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Pyrolysis of the Cyclooctatetraene Dianion[†]

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The solid potassium cyclooctatetraene dianion was heated from 300 to 1000 °C. Below 400 °C it did not produce any new products. However, at temperatures above 650 °C both hydrogen and methane gases are liberated and account for all of the volatile products. The nonvolatile products are polymeric in nature, and laser desorption mass spectroscopy reveals that they are held together by single bond linkages and linkages that result from [2 + 2] additions. The methane is proposed to result from the reaction between molecular hydrogen and carbenes.

Introduction

Some of the most kinetically and thermodynamically stable organic materials are represented by the polyaromatic hydrocarbons (PAH's). Heating benzene, a $4n + 2\ \pi$ electron annulene, to temperatures of over 1000 °C produces only one material: hot benzene. Despite the absence of new products, automerization (degenerate skeletal rearrangement) does take place.[1] Aromatic naphthalene acts in a manner similar to that of benzene when heated to temperatures well over 500 °C, but it and the other PAH's are not quite as resistant to fragmentation. It was discovered over a half century ago that naphthalene will liberate hydrogen under very high temperature pyrolysis conditions,[2] and very recently it was realized that C_{60} is produced from the high temperature (>1000 °C) pyrolysis of naphthalene.[3]

In contrast to the aromatic systems, cyclooctatetraene (COT), a $4n\ \pi$ electron annulene, polymerizes at room temperature.[4a] Even gentle warming (100 °C) of COT results in a myriad of products including four dimers, and polymeric materials.[4] Under more vigorous conditions (ca. 510 °C) dihydropentalene is formed.[5] The addition of two electrons to COT dramatically decreases its fragility. Under inert conditions the dianion of COT (a $4n + 2\ \pi$ electron system) behaves more like the neutral PAH's. The solid and tetrahydrofuran (THF)-solvated COT dianion salts have persisted for years at ambient temperatures on our shelves and resist both polymerization and thermal decomposition up to temperatures where Pyrex glass begins to soften (ca. 400 C).[6]

In contrast to the COT system, electron addition to the PAH's results in rendering the C−C and C−H bonds much more thermally labile. The thermal chemistry of the anion radicals of these materials contrasts dramatically with that of the neutral materials. Ten years ago it was found that warming the solid anion radical salt of naphthalene to just 100 °C results in the polymerization of the hydrocarbon with simultaneous generation of hydrogen gas.[7] These contrasting behaviors and the exciting high temperature chemistry of the PAH's[2] motivated us to investigate the high temperature behavior of the dianion of COT.

Experimental Section

Samples of the dianion of cyclooctatetraene (1−5 mmol) were generated via exhaustive reduction of COT in an evacuated apparatus on a potassium metal mirror in 10−30 mL of tetrahydrofuran (THF). After separation of the dianion solution from the excess metal, the solvent was removed under reduced pressure.[8] The solid $K^+{}_2COT^{2-}$ was then poured into a quartz glass tube, which was sealed from the apparatus.[9] This tube containing the $K^+{}_2COT^{2-}$ salt was connected to the high vacuum system through a U-tube, which was cooled in liquid nitrogen. After the line was pumped down to about 10^{-6} torr, the stopcock separating the $K^+{}_2COT^{2-}$ and the high vacuum system was opened, and the quartz tube was heated in a sand bath, Figure 1. The temperature was monitored with a nickel−chromium vs nickel−aluminum thermocouple by Omega (−200−1250 °C). The pressure in the vacuum system was monitored with a Fluid Precision Inc. capacitron pressure gauge to ±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 U-tube was obtained. In this system (Figure 1) 1 mmol of gas produces a pressure of about 150 torr.

When these noncondensable gases were exposed to a 300 °C Cu−CuO furnace, the pressure dropped 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, I_2 and ether were distilled into the quartz tube to oxidize any reactive anionic material. The ether and I_2 were then removed under reduced pressure, and the solids were extracted with toluene. Both the toluene soluble and toluene insoluble materials were submitted to laser desorption mass spectral analysis. Nothing, not even unreacted COT, was recovered in the U-tube. On the other hand, heating neutral COT under identical condition results in all of the COT being recovered in the U-tube, and no gases produced.

To insure that THF did not remain in the solid $K^+{}_2COT^{2-}$ salt, samples of it were quenched with D_2O, and the resulting D_2O solution was checked for the presence of THF using a ^1H 300 MHz NMR (Gemini-2000 by Varian). This procedure has been previously described.[9]

Spectroscopic analyses were carried out using a Nicole FT-IR using a gas cell fitted with sodium chloride windows. Matrix assisted laser desorption time of flight mass spectra

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[†] Dedicated Professor Glen A. Russell on the occasion of his 70th birthday.

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1995.

(1) Scott, L. T.; Roelofs, N. H.; Tsang, T. H. *J. Am. Chem. Soc.* **1987**, *109*, 5456.

(2) (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.

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

(4) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Annalen.* **1948**, *506*, 1. (b) Lord, R. C.; Walker, R. W. *J. Am. Chem. Soc.* **1954**, *76*, 2518. (c) Jones, W. O. *J. Chem. Soc.* **1953**, 2036. (d) Jones, W. O. *Chem. Ind.* **1955**, 16. (e) Schroder, G. *Chem. Ber.* **1964**, *97*, 3131. (f) Schroder, G.; Kirsch, G.; Oth, J. F. M. *Chem. Ber.* **1974**, *107*, 460.

(5) Jones, M.; Schwab, L. O. *J. Am. Chem. Soc.* **1968**, *90*, 6549.

(6) Results from this work.

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

(8) Stevenson, C. D.; Zigler, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 2513.

(9) The solid dianion salt is just $K^+{}_2COT^{2-}$ and does not have solvent (THF) incorporated in it, see Concepcion, R.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 1778.

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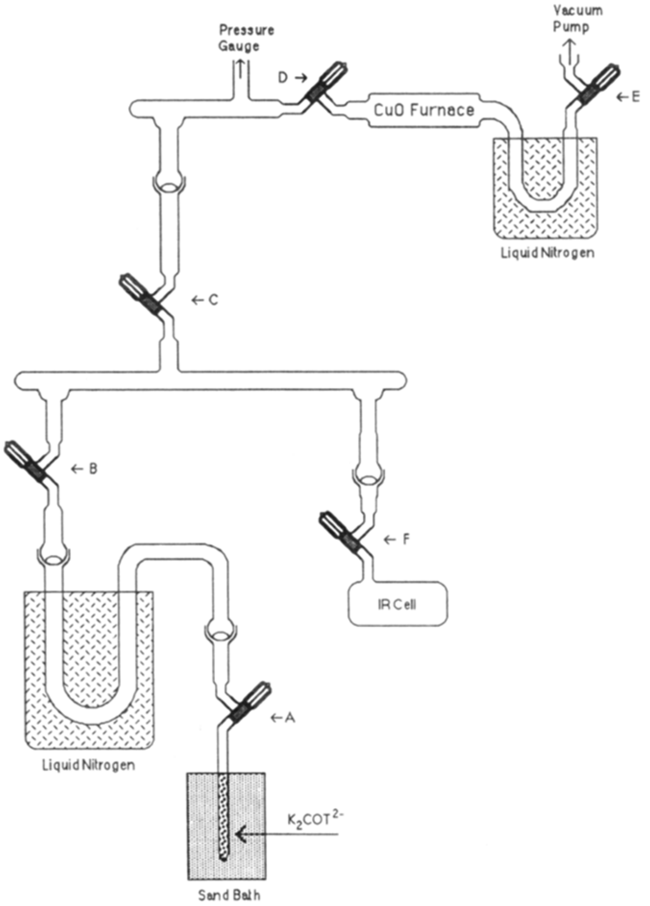


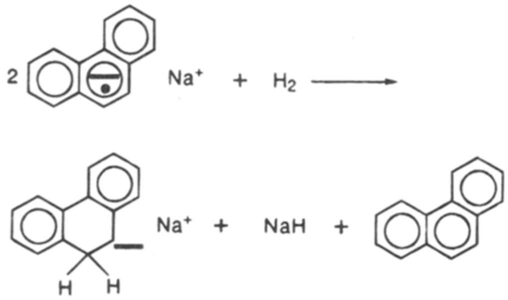
Figure 1. Apparatus used to analyze evolved gasses from the $M^+{}_2COT^{2-}$ pyrolysis. The dianion was heated with stopcock A, B, C, and F open. Thus the IR cell and the pressure gauge were exposed to the noncondensable (liquid N_2) evolved gases as they were formed. Hydrogen gas could be analyzed by closing stopcock F and opening stopcock D. This allowed the gases to enter the hot CuO furnace. The water produced in the furnace was caught in the adjoining U tube, which was immersed in liquid N_2.

were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

Results and Discussion

No apparent chemical alterations or gas evolution take place when a sample (ca. 1 mmol) of the solid potassium salt of cyclooctatetraene dianion ($K^+{}_2COT^{2-}$) is heated under static conditions to 380 °C for up to 8 h. However, when the sample is further heated to 650 °C, the evolution of noncondensable gases is detected. After 3 h, as much as 0.17 mol of gas/mol of dianion is evolved, Figure 2. Heating the sample to over 1000 °C results in the production of three times as much gas. The exposure of this gas mixture to a hot 300 °C Cu−CuO furnace results in a drop in the pressure to 5% of its original value and the consequent formation of water. This means that 95% of the gas is H_2 ($H_2 + CuO \rightarrow Cu + H_2O$). It seems probable that heating of the dianion results in the ejection of an electron to form the COT anion radical, which then polymerizes in a manner analogous to that of the naphthalene anion radical, Scheme 1.[7]

A granular black solid polymeric material remained after the completion of the pyrolysis. It was quenched under vacuum with I_2 in diethyl ether. Laser desorption mass spectral analysis of the quenched material reveals negative ion peaks at 208, 317, and 830, Figure 3. These are consistent with 2, 3, and 8 partially hydrogenated COT units linked together and are consistent with the mechanism proposed above. Since the reaction is essentially taking place in a hydrogen bath, the partially hydrogenated polymers are to be expected, because both the THF solvated and dry anion radical salts are known to readily take up H_2 as shown below.[10]



The IR spectral analysis of the noncondensable gasses, taken either before or after the oxidative removal of the

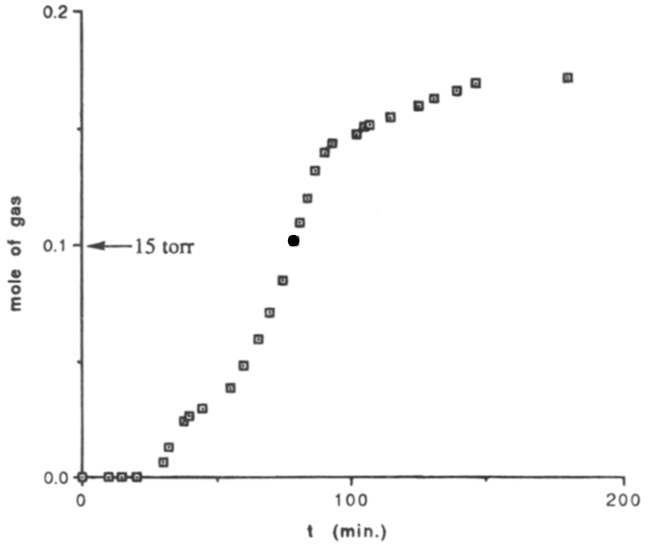
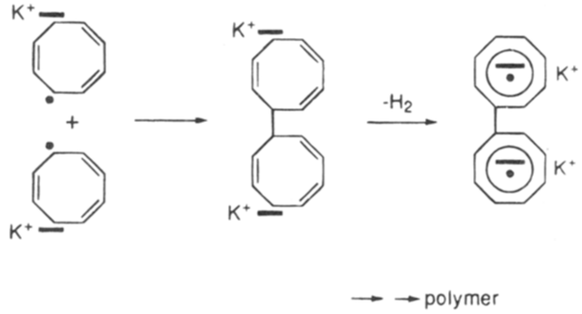


Figure 2. Plot of the number of moles of noncondensable gas evolved per mole of $K^+{}_2COT^{2-}$ produced from a 1.03 mmol sample of $K^+{}_2COT^{2-}$ as the salt was being heated to ca. 650 °C in a quartz glass vessel. Similar results were obtained from five separate reactions with various amounts (1 −2 mmol) of $K^+{}_2COT^{2-}$. After the sample is immersed in the oven, there is an induction period required to heat up the sample. This accounts for the near zero readings at the beginning of the experiments. Very similar results were obtained from samples of $Li^+{}_2COT^{2-}$.

Scheme 1



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

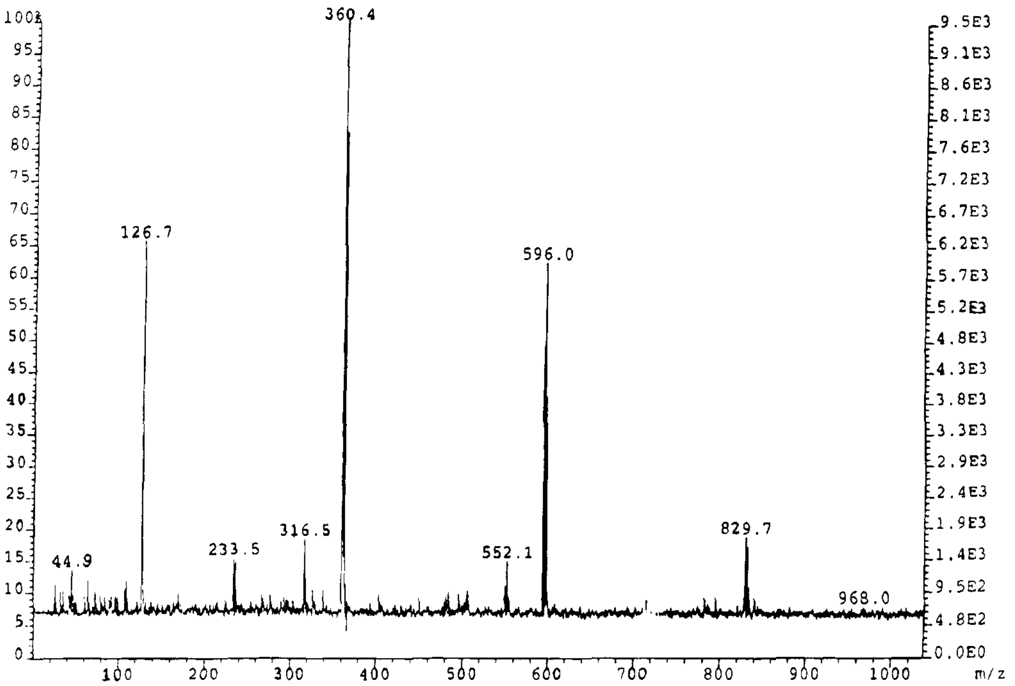
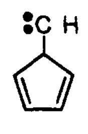


Figure 3. Negative ion laser desorption mass spectrum of the I_2-quenched toluene-washed soot. The toluene-extracted material also contains peaks at 830, 596, and 317, and in addition has a peak at 208 *m/z*.

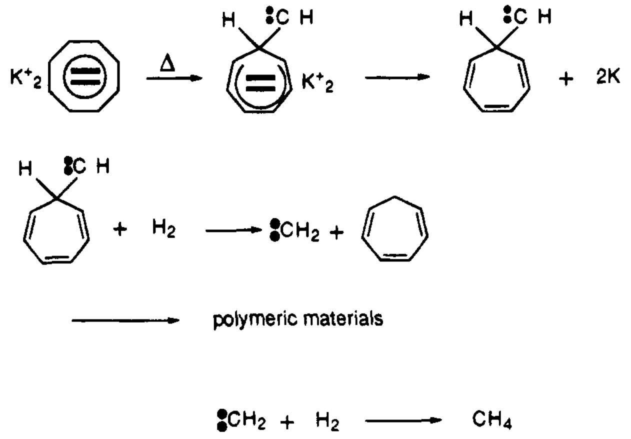
H_2, proves that the other gas is methane. As mentioned in the Experimental Section, the $K^+{}_2COT^{2-}$ samples are free of THF. To further insure that the methane did not originate from the THF, a sample was generated in THF-d_8. Methane (CH_4) was also generated from this sample, not CD_4. The CH_4 production is a surprising result, given that only one hydrogen is associated with each carbon in the starting material ($K^+{}_2COT^{2-}$). It isn't difficult to imagine reaction pathways where two hydrogens gather on a single carbon, but four hydrogens ending up on single carbon most likely requires the involvement of carbenes. Scott and co-workers proposed a mechanism for the high temperature automerization of 1,2-di-^{13}C-benzene that involves a carbene intermediate, structure I.[1] A mechanism involving structure II was, however, favored over that involving the intermediate carbene.[1]



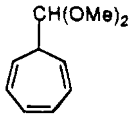
I

II

Scheme 2



An intermediate involving a structure that is analogous to Scott's proposed carbene nicely accounts for the observed methane gas, Scheme 2. At these elevated temperatures, it is expected that a cycloheptatrienyl system would eject its electrons immediately upon formation, and the ever present hydrogen would capture the newly formed carbene to form methane. The cycloheptatriene would be involved in the polymerization process at these temperatures, and we should observe some evidence of seven-member rings in the polymeric products. Indeed the positive ion laser desorption mass spectrum of the toluene soluble solids exhibits a peak at 397 *m/z*, which corresponds to 3 COT's and a tropylium cation connected via single bonds. The contraction of COT yielding a cycloheptatrienyl system is known to take place in number of reactions.[11] For example methanol adds to COT in the presence of mercury acetate to give III.[11a] Some polymerization can take place without hydrogen evolution, as it is known that the solvated anion radical of COT will undergo a [2 + 2] dimerization to form the dianion and anion radical of [16]annulene via IV.[12]



III

IV

Conclusion

The static pyrolysis of the solid potassium salt of the cyclooctatetraene dianion results in polymerization in-

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[11] (a) Cope, A. C.; Nelson, N. A.; Smith, D. S. *J. Am. Chem. Soc.* **1954**, *76*, 1100. (b) Eberson, L.; Nyberg, K.; Finkelstein, M; Peterson, R. C.; Ross, S. D.; Uebel, J. J. *J. Org. Chem.* **1967**, *32*, 16.

[12] (a) Stevenson, C. D., Burton, R. D.; Halvorsen, T. D.; Reiter, R. C. *J. Org. Chem.* **1993**, *50*, 4289. (b) Stevenson, C. D.; Nebgen, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 5501.

volving single bond linkages as well as some [2 + 2] additions. The formation of the former linkages results in the production of hydrogen gas, which can either hydrogenate the olefinic polymer or escape the reaction mixture in the form of H_2 or CH_4. It is proposed that the production of methane, which accounts for about 5% of the CH_4/H_2 mixture, comes from the capture of hydrogen by carbenes. These products contrast with those obtained from the very high temperature thermolysis of neutral COT, which are benzene, styrene, acetylene, and ethylene.[13]

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[13] Kubo, M. *J. Chem. Soc. Jpn. Pure Chem. Sect.* **1954**, *75*, 212.