting each experiment, the system was flushed with nitrogen at a flow rate of 50 ml/min for 1–2 min. Next, the gas selected for the experiment (N_2, Ar/N_2) was applied and bubbled inside the liquid at the desired flow rate and the discharge was turned on. After the desired treatment time, the discharge was turned off and the treated toluene was analyzed, as specified below. In all experiments performed, traces of a brownish sticky solid deposit were observed on the inner surface of the DBD tube and on the surface of the HV electrode at the end of the treatment. Although backflow of toluene vapors into the discharge zone is not expected to be strong, nevertheless, considering the prolonged (30–150 min) operation of the discharge, the deposits are most likely due to polymerization/oxidation of toluene vapors.

2.3 | Analytical procedures

Treated liquid toluene samples were analyzed by gas chromatography coupled with mass spectrometric and flame ionization detectors (GC–MS and GC/FID), using the following instruments: Agilent GC/MSD 6850/5973 equipped with a 30 m × 0.25 mm HP-5 column with 0.25-µm film thickness; Agilent 7890 GC/FID equipped with an Agilent 30 m × 0.53 mm Plot Q column.

3 | RESULTS AND DISCUSSION

A representative GC–MS trace is shown in Figure 2a. It was obtained from analysis of a toluene sample treated for 30 min with DBD generated by an AC voltage of 10 kV and a frequency of 15 kHz in pure nitrogen flowing at 100 ml/min.

The chromatogram contains several peaks, which were assigned to specific products based on their mass spectra and retention times, matching those of authentic samples, when available, used as standards. The observed products can be classified into three groups, collecting, respectively, N-containing compounds, hydrocarbons, and O-containing compounds. The first group is the focus of the present research and includes methyl pyridines (peak A), benzonitrile (peak F), methyl benzonitriles (also called cyano toluenes, peak M), and benzyl nitrile (peak N).
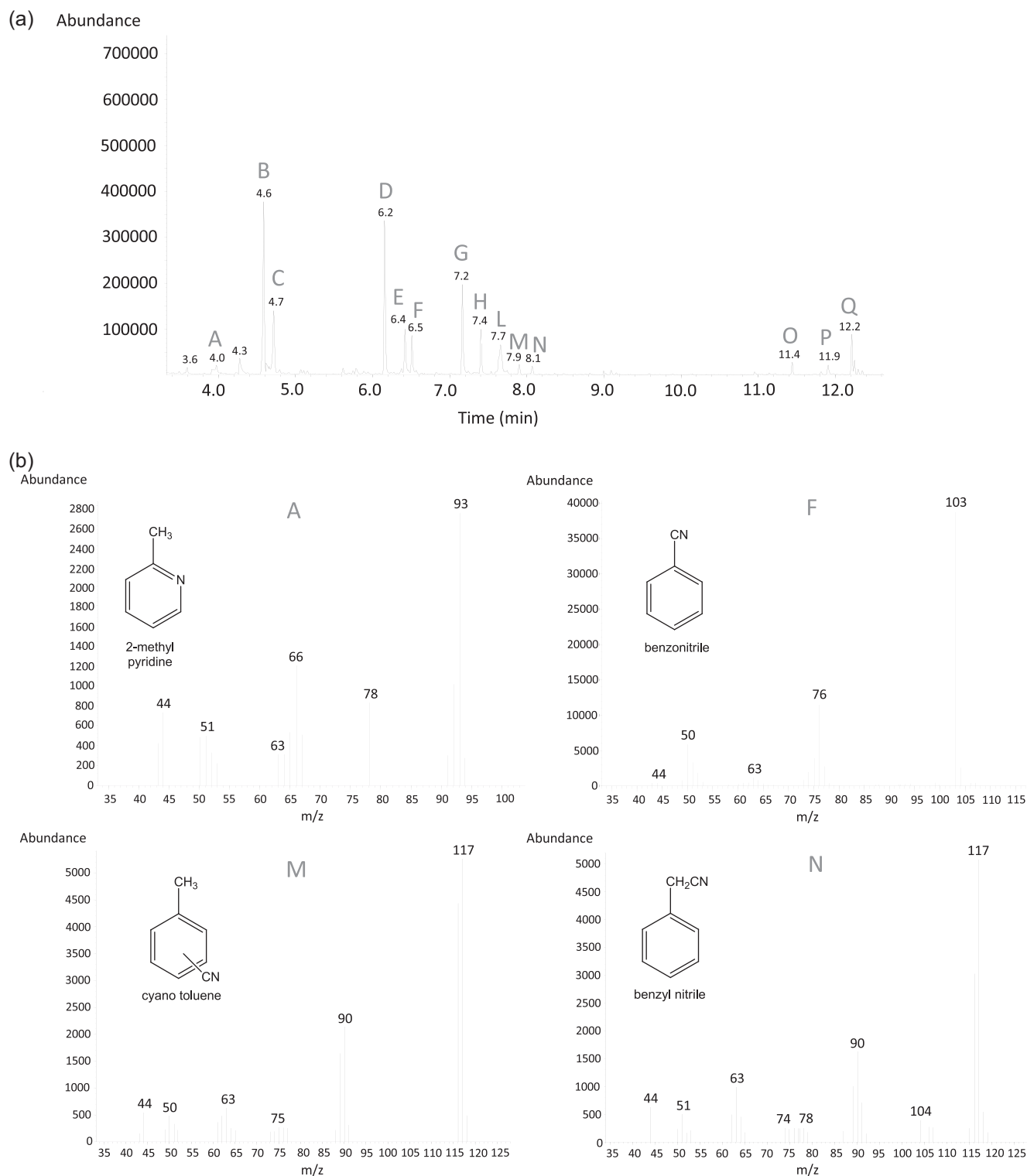
FIGURE 2 (a) Gas chromatography–mass spectrometry trace of a toluene sample treated for 30 min with DBD activated N_2 at a gas flow rate of 100 ml/min; (b) mass spectra and structures of major observed N-containing products

Representative mass spectra and structures of N-containing products are shown in Figure 2b. The second group includes a few hydrocarbons including ethylbenzene (peak B), methyl toluenes (xylenes) (peak C), as well as larger molecules, which can be indicated cumulatively as toluene dimers (peaks O, P, and Q) and identified as bibenzyl and isomeric benzyl toluenes. Finally, in the third group, O-containing compounds are found, notably benzaldehyde (peak D), benzyl alcohol (peak G), phenol (peak E), and hydroxy toluenes (peaks H and L).
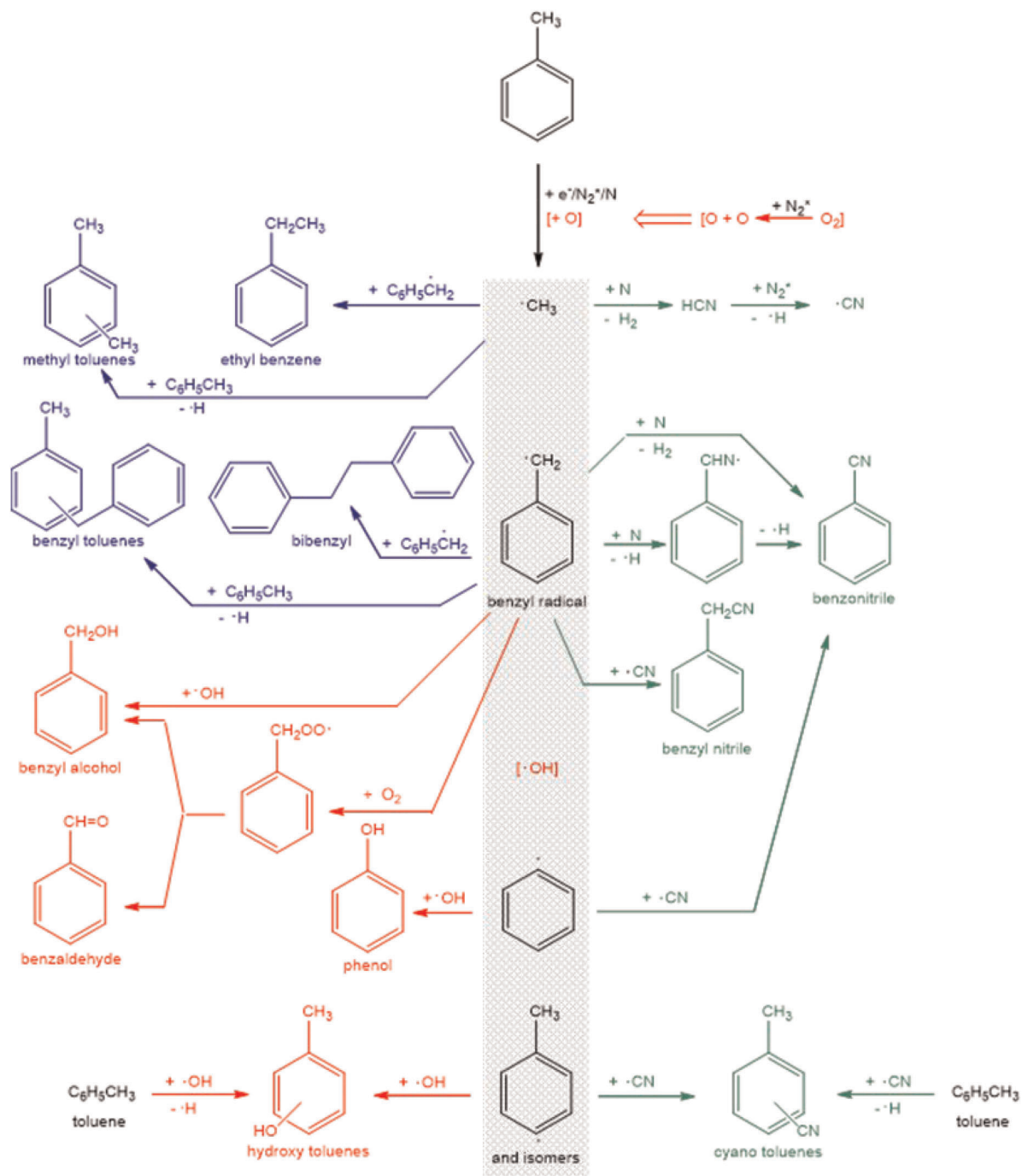
SCHEME 1 Major observed products, including N-containing products (green), hydrocarbons (blue) and O-containing products (red), and proposed routes for their formation. Inferred involved radicals are shown in the central column on a textured background. See main text for details

The presence of these products, in spite of the fact that air and oxygen were not purposely admitted in the reaction system, is attributed to residual oxygen, which efficiently quenches excited nitrogen species, as discussed later, and makes oxidation highly competitive. Experiments were run to investigate the effects of a few process variables on the obtained product distribution, namely (i) the N_2 flow rate, which was tested at 50, 75, and 100 ml/min; (ii) the

treatment time, which was set at 30, 75, 100, and 150 min; and (iii) the process gas nature and composition, which were tested using N_2/argon mixtures, as argon allows to ignite plasma at relatively low applied voltages[17] and might favor molecular nitrogen dissociation.[18] All these experiments produced results that are not significantly different from those reported in Figure 2. The structures of all major observed products, as well as possible routes for

their production, are shown in Scheme 1, which uses a color code to distinguish N-containing products (green), hydrocarbons (blue), and O-containing products (red). Scheme 1 is based on literature data on C–N bond formation from studies of the reactions of vaporized toluene within discharges in molecular nitrogen[15–17] and of the reactions of atomic nitrogen with hydrocarbons in planetary atmospheres.[19] The conclusions of the latter studies concerning methane and ethane were extrapolated here to the corresponding phenyl-substituted analogue, toluene.

As summarized in Scheme 1, in an N_2 DBD discharge, toluene can react with electrons,[15] with molecular nitrogen in excited states, indicated here with the short notation N_2^*,[15] and with atomic nitrogen.[19] Among the products of these reactions are the carbon-centered radicals shown in the central column of the scheme over a textured background, notably methyl ($\cdot CH_3$), phenyl ($\cdot C_6H_5$), benzyl ($\cdot CH_2C_6H_5$), and three isomeric (*ortho*-, *meta*-, and *para*-) methyl phenyl ($\cdot C_6H_4CH_3$) radicals. On the basis of known reactions of methane and ethane,[20] one could also expect that additional toluene-derived reactive species with C–N bonds (carbenes and nitrenes isomers $C_6H_5-CH=NH$, $C_6H_5-CNH_2$, $C_6H_5-CH_2N$) possibly form via reaction with excited nitrogen atoms, leading eventually to benzonitrile. These reactive species are not included in Scheme 1. In the presence of molecular oxygen, adventitious in our experiments, an additional efficient entry is available for benzyl radical via reaction of toluene with atomic oxygen. Atomic oxygen is produced via dissociative energy transfer reaction from N_2^* to O_2,[21,22] as indicated in the scheme, and is converted into the OH radical in the above-cited reaction with toluene. Thus, OH radicals are also available to react in this system, as discussed below, and are, therefore, included in the central column of the scheme. Benzyl radical is a key intermediate in the synthesis of benzonitrile via reaction with ground-state atomic nitrogen, which occurs along two parallel channels, as shown in Scheme 1.[15,20] Benzonitrile can also form via radical–radical combination of phenyl radical with cyano radical ($\cdot CN$), another reactive species of special relevance for the present study. The cyano radical forms in the reaction of N_2^* with HCN, which, in turn, is generated from methyl radical reacting with ground-state atomic nitrogen.[15] The cyano radical can give radical–radical combination reactions also with benzyl radicals to form benzyl nitrile, and with methyl-phenyl radicals (three distinct isomers) to form methyl benzonitriles. Another route to methyl benzonitriles is the reaction of the cyano radical with toluene according to the already mentioned, well-known radical addition/oxidation sequence, resulting in this case in the substitution of H by CN.

The observed hydrocarbon products (Figure 2a) are accounted for by analogous reactions of methyl and benzyl radicals with toluene (via an addition/oxidation sequence), leading to isomeric methyl toluenes (xylenes) and benzyl toluenes, respectively, and with the benzyl radical (via radical/radical combination), leading to ethylbenzene and bibenzyl, respectively (Scheme 1).

Finally, oxygen-containing products are attributed to well-known reactions initiated by O atoms and OH radicals, as described in the literature.[15,23] Worth reminding here is the efficient reaction, mentioned above, between N_2^* and O_2, leading to molecular oxygen dissociation,[21] which accounts for the important toluene oxidation channel observed also in a nitrogen discharge in the presence of only trace amounts of oxygen.

4 | CONCLUSIONS

The results of this study suggest the possibility to use the greenest of N sources, molecular nitrogen, at ambient temperature and atmospheric pressure in a simple discharge setup to achieve functionalization of toluene into valuable nitrogen-containing organic compounds. Using dielectric barrier discharge to activate molecular nitrogen and produce reactive nitrogen species in close proximity of liquid toluene, we obtained proof-of-principle results that this approach can be used to form new C–N bonds in suitably activated organic compounds. The study also highlights obstacles and limitations of the developed system and provides guidelines for further development of this novel approach to the synthesis of valuable organic products. Major issues to be considered include the formation of oxygenated products due to undesired oxygen present in the system and of hydrocarbons due to the reaction of toluene-derived carbon radicals with toluene. With regard to the first issue, optimization of the plasma source and the experimental setup will implement measures to rigorously exclude oxygen from the system, thus avoiding quenching of excited nitrogen and contextual oxygen atom formation, leading to undesired C–O products. As for hydrocarbons, their production will be limited by maximizing the plasma/liquid interface, thus favoring the reactions with nitrogen reactive species, which could be achieved, for example, by using multiple modules in sequence instead of a single module, as done in this study, or by developing a falling-film reactor design, as described in the literature for water treatment.[24] Emission spectroscopy characterization of the discharge and its afterglow will also guide the optimization of the setup to maximize the interaction of reactive nitrogen species with liquid toluene.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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