J. Org. Chem. **1997,** *62,* 2193−2197

Thermal and Laser Pyrolysis of Hydrocarbon Anion Radicals

Cheryl D. Stevenson,*[†] Charles V. Rice,[†] Paul M Garland,[†] and Brian K. Clark[‡]

Departments of Chemistry and Physics, Illinois State University, Normal, Illinois 61790-4160

Received August 1, 1996[⊗]

The solid anion radical salts resulting from the reductions of naphthalene, pyrene, perylene, benzo[*k*]fluoranthene, and biphenyl with lithium, cesium, and potassium metals were either pyrolyzed at 200−380 °C or irradiated with a pulsed frequency doubled Nd:YAG laser (532 nm wavelength). For both the pyrolytic and laser photolytic studies the only volatile products were hydrogen and methane. The hydrogen originated from the anionic polymerization of the anion radical. Evidence is presented that suggests that the methane results from a carbene intermediate, which in turn reacts with the H_2. Consistent with the H_2 formation, MALDS mass spectral analysis revealed the presence of dimers, trimers, and higher polymers of the polyaromatic hydrocarbon in the remaining nonvolatile products. There were considerably fewer low molecular weight oliomers produced via the laser photolysis than via the thermolysis.

Introduction

Some of the most kinetically and thermodynamically stable organic materials are represented by the polycyclic *aromatic* hydrocarbons (PAHs). However, they will liberate hydrogen under very high temperature pyrolysis conditions.[1] It would seem reasonable that the addition of an antibonding electron to these systems would result in the formation of anion radicals that would be less thermally stable due to the general bond order decrease. However, under inert atmospheres, these anion radicals are both kinetically and thermodynamically quite stable, in either solution or the solid state.[2] Just like their neutral analogs, solid and tetrahydrofuran (THF)-solvated PAH anion radical salts have persisted for years at ambient temperatures on our shelves. The thermodynamic stability of the solid and solvated PAH anion radicals is accounted for by their large crystal lattice and solvation enthalpies.[2]

A number of more complex solvated hydrocarbon anion radicals do undergo spontaneous chemical changes at ambient temperatures. For example, the anion radical of *cis*-stilbene spontaneously rearranges to the trans isomer,[3] and the anion radical of cyclooctatetraene dimerizes to form the [16]annulene anion radical.[4] Despite the variety of possible thermal anion radical rearrangements and decompositions, there have been no such reports for the PAH anion radical systems. Here, we report on the thermal and laser photolytic decomposition of the solid naphthalene anion radical salt (e.g., $K^+C_{10}H_8{}^{\bullet -}{}_{(s)}$).

Hydrogen gas from the pyrolysis of PAHs was discovered over a half a century ago,[1a] and recently it was discovered that sufficient thermal energy is added to gas-phase naphthalene at ∼1000 °C to get C−H bond cleavage and C_{60} formation.[5] Further, the initial synthesis of C_{60} was carried out by Kroto and co-workers[6] via the irradiation of a graphite target with a Nd:YAG laser beam. Upon noting these two experiments, it occurred to us that the addition of antibonding electrons to polyaromatic hydrocarbons could significantly reduce bond order and make the bond cleavage much more thermally accessible. It isn't until temperatures much higher than the softening point of Pyrex glass that neutral PAHs yield anything other than hot PAH's upon thermolysis. Other than a single report from our laboratory almost a decade ago involving anion radical ammonia complexes,[7] there have been no reports concerning the chemistry of anion radical pyrolysis. Further, there are no reports concerning the chemistry of laser photolysis of anion radicals.

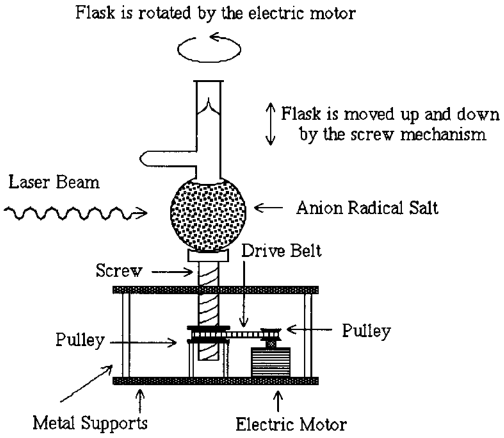


Figure 1. Support platform used to expose the anion radical salt to the laser beam. Because the position of the laser beam is fixed, the bulb is rotated by the electric motor and moved vertically by the screw mechanism.

Experimental Section

The anion radical salts were generated under high vacuum conditions via reduction of the neutral PAH with a stoichiometric amount of lithium, potassium, or cesium metal. THF, which was dried over sodium−potassium alloy, served as the solvent. After complete reduction, the dark colored anion

---

[†] Department of Chemistry.

[‡] Department of Physics.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1997.

(1) (a) Tilicheev, M. D.; Shchitikov, V. K. *Chem. Zentrbl. I* **1937**, 4583. (b) Kinney, C. R.; del Bel, E. *Ind. Eng. Chem.* **1954**, *46,* 548.

(2) (a) Stevenson, C. D.; Schock, L. E.; Concepcion, R.; Peterson, R. *J. Phys. Chem.* **1985**, *89*, 175. (b) Stevenson, C. D.; Schock, L. E. *J. Am. Chem. Soc.* **1983**, *105*, 3742. (c) Stevenson, C. D.; Schock, L. E.; Reiter, R. C. *J. Phys. Chem.* **1983**, *87*, 4004.

(3) Wang, H.; Levin, G.; Szwarc, M. *J. Am. Chem. Soc.* **1977**, *99*, 2642.

(4) Stevenson, C. D.; Burton, R. D.; Peters, S. J.; Reiter, R. C. *J. Org. Chem.* **1993**, *58*, 5838.

(5) Taylor, R. Langley, G. J.; Kroto, H. W.; Walton, D. R. M. *Nature* **1993**, *366*, 728.

(6) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318,* 162.

(7) Stevenson, C. D.; Espe, M. P.; Emaluelson, T. *J. Org. Chem.* **1985**, *50*, 4289.

S0022-3263(96)01487-9 CCC: $14.00

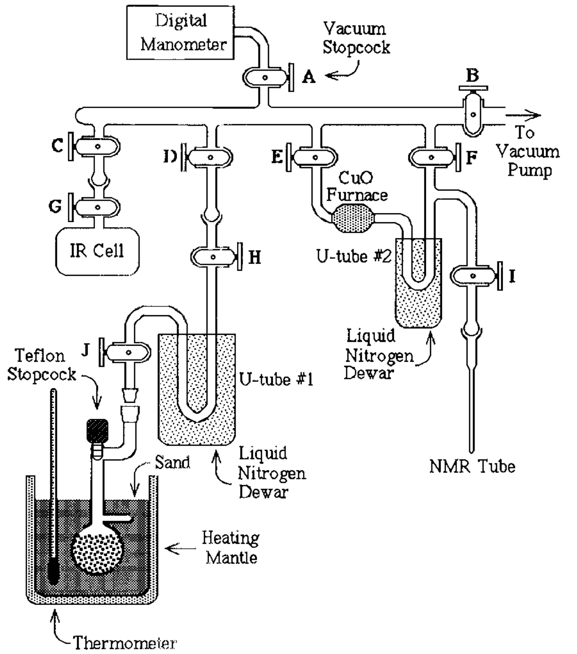
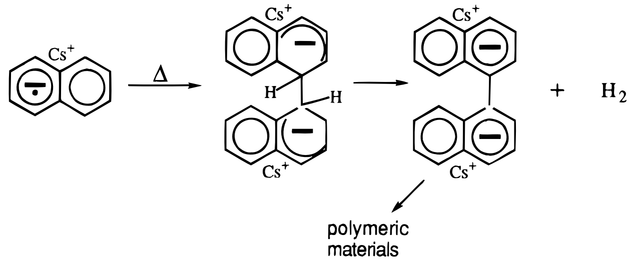
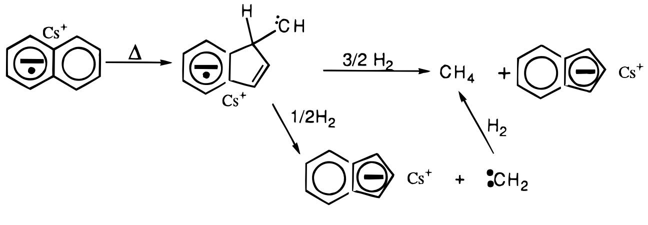


Figure 2. Illustration of the apparatus used for analyses of the gases resulting from the pyrolysis and laser photolysis. After laser irradiation, a Teflon stopcock was attached above the break seal and the bulb connected to the vacuum line. The break seal was broken with an iron bar, and the stopcock was opened, allowing the volatile products to enter the vacuum line.

Scheme 1



Scheme 2



radical solutions were poured into an evacuated round-bottom Pyrex bulb, and the THF was removed under reduced pressure while the contents of the bulb were stirred magnetically. This left a coating of the solid anion radical salt on the walls of the bulb. The solid anion radical salt was then exposed to an open vacuum for several more hours to complete the solvent removal. D_2O was added to some of these samples, and the D_2O solutions were then submitted to NMR analysis to verify the absence of THF as previously described.[8]

The bulbs were placed on the support platform, Figure 1, which enabled most of the anion radical salt to be exposed to the stationary laser beam by means of the screw mechanism.

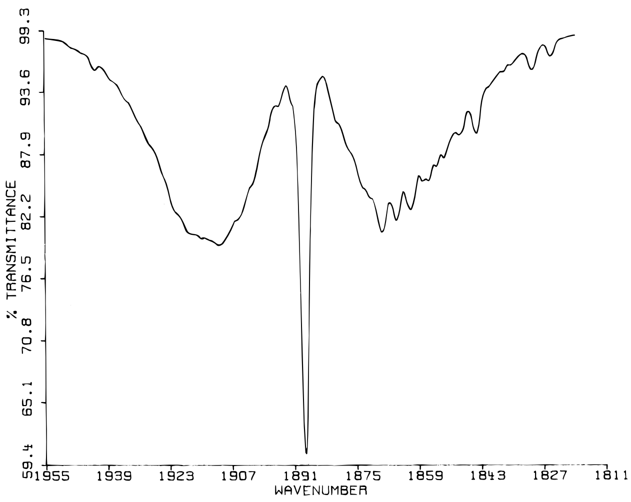


Figure 3. Gas-phase FT-IR spectrum of the reaction product that was frozen out at −142 °C resulting from the 380 °C pyrolysis of $Cs^+C_{10}H_8^{\bullet -}{}_{(solid)}$ under 530 mm of ethylene. The strong peak at 1444 cm^{-1} is due to a CH_2−CH_2 bending mode in cyclopropane (see: Pinchas, S.; Lauticht, I. *Infrared Spectra of Labelled Compounds*; Academic Press, Inc.: New York, 1971; p 80).

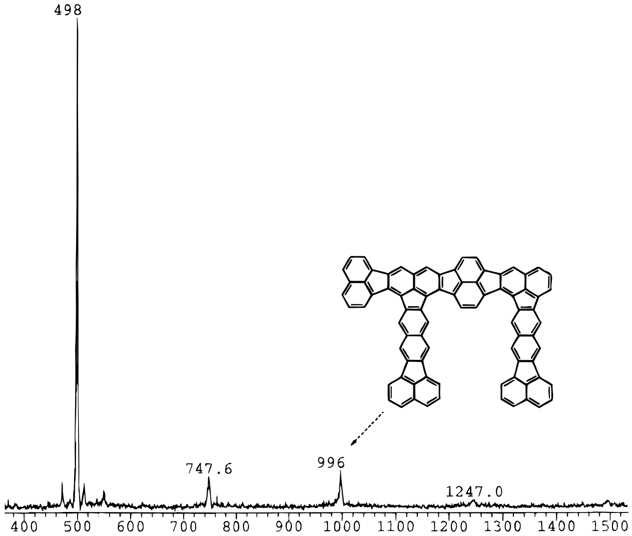


Figure 4. Matrix-assisted laser desorption mass spectrum of the solid products resulting from the static 380 °C pyrolysis of the cesium salt of benzo[*k*]fluoranthene anion radical solid salt. The structure shown or, more likely, a mixture of its isomers is the most likely material to give rise to the peak at $m/e = 996$.

The laser photons were generated using a Spectra Physics Quanta-Ray DCR-11-3 pulsed Nd:YAG laser with a HG-2 frequency doubling unit (Type II crystal). The wavelength of the laser beam was 532 nm wavelength, and each pulse contained 150 mJ of energy. The pulse length was either 2 or 200 ns.

After the laser irradiation was complete, a stopcock was attached above the break seal and the apparatus connected to the high vacuum system through a U-tube, which was cooled in liquid nitrogen, Figure 2. After the line was pumped down to about 10^{-6} Torr, the stopcock separating the bulb and the high vacuum system was opened and the break seal was broken. The pressure in the vacuum system was monitored with a Fluid Precision, Inc., capacitron pressure gauge to an accuracy of ±0.01 Torr. The final pressures ranged from 20 to 100 Torr. From the known volume of the vacuum system, the number of moles of noncondensable gases that passed through the liquid nitrogen cooled U-tube was obtained. In

---

[8] (a) Stevenson, C. D.; Wiedrich C. R.; Clark, G. *J. Phys. Chem.* **1981**, *85*, 374. (b) Stevenson, C. D.; Zigler, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 6558.

[9] Pinchas, S.; Laulicht, I. *Infrared Spectra of Labelled Compounds*; Academic Press: New York, 1971; p 67.

this system (Figure 2) 1 mmol of gas produces a pressure of about 150 Torr at 298 K.

The pyrolysis studies were carried out by simply heating the bulb containing the solid anion radical salts in a sand bath. This bulb containing the pyrolized material was then connected to the high vacuum system in an identical manner. The temperature of the sand bath was monitored with a nickel−chromium vs nickel−aluminum thermocouple by Omega (−200 to +1250 °C). Only the cesium salt of naphthalene was studied, as electron transfer back to the metal is absent with this case.

The noncondensable (at liquid nitrogen temperatures) gases were exposed to a 300 °C Cu−CuO furnace, Figure 2. This resulted in a pressure drop due to the oxidation of the H_2 to form water. In separate experiments mixtures of methane and hydrogen were injected into the system to verify that the hot CuO would selectively oxidize the H_2 leaving the CH_4. This vacuum system was fitted with a 10 cm gas IR cell, allowing us to take an IR sample at any time.

After completion of the pyrolysis or laser photolysis, I_2 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 a black sooty material is generated via the pyrolysis or laser photolysis, and it reacts explosively toward air prior to I_2 reoxidation. After reoxidation, the ether and I_2 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 mass spectroscopy (MALD-MS) analysis. Nothing, not even neutral PAH, was recovered in the liquid nitrogen cooled U-tube.

After the pyrolysis of the $Cs^+C_{10}H_8^{\bullet-}$ in an atmosphere of ethylene, the reaction flask and U-tube no.1 (Figure 2) were placed in a bath of solid−liquid methylcyclopentane (−142 °C). The entire system was then evacuated, leaving only condensable (at −142 °C) materials. The melting point of ethylene is −169 °C and that of cyclopropane is −128 °C. Thus, the −142 °C U-tube will trap (freeze) cyclopropane and not ethylene under vacuum conditions. Later, warming of the U-tube and reaction flask to room temperature allowed expansion of the condensable gas into the IR cell. Only cyclopropane was observed upon IR analysis.

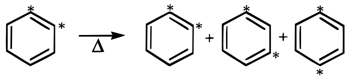
Results and Discussion

Pyrolysis Experiments with Naphthalene Anion Radical. When 0.58 g (4.5 mmol) of solid cesium naphthalene anion radical ($Cs^+C_{10}H_8^{\bullet-}{}_{(solid)}$) was heated at 380 °C for 8 h, 2.7 mmol of noncondensable gases were evolved, which resulted in a pressure of 38.6 mbar in the vacuum apparatus shown in Figure 2. Upon exposure of the gas to the Cu/CuO furnace, the pressure dropped by 80% (to 7.72 mbar), and the condensable product of the reaction in the furnace was collected in an NMR tube. ^1H NMR in deuteriated acetone/tetramethylsilane revealed this product to be water, which resulted from CuO + $H_2 \rightarrow H_2O$ + Cu. Thus, 80% of the original gas was hydrogen. This, in conjunction with the polymeric sooty material left in the original reaction flask, suggests the polymerization described in Scheme 1.

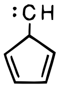
Infrared spectroscopy proved that all of the remaining gas was methane. In order to be certain that the naphthalene anion radical salt was the source of the methane, pyrolysis studies were carried out using perdeuteriated naphthalene. Indeed, an IR spectrum of the gaseous products revealed perdeuteriated methane.[10] Since each carbon in naphthalene only has either one or zero hydrogens attached, it is somewhat surprising that a carbon product with four hydrogens was produced. Certainly, some C−C bonds were being broken in the naphthalene. A reasonable mechanism for the formation of CH_4 that has come to our attention, via the work of Scott and co-workers,[11,12] involves the formation of a carbene. The liberated carbene would react with the hydrogen, which has been shown to be present, to give methane, reaction 1.

$$:CH_2 + H_2 \rightarrow CH_4 \qquad (1)$$

Scott and co-workers[11] observed the high temperature (over 1000 °C) automerization of [1,2-^{13}C]benzene, reaction 2. One of the suggested mechanisms for this rearrangement included a carbene intermediate (structure I), and the other mechanism involved benzvalene (structure II). The formation of an analogous carbene (structure III) during the anion radical pyrolysis could explain the observed formation of methane, Scheme 2.

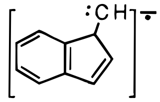


(2)



I

II



III

Thus, the anion radical depicted in structure III would react with hydrogen and lose the carbene moiety to yield the stable benzocyclopentadienyl anion, Scheme 2.

The granular black sooty material that remained after the pyrolysis yielded a single broad (line width ≈ 10 G) EPR line at $g = 2.00$ that persists even after exposure of the soot to I_2. This signal is consistent with that commonly observed from living polymers.[12] This is further consistent with the fact that the fast atom bombardment mass spectra and laser desorption mass spectra of the I_2 quenched soot shows the presence of 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 24 h in a Soxhlet. Submission of this toluene extract to laser desorption mass spectral analysis revealed just four peaks at 462, 500, 613, and 750 m/e units, respectively. The 750 peak corresponds to six naphthalene units minus 18 m/e units. This is consistent with six naphthalene units joined with the loss of a CH_2 and four hydrogen atoms. It could also be due to the joining of six naphthalenes with the loss of 18 hydrogens. The m/e = 500 peak probably comes from a naphthalene tetramer with the loss of 12 hydrogens. The 613 peak is nicely consistent with 500 plus 127 (a naphthalene − 1H) minus a CH_2 group. The peak at 462 m/e cannot originate from multiples of C_{10} moieties and necessarily requires disruption of the naphthalene skeleton and loss of carbons. Keep in mind that most of the soot was insoluble and presumably consisted of material with molecular weights even higher than 750.

---

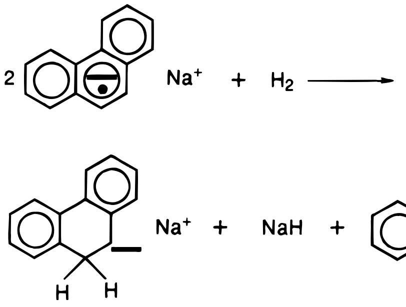
[10] (a) Scott, L. T.; Roelofs, N. H.; Tsang, T. H. *J. Am. Chem. Soc.* **1987**, *109*, 5456. (b) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692.

[11] Also see: Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235.

[12] (a) Stevenson, C. D.; Concepcion, R.; Block, A. M. B. *J. Phys. Chem.* **1977**, *81*, 367.(b) Smentowski, F. J.; Stevenson, C. D. *J. Phys. Chem.* **1970**, *74*, 2525. (c) Szwarc, M. In *Ions and Ion Pairs in Organic Reactions;* Szwarc, M., Ed.; John Wiley and Sons: New York, 1974; Vol. 2, Chapter 4.

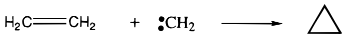
Toluene extracts of the polymeric soot did not yield a ^{133}Cs NMR signal. However, water extracts did yield a strong ^{133}Cs NMR signal at 0.0 ppm, relative to CsI in D_2O. Thus, the NMR data and the mass spectral data show no sign of either C_{60} or an endohedral C_{60-82}.

Replacement of the naphthalene with $C_{10}D_8$, as expected, yielded CD_4 as the only IR active gas. We attempted to capture the CH_2 with D_2 by carrying out the pyrolysis in the presence of D_2, but the anion radical reacted with the D_2 to form neutral deuterated naphthalene prior to thermolysis. This was not unexpected, because both the THF-solvated and dry anion radical salts are known to readily take up H_2 as shown for the phenanthrene system below.[13]



(3)

As further evidence for the formation of a carbene, we carried out the pyrolysis experiment on a 1:1 mixture of $Cs^+C_{10}D_8^{\bullet-}{}_{(solid)}$ and $Cs^+C_{10}H_8^{\bullet-}{}_{(solid)}$. This experiment did produce CH_2D_2 as well as the expected CHD_3 and CDH_3, which is consistent with −CD and −CH moieties being trapped by the D_2 and H_2 produced during the polymerizations, Scheme 1. Of course, many mechanisms are consistent with the these observations. However, when the pyrolysis was carried out in a flask charged with 530 torr of ethylene, cyclopropane (Figure 3) was found to be present in the gaseous products. Cyclopropane is the expected product from the reaction between carbene and ethylene, reaction 4.



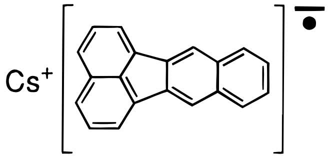
(4)

Laser Photolysis Experiments. The irradiation of $Cs^+C_{10}H_8^{\bullet-}{}_{(solid)}$ with 2 ns pulses using the apparatus shown in Figure 1 produced a high-temperature plasma, which was observed where the laser beam struck the salt. After the laser irradiation was complete, a stopcock was attached above the break seal and the apparatus connected to the vacuum line, Figure 2. The break seal was broken (under vacuum) with a small magnetic bar, and the products were analyzed using the procedure described in the Experimental Section.

As in the case of the pyrolysis experiments, the analysis of the gases showed the presence of both hydrogen and methane (95:5) but with a larger relative amount of hydrogen. Again, EPR also indicated the existence of living polymer in the soot, and ^{13}C and ^{133}Cs NMR in toluene-d_8 did not yield signals other than those for the solvent peaks. As with the thermolysis results, the same high molecular weight materials were detected by MALD-MS. Mass spectra of the toluene-soluble material did not show the low molecular weight material observed in the thermolysis.

When the duration of the laser pulses was increased by 2 orders of magnitude (200 ns), a brilliant purple plasma was seen. The longer pulses keep the anion radical at the plasma temperatures for a longer time, allowing more chemistry to occur. To prevent damage to the flask, the laser beam was focused on an interior carbon rod coated with the anion radical salt. However, MALD-MS indicted that the PAH was destroyed to such an extent that no polymerization products were observed. In fact, the only signals seen in the mass spectra are those for Cs^+ ion and Cs_2I^+ ion at 393.

Other Hydrocarbon Anion Radicals. Similar pyrolysis (200−380 °C) and laser photolysis studies were also carried out using the anion radicals of pyrene, perylene, benzo[*k*]fluoranthene, and biphenyl reduced with lithium, cesium, and potassium metals. In all 24 cases, both H_2 and methane were the only noncondensable gases formed, and the H_2:CH_4 ratio increased with the severity of the reaction conditions. The MALD-MS analysis of the soot produced from the 290 °C pyrolysis of the potassium pyrene anion radical salt exhibited peaks corresponding to the pyrene monomer ($C_{16}H_{10}$, $m/z = 202$), a dimer minus a CH_2 and two hydrogens ($C_{31}H_{16}$, $m/z = 388$), and a trimer minus a CH_2 and four hydrogens ($C_{47}H_{24}$, $m/z = 588$). MALD mass spectra of the soot from the 380 °C pyrolysis of the cesium benzo[*k*]fluoranthene anion radical (structure IV) exhibited peaks at 500 corresponding to two monomer units minus four hydrogens, 748 corresponding to three monomer units minus eight hydrogens, and 996 corresponding to four monomer units minus 12 hydrogens, Figure 4. Crowley et al.[14] recently reported that the pyrolysis of the benzo[*k*]fluoranthene neutral molecule also yields a species of mass ca. 750 along with C_{60}.



IV

Conclusions

The laser photolysis and thermal pyrolysis of a variety of hydrocarbon anion radicals in the solid state yield hydrogen and methane as the only gas-phase products. 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_2. The proposed mechanism involving carbenes is consistent with Scott and co-workers' results concerning their 900 °C pyrolytic automerization of naphthalene where they conclude: "the thermal automerization of naphthalene probably occurs by reversible formation of benzofulvene, either via carbenes or by direct dyotropic rearrangements."[10b]

Gas-phase naphthalene accepts an electron slightly exothermically (EA = +14.6 kJ/mol),[15] and the cesium anion radical salt has a crystal lattice energy of 630 kJ/mol.[9a] This, in conjunction with the ionization potential of cesium (−373 kJ/mol)[16] and heats of sublimation of Cs

---

[13] Ichikawa, M.; Soma, M.; Onishi, T.; Tamaru, K. *Bull. Chem. Soc. Jpn.* **1970**, *43,* 3672.

[14] Crowley, C.; Kroto, H. W.; Taylor, R.; Walton, D. R. M.; Bratcher, M. S.; Cheng, P.; Scott, L. T. *Tetrahedron Lett.* **1995**, *36,* 1215.

[15] Becker, R. S.; Chen, E. *J. Chem. Phys.* **1966**, *45,* 2403.

[16] Lotz, W. *J. Opt. Soc. Am.* **1967**, *57,* 873.

Scheme 3

(enthalpies in kJ/mol)

$$\begin{array}{lr}
C_{10}H_{8(gas)} + e^{-}{}_{(gas)} \rightarrow C_{10}H_{8}{}^{\bullet -}{}_{(gas)} & \Delta H^{\circ} = -14.6 \\
Cs_{(gas)} \rightarrow Cs^{+}{}_{(gas)} + e^{-}{}_{(gas)} & \Delta H^{\circ} = +373 \\
Cs_{(solid)} \rightarrow Cs_{(gas)} & \Delta H^{\circ} = +78.6 \\
Cs^{+}{}_{(gas)} + C_{10}H_{8}{}^{\bullet -}{}_{(gas)} \rightarrow & \\
\qquad Cs^{+}C_{10}H_{8}{}^{\bullet -}{}_{(solid)} & \Delta H^{\circ} = -630 \\
C_{10}H_{8(solid)} \rightarrow C_{10}H_{8(gas)} & \Delta H^{\circ} = +72.7 \\
\hline
C_{10}H_{8(solid)} + Cs_{(solid)} \rightarrow & \\
\qquad Cs^{+}C_{10}H_{8}{}^{\bullet -}{}_{(solid)} & \Delta H^{\circ} = -120
\end{array}$$

and naphthalene,[17] places the $Cs^{+}C_{10}H_{8}{}^{\bullet -}$ solid anion radical salt energetically downhill from Cs and $C_{10}H_8$ in their standard states by more than 100 kJ/mol, Scheme 3. Thus, from a thermochemical point of view, it might seem surprising that heating the anion radical salt to just 150 °C yields polymerization along with the liberation of hydrogen and methane gases. The small heats of formation of the polymeric soot must account for this fact.

A variety of high molecular weight species (>1000) is formed, and there is no indication of the formation of either C_{60} or endohedral fullerenes.

Acknowledgment. We wish to thank the National Science Foundation (Grant No. CHE-9011801) and the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

JO961487Q

---

[17] (a) Hicks, W. T. *J. Chem. Phys.* **1963**, *38*, 1873. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970; p 170.