J. Org. Chem. **2002,** *67,* 119−124

Pyrolysis of *p*-Benzosemiquinone

Cheryl D. Stevenson,* Lance J. Heinle, and Richard C. Reiter

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

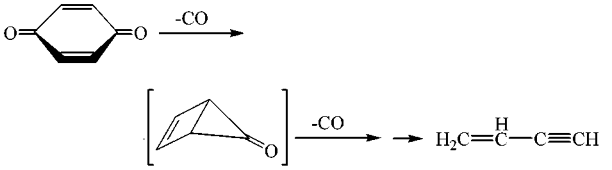
stevenson@xenon.che.ilstu.edu

Received June 25, 2001

In contrast to the thermolysis of *p*-benzoquinone, which does not decompose until the temperature is over 800 °C, and then primarily yields vinylacetylene, the corresponding anion radical, precipitated from liquid ammonia [$Na^+(NH_3)C_6H_4O_2^{\bullet-}$], decomposes at 380 °C and fragments primarily into phenol, hydroquinone, ammonia, methane, carbon monoxide, hydrogen, and minor amounts of other simple compounds. When the benzoquinone is replaced with perdeuteriobenzoquinone, deuterium and hydrogen are randomly scrambled into the products, and both ND_3 and CH_4 are formed. When the hot pyrolysis container is completely sealed, preventing the escape of volatile materials, *p*-aminophenol, as opposed to phenol, is the major liquid product.

Introduction

The literature is replete with results from the pyrolytic treatment of neutral organic compounds,[1] but there are only a few papers (all from our laboratory) regarding the pyrolysis of the anion radicals of these compounds.[2] Nearly 30 years ago Hageman and Wiersum[3] found that the pyrolysis of *p*-benzoquinone at 850 °C yields vinylacetylene (70%) (reaction 1), smaller amounts of benzene, styrene, indene, and phenylacetylene, and traces of toluene and naphthalene. Since we have previously observed the activation of C−C and C−H bonds in polyaromatic hydrocarbons (PAHs) via electron addition,[2] we were motivated to determine if the addition of an electron would result in analogous bond activation in quinones.



(1)

In carbonaceous meteorites, most of the carbon is tied up in kerogen which, in turn, contains a number of PAH's.[4] In 1999, Zare and co-workers reported that UV radiation, under astrophysical conditions at 10 K, of PAH's encrusted in water ice, can lead to the formation of a number of oxygenated organic compounds including alcohols, quinones, ethers, and hydrogenated PAHs.[5] These findings are important because quinones are important biological and prebiotic compounds and are essential for electron transport in simple organisms. Large pieces of asteroids, which have collided with Earth during the prebiotic phase of our planet, are also known to contain quinones.[6] Since considerable heat is generated during the terrestrial entry of asteroid material, it occurred to us that the products produced in the pyrolysis of quinoid materials may also be of prebiotic interest. However, neutral *p*-benzoquinone resists pyrolytic damage up to temperatures of 800 °C.[7] Perhaps some prebiotic compounds were produced via the pyrolysis of quinone anion radicals.

Many quinones undergo spontaneous electron transfer from a number of solvent systems in the presence of visible and UV radiation, producing the semiquinone.[8] Further, the resulting semiquinone is expected to be much more sensitive to thermal degradation than is the parent quinone. This is analogous to the observations obtained from the PAH systems. For example, naphthalene does not begin to undergo thermal degradation until temperatures reach nearly 1200 °C. On the other hand, the addition of a single electron activates the C−H and C−C bonds.[2a] Even relatively gentle warming of the naphthalene anion radical to 100 °C results in the formation of H_2 and CH_4. The CH_4 appears to result from the formation of carbene (Scheme 1). Other than polymeric materials, methane has remained the only organic compound isolated from the pyrolysis of PAH anion radicals. To date these pyrolysis studies have included the anion radicals of naphthalene, perylene, pyrene, benzofluoranthene, and biphenyl.[2]

In view of the results with the PAH anion radicals, we anticipated that an analogous set of bond activations would occur upon the single electron addition to benzoquinone. More interestingly, if carbenes are also involved in the pyrolysis of the benzoquinone anion radical, a variety of oxygenated organic compounds may result. We anticipated that some of these might even be of prebiotic importance. The possibility of the formation of important prebiotic compounds containing nitrogen is even greater, due to the presence of ammonia in asteroid material, which is solvating the cation−anion radical ion pair.[9] Nitrogen liberated from the ammonia ligating the cation

---

(1) Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980.

(2) (a) Stevenson, C. D.; Rice, C. V.; Garland, P. M.; Clark, B. K. *J. Org. Chem.* **1997**, *62*, 2193. (b) Batz, M L.; Garland, P. M.; Reiter, R. C.; Sanborn, M. D.; Stevenson, C. D. *J. Org. Chem.* **1997**, *62*, 2045. (c) Stevenson, C. D.; Garland, P. M.; Batz, M. L. *J. Org. Chem.* **1996**, *61*, 5948.

(3) Hageman, H. J.; Wiersum, U. E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 334.

(4) Allamandola, L. J.; Tielens, A. G. M.; Barker, J. R. *Astrophys. J. Suppl. Ser.* **1989**, *71*, 733.

(5) Zare, R. N.; Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J.; Gillette, J. S.; Clemett, S. J. *Science* **283**, *135*, 1999.

(6) Bernstein, M. P.; Sandford, S. A.; Allamandola, L. J. *Sci. Am.* **1999**, *July*, 42.

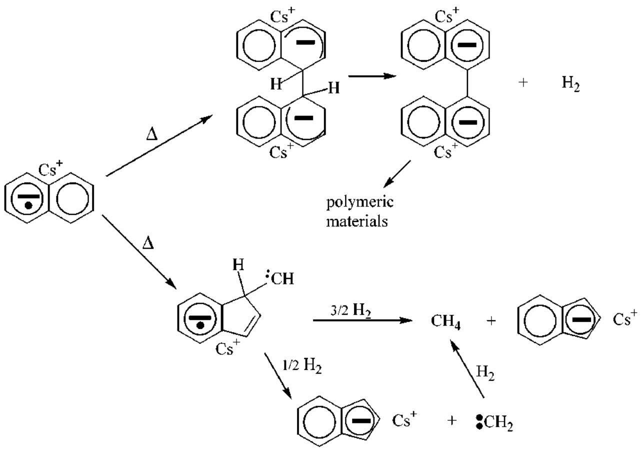
(7) Hageman, H. J.; Wiersum, U. E. *Tetrahedron* **1971**, *45*, 4329.

(8) Kim, Y. S.; Stevenson, C. D. *J. Phys. Chem. A* **1999**, *103*, 7139.

(9) Gerakines, P.; Schutte, W. A.; Ehrenfreund, P. *Astron. Astrophys.* **1996**, *312*, 289.

10.1021/jo010646p CCC: $22.00

Scheme 1



of the solid sodium semiquinone ion pair $\{Na^+(NH_3)C_6H_4O_2^{\bullet-}\}$ could conceivably be found in pyrolysis products. As a precedent, fragments of 18-crown-6, "solvating" the cation of solid benzene anion radical salt $\{K^+(18\text{-crown-}6)C_6H_6^{\bullet-}\}$ were found in its pyrolysis products.[10] Ammonia can efficiently serve both as a solvent and as an electron donor in a photoinitiated electron transfer to *p*-benzoquinone.[8] Despite this fact, to generate large quantities of benzosemiquinone in liquid ammonia, the present studies were carried out using sodium metal as a reducing agent.

Results and Discussion

Exposure of dilute solutions of benzoquinone in liquid ammonia to sodium metal results in bluish solutions that yield strong well-resolved signals upon EPR analysis. However, the EPR spectrum (Figure 1a) not only shows the expected 1:4:6:4:1 splitting (a_H = 2.42 G for 4 Hs) pattern for the free solvated semiquinone but the signal from a second species is also present. Computer simulation, Figure 1b, reveals that the second species exhibits couplings of 2.48 G for 2 Hs and 1.14 G for the second set of two equivalent protons. Although ion-associated and free solvated anion radicals have not been previously observed simultaneously in liquid NH_3, this second species appears to be an ion-associated benzosemiquinone. The identity of the ion-associated species is confirmed by the observation of more free solvated ion in dilute solutions and more ion-associated species in the more concentrated solutions. Further, the addition of sodium cations (sodium perchlorate) increases the relative intensity of the spectrum of the ion pair relative to that due to the free solvated ion.

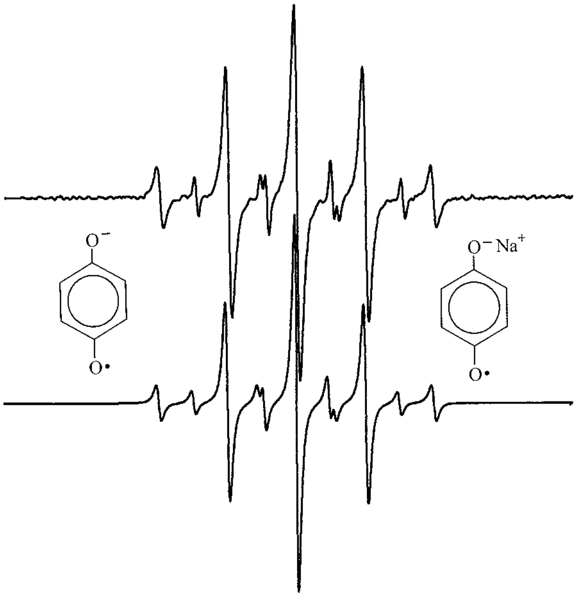
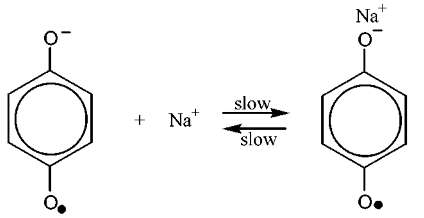
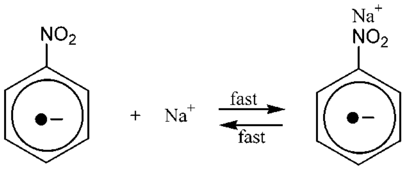


Figure 1. (Upper) EPR spectrum (20 G sweep width) recorded at 25 °C with a modulation amplitude of 0.05 G of p-benzoquinone reduced with sodium metal in liquid ammonia. The computer simulation (lower) was generated using coupling constants of 2.42 G (4 Hs) for the free solvated *p*-benzosemiquinone and 2.48 G (2 Hs) and 1.14 G (2 Hs) for the solvent-separated ion pair of *p*-benzosemiquinone. The ratio of $[C_6H_4O_2^{\bullet-}]/[C_6H_4O_2^{\bullet-},Na^+]$ = 2.0, and the peak-to-peak line width is 0.12 G for both species. The ion associated species is shifted upfield by 0.25 G.

The EPR spectra of the ion pair and of the free ion are observed simultaneously because the rate of dissociation and association (reaction 2) are slow on the EPR time scale. The close interaction between one of the oxygens and the sodium cation splits the equivalency of the four protons. There are many examples of such ion association processes that have been observed in liquid ammonia, e.g. reaction 3, but in all previous cases the forward and reverse kinetics have been sufficiently fast to result in the observation of only the time average EPR spectrum.[11,12]

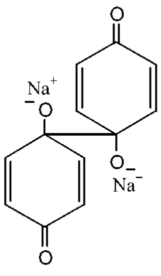


(2)



(3)

Evaporation of the solvent shifts reaction 2 to the right. Complete removal of the volatile solvent under high vacuum leaves a dark brown solid that contains a substantial amount of pinacolate at ambient temperatures, structure I.[13] Warming the pinacolate drives it back to the original anion radical salt. This is demon-



I

---

[10] Stevenson, C. D.; Morgan, G. *J. Org. Chem.* **1998**, *63*, 7694.

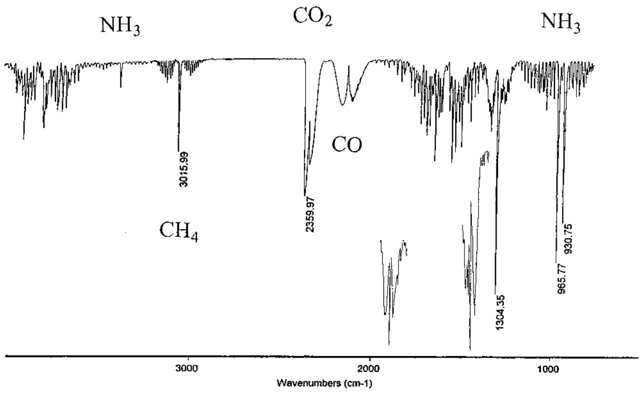
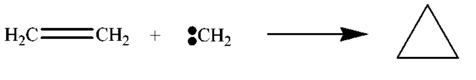


Figure 2. Gas-phase FT-IR spectrum of the gaseous products produced by the 380 °C pyrolysis of $[Na^+(NH_3)C_6H_4O_2^{\bullet-}]_{(solid)}$. When ethylene was present during the pyrolysis, the presence of cyclopropane in the gas-phase products was evidenced by the presence of the (inset) bands at 1444 and 1888 cm^{-1} (see Pinches, S.; Lauticht, I. *Infrared Spectra of Labeled Compounds*; Academic Press, Inc.: New York, 1971; p 80).

strated by an increase in the EPR signal due to $Na^+(NH_3)C_6H_4O_2^{\bullet-}$ that is observed upon warming the dark brown solid. The addition of water to the solid residues followed by titration of both refluxed and unheated samples with dilute HCl solutions proved that the ratio of ligated ammonia to benzoquinone anion radical is 1:1.

Heating sealed evacuated bulbs containing samples of $Na^+(NH_3)C_6H_4O_2^{\bullet-}$ (this anion radical salt is the substance undergoing pyrolysis) to 380 °C results in the formation of several gas-phase products. In addition, a considerable amount of liquid material was collected in an attached sidearm, which was maintained at room temperature, see Experimental Section. The sidearm represents a room temperature "escape" for the condensable portion of the hot pyrolysis mixture. All of the gas-phase products (products not condensable at liquid nitrogen temperature) combined represent 5 mol % of the initial benzoquinone. FTIR studies of the gases revealed the presence of CO, CO_2, CH_4, NH_3, and traces of ethane (Figure 2). Further, exposure of the noncondensable (liquid nitrogen) portion of these gases to a solution of cyclohexene in toluene containing palladium on activated charcoal produced cyclohexane. Hence, hydrogen was also produced during the pyrolysis.

Since benzoquinone does not possess a carbon containing more than one hydrogen, the formation of methane was rather surprising. A plausible explanation is the existence of a carbene intermediate. To substantiate its presence, the pyrolysis of the benzosemiquinone anion radical salt was carried out in a flask charged with 400–500 Torr of ethylene. FTIR analysis showed the clear presence of cyclopropane in the gaseous products (Figure 2). Cyclopropane is the expected product from the reaction between carbene and ethylene (reaction 4).[14]

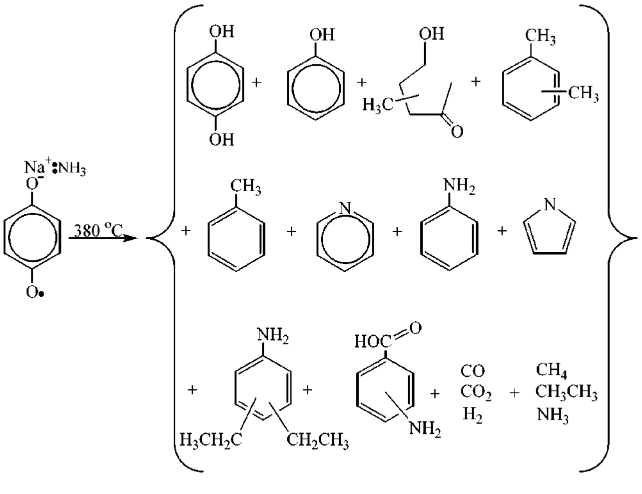


(4)

Table 1. Approximate Relative Product Ratios for the Liquids Products Formed during a Typical 380 °C, 16 h Pyrolysis of $[Na^+(NH_3)C_6H_4O_2^{\bullet-}]_{(solid)}$ Carried Out with and without a Cool Side Arm

product	percentage with side arm	percentage without side arm
phenol	90	2
hydroxymethylpentanone	4	1
xylene	3	1
toluene	1	<1
aniline	<1	<1
pyrrole	<1	<1
pyridine	<1	<1
p-aminophenol	none found	94

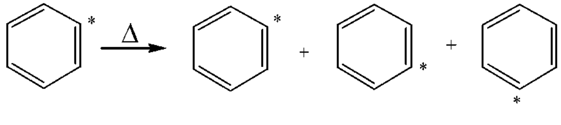
Scheme 2



A colorless liquid was collected in the sidearm. The mass of this liquid represents about 20% of the initial mass of benzoquinone used in the reaction. GC-MS analysis of this liquid revealed that it is 90% phenol (94 m/e), and this was confirmed by NMR. The other 10% is made up of hydrocarbons and nitrogen-containing compounds. The nitrogen-containing compounds produce parent peaks at m/e = 93, 67, and 79 corresponding to aniline, pyrrole, and pyridine. The hydrocarbons and oxygenated hydrocarbon compounds yield parent peaks at m/e = 92, 106, and 116. These correspond to toluene, xylene (*o*-, *m*-, and *p*-) and hydroxymethylpentanone. The percentages of these compounds vary with the exact temperature and reaction time. However, the results from a typical experiment are shown in Table 1.

A black solid remains in the bottom of the reaction flask, which accounts for the remainder (ca. 75%) of the sodium benzoquinone anion radical. This black solid is totally water-soluble and consists primarily of the sodium salts of hydroquinone ($NaC_6H_5O_2$ and $Na_2C_6H_4O_2$). Other minor constituents of this solid yield MS peaks at m/e = 149 and 137. The mass spectral patterns suggest that they are due to one or more of the isomers of diethylaniline and aminobenzoic acid. All of the products produced during the pyrolysis of $[Na^+(NH_3)C_6H_4O_2^{\bullet-}]_{(solid)}$ are shown in Scheme 2.

Scott and co-workers[15] observed that at high temperatures (over 1000 °C) [1,2-^{13}C]benzene underwent automerization, reaction 5 (where the * indicates a ^{13}C). One



(5)

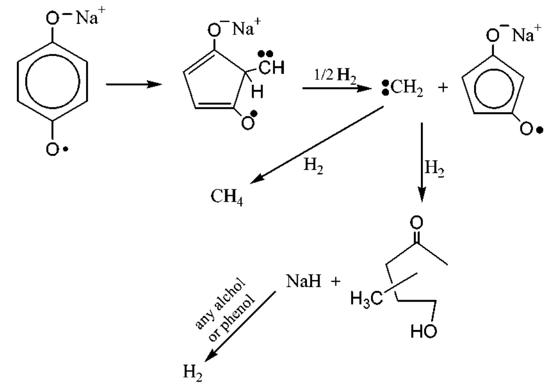
---

(11) Stevenson, C. D.; Reiter, R. C.; Ross, D. G.; Frye, D. G. *J. Phys. Chem.* **1984**, *88*, 1854.

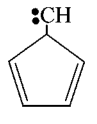
(12) Smentowski, F. J.; Stevenson, C. D. *J. Am. Chem. Soc.* **1968**, *90*, 4661.

(13) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 2nd ed.; Boston, 1968; Chapter 28.4.

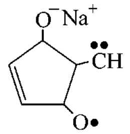
Scheme 3



of the proposed mechanisms for the rearrangement included a carbene intermediate (structure II). Since hydrogen gas is produced during the pyrolysis, the formation of a carbene that is analogous to that proposed by Scott and co-workers (structure III) would explain the



II

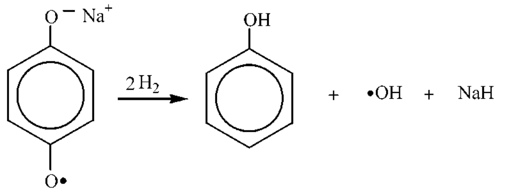


III

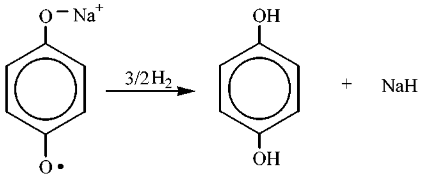
formation of a number of our observed products including methane and hydroxymethylpentanone (Scheme 3) and ethane (reaction 6).

$$CH_4 + :CH_2 \longrightarrow CH_3{-}CH_3 \qquad (6)$$

Since H_2 and carbene are observed, a likely route to hydroxymethylpentanone involving a sodium cyclopentadienone anion radical is presented in Scheme 3. The presence of hot hydrogen also accounts for the large quantities of phenol, which simply comes from the hydrogenation of benzosemiquinone, reaction 7. Hydrocarbon anion radicals are known to undergo rapid hydrogenation, forming NaH even at room temperature, see reaction 8.[16] The hydroquinone can be accounted for



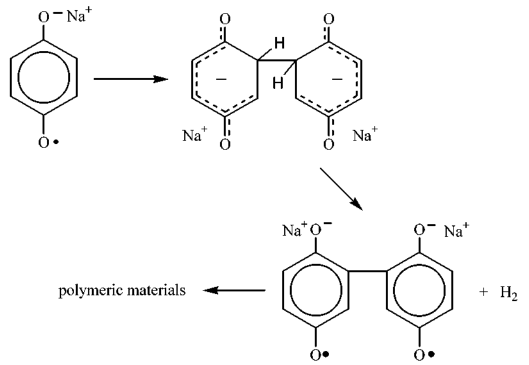
(7)



(8)

via the partial hydrogenation of the anion radical. Sodium hydride reacts with dihydroxybenzene (yielding $C_6H_4OHO^-,Na^+$), accounting for the absence of large amounts of sodium hydride left in the reaction flask. Scheme 3 and reactions 6−8 account for all of the major hydrocarbons and oxygenated hydrocarbon products observed during the pyrolysis.

Scheme 4



Since so many of the products contain hydrogen, and no more than one hydrogen exists on any carbon of benzosemiquinone, the ammonia must represent a source of hydrogen. To substantiate this, the pyrolysis was carried out using perdeuterated benzoquinone. Indeed, the pyrolysis carried out with $[Na^+(NH_3)C_6D_4O_2^{\bullet -}]_{(solid)}$ yields ND_3, ND_2H, and NDH_2 as well as CH_4. The formation of perprotiated methane proves that the ammonia is a major source of hydrogen, since no carbon had any protons bonded to it prior to pyrolysis. Substantial amounts of N_2 must have also been produced, but since it is inert and IR inactive, its presence was not confirmed. This experiment also produced several partially protiated phenols including $C_6H_4D_2O$, $C_6H_5D_1O$, $C_6H_3D_3O$, and $C_6H_2D_4O$. The formation of all four isotopic isomers of ammonia also substantiates the fragmentation of the ammonia.

Analogous pyrolysis experiments were also carried out in quartz glass at the temperatures where Scott and co-workers observed the automerization of benzene. The $[Na^+(NH_3)C_6D_4O_2^{\bullet -}]_{(solid)}$ samples were exposed to the 1100 °C temperature for only 1 h. Under these high-temperature conditions, phenol is produced at a much lower yield, ~20%, and the solid left in the bulb is not hydroquinone but is an insoluble graphitic material. Again IR revealed the formation of CO, CO_2, CH_4, and NH_3. The greatest difference between the lower and high temperature pyrolysis is the formation of large amounts of polymeric material in the latter and the complete lack of it in the former. Even lowering the reaction time to 10 min did not decrease the amount of polymeric material. At 1100 °C there is sufficient energy to allow the formation of intermolecular C−C bond formation, Scheme 4, that is analogous to that formed during the pyrolysis of the PAH anion radicals.[2]

A hot comet entering the prebiotic terrestrial atmosphere could eject materials during the pyrolysis. The contents of the cold sidearm may represent the liquid materials so ejected. To simulate the conditions where the liquids cannot escape, such as in the interior of the meteorite, experiments were carried out with the entire reaction vessel immersed in the hot (380 °C) sand bath for 16 h. The liquid products were distilled from the solid hydroquinone and hydroquinone salts. The major con-

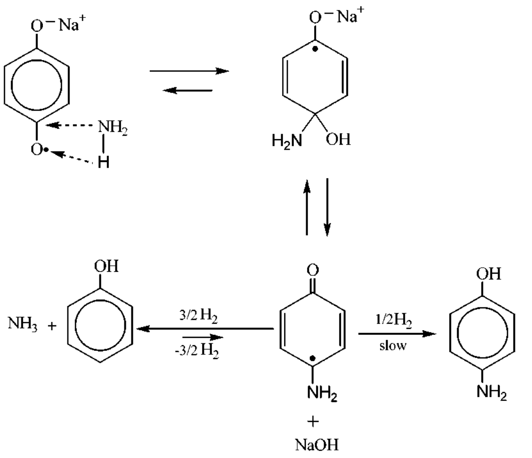
---

(14) Stevenson, C. D.; Concepcion, R.; Block, A. M. B. *J. Phys. Chem.* **1977**, *87*, 367.

(15) (a) Scott, L. T.; Roelofs, N. H.; Tsang, T. H. *J. Am. Chem. Soc.* **1987**, *109*, 5456. (b) Also see: Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235.

(16) Ichikawa, M.; Soma, M.; Onishi, T.; Tamaru, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3672.

Scheme 5



stituent of these liquids proved to be *p*-aminophenol (94%). Phenol was only a minor constituent (2%). In contrast, no *p*-aminophenol was found in the pyrolysis experiments where the liquid products could escape the hot reaction mixture. Since phenol is the major liquid product produced when the newly formed materials can escape the reaction mixture, the *p*-aminophenol must result from a reaction involving the phenol. Under these somewhat extreme conditions, the ammonia, hydrogen, and a small, but finite, amount of an intermediate may be in equilibrium in the gas phase. Hence, only if the phenol can escape can the reaction involving the intermediate forming *p*-aminophenol be avoided. These results are consistent with Scheme 5.

Summary

In contrast to the pyrolytic behavior of neutral *p*-benzoquinone, which is thermally stable up to 800 °C and is dominated by reaction 1 at more elevated temperatures, the anion radical of *p*-benzoquinone degrades at 380 °C. The thermolysis of *p*-benzoquinone yields vinylacetylene as the principal organic product,[3] while the corresponding pyrolysis of the ammonia-ligated anion radical yields phenols (Scheme 5).

Hence, it is clear that the addition of a single electron dramatically alters the thermal fragmentation pattern of *p*-benzoquinone, as a number of gases are emitted including CO, CH_4, NH_3, C_2H_6, and CO_2. Isotopic studies have shown that the N−H bonds in the ammonia, and the C−H bonds in the semiquinone, are disrupted during the semiquinone pyrolysis. The results indicate that a number of organic compounds that may be of prebiotic importance can be formed in small amounts via semiquinone pyrolysis (see Scheme 1). Unfortunately, no traces of any (hoped for) amino acids were found in the pyrolysis of the parent *p*-benzosemiquinone. The results do suggest, however, that a wide variety of organic materials may be emitted from hot semiquinones with more complex structures such as those found in the Zare study.[5]

Experimental Section

p-Benzoquinone, in 50 mL of liquid ammonia, was reduced with an equivalent of sodium metal to its anion radical in a three-neck, 250 mL, round-bottom bulb under inert (under Ar) conditions. The resulting deep blue solutions were stirred while the solvent was allowed to evaporate under reduced pressure.

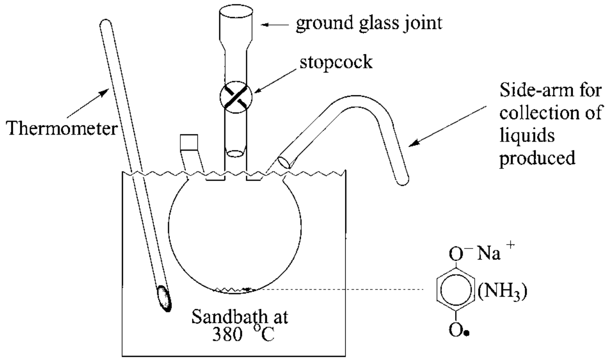


Figure 3. Apparatus used for the 380 °C pyrolysis of the $[Na^+(NH_3)C_6H_4O_2^{\bullet-}]_{(solid)}$. The liquid condensable products were collected in the sidearm. After cooling the apparatus was attached to the vacuum system via the ground glass joint.

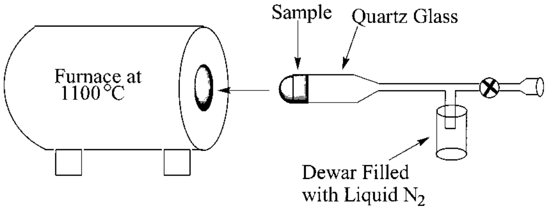


Figure 4. Apparatus used for the 1100 °C pyrolysis of the $[Na^+(NH_3)C_6H_4O_2^{\bullet-}]_{(solid)}$. The condensable products were collected in the sidearm immersed in the liquid nitrogen bath.

After the removal of all of the visible liquid ammonia, the contents of the apparatus were exposed to an active vacuum (10^{-3} Torr) to ensure the removal of all unligated ammonia. The bulb was then immersed in a sand bath and heated at 380 °C (Figure 3). After 16 h the bulb was allowed to cool to room temperature. It was then attached to a vacuum line equipped with a manometer and an IR cell. Opening the stopcock typically resulted in a pressure of 210 Torr. The glass sidearm was then sealed from the apparatus with a hand torch. The contents were subsequently dissolved in $CDCl_3$ and submitted to NMR and GC-MS analysis. The contents of the reaction bulb were exposed to air and collected.

Pyrolysis times as short as 2 h were tested, and the major products are the same but some anion radical remained in the reaction flask. Increasing the time to 16 h increased the amounts of the products and depleted the unreacted anion radical. Control experiments carried out with the starting material, benzoquinone without ammonia, did not yield any products other than sublimed benzoquinone.

A quartz apparatus was built for experiments carried out at temperatures of 1100 °C (Figure 4). The anion radical sample was prepared in the same manner as in previous experiments. A furnace was utilized to create and maintain the desired temperature of 1100 °C. Exposure to the heat source lasted only up to an hour, as a reaction was noticed instantaneously. No difference in the products was noticed upon varying the reaction time from 10 to 60 min. The apparatus, once again, had a glass sidearm that was cooled to collect any liquids produced. Hence, polymerization takes place faster than volatile products can escape the reaction vessel. This apparatus also had a stopcock attached to it to allow for FTIR analysis of the gas-phase products.

EPR spectra were recorded on a Bruker ER-200 EPR spectrometer equipped with a Bruker ER-4111 variable temperature controller. Mass spectral data were obtained on a Hewlett-Packard 6890/5973 gas chromatograph/mass spectrometer system containing a 30-m, 0.25 mm ID capillary column of methylphenyl silicone. With the exception of the hydroxymethylpentanone, the identities of all of the liquid products were confirmed by injecting the authentic materials into the GC mass spectral system and the observation of identical retention times and mass spectral patterns. The mass spectral fragmentation pattern of hydroxymethylpentanone shows the parent peak at 116 and large peaks fragmentation peaks at 101 (loss of methyl), 58, 59, and 43 m/e.

NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer. Matrix assisted LASER desorption time-of-flight mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois. The MALDI analyses showed no hint of the formation of polymeric compounds or fullerenes.

Acknowledgment. We thank the National Science Foundation for support of this work.

JO010646P