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Surface Reactions

Birch Reduction of Benzene in a Low-Temperature Plasma**

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We describe the observation of the highly selective, albeit modest-yielding, dihydrogenation of benzene and other arenes in a low-temperature plasma (LTP) of helium at atmospheric pressure. The reduction of benzene is of great interest as a model for the hydrogenation of aromatic compounds.[1] Benzene reduction has been achieved by using various heterogeneous and homogeneous chemical systems in the solid, liquid, and gas phases.[2] Full reduction to cyclohexane (C_6H_{12}) is the usual result of benzene hydrogenation, because of the high thermodynamic stability of this product. Other than the sodium/alcohol Birch reduction[3] and some well-controlled metal-catalyzed reductions,[4,5] the partial reduction of benzene to cyclohexadiene with high selectivity is very challenging. Unlike metal-catalyzed hydrogenations, in which molecular hydrogen is used as the hydrogen source, in the Birch reduction an alcohol functions as the proton donor while the alkali metal acts as an electron donor, with cyclohexadienes being formed as the reduction products. Partial reduction of nitrogen-containing aromatic compounds has been encountered in the gas phase,[6,7] however, there are no reports of gas-phase dihydrogenation of benzene that give significant yields or selectivity.[8]

Figure 1 shows the experimental setup used for conducting the plasma processing of organic compounds (for details see the Supporting Information). Headspace vapors of samples are carried by the discharge gas (helium) through a discharge chamber, where a helium plasma is sustained by dielectric barrier discharge[9] at atmospheric pressure. The resulting ionic species are introduced into the mass spectrometer by on-line mass analysis (that is, no ionization source is used except for the plasma system itself).

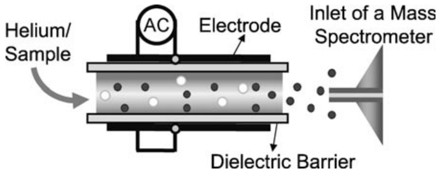

Figure 1. Schematic view of the experimental setup consisting of an atmospheric pressure low-temperature plasma (LTP) ion source configured to provide a dielectric barrier discharge (DBD) and to allow product ions and neutral species to be swept into a mass spectrometer.

Typical LTP mass spectra derived from benzene, toluene, and naphthalene are shown in Figure 2 A–C. The major signal in the spectrum of each of these arenes has a mass 2 Da above that of the reactants. Interestingly, neither molecular radical cations ($M^{\bullet+}$) nor the protonated molecules ($[M+\text{H}]^+$), which are normally detected using atmospheric pressure ionization, are observed. Besides the $[M+2]^{\bullet+}$ signals, lower abundance ions with masses 16 Da and 32 Da higher than the molecular mass of the reactant are also present, indicating that oxidation accompanies reduction. The neutral products formed from the LTP treatment of benzene were collected cryogenically and analyzed off-line by EI/GC/MS and tandem mass spectrometry (for details see the Supporting Information). These data show that no benzene remains after passage though the discharge chamber. The major products include 1,3- and 1,4-cyclohexadiene (C_6H_8), phenol (C_6H_5OH), and biphenyl ($C_{12}H_{10}$). Clearly, the $[M+2]^{\bullet+}$ signal corresponds to dihydrogenation of the benzene ring ($[M+2\text{H}]^{\bullet+}$) and the $[M+16]^{\bullet+}$ signal is due to oxygen addition ($[M+\text{O}]^{\bullet+}$). Compounds such as 1,4-cyclohexadiene, 4-methyl-1,3-dioxolane, and pyridine were also subjected to LTP, and the corresponding spectra are shown in Figure 2 D–F. The major ionic species are the molecular ions ($M^{\bullet+}$, $[M-\text{H}]^+$, $[M+\text{H}]^+$), similar to what has been reported for glow-discharge ioniza-

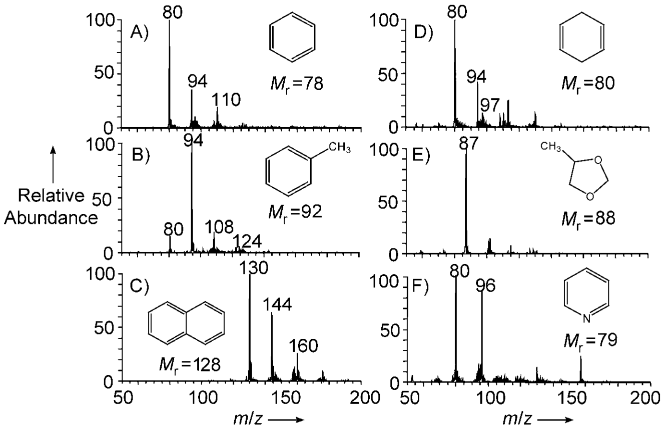

Figure 2. LTP mass spectra of: A) benzene, B) toluene, C) naphthalene, D) 1,4-cyclohexadiene, E) 4-methyl-1,3-dioxolane, and F) pyridine.

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tion[10] and atmospheric pressure chemical ionization (APCI).[11]

A certain degree of oxidation is also observed for these compounds, but no signal corresponding to a reduced species is detected. Molecules with a variety of functional types were also subjected to LTP and their product ions were analyzed by mass spectrometry (Table S1 in the Supporting Information). Similar to the results shown in Figure 2, reduction by dihydrogenation was observed for arenes but not for other types of compounds, even those having functional groups susceptible to reduction. It is also remarkable that under the LTP conditions, the reduction of benzene stops after the addition of two hydrogen atoms to form cyclohexadiene products (C_6H_8), in spite of the fact that complete hydrogenation is thermodynamically more favorable once the aromatic system is destroyed.[12]

To elucidate the reaction mechanism, efforts were directed at finding the source of the added hydrogen. Hydrogen atoms from benzene, trace molecules in the environment, and adsorbate on the discharge surfaces are all possible contributors to the reduction. The possibility of benzene itself acting as the hydrogen source was precluded by analyzing the LTP mass spectrum of hexadeuterobenzene (C_6D_6, $M_r = 84$). If hydrogen was provided from benzene, the reduction product ions should appear at m/z 88 (addition of two deuterium atoms). However, the base signal occurs at m/z 85 with ions at m/z 86 and 84 of much lower abundances, but no signal at m/z 88 (Figure S2 in the Supporting information). The observation of abundant ions of m/z 85 is most likely due to back exchange of deuterium to hydrogen from the initially formed dihydrogenation product ($[C_6D_6{+}2\,H]^{\cdot+}$) at m/z 86. The possibility of hydrogen arising from chemicals in the surrounding environment such as water and methanol (a common solvent) is highly unlikely. This is evident from the fact that after feeding deuterated water or methanol into the plasma system during the LTP treatment of benzene, the dominant signal was still at m/z 80 (Figure S3 in the Supporting Information). The chance that surface physisorbed water may contribute was also ruled out by using properly baked discharge surfaces.

Based on the above results, the only remaining hydrogen source is the discharge surface, which is made of glass. Since glass is terminated by silicon-bound OH groups,[13] it can potentially provide hydrogen atoms for reduction. To test this possibility, two thin sections of silicon wafer were inserted into the discharge chamber to cover the glass slides which comprise the surfaces at the top and bottom of the chamber. In this case, the glass slides still functioned as a dielectric barrier to maintain a stable plasma, but it is the silicon wafer with a surface terminated with silicon atoms that is exposed to the plasma. The corresponding LTP mass spectrum of benzene is shown in Figure 3A. The base signal is now the molecular ion of benzene at m/z 78, with the reduction product at m/z 80 appearing in relatively lower abundance. Since the entire area of the discharge chamber was not covered by silicon, the exposed glass surface might contribute to the observation of ions at m/z 80. To confirm the role of covalently bound surface hydrogen atoms in the reduction of benzene, the silicon wafer surface was modified so that hydrogen was the terminating group.[14] The corresponding mass spectrum of benzene after LTP treatment is shown in Figure 3B. As expected, the intensity of the $M^{\cdot+}$ ions of benzene (m/z 78) decreases significantly, while ions corresponding to the reduction product $[M{+}2\,H]^{\cdot+}$ (m/z 80) become the base signal. The above results indicate that benzene reduction involves hydrogen atoms covalently bound to the discharge surface.

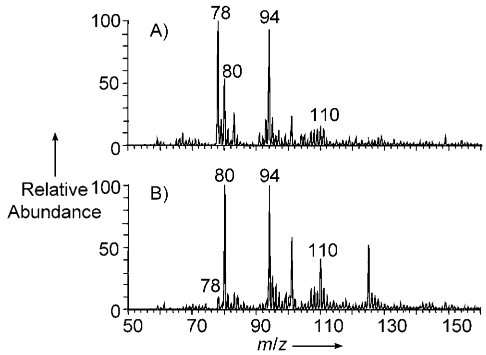
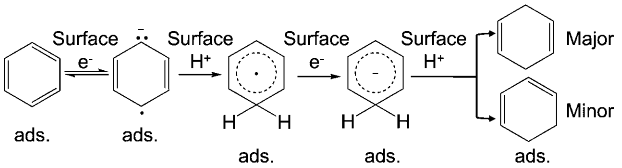


Figure 3. LTP mass spectra of benzene with: A) a discharge chamber containing a silicon wafer surface exposed to the plasma, and B) a discharge chamber containing an Si–H-modified silicon wafer exposed to the plasma.

A surface-assisted benzene reduction pathway is proposed, as shown in Scheme 1. The efficient diffusion of electrons from the plasma to the surface means the discharge surface is negatively charged.[15] Electrons with low binding energies (ca. 1 eV) are adsorbed onto the discharge surface and can diffuse across it or recombine with positively charged entities. In the first step of the reduction, the adsorbed benzene molecule is proposed to capture an adsorbed electron in its vicinity on the discharge surface, thereby giving rise to an adsorbed benzene radical anion intermediate. The proposed next step for the reduction of benzene involves charge neutralization by reaction of the benzene radical anion with a positively charged group on the surface, which provides a hydrogen atom for the first proton addition step. One possible donating entity in the case of the glass surface is $(\cdots\mathrm{Si{-}O^{\cdot}}\cdots\mathrm{H})^{+}$. The addition of a second electron followed by another proton will form the cyclohexadiene product, which could be collected as such or ionized in the plasma to yield the observed $[M{+}2\,H]^{\cdot+}$ ions. GC/MS analysis of the benzene reduction products showed 1,4-cyclohexadiene as the major reduction product, in a yield 2.5 times greater than that of the co-product 1,3-cyclohexadiene. It is likely that some 1,3-cyclohexadiene is formed from 1,4-cyclohexadiene as a result of isomerization promoted by its greater stability.[16] The



Scheme 1. Mechanism for the surface-assisted reduction of benzene in an LTP. Benzene molecules are adsorbed (ads.) on the discharge surface during reduction and this is followed by desorption of the reduction products into the gas phase.

further reduction of 1,4-cyclohexadiene is not favorable because of its low reactivity toward electron addition,[16,17] which results in dihydrogenation being the main reduction pathway. Efforts have been made to identify the proposed reaction intermediates—including benzene radical anions, cyclohexadienyl radicals, and cyclohexadienyl anions. However, their unstable nature precludes analysis in the gas phase; this is in contrast to recent studies of solution-phase reaction intermediates by mass spectrometry.[18–20] Clearly, further experimental and theoretical investigations are needed to verify the proposed mechanism. We also note the similarities between reduction in the LTP plasma and the conditions employed in the Birch reduction. Both reactions are initiated by the addition of a single electron and followed by protonation, with 1,4-cyclohexadiene observed as the major product. In both cases only arenes can be reduced effectively, while weak aromatic systems including pyridine and furan or other functional groups are less prone to reduction. Substantial differences in the reaction environment exist, especially the fact that unlike the Birch reduction, the present system is heterogeneous and the addition of proton donors cannot directly influence the reaction, as shown by the results of deuterated methanol or water addition.

Another most interesting phenomenon in the plasma treatment of benzene is that oxidation accompanies reduction. As shown in Figure 2 A, ions occur at m/z 94 and 110,and were identified by MS/MS as phenol and dihydroxybenzene, respectively. The formation of phenol by benzene oxidation has been observed under different atmospheric ionization conditions. It is believed that the addition of an $O(^3P)$ atom to the benzene ring followed by 1,2-hydrogen transfer results in the production of phenol.[21] Adding oxygen gas (5% volume) to the helium plasma, however, reduced the extent of phenol production (as judged from the abundance of ions at m/z 94), and dramatically increased another signal at m/z 97 (Figure S4 in the Supporting Information). The identity of the ions at m/z 97 was interrogated by adding $^{18}O_2$ to the LTP and conducting tandem mass spectrometry studies (Figure S4 in the Supporting Information). Its composition is most likely $C_6H_9O^+$; however, the structure of this ion has not been identified since several possible conformers can interconvert under ion-trap collision-induced dissociation (CID) conditions. The formation of $C_6H_9O^+$ ions at a higher oxygen concentration likely involved subsequent oxidation of the benzene reduction product (C_6H_8; for details see the Supporting Information). The effect of the discharge gas flow rate on benzene redox reactions in the LTP system was also evaluated. It is interesting to note that with an increase in the helium gas flow rate, the relative abundances of the reduction product at m/z 80 and the oxidation product at m/z 97 are increased, while that of the oxidation product at m/z 94 is decreased (Figure S5 in the Supporting Information). The possible contributing factors are discussed in the Supporting Information.

In summary, partial reduction of benzene together with oxidation has been observed in a low-temperature helium plasma at atmospheric pressure. Mechanistic studies suggest that the reduction occurs at the discharge surface and is initiated by the capture of low-energy electrons from the surface, followed by protonation by acidic hydrogen atoms from surface hydroxy groups (in the case of glass). This heterogeneous reduction, similar to the homogeneous Birch reduction, is unique in its high selectivity for arenes and its exclusive formation of dihydrogen reduction products. The simultaneous benzene oxidation is believed to be due to gas-phase reactions induced by oxidative radicals such as triplet O and $OH^{\bullet}$ derived from oxygen or water in the discharge environment. The overall yield of the benzene dihydrogenation products under the current experimental conditions is limited because of the occurrence of other competitive reactions such as oxidation and dimerization. Future studies are needed to optimize the reduction of benzene in a plasma system for the reaction to be applicable in synthesis. The surface Birch reduction reaction exemplifies the rich but little explored chemistry that occurs at the discharge surface in a plasma. It also has longer term potential for synthetic chemistry, considering the simplicity and low cost of implementing LTP, the rapid reactions, and the easy sample handling processes.

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