

# Thermolysis of the Benzene Anion Radical 18-Crown-6 Complex

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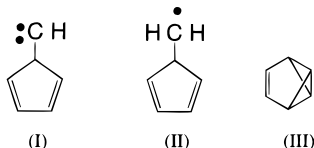
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The C–O and C–H bonds of 18-crown-6 are activated when 18-crown-6 is complexed with the potassium salt of the benzene anion radical. Evacuated glass bulbs containing the solid anion radical salt of potassium 18-crown-6 benzene anion radical were plunged into a bath at 320 °C, resulting in mini-explosions and generating a series of compounds including dioxane, 2-methyl-1,3-dioxolane, divinyl ether, hydrogen, methane, and 15-crown-5. Deuterium labeling studies proved that all of these compounds originated from the 18-crown-6. Further, these labeling studies were an aid in discerning the mechanism of the decomposition. Benzene, 1,4-cyclohexadiene, and cyclohexene were also generated. The last two originated from the reaction of the anion radical of benzene with hydrogen.

## Introduction

The addition of a single electron to the  $\pi$  cloud of polyaromatic hydrocarbons (PAHs) activates the C–C and C–H bonds, rendering their alkali-metal solid anion radical salts susceptible to thermal decomposition at temperatures just above 100 °C.<sup>1,2</sup> This low-temperature thermal decomposition liberates H<sub>2</sub> and methane along with the formation of dimers, trimers, and higher polymers and is analogous to the very high temperature pyrolysis of PAHs where H<sub>2</sub> is also liberated<sup>3</sup> and fullerenes are formed.<sup>4</sup> Hence, PAHs can be polymerized only at temperatures above the softening point of Pyrex glass, while thermolysis following single-electron reduction is the only method for the low-temperature polymerization of PAHs.

The hydrogen results from an anionic polymerization of the anion radical, and the methane is believed to come from the formation of an intermediate carbene followed by its capture of H<sub>2</sub>.<sup>2,5</sup> The proposed mechanism, involving carbenes, is consistent with Scott's and co-worker's results concerning their 900 °C pyrolytic automerization of naphthalene, regarding which they conclude "the thermal automerization of naphthalene probably occurs by reversible formation of benzofulvene, either via carbenes or by direct dyotropic rearrangements."<sup>6</sup> However, recent experiments by Hopf et al.<sup>7</sup> showed that benzene will automerize at temperatures as low as 800 °C when hydrogen serves as the carrier gas. Their work strongly suggests that the mechanism actually involves a radical-driven process where I as opposed to II or III is involved



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in the automerization mechanism.<sup>6</sup> The extreme interest in the high-temperature behavior of aromatic molecules,<sup>6–15</sup> is in contrast with the analogous lower temperature behaviors of their anion radicals<sup>3,5</sup> motivated us to investigate the thermolysis of the anion radical of the most common of all aromatic systems: **benzene**.

Unfortunately, the solid (solvent-free) anion radical salt of benzene is not stable toward return of the electron back to the alkali metal.<sup>16a</sup> This problem can be circumvented by addition of 18-crown-6 to the system.<sup>16</sup> The encapsulation of the metal cation in the crown ether thermodynamically disfavors electron return and renders

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$K^+\{18C6\}C_6H_6^{\cdot-}$  (solid) kinetically and thermodynamically stable under inert conditions.<sup>16</sup> We did not anticipate thermolysis products arising from the crown ether itself, as the electron resides totally on the benzene system and 18-crown-6 and 18-crown-6 containing alkali-metal cations resist decomposition at the temperatures of our thermolysis studies.<sup>17</sup>

### Results and Discussion

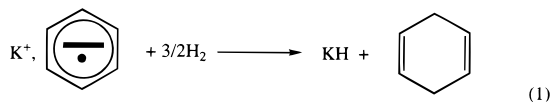
In a typical experiment involving 1.9 millimol (50.7 mg) of solid potassium 18-crown-6 benzene anion radical salt heated at 320 °C for 30 s, 0.73 millimol of noncondensable gases, which passed through a liquid-nitrogen-cooled U-tube were evolved. A small amount (4.4 mg) of light condensable liquids were found in the U-tube, and 41.0 mg of a black sooty polymeric material was left in the reaction flask.

The noncondensable gases resulted in a pressure of 10.75 millibar in the vacuum apparatus. Upon exposure of the gas to the Cu/CuO furnace, the pressure dropped by 59.6% (to 4.33 millibar), and the condensable product of the reaction in the furnace proved to be water ( $CuO + H_2 \rightarrow H_2O + Cu$ ). Thus, 59.6% (0.435 millimol or 0.87 mg) of the original gas was hydrogen. The hydrogen generated from the pyrolysis was also exposed to a stirred mixture of cyclopentene containing palladium on activated carbon in toluene. This resulted in the formation of cyclopentane. FT-IR analysis of the evolved gas proved that the remaining 40.4% (0.29 millimol or 4.6 mg) was methane.

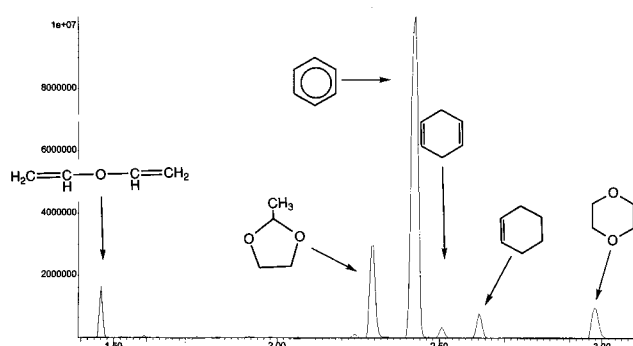
The amount of condensable material, noncondensable gases, and polymeric soot is sufficient to provide mass balance. Further, this experiment, using various amounts of solid potassium 18-crown-6 benzene anion radical salt, has been performed more than 20 times with nearly identical results. Hence, this reaction is very reproducible.

When the same pyrolysis was carried out with perdeuterated benzene replacing benzene, a similar mixture of gases was obtained. Exposure of these noncondensable gases to the cyclopentene mixture did not yield the expected dideuterated cyclopentane but again resulted in cyclopentane. Further, the resulting methane proved to be  $CH_4$  with no detectable traces of deuterated methane. Surprisingly, both the hydrogen and the methane apparently came from the 18-crown-6.

Condensable material was found in the liquid-nitrogen-cooled U-tube resulting from the pyrolysis of  $K^+\{18C6\}C_6H_6^{\cdot-}$  (solid). GC analysis proved this mixture to contain of six constituents (Figure 1). The most abundant constituent (retention time 2.41 min) proved to be benzene. This must have resulted from ejection of its antibonding electron. Consistent with this was the presence of both 1,4-cyclohexadiene and cyclohexene in the mixture (retention times 2.51 and 2.62 min), which must have resulted from the reaction of the benzene anion radical with  $H_2$  (reaction 1).<sup>2,18</sup> When  $K^+\{18C6\}$ -



$C_6D_6^{\cdot-}$  (solid) was substituted for  $K^+\{18C6\}C_6H_6^{\cdot-}$  (solid), the analogous products proved to be 1,2,3,4,5,6-hexadeuterio-1,4-cyclohexadiene and 1,2,3,4,5,6-hexadeuteriocyclohexene.



**Figure 1.** GC trace of the low-molecular-weight materials produced by the pyrolysis of potassium 18-crown-6 benzene anion radical. These compounds were caught in the liquid-nitrogen-cooled U-tube.

clohexene. In fact, these two materials and perdeuterated benzene were the only products found to contain deuterium resulting from any of the  $K^+\{18C6\}C_6D_6^{\cdot-}$  (solid) studies, as all of the remaining products resulted from the decomposition of the crown ether.

Evidently the high thermal energy coupled with the Coulombic pull of the potassium cation on the odd electron results in the expected ejection of the electron from the benzene. However, before it can be recaptured by  $K^+$ , the electron is "intercepted" by the crown ether. The electron capture by the crown is probably due to the electropositive nature of the oxygen atoms that is induced by the encapsulated potassium cation. The crown, now containing an extra electron, is in the form of a very short lived anion radical. The 18-crown-6 anion radical is a  $\sigma$  radical, which is known to cleave to an anion and a neutral radical.<sup>19</sup> Further, ether linkages in anion radicals are known to cleave in a similar manner (Scheme 1).<sup>20</sup>

All of the products except benzene and the hydrogenated benzenes (Figure 1) result from the dismemberment of the 18-crown-6 (Scheme 1). The use of perdeuterated benzene did not alter the isotopic composition of any of these decomposition products, as evidenced by both GC-mass spectral (Figure 1) and  $^1H$  NMR analysis. Attack of the methylene radical on the second oxygen followed by cleavage of the carbon-second oxygen bond results in dioxane, which is found at retention time 2.98 min in Figure 1. If water is simultaneously lost, the result is the formation of divinyl ether, which was also found (retention time of 1.46 min in Figure 1). The peak at retention time 2.29 min (Figure 1) proved to result from 2-methyl-1,3-dioxolane, which simply results from 1,2-hydrogen migration followed by attack of the methine carbon radical upon the oxygen atom. Note that the fragment left after the departure of dioxane, 2-methyl-1,3-dioxolane, or divinyl ether can undergo an analogous loss of another molecule.

No water was found in the reaction products. However, it would react with the potassium hydride (formed via reaction 1) and any potassium metal to yield hydrogen

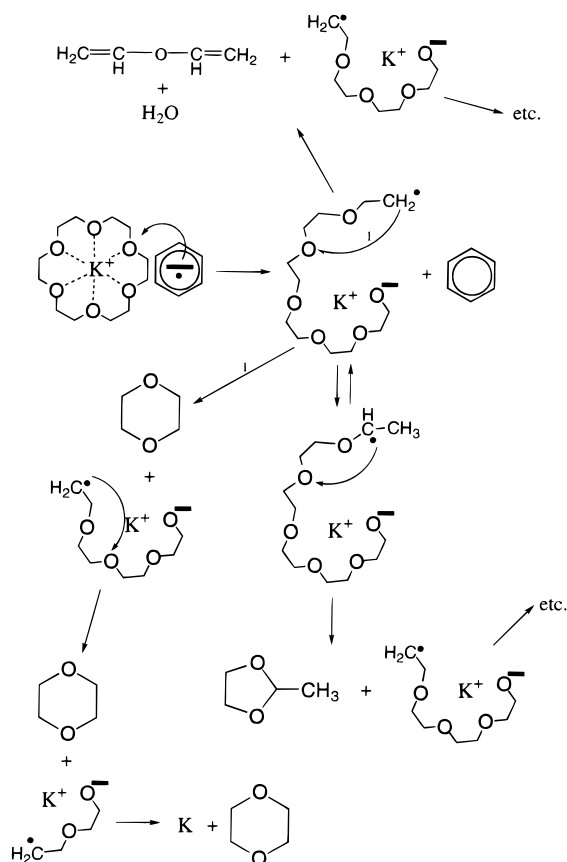
(17) 18-Crown-6 samples that were dissolved in tetrahydrofuran saturated in potassium iodide, followed by solvent removal, resisted any thermal decomposition at 320 °C.

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Scheme 1



gas, which is observed. Once the crown ether is broken, some electron return to the exposed  $K^+$  would be expected, thus providing a mechanism for the generation of potassium metal.

The granular black sooty material, which remained in the reaction flask after the pyrolysis, was exposed to  $I_2$ . The fast atom bombardment mass spectra and laser desorption mass spectra of the  $I_2$ -quenched soot shows the presence of only high-molecular-weight material. After the addition of  $I_2$  (in ether) and treatment with sodium thiosulfate to remove the excess iodine, the soot was extracted with toluene for 12 h in a Soxhlet apparatus. Submission of this toluene extract to laser desorption mass spectral analysis revealed the presence of a vast number of high-molecular-weight polymeric compounds with prominent  $m/e$  values of 1104, 856, and 582. These heavy materials are expected from the formation of polyethers. Closure of the radical produced after the initial dioxane formation (Scheme 1) would produce some 15-crown-5. Indeed, prominent peaks at  $m/e$  220 (the molecular weight of 15-crown-5) and 204 (loss of O) suggests the presence of 15-crown-5 in the toluene extracts.

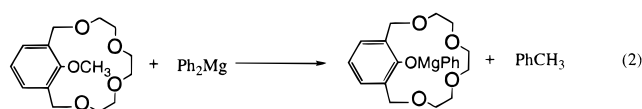
It should be noted that the pyrolysis described above at 320 °C can be carried out under milder conditions with similar results but with fewer condensable products. Benzene makes up a larger portion of the condensable products at lower pyrolysis temperatures. When the pyrolysis is carried out for 20 s at 200 °C, benzene and a small amount of cyclohexene (in a 17:1 ratio) are the only products caught in the U-tube.

The experiments described above were repeated using naphthalene and perdeuterated naphthalene in place of the benzene, and identical results were obtained. Again

the same products were obtained from the 18-crown-6 and the  $CH_4$  and  $H_2$  were found to come from the crown as opposed to the naphthalene.

The addition of electrons to polyaromatic hydrocarbons results in thermal C-C and C-H bond activation;<sup>1,2</sup> however, if 18-crown-6 is present, there is more bond activation in the crown than in the PAH. The remarkable affinity that the macrocyclic ethers have for metal cations is of fundamental importance in coordination chemistry, and the presence of a crown ether assists the electron transfer from a metal to an acceptor ( $M + \text{crown} + A \rightarrow M^+ - \text{crown} - A^-$ ). The thermally induced return of the electron is, on the other hand, a much more involved process.

It has been previously observed by Bickelhaupt and co-workers<sup>21</sup> that (2-methoxy-1,3-xylylene)-15-crown 4 undergoes a rather efficient ether cleavage in the presence of organomagnesium reagents at 100 °C (reaction 2). This reaction does not involve cleavage of the outer



perimeter of the crown ether structure, but it does show that the ether linkages can be activated in the presence of organic anions. Richey et al.<sup>22</sup> did, however, observe cleavage of one of the short bridges of 2,1,1-cryptand to vinyl and (metalated) hydroxyethyl groups, when solutions of the cryptand were exposed to dialkylmagnesium compounds. It seems likely that we are observing an analogous activation of the ether linkages in the 18-crown-6 in the presence of the very basic benzene anion radical.

The liberation of methane and hydrogen were expected, as these are typically the major gas-phase products produced during anion radical pyrolysis.<sup>2,5,23</sup> The hydrogen is lost upon polymerization of the anion radical. The new carbon-carbon bonds replace the carbon-hydrogen bonds in the monomer.<sup>2,5,23</sup> The methane is believed to come from the hydrogenation of a radical ( $\cdot CH_2CH_2O - - + H_2 = CH_4 + \cdot CH_2O - -$ ) or via the capture of hydrogen by a carbene intermediate.<sup>2,5,23</sup>

## Experimental Section

The anion radical salts were generated under high-vacuum conditions via reduction of neutral benzene on a freshly distilled potassium mirror. The benzene, which was dried over sodium-potassium alloy, served as the solvent.<sup>15</sup> After complete reduction, the dark-colored anion radical solutions were poured into an evacuated round-bottom Pyrex bulb, and excess benzene was removed under reduced pressure while the contents of the bulb were stirred magnetically. The remaining solid anion radical salt was then exposed to an open vacuum for several more hours to complete the solvent removal.

The pyrolysis studies were carried out by plunging the bulb containing the solid anion radical salts into a hot (320 °C) sand bath. This procedure results in an apparent explosion of the salt and the generation of a puff of smoke. The bulb containing

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the pyrolyzed material was then connected to the high-vacuum system. The temperature of the sand bath was monitored with a nickel–chromium vs nickel–aluminum thermocouple by Omega (–200–1250 °C).

The noncondensable (at liquid-nitrogen temperatures) gases were exposed to a 300 °C Cu–CuO furnace. This resulted in a pressure drop due to the oxidation of the H<sub>2</sub> to form water, which was collected in a U-tube. The water produced in the furnace was caught in the adjoining U tube, which was immersed in liquid N<sub>2</sub>. H<sub>2</sub> and D<sub>2</sub> discrimination was carried out by replacing the NMR tube with a bulb containing cyclopentene with the hydrogenation catalyst. In separate experiments mixtures of methane and hydrogen were injected into the system to verify that the hot CuO would selectively oxidize the H<sub>2</sub>, leaving the CH<sub>4</sub>. This vacuum system was fitted with a 10 cm gas IR cell, allowing us to take an IR (Nicolet 5SXC FTIR spectrometer) sample at any time.

After completion of the pyrolysis, I<sub>2</sub> and ether were distilled into the bulb containing the reaction mixture. This was done to oxidize any reactive anionic material. It should be noted that the black sooty material generated via the pyrolysis reacts

explosively toward air prior to I<sub>2</sub> reoxidation. This explosive nature is probably due to the presence of highly reactive anionic living polymers.<sup>23</sup> After reoxidation, the ether and I<sub>2</sub> were removed under reduced pressure, and the solids were extracted with toluene. Both the toluene-soluble and toluene-insoluble materials were submitted to matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS) analysis.

The liquid-nitrogen-cooled U-tube was sealed from the line on both sides. The tube was then broken open under chilled conditions, and either CDCl<sub>3</sub> (for NMR analysis) or dodecane (for GC–mass spectral analysis) was added. The NMR spectra were recorded on a Varian Mercury 400 MHz instrument, and the GC mass spectral data were collected on a Hewlett-Packard HP 5890 GC system connected to a Hewlett-Packard 5973 mass selective detector.

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