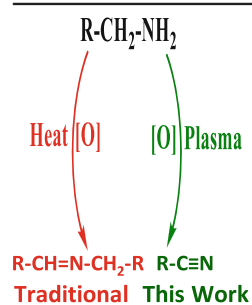


Direct and Efficient Dehydrogenation of Tetrahydroquinolines and Primary Amines Using Corona Discharge Generated on Ambient Hydrophobic Paper Substrate

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Abstract. The exposure of an aqueous-based liquid drop containing amines and graphite particles to plasma generated by a corona discharge results in heterogeneous aerobic dehydrogenation reactions. This green oxidation reaction occurring in ambient air afforded the corresponding quinolines and nitriles from tetrahydroquinolines and primary amines, respectively, at >96% yields in less than 2 min of reaction time. The accelerated dehydrogenation reactions occurred on the surface of a low energy hydrophobic paper, which served both as container for holding the reacting liquid drop and as a medium for achieving paper spray ionization of reaction products for subsequent characterization by ambient mass spectrometry. Control experiments indicate superoxide anions ($O_2^{\bullet-}$) are the main reactive species; the presence of graphite particles introduced heterogeneous surface effects, and enabled the efficient sampling of the plasma into the grounded analyte droplet solution.

Keywords: Mass spectrometry, Paper spray ionization, Corona discharge, Aerobic oxidation, Quinoline synthesis, Heterogeneous dehydrogenation

Received: 22 August 2016/Revised: 22 September 2016/Accepted: 27 September 2016/Published Online: 20 October 2016

Introduction

Oxidation reactions are challenging in terms of energy and waste management requirements, but when made catalytic, these reactions have the potential to provide facile pathways to atom-efficient synthesis [1, 2]. The use of oxygen as oxidant [3, 4] is a recent advancement capable of replacing toxic metal oxidants like manganese dioxide, silver oxide, and lead tetraacetate [5, 6]. Both homogeneous and heterogeneous catalytic aerobic oxidation methods that involve transition metals (e.g., Ru, Cu, Fe, etc.) have been developed for amines and alcohols. For example, in combination with a hydrogen acceptor (e.g., quinone) as co-catalyst, and $O_2/Co(salen)$ as oxidant, ruthenium-based compounds have been used in a multi-catalytic oxidation of alcohols and amines [7]. The requirement

of high loading of the hydrogen acceptor has led to the rational design of o-quinone-based Ru catalysts for amine oxidation [8]. First row transition metals are often used with stable radicals such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and its derivatives to achieve aerobic oxidation [9, 10]. Instead of oxygen, earlier studies employed electrochemical methods to generate the oxoammonium salt from TEMPO, which was thought to be the active species for the oxidation process [11]. In the present work, we report a nonmetallic aerobic oxidation of amines using plasma generated from corona discharge. To enable direct analysis of the reaction mixture, a drop of amine solution was placed on a hydrophobic paper triangle and was exposed to the reactive plasma; in this way, the paper served both as a container for bulk-phase reaction and as a means to achieve ambient paper spray (PS) ionization at atmospheric pressure for subsequent characterization by mass spectrometry (MS).

Electrical discharge is formed when an electric charge passes through a material (gas, liquid, or solid) which does not normally conduct electricity. The chemistry of the discharge is driven by electrons causing ionization, molecule excitation, and the production of radicals. Gaseous ions formed are accelerated by the electric field and undergo collisions with

Electronic supplementary material The online version of this article (doi:10.1007/s13361-016-1516-8) contains supplementary material, which is available to authorized users.

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neutral gas molecules. This exchange of momentum, and the subsequent cascading effect, generates a bulk fluid of plasma motion [12, 13], which we sample for the oxidative reactions reported in this study. In ambient air, ozone (O_3) is determined to be a major product in corona discharge according to the following reactions ($M = O_2$ or other molecular gases in air) [14, 15]:



It has also been shown experimentally using ferrous sulfate and superoxide dismutase that superoxide anions ($O_2^{\bullet -}$) are created [15, 16]; these anions are formed by attachment of thermalized electron to oxygen in air. In a recent study [17], we showed that $O_2^{\bullet -}$ anions produced in photo-redox reactions were the main active species for the dehydrogenation of tetrahydroquinolines in ambient air. Therefore, we wished to test the possibility of achieving dehydrogenation of amines after exposure to $O_2^{\bullet -}$ in plasma. Indeed, hydrogen atom abstraction capacity for such reactive oxygen species is well-known [18–20], even from alkanes. This subject has been studied extensively in gas-phase experiments [21, 22], which typically involve oxygen-centered radical species present at surfaces. Proton coupled electron transfer reactions have also been reported, which usually culminate in the formation of $[M^{(n-1)+} - OH]$ [23], an active species in heterogeneous catalysis of amines.

In recent years, plasma-based ionization methods have become popular in which various species in the plasma, including excited metastable molecules, electrons, and ionic species have been used to sample analytes present on an ambient surface. Examples of plasma-based ambient ion sources include direct analysis in real time [24], flowing atmospheric-pressure afterglow [25], low-temperature plasma [26], dielectric barrier discharge ionization [27], desorption atmospheric-pressure chemical ionization [28], microhollow cathode discharge microplasmas [29], etc. Mechanism of ionization include protonation, penning ionization, electron capture, and charge transfer. Apart from ion production for analytical MS, chemical transformations leading to unique products compared with the starting analyte have been reported. For instance, dihydrogenation of benzene (Birch reduction) was observed in the presence of low-temperature plasma [30]. Replacement of one carbon in benzene with nitrogen was also observed when exposed to low-temperature plasma in the presence NO gas [31].

The current experiment is unique in that we utilize liquid drops present on ambient paper surface as miniaturized reaction systems to study the susceptibility of linear primary amines

(e.g., hexylamine and decylamine) and tetrahydroquinolines (secondary amines such as 1,2,3,4-tetrahydroquinoline, 8-methyl-1,2,3,4-tetrahydroquinoline, and 6-methoxy-1,2,3,4-tetrahydroquinoline) toward dehydrogenation, in which the elimination of four hydrogen atoms (4 H) facilitated the formation of the corresponding nitriles and quinolines, respectively. The paper was made hydrophobic to prevent spreading and rapid evaporation of amine solution, which was typically composed of methanol/water (2:1, vol/vol). Graphite (5 mg per mL amine solution) was used as a catalyst, allowing for easy disposal of the paper substrate after products extraction. In the current work, the extracted nitrile and quinoline products were characterized by MS after online extraction and PS ionization [32–35]. Therefore, the experimental procedure consisted of two separate steps: (1) exposure of methanol/water drop containing amine to electrical discharge generated by applying +5 kV DC voltage, followed by (2) PS-MS analysis of reaction products achieved using +3 kV and acetonitrile spray solvent. By doping KI into the amine solution, the presence of iodine (I_2) was visibly detected, providing mechanistic insight that suggest the involvement of superoxide anions in the dehydrogenation reaction.

Experimental

Dehydrogenation on Ambient Hydrophobic Paper Surface

The experimental set-up enabling the use of plasma for dehydrogenation reactions consisted of hydrophobic paper (prepared in-house) and a conductive metal wire (e.g., stainless steel). In a typical experiment, a drop (10 μ L) of the amine reactant solution prepared in methanol/water (2:1, vol/vol) mixture was placed on the hydrophobic paper triangle and the conductive metal wire was suspended 5 mm above the droplet in ambient air (Figure 1a). High DC voltage of +5 kV was applied to the metal wire while the hydrophobic paper was grounded; in this way, the plasma generated at the tip of the metal wire was electrically directed toward the grounded amine solution present on the paper (Figure 1b). An optimized amount (5 mg/mL) of graphite particles were added to the reacting solution as catalyst, and to facilitate electrical conduction. A second experiment was performed in which the DC high voltage was applied to the hydrophobic paper and the metal wire grounded. In both experiments, discharge was induced until the amine solution dried; this end point was marked by the discharge traveling directly to the alligator clip holding the grounded paper (Figure 1c). Video of the experimental setup was recorded using Samsung Galaxy S5 cell phone with which LS-Pro Macro lens (15 \times magnification) was attached. The observed reaction yields were calculated using the following equation:

$$\text{Observed yield} = [I_{\text{product}} / (I_{\text{reagent}} + \Sigma I_{\text{all products}})] \times 100\%,$$

where I = absolute ion intensities; I_{product} = product of interest, $\Sigma I_{\text{all products}}$ = all other observed products.

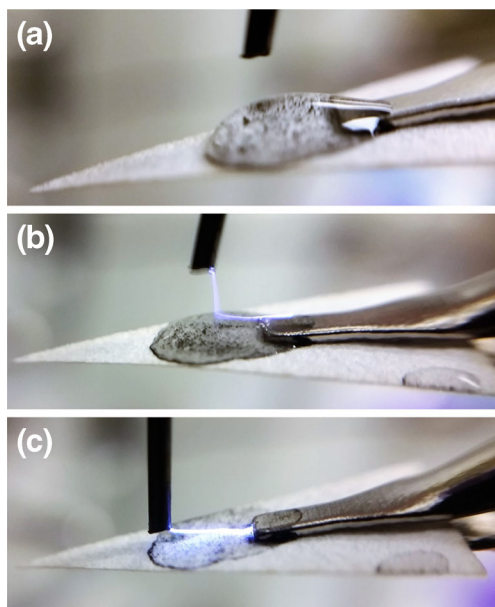


Figure 1. Experimental set-up for using aqueous-based solution present on hydrophobic paper to sample plasma generated by corona discharge. Paper triangle is held in place by a grounded stainless steel alligator clip whilst a direct current (DC) voltage of +5 kV was applied to stainless steel wire. Photographs showing (a) onset of experiment with no voltage applied, (b) discharge going through solution when voltage is applied, (c) discharge going toward grounded clip with no contact with dried solution

Paper Spray Ionization Mass Spectrometry (PS-MS)

After surface reaction, the conductive metal wire was removed and the hydrophobic paper triangle containing the dried reaction mixture was placed in front of an ion trap mass spectrometer. Reaction products were extracted with 20 μ L pure acetonitrile (3 \times within 60 s interval) and ionized on-line using paper spray ionization after applying 3 kV DC voltage to the wet hydrophobic paper triangle. No discharge was induced during this analysis period and so no significant reaction was observed during analysis, as shown by the control experiments. This PS-MS sample analysis condition involved the generation of charge micro-droplets containing the extracted reaction product and ionization via proton transfer. The ionized species were transferred to the inlet of the mass spectrometer for subsequent characterization through the measurement of mass-to-charge (m/z) ratio and in tandem MS (MS/MS) experiments. All MS experiments were performed using a Thermo Fisher Scientific Velos Pro LTQ linear ion trap mass spectrometer (San Jose, CA, USA). MS parameters used were as follows: 150 $^{\circ}$ C capillary temperature, three microscans, and 60% S-lens voltage. Thermo Fisher Scientific Xcalibur 2.2 SP1 software was applied for MS data collecting and processing. Tandem MS with collision-induced dissociation (CID) was utilized for analyte identification. An isolation window of 1.5 Th (m/z units) and a normalized collision energy of 30%–35% (manufacturer's unit) was selected for the CID experiment. Thermo Q-

Exactive Orbitrap mass spectrometer was used for high resolution measurements.

Hydrophobic Paper Preparation

Using a digital template, paper triangles were cut from chromatography paper (No.1) with an Epilog Legend 36EXT laser using 15% power at 1000 Hz. The cut paper triangles were silanized using trichloro(3,3,3-trifluoropropyl) silane vapor under vacuum, inside a desiccator for 4 h [33]. Typically, 0.5 mL of the silanization reagent was used for four to five sheets of paper. Paper size was approximately 80 mm² (base width of 9.5 mm, height of 16.6 mm).

Chemicals and Reagents

1,2,3,4-Tetrahydroquinoline, 8-methyl-1,2,3,4-tetrahydroquinoline, 6-methoxy-1,2,3,4-tetrahydroquinoline, hexylamine, decylamine, trichloro(3,3,3-trifluoropropyl) silane, methanol, and acetonitrile were purchased from Sigma-Aldrich (St. Louis, MO). Potassium iodide solution (10%) was purchased from GFS Chemicals (Powell, OH). Prismacolor Ebony graphite drawing pencil (#14420) was purchased from a local store. The embedded pure graphite was removed and ground into a fine powder using mortar and pestle.

Results and Discussion

Optimization and Dehydrogenation of Tetrahydroquinolines

Recently, catalytic dehydrogenation of tetrahydroquinolines to quinolines has attracted much interest, especially in the area of developing mild reaction conditions for high yield. As discussed in the introduction, current efforts utilize transition-metal-based catalysts that require hours of reaction times and moderately high temperatures (typically >100 $^{\circ}$ C). New synthetic strategies that allow (1) accelerated reaction rates, (2) low pressures of O₂, (ambient air), and (3) the avoidance of costly or toxic additives, are still desirable. In this study, dehydrogenation of tetrahydroquinolines was achieved by exposing liquid droplet present on ambient paper surface and containing the amine reactant to plasma generated by a corona discharge. A paper spray mass spectrum of the extracted surface reaction product is shown in Figure 2d. This data was recorded after 2 min of plasma exposure to 8-methyl-1,2,3,4-tetrahydroquinoline (8-methyl-THQ; MW 147) solution, in the presence of graphite particles (Scheme 1). High abundance of ions corresponding to the expected dehydrogenation product, 8-methyl quinoline, (m/z 144) was observed; this peak corresponds to a loss of 4 Da compared with that of reactant at m/z 148. For the purposes of comparison, MS analysis of the plasma reaction performed in the absence of graphite particles is shown in Figure 2c, as well as the paper spray mass spectrum for the same 8-methyl-THQ solution recorded in the absence of discharge (Figure 2a). Another spectrum was also recorded after 2 min of drying the droplet in the presence of graphite particles but in the absence of electrical discharge (Figure 2b).

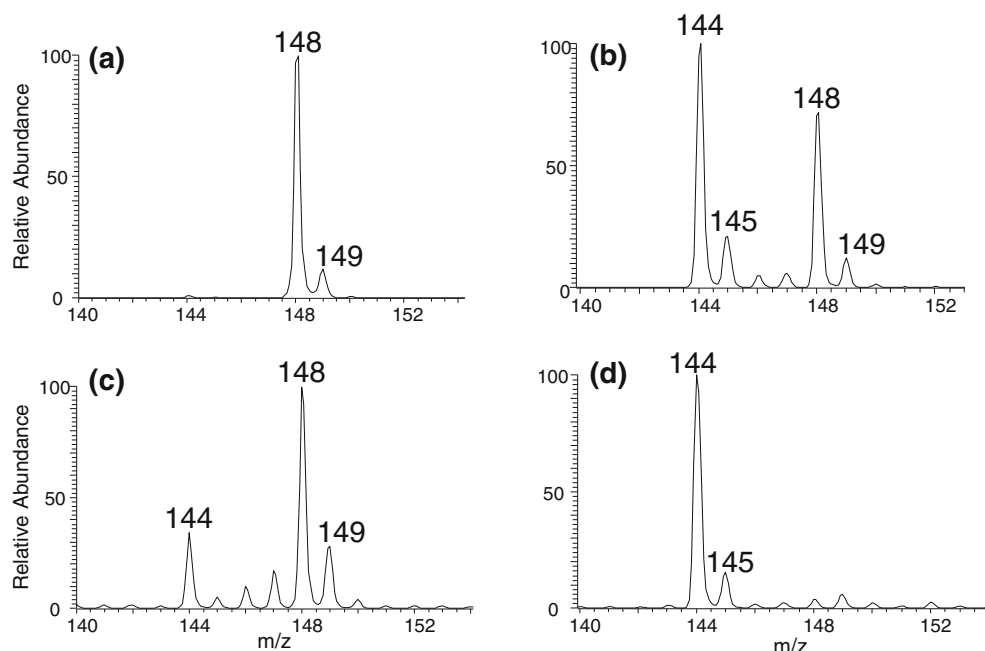


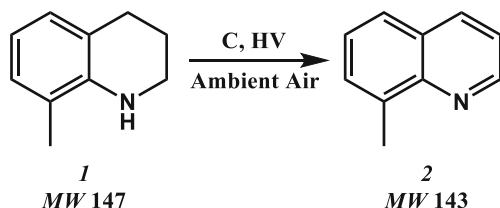
Figure 2. Paper spray mass spectra of pure 8-methyl-1,2,3,4-tetrahydroquinoline (*MW* 147) recorded (a) from fresh reactant, without drying, and in the absence of electrical discharge, (b) after 2 min of drying in the absence of discharge but in the presence of graphite particles, (c) after 2 min exposure to electrical discharge in the absence of graphite particles, and (d) after 2 min exposure to electrical discharge in the presence of graphite particles. All spectra were recorded using 3 kV spray voltage and 60 μL acetonitrile spray solvent

Collectively, the data demonstrate that the PS-MS analysis step did not contribute to the observed dehydrogenation reaction. The high abundance of unreacted amine detected at m/z 148 in Figure 2c exemplifies the importance of the graphite particles, providing 58% of 8-methyl quinoline product in the absence of discharge (Figure 2b). Note that only 5% of product yield was observed after drying 8-methyl-THQ in the absence of both graphite and discharge (Supplementary Figure S1B, Supporting Information). Inducing corona discharge in the presence of graphite particles for just 2 min afforded 96% conversion from 8-methyl-THQ into 8-methyl quinoline. A 26% yield was calculated for the control experiment performed without added graphite (Figure 2c).

The effect of graphite on reaction yield became clearly visible when the amount doped into solution was varied from 0 to 10 mg/mL. In this case, the role of graphite was judged by visually inspecting the appearance of a deep brown color that resulted from iodine (I_2) formation. Through surface/adsorption

effects, we expected increased amount of graphite to make possible effective sampling of the reactive oxygen species in the plasma (O_3 , $\text{O}_2^{\cdot-}$, etc.); these and the by-product (H_2O_2) from dehydrogenation all react with iodide (I^- ; colorless) to give iodine (I_2 ; brown). Therefore, KI [15 μL (10%) per mL of reactant] was added to the 8-methyl-THQ solution to allow in-situ generation of I_2 . In our experiments, the intensity of the brown color was dependent on the amount of graphite particles doped into the 8-methyl-THQ solution (Supplementary Figure S2, Supporting Information). No color change was observed when no discharge was induced, indicating the absence of $\text{O}_2^{\cdot-}$ anions and other reactive species. Conversely, generation of plasma in the absence of graphite particles yielded a slight color change, though the resultant brown color was less intense compared with 8-methyl-THQ solutions containing increasing amounts of graphite. This confirms results from MS, which showed 26% product yield under similar conditions. Aside from detection of color change, we also observed gas evolution during the discharge exposure period (Video S1, Supporting Information). We believe this could be due to O_3 production as predicted in Equation 3 above.

The type of the metal wire used for the plasma generation was found to influence the PS-MS analysis step after surface reaction. For example, electro-corrosion (the corrosion of metallic parts by external currents) was observed when using copper wire and Cu ions released into the reactant solution. Under this experimental condition, neither the reactant 8-methyl-THQ nor its dehydrogenation product could be detected in the subsequent PS-MS analysis. Instead, acetonitrile



Scheme 1. Conversion of 8-methyl-1,2,3,4-tetrahydroquinoline (**1**) to 8-methyl quinoline (**2**) in ambient air using DC high voltage (HV) and graphite (C) particles

adducts of Cu ions $[\text{Cu}(\text{CH}_3\text{CN})_2]^+$ were observed in large quantities at m/z 145 and 147 (Supplementary Figure S3, Supporting Information), with 2:1 relative abundances for ^{63}Cu and ^{65}Cu isotopes, respectively, which masked the ions of interest. The same species were detected in a reverse experiment where the DC voltage was applied to the hydrophobic paper containing the reactant solution while the Cu wire was grounded. To solve this problem, stainless steel wires and alligator clips were used throughout the experiment, as they were found to be resistant to electro-corrosion. The stainless steel set-up was effective for both forward (paper grounded and voltage applied to metal wire) and reverse (voltage applied to paper and metal wire grounded) experiments (Supplementary Figure S4, Supporting Information).

The last experimental design consideration concerned the nature of paper (hydrophilic versus hydrophobic) used for holding reactant solution. The high surface energy of untreated hydrophilic paper (~ 65 mN/m) facilitated solvent spreading and, thus, rapid evaporation. Although accelerated reactions rates have recently been observed under such limited solvent/thin film conditions [36–39], limited dehydrogenation reaction product was detected in the current study when hydrophilic paper was used. We attribute this observation to the inability to direct the plasma to the specific area of the paper containing the liquid film sample. In fact, without a bridging solvent, the plasma travels toward the grounded alligator clip holding the paper in place with no contact with the reactants on the paper surface (Figure 1c). With the silanized hydrophobic paper (surface energy, 44 mN/m) [33], wetting is minimized and the plasma is effectively sampled; this allows the miniaturization of chemical reactions using only small volumes of reactant solution. In the current experiment, a 10 μL aqueous-based droplet enables 2 min of reaction time before drying. As already shown, this reaction time is sufficient to convert more than 96% of 8-methyl-THQ into the corresponding quinoline. By using an organic solvent such as acetonitrile for product extraction, the same hydrophobic paper surface served as a medium to achieve ambient PS ionization that transfers the reaction product to the mass spectrometer while leaving the dried graphite particles behind. Three successive extractions, each with 20 μL acetonitrile, eluted a total of 81% of the product from the dried graphite particles in less than 60 s (Supplementary Figure S5, Supporting Information).

Using the optimized experimental conditions/materials, the plasma-induced dehydrogenation procedure was applied for the oxidation of 1,2,3,4-tetrahydroquinoline (THQ, MW 133) and 6-methoxy-1,2,3,4-tetrahydroquinoline (6-methoxy-THQ, MW 163) at atmospheric pressure and temperature. The results of this experiment are shown in Figure 3, where the corresponding quinolines were detected at m/z 130 and 160 as protonated species for quinoline and 6-methoxy quinoline, respectively. These peaks, resulting from the removal of four hydrogen atoms were confirmed by high resolution measurements in which errors less than 2 ppm were observed (Supplementary Figures S6–S8, Supporting Information). High and comparable yields of 93% and 91% were calculated,

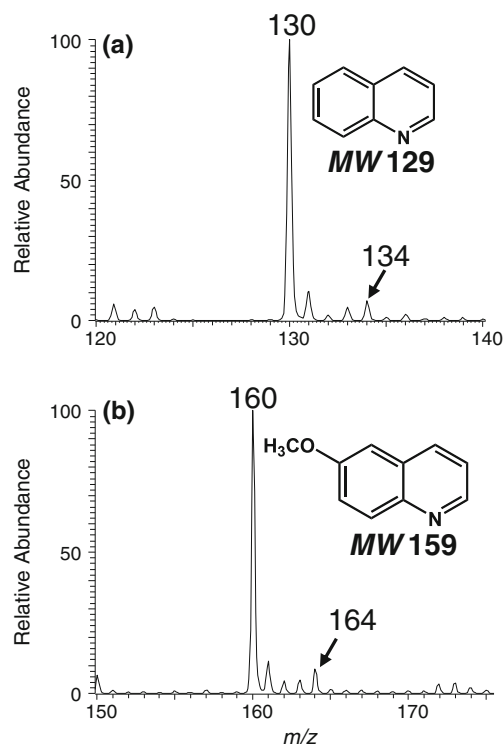
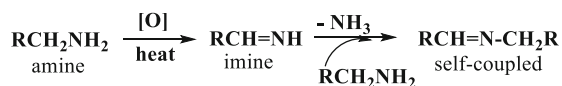
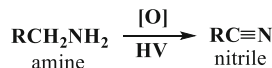


Figure 3. Paper spray mass spectra recorded after 2 minute plasma-based dehydrogenation reaction (in the presence of graphite particles) involving (a) 1,2,3,4-tetrahydroquinoline (MW 133) and (b) 6-methoxy-1,2,3,4-tetrahydroquinoline (MW 163) to produce the corresponding quinolines at m/z 130 and 160, respectively. All spectra were recorded using 3 kV spray voltage and 60 μL acetonitrile spray solvent

respectively, for THQ and 6-methoxy-THQ reactants. We believe this finding is significant because the catalytic approach described herein is a simple and effective method for obtaining quinolines in ambient air using off-the-shelf graphite particles as catalyst under the conditions of applied high DC voltage. The current procedure has potential to alleviate concerns (e.g., explosive hazards) in traditional aerobic reactions typically involving the mixing of catalyst, reactant, and the gaseous (O_2) oxidant in organic solvent in the presence of heat.

We note that for all three tetrahydroquinolines tested, the dehydrogenation reaction proceeded smoothly to the preferred product without the detection of the dihydroquinoline intermediates (i.e., removal of two hydrogen atoms) in the 2 min reaction time. This included the sterically demanding conversion of 8-methyl-THQ into 8-methyl-quinoline. This suggests that the current reaction condition is energetic and occurs faster compared with the traditional aerobic dehydrogenation reactions, which require hours of reaction time. Although this enhanced reaction rate may be due to reactant confinement and concentration effects resulting from solvent evaporation, we believe the observed catalytic effect is heterogeneous in nature, occurring mostly at the surfaces of the graphite particles. The combined effect is expected to limit the diffusion of the dihydroquinoline intermediates and allow rapid conversion into the final product. This expectation was further investigated

Traditional Aerobic Oxidation:**This Work:****Scheme 2.** Possible aerobic oxidation pathways for primary amines

by employing linear primary amines ($\text{R-CH}_2\text{NH}_2$) such as hexylamine and decylamine. Depending on reaction conditions, primary amines can be converted into three possible products (Scheme 2): (1) imine (R-CH=NH) via the removal of two hydrogen atoms, (2) nitriles ($\text{R-C}\equiv\text{N}$) through the removal of four hydrogen atoms, and (3) $\text{R-CH}_2\text{N=CH}_2\text{-R}$ via the elimination of ammonia in a self-coupling reaction between imine and unreacted amine. Formation of nitriles in aerobic oxidation is rare because of intrinsic self-coupling properties of the primary amine substrates. Interestingly, successful methods for nitrile production mostly relied on heterogeneous catalysis [40–43].

Dehydrogenation of Primary Alkylamines

Mass spectra results obtained after exposing aqueous solutions of hexylamine (MW 101) and decylamine (MW 157) to DC corona plasma are shown in Figure 4c and d, respectively. In the absence of plasma, both primary amines were detected as

protonated species at m/z 102 and 158 (Figure 4a and b). A completely different mass spectrum was recorded for hexylamine after 2 min of plasma exposure; a species at m/z 98 was detected (Figure 4c), which we interpret to result from the protonation of the corresponding nitrile (MW 97) after hexylamine undergoes a loss of four hydrogen atoms. This expectation was confirmed in MS/MS experiments (see insert, Figure 4c) using collision-induced dissociation (CID) where the ion at m/z 98 fragmented to give fragment ions at m/z 81, 70, and 57 through the release of neutral NH_3 (MW 17), $\text{CH}_2=\text{CH}_2$ (MW 28), and $\text{CH}_2=\text{C=NH}$ (MW 41), respectively. A yield >92% was calculated for nitrile production from hexylamine with no detectable amounts of imine or self-coupling products. These results confirm the presence of a fast energetic heterogeneous reaction system. The result of the decylamine reaction is shown in Figure 4d. Here too, the nitrile formation was apparent from the presence of a peak at m/z 154. CID MS/MS of ion at m/z 154 showed predominant fragment ions at m/z 126, 98, and 70 (Figure 5c) via successive elimination of ethylene ($\text{CH}_2=\text{CH}_2$, MW 28). A minor ammonia loss was observed yielding a fragment ion at m/z 137. The yield for this nitrile production was calculated as >80%. While no imine product was observed, we detected <3% production of the self-coupled product at m/z 296. [Note: proton affinity of hybridized orbitals decrease in this order $\text{sp}^3 > \text{sp}^2 > \text{sp}$ [44]; thus, the ionization efficiency of nitrile (having sp nitrogen) is expected to be less than that for the self-coupled product (with sp^2 nitrogen)]. Given that decylamine ($\text{PA} = 930.4 \text{ kJ/mol}$) and

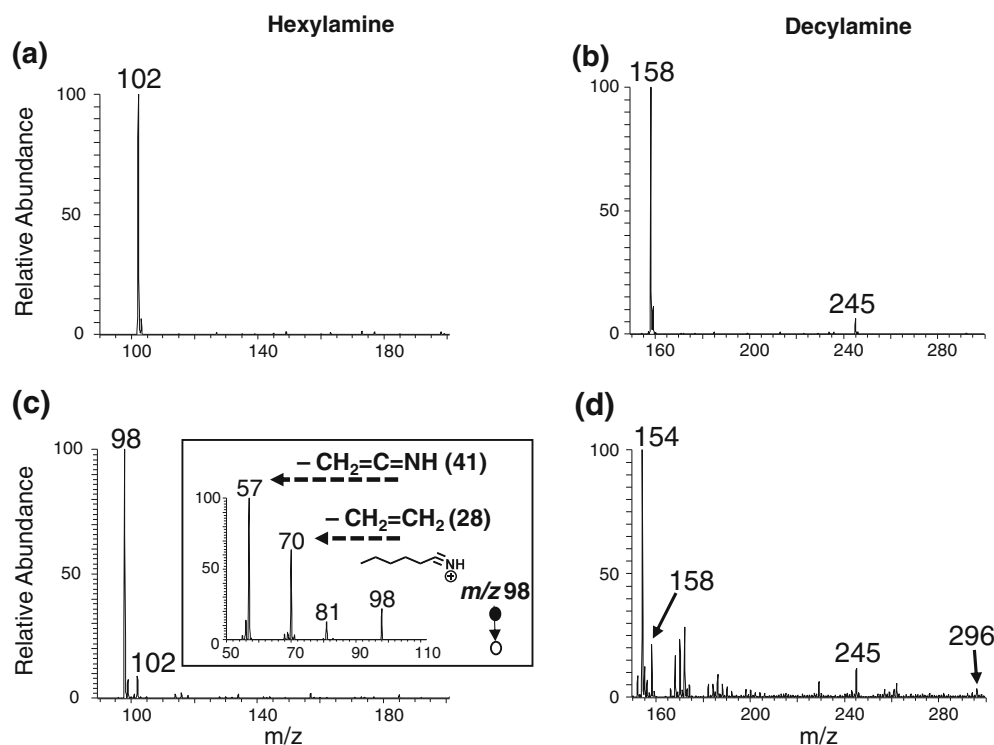


Figure 4. PS-MS mass spectra of hexylamine (MW , 101) and decylamine (MW , 157) recorded before (a), (b) and after (c), (d) plasma exposure. Dehydrogenation reaction leading to nitrile formation (m/z 98 and 154) occurred after exposing the amines to plasma for only 2 min at +5 kV

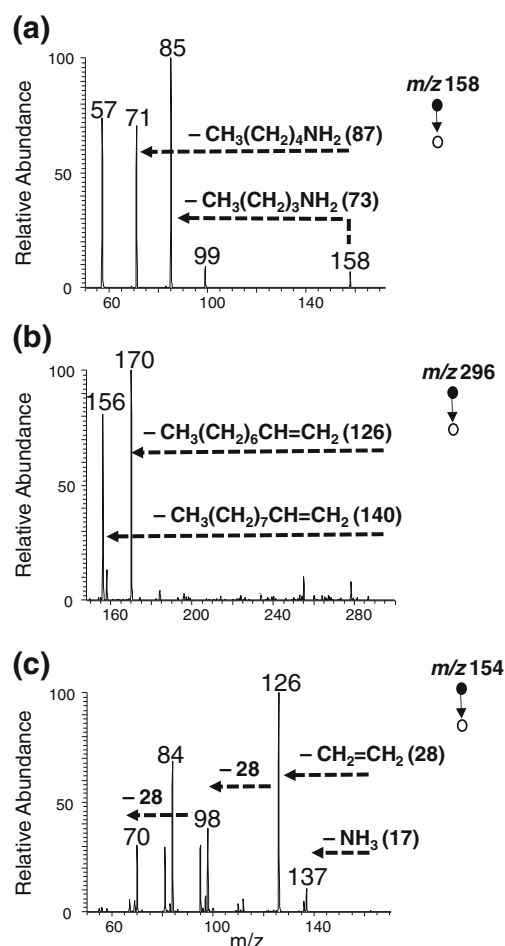


Figure 5. Tandem MS product ion mass spectra for species at (a) m/z 158 (protonated unreacted decylamine), (b) m/z 296 (protonated self-coupled product of decylamine), and (c) m/z 154 (protonated nitrile reaction product from decylamine)

hexylamine (PA = 927.5 kJ/mol) have comparable basicities, we believe the differences in self-coupling abilities might be influenced by their size. The fragmentation pattern of the self-coupled product ion (m/z 296) is contrasted with that of the unreacted amine (m/z 158) in Figure 5a, b, where the former ion gives fragment ions at m/z 170 and 156 through the elimination of 1-nonene (MW 126) and 1-decene (MW 140), respectively. The amine, on the other hand, dissociates through the release of neutral propylamine (MW 59), butylamine (MW 73), pentylamine (MW 87), and hexylamine (MW 101) species, yielding fragment ions at m/z 99, 85 (major), 77, 57, respectively (Figure 5a). Unlike the tetrahydroquinoline reactants that showed significant dehydrogenation reaction in the presence of graphite with no induced discharge, no nitrile product was detected for the primary amines under similar conditions (Supplementary Figure S9, Supporting Information). This result clearly reveals the role of corona discharge, with the graphite particles facilitating the generation and confinement of the $O_2^{\cdot-}$ anions for subsequent reaction with the amines through heterogenous catalysis.

Conclusions

A heterogeneous droplet-based reaction system is described for effective sampling of plasma generated from corona discharge at atmospheric pressure. The droplet reaction system was created by a mismatch in surface energies between the hydrophobic paper surface and aqueous-based reactants. Other important experimental considerations (aside from surface energy differences) include the nature of the conductive wire (e.g., copper versus stainless steel) from which the plasma is generated, solvent system for amine reactants, and volume of paper spray solvent. Using this confined-volume micro-reactor system, the susceptibility of tetrahydroquinolines and primary amines toward dehydrogenation was investigated in ambient air at room temperature and pressure. Both groups of chemical species underwent complete dehydrogenation (i.e., removal of four hydrogen atoms) in less than 2 min of plasma exposure time, affording up to 96% product yield in the case of 8-methyl-1,2,3,4-tetrahydroquinoline. As confirmed by the production of a brown-colored iodine (I_2) precipitate in the presence of KI, we believe superoxide anions ($O_2^{\cdot-}$) are the main active species causing the observed hydrogen abstraction effects. The process is selective (i.e., no oxygen addition was observed); the tetrahydroquinolines (1,2,3,4-tetrahydroquinoline, 8-methyl-1,2,3,4-tetrahydroquinoline, and 6-methoxy-1,2,3,4-tetrahydroquinoline) produced the corresponding quinolines whilst the primary amines (hexylamine and decylamine) yielded the corresponding nitrile. The self-coupled aerobic oxidation product typically observed for primary amines was detected in <3% yield for decylamine. For all species tested, an enhanced rate of dehydrogenation (>3x) was observed in the presence of graphite particles, which we attribute to increased conductivity and surface effects during reaction. Corona discharge appears to be an efficient source to generate highly reactive species in ambient air for dehydrogenation and, through the combination with hydrophobic paper, direct analysis of the reaction mixture is enabled without extensive sample workout.

Acknowledgments

The authors acknowledge support for this research by the Ohio State University start-up funds and U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Condensed Phase and Interfacial Molecular Science, under award number DE-SC0016044.

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