J. Am. Chem. Soc. **1983**, *105*, 4239–4243

The opposite would be expected for a reversed ordering of these levels. What is actually seen (Figure 8) is that at higher photon energy the high- and the low-energy sides of the band give distinctively different β values, the ones for the low-energy side being systematically lower. In this analysis, the implicit assumption is that the β over a vibrational envelope is fairly constant. When there is extensive overlap in the photoelectron spectrum between two bands, however, vibronic interaction might occur.[4] In addition, a skewing of the broad distribution of the band shape may give rise to a spectrum that is not free from contribution of both orbitals. Nevertheless, it is believed that at these extreme ends one or the other orbital is dominant so that at least the qualitative behavior of β (E_p) can be plotted. The low-energy side β (E_p) curve (×) (Figure 8) does not show a rapid increase in β values as the photon energy increases. The behavior of the low-energy side (×) curve is also similar to the β curves reported for nonbonding orbitals in the other azabenzenes and it appears to be consistent with an assignment to a nonbonding orbital.

The high-energy side β (E_p) curve (☆) (Figure 8) does rise with photon energy reflective of a contribution from the π orbital which was lacking for the low-energy side. Therefore, the relative ordering for the first two ionic levels in pyridine is confirmed to be n at lower ionization energy followed by π. A subtle difference in the β values as a function of photon energy is shown by the data for pyridine and fluorosubstituted pyridines. There is a shift to lower β values for π orbitals due to the presence of fluorine. For the second π orbital the maximum β values in pyridine at electron kinetic energy of 16.5 eV is 1.233; in 2-fluoropyridine at an electron kinetic energy of 16.3 eV the β value is 0.884; and in pentafluoropyridine at electron kinetic energy of 15.6 eV the β value is 0.895. This effect was previously seen for benzene and hexafluorobenzene[3,4] and appears so far to be a general effect on β.

When the β values reported here are compared to the 21.22-eV He I values[12] for pyridine and pentafluoropyridine, it is seen that the He I data are systematically higher by approximately 0.2 β unit. It is also obvious from the shape of the β curve with photon energy that orbitals which are measured with line sources at 21.22 eV must yield electron kinetic energies sufficiently high to circumvent the threshold effects. If this is not the situation, the β values for n and π orbitals appear to be identical. For example, for pentafluoropyridine the 21.22-eV line source gives identical β values of 0.6 for the first and third bands identified as π and n, respectively. The data presented here at 21.22 eV show identical β values of 0.45, but at a photon energy of 27 eV, the β values are 0.9 and 0.5, respectively. Clearly, the ability to produce electrons of different kinetic energies provides another dimension in distinguishing the orbital producing the photoelectron.

Conclusion

A systematic study of the angular distribution parameter, β, has been determined for a series of azabenzenes over the photon energy range from 12 to 27 eV. From these results generalizations can be made regarding the relative behavior of β for the π and n orbitals. The value of β for the π orbitals rises more rapidly with photon energy than the n orbitals to a value close to or greater than 1.0 for energies approximately 15 eV above the ionization threshold. In contrast, the value of β for the nonbonding n orbitals is fairly constant as a function of photoelectron energy and remains relatively low (below a value of 0.5 unit of β). Using these generalizations, it has been possible to assign the order of binding energy levels in pyridine. Generalization on the behavior of β as a function of orbital types must be approached with great caution. They should be made preferably for a limited series of homologous compounds. Nevertheless, as in the present case of the azabenzenes such generalizations do seen appropriate. In evaluating the systematic behavior of β as a function of photon energy for various molecular orbitals, it may be desirable to extend the energy range. It is hoped that theoretical calculations on the angular distribution parameters will lead to a better understanding of the observed behavior of β for different molecular orbital types. Besides offering a means of fingerprinting an orbital, and thus helping the assignment of the ionization levels in a molecule, a systematic study of the energy dependence curves of β gives an opportunity to characterize the nature of molecular orbitals and the dynamics of the photoionization process in molecules.

Acknowledgment. The authors thank M. O. Krause of Oak Ridge National Laboratory for making available his spherical sector analyzer.

Registry No. Pyridine, 110-86-1; 2-fluoropyridine, 372-48-5; pentafluoropyridine, 700-16-3; pyrazine, 290-37-9; pyrimidine, 289-95-2.

Chemical Properties of the Gas-Phase Benzvalene Radical Cation

D. L. Miller and M. L. Gross*

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588.

Received November 15, 1982

Abstract: The nature of the gas-phase benzvalene radical cation has been explored by means of comparative ion–molecule reactions studied by Fourier transform mass spectrometry and by comparative collision-induced dissociation spectra obtained by mass spectrometry/mass spectrometry. It is found that this C_6H_6 radical cation has a unique structure different from previously studied C_6H_6 radical cations, including ionized benzene. We conclude that the structure is similar to that of its neutral precursor. The rate constant of the reaction with neutral butadiene has also been measured and compared with the rate constant of the reaction of ionized fulvene and butadiene.

Perhaps one of the most studied systems in gas-phase ion chemistry is that of the C_6H_6 radical cation,[1–28] in particular that of ionized benzene. This is due in large part to questions concerning the nature of the gas-phase ion structure. Benzene requires

---

(1) Beynon, J. H.; Fontaine, A. E. *Chem. Commun.* **1966**, 177.

(2) Keough, T.; Ast, T.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 245.

(3) (a) Jones, E. G.; Bauman, L. E.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 185; (b) Cooks, R. G.; Kim, K. C.; Keough, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *15*, 271.

0002-7863/83/1505-4239$01.50/0

approximately 4.7 eV[20] of internal excitation for fragmentation to occur due to its stable structure. Thus, it is possible that electronic excitation, ring opening, and carbon and/or hydrogen isomerization via valence or structural isomers may occur prior to fragmentation.

With these possibilities in mind, we report here the first examination of the gas-phase chemistry and properties of the C_6H_6 radical cation generated from tricyclo[3.1.0.0^{2,6}]hex-3-ene (I)

I

(referred to as benzvalene for the rest of this paper). One purpose of this investigation is to see if ionized benzene (and other isomers) and benzvalene have interconverted prior to decomposition. The study was carried out by examining the gas-phase ion–molecule reaction chemistry of the radical cation from benzvalene with the use of Fourier transform mass spectrometry (FTMS)[29] and the collision-induced dissociation (CID)[30] spectra obtained with the use of mass spectrometry/mass spectrometry (MS/MS).

Experimental Section

Instrumentation. The instrument used in the ion–molecule reaction studies was a modified Varian ICR-9 Fourier transform ion cyclotron resonance spectrometer which has been described in the recent literature.[31] Typical conditions used in these experiments were the following: sample pressure, between 8×10^{-7} and 3×10^{-6} torr; ionizing energy, 12–15 eV; instantaneous emission current, 20 nA; magnetic field, 1.2 T; trap voltage, 1 V; excitation bandwidth, 300 kHz; and excitation sweep rate, 5.7×10^8 Hz/s. All experiments were done in the mixer mode with the "quench" pulse on. Five-hundred time-domain transients were acquired and averaged in most cases. The reagent neutrals were admitted into the FTMS through the standard inlet system. However, the benzvalene was admitted through a glass-lined inlet system of our own design and manufacture to prevent its isomerization to benzene upon staying in contact with stainless steel for extended periods of time.[29]

The rate-constant measurements were performed on a pulsed mode ICR.[32] The pulse sequence, including the delay time between ionization and analysis, was controlled by an Intel Model 8039 microprocessor and an interface of our own design and manufacture. Absolute pressure measurements were obtained from a Veeco RG1000 ionization gauge which had been calibrated against a Datametrics Baracel Electronic Manometer, Model 1173.

The apparatus used in the collision-induced dissociation (CID) studies was a Kratos MS50 triple-analyzer mass spectrometer of EBE geometry, which has been described elsewhere.[33] Typical conditions used in this study were the following: mass resolution, 10000; source temperature, 150 °C; second energy slit, 0.5 mm; and ionizing energy, 70 eV. The CID spectra were taken by using the following procedure. The first electrostatic analyzer and the magnet were adjusted to pass C_6H_6 radical cations. The target gas (He) was then introduced to the collision chamber until the precursor ion intensity was suppressed to $^1/_2$ of its original value due to scattering, decomposition, and neutralization (charge exchange). The second electrostatic analyzer potential was then scanned to acquire the spectrum of the decomposition products.

The samples of benzene and 1,5-hexadiyne were introduced into the ion source by using a heated reservoir probe supplied by the manufacturer. The samples of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride and 2,4-(*N*-phenylurazol-1,2-diyl)tricyclo[3.1.0.0^{3,6}]hexane were introduced into the ion source by using the solid sample probe which was held at ambient temperature. The samples were slowly sublimed from the probe by slow heat transfer from the hot ion source. The samples of 2,4-hexadiyne, 1,3-hexadien-5-yne, and 3,4-dimethylenecyclobutene were introduced into the ion source by using the reagent gas inlet system supplied by the manufacturer. The sample of benzvalene required special handling due to its tendency to isomerize to benzene when in contact with metals as mentioned previously. An all-glass reservoir probe containing a glass molecular leak was constructed as a replacement for the solids probe, and it was used to introduce the benzvalene directly into the ion source.

Materials. All compounds used in the ion–molecule reaction studies as reagent neutrals were purchased from standard commercial sources and their purity checked by mass spectrometry. The C_6H_6 isomers, benzene, 1,5-hexadiyne, and 2,4-hexadiyne, were also purchased from commercial sources and were 98% pure as guaranteed by the manufacturer. All reagents used in the synthesis were analytical reagent grade.

1,3-Hexadien-5-yne was synthesized by the method of Sondheimer, Ben-Efain, and Goani.[34] The material was purified by preparative GLC on a 1.8 m × 6.4 mm column with 3% SE-30 on Chromosorb W at 60 °C, and its purity was checked by ultraviolet analysis. We obtained a molar absorptivity of 2540 at 252 nm with cyclohexane as solvent (lit.[34] 2520).

Benzvalene was synthesized according to the method of Katz, Wang, and Acton.[35] Samples were purified by GLC as needed on a 1.8 m × 6.4 mm glass column packed with 45/60 AW Chromosorb G coated with 5% didecyl phthalate and 1.25% triethanolamine. Typical conditions were the following: column temperature, ambient; flow rate, 80 cm^3/min; injector and detector, 70 °C. Analysis by ^{1}H NMR showed multiplets at δ 2.0, 3.7, and 5.95 (lit.[36] δ 1.9, 3.68 5.95).

3,4-Dimethylenecyclobutene was synthesized by the method of Collier, Hefferman, and Jones.[37] The product was purified by GLC (6 m SE-30 column at 50 °C, flow rate of 60 cm^3/min). ^{1}H NMR showed peaks at δ 4.6, 4.7, and 6.8 (lit.[37] δ 4.7, 4.8, and 6.8).

---

(4) Baer, T.; Willet, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076.

(5) (a) Franklin, J. L.; Carrol, S. R. *J. Am. Chem. Soc.* **1969**, *91*, 5490; (b) Franklin, J. L.; Carrol, S. R. *Ibid.* **1969**, *91*, 6564.

(6) Borchers, F.; Levsen, K. *Org. Mass Spectrom.* **1975**, *10*, 584.

(7) Cooks, R. G.; Beynon, J. H.; Litton, J. F. *Org. Mass. Spectrom.* **1975**, *10*, 503.

(8) Koppel, C.; Schwarz, H.; Borchers, F.; Levsen, K. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *21*, 15.

(9) Gross, M. L.; Russell, D. H.; Aerni, R. J.; Broncyzk, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 3603.

(10) Russell, D. H.; Gross, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 6279.

(11) Jones, E. G.; Bhattacharya, A. K.; Tiernan, T. O. *Int. J. Mass. Spectrom. Ion Phys.* **1975**, *17*, 147.

(12) Beynon, J. H.; Caprioli, R. M.; Perry, W. O., Baitinger, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 6828 and references therein.

(13) Gross, M. L.; Aerni, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 7875.

(14) Momigny, J.; Brakier, M. L.; D'or, L. *Bull. Cl. Sci., Acad. R. Belg.* **1962**, *48*, 1002.

(15) (a) Andlauer, B.; Ottinger, C. *J. Chem. Phys.* **1971**, *55*, 1471; (b) Andlauer, B.; Ottinger, C. *Z. Naturforsch.* **1972**, *27*, 293.

(16) Bursey, M. M.; Tibbets, F. G.; Little, W. F.; Rausch, M. D.; Moser, G. A. *Tetrahedron Lett.* **1969**, 3469.

(17) Chupka, W. A. In "Chemical Spectroscopy and Photochemistry in the Vacuum Ultraviolet"; Sandorfy, C., Ausloos, P. J., Robin, M. B., Eds.; D. Reidel: Boston, 1974.

(18) Smith, R. D.; Futrell, J. H. *Org. Mass Spectrom.* **1976**, *11*, 445.

(19) Jonsson, B.; Lindholm, J. *Ark. Fys.* **1968**, *39*, 65.

(20) Rosenstock, H. M.; Larkins, J. T.; Walker, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 309.

(21) Rosenstock, H. M.; McCulloh, K. E.; Lossing; F. P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 327.

(22) (a) Eland, J. H. D. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 457; (b) Eland, J. H. D.; Schulte, H. *J. Chem. Phys.* **1975**, *62*, 3835.

(23) Gallup, G. A.; Steinheider, D.; Gross, M. L. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 185.

(24) Frieser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35.

(25) Smith, R. D.; Decorpo, J. J.; Futrell, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *26*, 279.

(26) Wexler, S.; Pobo, L. G. *J. Chem. Phys.* **1970**, *74*, 257.

(27) Panczel, M.; Borossoy, J. *Magy. Kem. Foly.* **1980**, *86*, 102.

(28) Dannacher, J.; Stadelmann, J. P.; Vogt, J. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 69.

(29) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A.

(30) McLafferty, F. W.; Kornfeld, R.; Haddon, W. F.; Levsen, K.; Sakai, I.; Bente, P. F., III; Tsai, S.-C.; Schuddemage, H. D. R. *J. Am. Chem. Soc.* **1973**, *95*, 3886.

(31) Ledford, E. B., Jr.; Ghaderi, S.; White, R. L.; Spencer, R. B.; Kulkarni, P. S.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1980**, *52*, 463.

(32) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1978**, *49*, 111.

(33) Gross, M. L.; Chess, E. K.; Lyon, P. A.; Crow, F. W.; Evans, S.; Tudge, H. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 243.

(34) Sondheimer, F.; Ben-Efain, D. A.; Goani, Y. *J. Am. Chem. Soc.* **1961**, *83*, 1682.

(35) (a) Katz, T. J.; Wang, E. J. Acton, N. *J. Am. Chem. Soc.* **1971**, *93*, 3782; (b) *Org. Synth.* **1973**, *53*, 1824.

(36) Wilzbach, K. E.; Ritscher, J. S.; Kaplan, L. *J. Am. Chem. Soc.* **1967**, *89*, 1031.

(37) Collier, B. A. W.; Hefferman, M. L.; Jones, A. J. *Aust. J. Chem.* **1968**, *21*, 1807.

Bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride was synthesized by the method of van Tamelen, Pappas, and Kirk.[38] The product was sublimed at 50 °C and 0.01 mm and its melting point was 157–160 °C (lit.[38] mp 162–163 °C). The ^{1}H NMR showed multiplets at δ 3.42, 3.6, and 6.44 (lit.[38] δ 3.49, 3.66, and 6.49).

2,4-(*N*-Phenylurazol-1,2-diyl)tricyclo[3.1.0.0^{3,6}]hexane was synthesized by the method of Katz and Acton.[39] ^{1}H NMR analysis of the product gave multiplets at δ 7.4, 5.1, 3.3, 2.7, and 2.45 (lit.[39] δ 7.45, 5.02, 3.2, 2.63, 2.6).

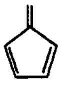
Results and Discussion

Ion–Molecule Reaction Studies. In previous studies,[9,10] it was demonstrated that various C_6H_6 radical cations can be distinguished on the basis of comparative ion–molecule reactions as a test of structural difference. These same reactions were employed to examine the C_6H_6 radical cation from benzvalene.

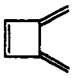
Reaction of Ionized Benzvalene with 2-Iodopropane. In the previous work,[9] we demonstrated that ionized benzene exhibited a unique ion–molecule reaction with 2-iodopropane to yield a product with a composition of $C_9H_{13}^+$ (see eq 1).[40] The acyclic isomers and the cyclic isomers fulvene (II)[10] and 3,4-dimethylenecyclobutene (DMCB; III) did not exhibit this reaction. The corresponding reactivity of the benzvalene radical cation with 2-iodopropane was examined as a starting point.

Benzvalene and 2-iodopropane were introduced into the cell of the FTMS, and a series of variable delay experiments ranging from 0 to 500 ms were carried out by using different pressure ratios of the compounds. No *m/z* 121 peak (less than 2% of that found for benzene) was observed under any of the conditions used. Peaks were observed at *m/z* 78, 91, 115, 128, 141, and 155 which correspond to the peaks of the products of the reaction of the benzvalene molecular ion with its neutral (verified by double-resonance ion ejection of *m/z* 78). Peaks were also observed at *m/z* 170 and 213, corresponding to the peaks of the molecular ion of 2-iodopropane and a propylated molecular ion. On the basis of comparative ion–molecule reactions with 2-iodopropane as neutral reactant it can be seen that the benzvalene radical cation has not isomerized to the benzene radical cation.

$$C_6H_6^{+\cdot} + 2\text{-}C_3H_7I \rightarrow C_9H_{13}^+ + I \qquad (1)$$



II



III

Internal Ion–Molecule Chemistry of Benzvalene. Ionized benzene does not exhibit bimolecular reactivity with neutral benzene under the conditions employed in these experiments (ca. 10^{-6} torr; variable delay times). However, the acyclic and other cyclic isomers exhibit a rich ion chemistry. Unfortunately, these results yield no structural information about the C_6H_6 radical cation since it is impossible to determine if it is the ion or the neutral that is responsible for the abundant internal ion chemistry (see eq 2–6). Nevertheless, it is possible to modify the experiment to confirm that ionized benzvalene is not isomerizing to the benzene radical cation.

$$C_6H_6^{+\cdot} + C_6H_6 \rightarrow [C_{12}H_{12}^{+\cdot}]^* \rightarrow C_{12}H_{11}^+ \; H\cdot \qquad (2)$$

$$\rightarrow C_{11}H_9^+ + CH_3\cdot \qquad (3)$$

$$\rightarrow C_{10}H_8^{+\cdot} + C_2H_4 \qquad (4)$$

$$\rightarrow C_9H_7^{+\cdot} + C_3H_5\cdot \qquad (5)$$

$$\rightarrow C_7H_7^+ + C_5H_5 \qquad (6)$$

[$^2H_6$]Benzene was added to the FTMS cell and mixed with benzvalene. No new ion-molecule products were found, and the intensities of the product ions did not change. The C_6D_6 simply acted as an inert diluet. Thus, we observed that ionized benzvalene does not react with neutral [$^2H_6$]benzene and that ionized C_6D_6 is unreactive with neutral benzvalene.

The results of the ion–molecule reactions of ionized benzvalene with its neutral are similar to those obtained for the acyclic C_6H_6 isomers and the cyclic C_6H_6 isomers. Thus, it is possible that ionized benzvalene has isomerized to another structure besides benzene. This possibility can be investigated by employing other neutrals to test the reactivity.

Reaction of Ionized Benzvalene with Methyl Vinyl Ether. It has been shown that methyl vinyl ether (MVE) does not react with the C_6H_6 radical cations produced from ionized acyclic C_6H_6 isomers or with ionized benzene under the conditions employed in these experiments.[9] Reaction of ionized benzvalene with MVE, however, gave rise to a single peak at *m/z* 104 that was shown by double-resonance experiments to be due entirely to reaction of ionized benzvalene with neutral MVE. The *m/z* 104 peak is presumably due to loss of methanol from the benzvalene/MVE collision complex (eq 7). Thus, it may be seen that the C_6H_6 from benzvalene is different than the C_6H_6 radical cations from the acyclic isomers. However, the cyclic isomers fulvene and DMCB also react with MVE to form the *m/z* 104 ion. Nevertheless, it is possible to distinguish the benzvalene radical cation from the two cyclic isomers on the basis of other features. MVE reacting with ionized fulvene yields a peak at *m/z* 136 that is not seen for benzvalene. Ionized DMCB shows not only the peak at *m/z* 136 but also an additional peak at *m/z* 121 due to loss of a methyl group from the collision complex.

$$C_6H_6^{+\cdot} + C_3H_6O \rightarrow [C_9H_{12}O^{+\cdot}]^* \rightarrow C_8H_8^{+\cdot} + CH_3OH \qquad (7)$$

Reaction of Ionized Benzvalene with Furan. The ion-molecule chemistry of ionized benzvalene with neutral furan was examined in order to add additional credibility to the postulate of different ion structures. The C_6H_6 radical cation from fulvene does not react with neutral furan whereas the C_6H_6 from DMCB reacts with furan to form three secondary ions: a detectable collision complex $C_{10}H_{10}O^+$, $C_9H_7O^+$, and $C_8H_5O^+$ or $C_9H_9^+$.[9] Reaction of ionized benzvalene with neutral furan yields no ion–molecule reaction products. Only the chemistry of the molecular ions with their respective neutrals is seen. At this point, the C_6H_6 radical cations from DMCB and benzvalene may be dismissed as having the same ion structure. However, a more definitive reaction is still desired to distinguish benzvalene and fulvene.

Ion–Molecule Reaction Chemistry of Ionized Benzvalene with 1,3-Butadiene. 1,3-Butadiene was chosen as the next reagent neutral to be reacted with ionized benzvalene because its reactivity with ionized fulvene is well known.[10] When ionized benzvalene is mixed with neutral 1,3-butadiene, only one bimolecular product is observed, the formation of $C_9H_9^+$ (*m/z* 117) resulting from the loss of a methyl group from the collision complex (eq 8).

$$C_6H_6^{+\cdot} + C_4H_6 \rightarrow [C_{10}H_{12}^{+\cdot}]^* \rightarrow C_9H_9^+ + CH_3\cdot \qquad (8)$$

Double-resonance experiments show that the reaction involves exclusively ionized benzvalene. This result is different from that observed for the C_6H_6 radical cation from fulvene in which three products are observed—$C_{10}H_{11}^+$, $C_9H_9^+$, and $C_8H_8^+$. Ionized benzvalene produces only $C_9H_9^+$. Enough differences are observed in the ion-molecule reactions that we conclude that ionized benzvalene has a different gas-phase structure than ionized fulvene.

However, two complicating factors must be addressed. These are possible internal energy effects and the possibility of mixtures of ion structures. It is conceivable that ionized benzvalene (ΔH_f = 299 kcal)[41] is isomerizing to the most stable forms of the C_6H_6 radical cation, namely benzene (ΔH_f = 233 kcal)[42] or fulvene (ΔH_f = 240 kcal).[43] This would result in benzene or fulvene ions containing 66 and 59 kcal, respectively, of excess energy which could effectively close the reaction channels leading to $C_{10}H_{11}^+$ and $C_8H_8^+$ from neutral 1,3-butadiene and ionized fulvene, for

---

[38] van Tamelen, E. E.; Pappas, Kirk, K. L. *J. Am. Chem. Soc.* **1971**, *93*, 6092.

[39] Katz, T. J.; Acton, N. *J. Am. Chem. Soc.* **1973**, *95*, 2738.

[40] Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.*, in press.

[41] Bischof, P.; Gleiter, R.; Muller, E. *Tetrahedron* **1976**, *32*, 2769.

[42] Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1969**, 26.

[43] Heilbronner, E.; Gleiter, R.; Hopf, H.; Hornung, V.; de Meijere, A. *Helv. Chim. Acta* **1971**, 783.

example, and lead to a false conclusion as to the ion structure involved.

We can discount internal energy effects on the basis of the following observations. As mentioned previously, all of the ion–molecule reactions were monitored from 0 to 500 ms. If the isomerization to a "hot" benzene or fulvene radical cation is occurring, one might expect that the excess energy may prevent certain products from forming. However, at longer delay times, the "hot" ions would have experienced a number of stabilizing collisions (ca. 100 by 500 ms) which would drain off excess energy and reopen the reaction channels. This was never observed. A case in point is the ionized benzene and 2-iodopropane reaction. For benzvalene, at no delay time is the *m/z* 121 product characteristic of ionized benzene observed. Thus, we may tentatively discount excess internal energy from exothermic isomerizations as an important factor in the chemistry observed.

One reason for uncertainty in the interpretation that internal energy effects are not important is based on measurements of the rates of dissociation of internal energy selected C_6H_6 radical cations.[4] Ionized benzene, 1,5-hexadiyne, and 2,4-hexadiyne with identical internal energies dissociate with identical rate constants which has been interpreted to indicate isomerization of the 1,5- and 2,4-hexadiyne ions to the most stable benzene structure. Yet these ions exhibit dramatically different reactivities with 2-propyl iodide.[9] It is possible that isomerization occurs without activation and, if so, the observed reactivities are determined by internal energy rather than ion structure. If this were true for the benzvalene radical cation, it would mean that 100 collisions were insufficient to thermalize the ion which would be quite unexpected.

The possibility of a mixture of ion structures formed upon ionization of benzvalene neutral may also be discounted on the basis of the ion–molecule reaction chemistry. In most cases, the benzvalene displays totally different ion chemistry with a particular reagent neutral than do the other isomeric forms (e.g., ionized benzene with 2-iodopropane). Only for ionized benzvalene and fulvene are common products formed which may indicate a mixture of ion structures. We may also discount this possibility on the basis that ionized fulvene always displays a richer chemistry (gives more ionic products) with a particular reagent neutral than ionized benzvalene does. If fulvene radical cation is formed in the ionization of benzvalene, this richer chemistry should be observed.

Preliminary Study of the Mechanism of the Reaction of Ionized Benzvalene and Neutral 1,3-Butadiene. The reaction mechanism of the benzvalene–butadiene system is of interest to us since it may occur by a gas-phase cycloaddition process, a general subject under careful study in this laboratory. Few experimental data exist concerning the cycloaddition chemistry of open-shell systems which makes it difficult to develop a set of selection rules for these systems.

The reaction of ionized benzvalene with neutral 1,3-butadiene was investigated by using isotopically labeled butadiene; specifically, [1,1,4,4-$^2H_4$]1,3-butadiene, [$^2H_6$]1,3-butadiene, and [1-^{13}C]1,3-butadiene were reacted with benzvalene, and the isotopic distribution of the products of methyl loss from the collision complex was monitored.

Reaction of Ionized Benzvalene with [1,1,4,4-$^2H_4$]1,3-Butadiene. When ionized benzvalene reacted with neutral [$^2H_4$]butadiene in the FTMS, extensive but incomplete hydrogen and deuterium exchange was observed (Table I). However, some subtle features could be discerned. The loss of CH_2D is markedly smaller than the amount predicted for statistical exchange while the loss of CHD_2 is 1.5 times larger than that for statistical exchange. These observations may be interpreted as showing that a large portion of the methyl loss arises from the original butadiene moiety. Unfortunately, we are unable to evaluate any isotope effects that accompany the transfer of H or D.

Reaction of Ionized Benzvalene with [$^2H_6$]1,3-Butadiene. Extensive hydrogen–deuterium exchange was also observed for the collision complex of the benzvalene/[$^2H_6$]butadiene reactions. The observed loss of CD_3 from the collision complex is 3 times larger than that predicted for total exchange (Table I). This observation is in accord with the results found for the [1,1,4,4-$^2H_4$]butadiene and substantiates that a major portion of the methyl loss arises from the original butadiene moiety. This is supported by the fact that loss of CH_2D is 2.5 times smaller than that predicted for statistical loss.

Table I. Isotopic Distribution for the Reaction of Benzvalene with Deuterium-Labeled 1,3-Butadiene[a,b]

neutral product	[1,1,4,4-$^2H_4$]1,3-butadiene	[$^2H_6$]1,3-butadiene
$\cdot CH_3$	24 (25)[c]	9 (9)[c]
$\cdot CH_2D$	40 (51)	17 (41)
$\cdot CHD_2$	37 (22)	46 (41)
$\cdot CD_3$	0 (2)	29 (9)

[a] Ionizing energy = 12.0 eV. [b] Values are the means of at least five measurements. Precision is better than ±10% relative standard deviation. [c] Numbers in parentheses are the calculated values assuming statistical distributions.

The information from the deuterium labeling allows us to suggest a large methyl loss from the original butadiene moiety, but the extensive exchange of the hydrogens and deuteriums prevents the assignment of a detailed mechanism. For this reason, we chose to examine the ion–molecule chemistry by using ^{13}C-labeled butadiene which should provide information on the nature of the carbon skeleton of the intermediate.

Reaction of Ionized Benzvalene with Neutral [1-^{13}C]1,3-Butadiene. The loss of $^{13}CH_3$ compared to the loss of CH_3 from the collision complex formed in the reaction with the [1-^{13}C]1,3-butadiene was found to be 1:4; that is, 80% of the methyl loss is CH_3 while 20% is loss of $^{13}CH_3$. Since the [1-^{13}C]1,3-butadiene molecule is symmetrical, we can multiply the measured intensity for loss of $^{13}CH_3$ by two to obtain the label distribution that would be obtained for [1,4-$^{13}C_2$]1,3-butadiene reacting as the labeled neutral. By doing this we can see that 40% of the methyl loss originates from the termini of the original butadiene moiety. This, coupled with the conclusion from the deuterium-labeling studies that a large part of the methyl loss comes from the original butadiene, allows us to suggest that the center carbons of the butadiene are also expelled as the methyl group. The best explanation for this would be formation of a cycloadduct by either a stepwise or a concerted process involving the termini of the butadiene. A tentative collision complex would be produced by a cycloaddition of the benzvalene as the dienophile and the butadiene as the diene (see eq 9).


(9)

Further support for this mechanism would require the synthesis of [2,3-$^{13}C_2$]1,3-butadiene. Thus far, we have been unable to prepare a sufficiently pure sample for testing the mechanism.

Rate-Constant Studies. The rate of reaction of fulvene with 1,3-butadiene has been reported previously.[10] We chose to determine the rate of reaction of ionized benzvalene with neutral butadiene and see how it compared to that of ionized fulvene.

We obtained a rate of 6.7×10^{-10} cm^3 mol^{-1} s^{-1} for the reaction of ionized benzvalene with neutral butadiene as compared to 1.0×10^{-9} cm^3 mol^{-1} s^{-1} for ionized fulvene and butadiene.

A comparison of the experimental rate and the theoretical rate calculated by the Langevin method[44] (1.3×10^{-9} cm^3 mol^{-1} s^{-1}) shows good agreement. If we assume that the collision frequency obtained from the Langevin calculation is the best estimate of the experimental collision frequency, we conclude that approximately 50% of the benzvalene ion–neutral butadiene collisions lead to product formation.

Collision-Induced Dissociation Studies. Cooks, Beynon, and Litton[7] studied the CID spectra of benzene and its linear isomers 1,5- and 2,4-hexadiyne. They observed that all three molecules gave essentially identical spectra. However, when these C_6H_6

---

(44) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

Table II. Collision-Induced Dissociation Spectra of Selected $[C_6H_6]^{+\cdot}$ Radical Cations[a-d]

	m/z										
$[C_6H_6]^{+\cdot}$ source	63	62	61	52	51	50	39	38	37	27	26
benzene	4.4	2.7	1.9	16.1	27.8	22.7	9.0	6.4	4.8	1.7	2.7
benzvalene	1.6	2.8	3.3	36.9	29.0	7.7	2.2	5.8	7.0	2.2	2.4
bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride	5.2	3.0	2.2	16.1	24.3	21.9	9.2	6.3	5.3	2.3	4.1
1,5-hexadiyne	5.0	2.5	1.8	26.6	21.4	19.4	9.8	5.0	4.4	1.8	2.7
2,4-hexadiyne	6.9	7.6	5.7	17.2	24.1	19.3	5.8	4.5	4.8	2.1	2.0
1,3-hexadien-5-yne	5.9	3.0	2.0	20.2	23.7	20.2	9.6	5.6	4.6	2.5	2.6
3,4-dimethylenecyclobutene	7.0	3.8	2.4	20.3	25.2	18.6	9.2	5.0	4.3	1.7	2.6
2,4-(*N*-phenylurazol-1,2-diyl)tricyclo[3.1.0.0^{3,6}]hexane	4.8	2.5	2.0	19.8	25.8	21.2	8.6	5.7	4.8	1.9	2.8

[a] Abundances relative to the sum of all peaks. [b] Values are the means of at least three measurements. [c] The reproducibility was better than ±5% relative standard deviation for benzene, 1,5- and 2,4-hexadiyne, 1,3-hexadien-5-yne, and DMCB, the rest were better than ±10%. [d] Ionizing energy 70 eV.

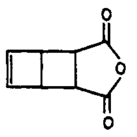
isomers were examined by charge stripping (formation of a doubly charged ion by interaction at high kinetic energy with a neutral gas molecule), differences were found. The relative cross sections for charge stripping were 8:2:1 for benzene, 1,5-hexadiyne, and 2,4-hexadiyne, respectively. The authors interpreted these results in terms of at least two different structures of C_6H_6 radical cations. There are other examples which show that charge stripping may be a better method for identification of isomers than CID.[45-48]

Borchers and Levsen[6] examined the C_6H_6 radical cations produced from benzene, its acyclic isomers, 1,5- and 2,4-hexadiyne, and more complex molecules as they fragmented. They suggested that the C_6H_6 radical cations isomerize to a common structure or mixture of structures. Only the CID spectra of the hexadiynes showed significant differences which are explained by proposing that the molecular ions of these particular compounds partially retained the structures of their neutral precursors.

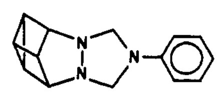
Results from another CID study[8] were interpreted to show that the C_6H_6 radical cation produced from direct ionization of [1-^{13}C]1,3-hexadien-5-yne isomerizes to a benzene radical cation prior to acetylene elimination. This was interpreted to mean that the hydrogen-exchange process in the benzene molecular ion occurs by reversible reactions in which acyclic species take part.

The common point in all the CID studies to date is that the benzene molecular ion does not give a distinct CID spectrum when compared to its acyclic isomers, particularly 1,3-hexadien-5-yne. Therefore, isomerization of benzene to an acyclic form was proposed. These interpretations are contradicted by the low energy ion–molecule reaction studies of Gross et al.[9] in which it was shown that the C_6H_6 radical cations from benzene and the acyclic isomers were different.

The CID Spectra of Some Selected C_6H_6 Radical Cations. The CID spectra of benzene, the acyclic isomers 2,4- and 1,5-hexadiyne and 1,3-hexadien-5-yne, the cyclic isomers benzvalene and 3,4-dimethylenecyclobutene, and the C_6H_6 radical cations produced from the decomposition of bicyclo[2.2.0]hex-5-ene-2,3-dicarboxlic anhydride (IV) and from 2,4-(*N*-phenylurazol-1,2-diyl)tricyclo-[3.1.0.0^{3,6}]hexane (V) were obtained. Major differences can be seen in the CID spectra of benzvalene, 1,5- and 2,4-hexadiyne, and DMCB when compared to the CID spectra of the other C_6H_6 radical cations (see Table II). The other spectra of the C_6H_6 radical cations were essentially identical with each other.



IV



V

The lack of difference in the CID spectra of benzene, 1,3-hexadien-5-yne, and the C_6H_6 radical cations generated from the more complex molecules can be interpreted to mean that these ions have isomerized to a common structure or mixture of structures. However, it has been shown that identical CID spectra do not necessarily mean identical ion structures.[44] The data from low energy ion–molecule reactions appear to be a better criterion for judging the ion structures for these particular ions.

Although the CID spectra of some of the C_6H_6 radical cations are not distinctive, this is not true for the spectra of ions from benzvalene, the hexadiynes, and DMCB. The CID spectrum of benzvalene shows a much larger loss of acetylene than the other C_6H_6 radical cations. Also much smaller methyl, ethylene, and C_3H_3 losses were observed. The favored loss of acetylene and the diminished loss of methyl, ethylene, and C_3H_3 are consistent with an ion structure retaining at least some cyclic characteristics.

The small loss of C_3H_3 from benzvalene reveals another distinct aspect of the benzvalene CID spectrum. A sharp peak due to charge stripping is seen superimposed on the broader *m/z* 39 CID peak. In the CID spectra of all the other C_6H_6 radical cations, the $C_3H_3^+$ peak is much larger (at least a factor of 3) and obscures the charge stripping peak if it is present at all.

For the cyclic isomer DMCB, a larger loss of methyl is seen compared to all the other C_6H_6 radical cations except that from 2,4-hexadiyne which has a comparable loss. However, the hexadiyne shows much larger losses of 16 and 17 mass units and a smaller loss of C_3H_3 than does DMCB, thus enabling a distinction to be made. The ionized 1,5-hexadiyne also shows distinct loss of acetylene, and that enables it to be distinguished from the other isomers. Our spectra of the ionized hexadiynes are in agreement with the previous reports.[6]

Conclusion

The chemical properties of the gas-phase benzvalene radical cation and other selected C_6H_6 radical cations have been examined with the use of Fourier transform mass spectrometry and collision-induced dissociation and compared to the results of previous work. We conclude that the benzvalene radical cation has a unique structure based on the low energy ion–molecule reaction chemistry. This is confirmed by the results of the CID experiments where it was observed that benzvalene exhibited a unique spectrum when compared to the CID spectra of the other C_6H_6 radical cations examined. We also find that it is possible to distinguish the C_6H_6 radical cation from DMCB by CID.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 80-08008) and by the Midwest Center for Mass Spectrometry (NSF Grant CHE 78-18572).

Registry No. I, 659-85-8; I radical cation, 81050-63-7; III, 5291-90-7; IV, 3097-60-7; V, 85554-23-0; 1,3-butadiene, 106-99-0; benzene, 71-43-2; 1,5-hexadiyne, 628-16-0; 2,4-hexadiyne, 2809-69-0; 1,3-hexadien-5-yne, 10420-90-3.

---

(45) Bowen, R.; Barbalas, M. P.; Pagano, F. P.; Todd, P. J.; McLafferty, F. W. *Org. Mass Spectrom.* **1980**, *15*, 51.

(46) Holmes, J. L.; Terlouw, J. K.; Burgers, P. C.; Rye, R. T. B. *Org. Mass Spectrom.* **1980**, *15*, 149.

(47) Miller, D. L.; Gross, M. L. *Org. Mass Spectrom.*, in press.

(48) Miller, D. L.; Gross, M. L. *J. Am. Chem. Soc.*, to be submitted.