Chemical Properties of the Fulvene Radical Cation: A Cycloaddition with 1,3-Butadiene

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Abstract: The chemical reactivity of the fulvene radical cation has been measured and compared with those of the benzene and various acyclic isomeric radical cations. This was accomplished by studying their reactivities in ion–molecule reactions observed using ion cyclotron resonance spectrometry (ICR). The fulvene radical cation exhibits considerably different properties from the other $[C_6H_6]^{+\cdot}$ isomers, and this is interpreted in terms of a unique structure for ionized fulvene which is not subject to ring opening or isomerization to benzene. One of the reactions of the fulvene cation, that with 1,3-butadiene, was examined in detail using dueterium and C-13 labeling. The intermediate complex has been assigned as a cycloadduct formed by an ionic analogue of a [6 + 4] cycloaddition.

In this paper, we report a study of the chemistry of ionized fulvene in order to compare its chemical properties with other $[C_6H_6]^{+\cdot}$ isomers. The structures of stable and decomposing C_6H_6 radical cations have been the subject of numerous experimental and theoretical studies.[1,2] Even with this large volume of experimental data, a clear and consistent understanding of the structure(s) and chemical properties of various C_6H_6 ions is only now beginning to emerge. Our present understanding of this important gas-phase ion has evolved because of the utilization of a large number of experimental methods including high-pressure mass spectrometry,[3] ion cyclotron resonance (ICR),[2a,4] defocused metastable methods,[5] collision-induced dissociation (CID),[6] isotopic labeling[7] (both ^2H and ^{13}C), photoion–photoelectron coincidence

spectroscopy (PIPECO),[8] emission spectroscopy,[9] and ionization/appearance energy measurements.[10]

Our work is directed at the question of whether structure is preserved upon ionization of organic molecules, and we have chosen C_6H_6 isomers as one model system for investigating this point. The answer to this question depends on the barrier heights for isomerization on various potential energy surfaces. Our experimental approach is to investigate the chemical properties of $[C_6H_6]^{+\cdot}$ as a function of neutral precursor structure. Of the various techniques mentioned above, high-pressure mass spectrometry, CID, and ICR are appropriate for the required studies of stable or nondissociating ions. We have chosen to study chemical reactivity in near-thermal ion–molecule reactions using ICR.

For highly activated dissociating ions, the possibility exists for isomerization and/or rearrangement reactions because activation energies for these processes can be lower than for fragmentation channels. Competitive or dominant isomerization is particularly important for systems which have high activation energies for dissociation. The molecular ion of benzene is a good example because the lowest energy fragmentation barrier is nearly 5 eV. Moreover, the ground-state heats of formation for the acyclic and cyclic C_6H_6 cation isomers are below the threshold for benzene decomposition. Thus, it is possible for a variety of C_6H_6 radical cations to interconvert at energies below the dissociation threshold.

However, we have found that the ion–molecule reaction chemistry of C_6H_6 radical cations which have insufficient energy to dissociate is consistent with unique structures for ionized benzene and acyclic isomers.[2a] Specifically, C_6H_6 ions from benzene react with 2-propyl iodide to form $C_9H_{13}^+$, whereas acyclic

(1) "Stable" ions refer to those of insufficient energy to decompose within a few milliseconds; "decomposing" ions have been activated to decompose at times less than a few milliseconds.

(2) For leading references, see: (a) Gross, M. L.; Russell, D. H.; Aerni, R. J.; Bronczyk, S. A. *J. Am. Chem. Soc.* **1977**, *99*, 3603. (b) Rosenstock, H. M.; McCulloh, K. E. *Int. J. Mass Spectrum. Ion Phys.* **1977**, *25*, 327.

(3) (a) Barker, R. *Chem. Ind. (London)* **1960**, 233. (b) Henglein, A. *Z. Naturforsch A* **1962**, *17*, 44. (c) Field, F. H.; Hamlet, P.; Libby, W. F. *J. Am. Chem. Soc.* **1967**, *89*, 6035. (d) Virin, L. I.; Safin, Y. A.; Dzhagatspanyan, R. F. *Khim. Vys. Energ.* **1967**, *1*, 417. (e) Giardini-Guidoni, A.; Zocchi, F. *Trans. Faraday Soc.* **1968**, *64*, 2342. (f) Wexler, S.; Clow, R. P. *J. Am. Chem. Soc.* **1968**, *90*, 3940. (g) Field, F. H.; Hamlet, P.; Libby, W. F. *Ibid.* **1969**, *91*, 2839. (h) Lifshitz, C.; Reuben, B. G. *J. Chem. Phys.* **1969**, *50*, 951. (i) Wexler, S.; Pobo, L. G. *J. Phys. Chem.* **1970**, *74*, 257. (j) Friedman, L.; Reuben, B. G. *Adv. Chem. Phys.* **1971**, *19*, 33. (k) Stockdale, J. A. D. *J. Chem. Phys.* **1973**, *58*, 3881. (l) Jones, E. G.; Bhattacharya, A. K.; Tiernan, T. O. *Int. J. Mass Spectrum. Ion Phys.* **1975**, *17*, 147. (m) Sieck, L. W.; Gordon, R., Jr. *Ibid.* **1976**, *19*, 269.

(4) (a) Anicich, V. G.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *11*, 329. (b) Freiser, B. S.; Beauchamp, J. L. *Chem. Phys. Lett.* **1975**, *35*, 35.

(5) (a) Bursey, M. M.; Tibbetts, F. G.; Little, W. F.; Rausch, M. D.; Moser, G. A. *Tetrahedron Lett.* **1969**, 3469. (b) Jones, E. G.; Bauman, L. E.; Beynon, J. H.; Cooks, R. G. *Org. Mass Spectrom.* **1973**, *7*, 185. (c) Keough, T.; Ast, T.; Beynon, J. H.; Cooks, R. G. *Ibid.* **1973**, *7*, 245. (d) Cooks, R. G.; Kim, K. C.; Keough, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *15*, 271.

(6) (a) Cooks, R. G.; Beynon, J. H.; Litton, J. F. *Org. Mass Spectrom.* **1975**, *10*, 503. (b) Borchers, F.; Levsen, K. *Ibid.* **1975**, *10*, 584.

(7) (a) Beynon, J. H.; Caprioli, R. M.; Perry, W. O.; Baitinger, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 6828, and references cited therein. (b) Gross, M. L.; Aerni, R. J. *Ibid.* **1973**, *95*, 7875.

(8) (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. (c) Dannacher, J. *Chem. Phys.* **1978**, *29*, 333.

(9) Allan, M.; Maier, J. P.; Marthaler, O.; Kloster-Jensen, E. *Chem. Phys.* **1978**, *29*, 331.

(10) (a) Andlauer, B.; Ottinger, Ch. *J. Chem. Phys.* **1971**, *55*, 1471. (b) Andlauer, B.; Ottinger, Ch. *Z. Naturforsch A* **1972**, *27*, 293. (c) Smith, R. D.; Futrell, J. H. *Org. Mass Spectrum.* **1976**, *11*, 445. (d) Jonsson, B.; Lindholm, E. *Ark Fys.* **1968**, *39*, 65. (e) Lifschitz, C.; Peers, A. M.; Weiss, M.; Weiss, J. J. *Adv. Mass Spectrom.* **1974**, *6*, 87. (f) Gordon, S. M.; Reid, N. W. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *18*, 379.

C_6H_6 radical cations only undergo a charge exchange reaction.

Other ion–molecule reactions of C_6H_6 radical cations assigned acyclic structures serve to support this picture. For example, these ions react with neutral acyclic C_6H_6 molecules and with 1,3-butadiene, whereas ionized benzene exhibits none of this chemistry.[2a] Other support for the concept of nonequilibration between ionized benzene and its acyclic isomers can be found in charge-stripping experiments[6a] but not in collision-induced dissociation.[6b]

Although the foregoing discussion pertains to nondecomposing $[C_6H_6]^+\cdot$, the existence of distinctive structures for certain dissociating C_6H_6 ions has been demonstrated also.[9] Based on the emission spectra of 1,3-hexadiyne and 2,4-hexadiyne radical cations, it has been concluded that a major fraction of these ions do not isomerize to benzene or to 1,4- or 1,5-hexadiyne even when activated above the threshold for fragmentation.

Another property of ionized benzene sufficiently activated to decompose is the propensity for carbon and hydrogen isomerization (scrambling).[7] The results have been interpreted to indicate that the hydrogen and carbon atoms are completely randomized prior to unimolecular dissociation, and that there are separate mechanisms for each of these processes. Of course, this must mean the ionized benzene must isomerize to some other structure prior to or concurrent with dissociation. Possible rearrangements which could be invoked are valence isomerizations or ring contractions (such as to fulvene). Hydrogen atom scrambling could take place via ring-opened isomers or even on the intact benzene skeleton.[11]

Isomerization of benzene ions to the fulvene structure (**1**) is
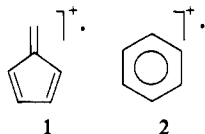
slightly endothermic [ΔH_f (fulvene radical cation) $\simeq$ 240 kcal; ΔH_f (benzene ion) $\simeq$ 233 kcal], and therefore it is an attractive intermediate for explaining carbon and hydrogen atom randomization processes in activated ions.[12] Moreover, beginning with the fulvene structure of $[C_6H_6]^+\cdot$, an exothermic rearrangement to the benzene structure would release $\sim$6 kcal/mol provided that there is no large activation energy. Conversely, the activation energy for ring opening to give an acyclic $[C_6H_6]^+\cdot$ would be large (at least 50–60 kcal). Evidence for or against this proposal can be obtained by a comparative study of benzene and fulvene.

A second reason for extending our C_6H_6 research to fulvene is that the radical cation should be an attractive candidate for cycloadditions provided, of course, its structure is retained upon ionization. Cycloaddition ion–molecule reactions have been of considerable interest to us, and they have been the subject of previous publications from this laboratory[13] and others.[14]

Results and Discussion

Reaction of Ionized Fulvene and Neutral Benzene. As we have reported previously, no bimolecular "dimerization" of ionized benzene and neutral benzene to give $[C_{12}H_{12}]^+\cdot$ occurs under the single collision condition of the ICR experiment. Furthermore, $[C_6H_6]^+\cdot$ from acyclic sources is also unreactive with neutral benzene thus ruling out these ions as precursors to the bimolecular formation of $[C_{12}H_{12}]^+\cdot$ observed by Jones et al.[31]

To determine whether the fulvene radical cation is the reactant in the bimolecular formation of $[C_{12}H_{12}]^+\cdot$, we investigated the ion–molecule reaction chemistry of ionized fulvene and neutral benzene. Under our experimental conditions (pressure range 10^{-6}–10^{-4} Torr and electron ionizing energies between 10 and 25 eV), no condensation products were observed when **1** and benzene-d_6 were mixed in the ICR cell. Instead, the only ion–molecule

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

(12) For a comparison of the heats of formation of various $C_6H_6^+\cdot$ radical cations, see Table I in ref 2a.

(13) Russell, D. H.; Gross, M. L. *Lect. Notes Chem.: Ion Cyclotron Reson. Spectrom.* **1978**, *7*, 209–231, and references cited therein.

(14) van Doorn, R.; Nibbering, N. M. M.; Ferrer-Correia, A. J.; Jennings, K. R. *Org. Mass Spectrom.* **1978**, *13*, 729.

product ion	m/z	rel intensity[b]
$C_{12}H_{12}$	156	1
$C_{12}H_{11}$	155	37
$C_{11}H_9$	141	36
$C_{10}H_8$	128	11
C_9H_9	117	3
C_9H_8	116	2
C_9H_7	115	6
C_8H_8	104	4

[a] At a total fulvene pressure of 5×10^{-6} torr and an ionizing energy of 10.5 eV. [b] Expressed as a percent of total product ion intensity which was normalized by dividing ion intensity by the mass of the ion observed.

reaction found is a charge exchange reaction of the benzene radical cation with a fulvene neutral (eq 1). Since the ionization potential
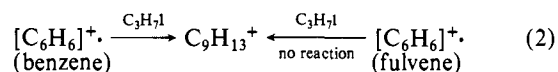
$$C_6H_6 + C_6D_6^+\cdot \rightarrow C_6H_6^+\cdot + C_6D_6 \qquad (1)$$
$$\text{(fulvene) (benzene)}$$
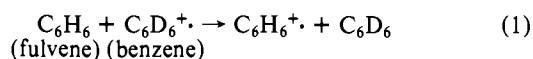
of fulvene (IP = 8.36[15]) is lower than that of benzene (IP = 9.25 eV[16]), the charge exchange is not unexpected.

Based on these observations, we may rule out fulvene as the precursor for the bimolecular formation of $[C_{12}H_{12}]^+\cdot$ as found in the benzene system.[31]

Reactions of Ionized Fulvene with Neutral Fulvene and 2-Propyl Iodide. Ionization of fulvene in the ICR cell produces a situation similar to that of the acyclic benzene isomers; that is, a rich variety of secondary product ions are found. Specifically, the major secondary ions are $[C_{12}H_{12}]^+\cdot$, $[C_{12}H_{10}]^+\cdot$, $C_{11}H_9^+$, $[C_{10}H_8]^+\cdot$, $C_{10}H_7^+$, $C_9H_7^+$, and $[C_8H_8]^+\cdot$ (see Table I for relative intensities). Clearly, the prolific ion–molecule reaction chemistry in a mixture of ionized and neutral fulvene is in sharp contrast to the inertness of the benzene ion and of ionized fulvene with neutral benzene.

Final confirmation for the lack of correspondence between ionized fulvene and benzene is the lack of reactivity of the fulvene ion and 2-propyl iodide (eq 2). The rate constant for the reaction
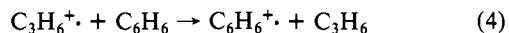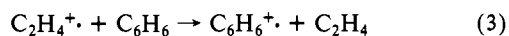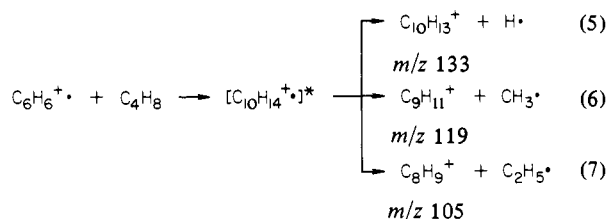
$$[C_6H_6]^+\cdot \xrightarrow{C_3H_7I} C_9H_{13}^+ \xleftarrow[\text{no reaction}]{C_3H_7I} [C_6H_6]^+\cdot \qquad (2)$$
$$\text{(benzene)} \qquad\qquad\qquad\qquad\quad \text{(fulvene)}$$

is <0.01 that of ionized benzene and 2-propyl iodide (i.e., $<1.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}).

Ion–Molecule Chemistry of Ionized Fulvene and Neutral Alkenes. Based on these results, any significant interconversion of ionized benzene and fulvene can be dismissed. This conclusion holds for ions which have *not* been activated to dissociate. However, at this point we cannot rule out ring opening of the fulvene ion to give an acyclic C_6H_6 structure. In fact, both ionized fulvene and acyclic C_6H_6 ions react with 1,3-butadiene (vide infra) and with their neutral precursors.

As a starting point for a comparison study of ionized fulvene and acyclic isomers, simple alkenes were chosen as reagent neutrals. No condensation product ions were observed when ethene or propene are mixed in the ICR cell with fulvene or with C_6H_6 ions from various acyclic isomers. However, a charge exchange reaction was found involving the alkene molecular ion and neutral C_6H_6 (eq 3 and 4).

$$C_2H_4^+\cdot + C_6H_6 \rightarrow C_6H_6^+\cdot + C_2H_4 \qquad (3)$$

$$C_3H_6^+\cdot + C_6H_6 \rightarrow C_6H_6^+\cdot + C_3H_6 \qquad (4)$$

In mixtures of the $[C_6H_6]^+\cdot$ sources and 1- or 2-butene, three ion–molecule product ions are observed. From pulsed double resonance experiments, these secondary ions are formed exclusively by reactions of $[C_6H_6]^+\cdot$ from fulvene (eq 5–7), but when an

(15) Heilbronner, E. H.; Gleiter, R.; Hopf, H.; Hornung, V.; deMeigere, A. *Helv. Chim. Acta* **1971**, *54*, 783.

(16) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Hernon, J. T.; Draxl, K.; Field, F. H. *Natl. Stand. Ref. Data Ser. Natl. Bur. Stand.* **1969**, *26*.

$$C_6H_6^+ \cdot \ + \ C_4H_8 \ \longrightarrow \ [C_{10}H_{14}^{+} \cdot]^* \ \begin{cases} \longrightarrow C_{10}H_{13}^+ + H \cdot & (5) \\ & m/z\ 133 \\ \longrightarrow C_9H_{11}^+ + CH_3 \cdot & (6) \\ & m/z\ 119 \\ \longrightarrow C_8H_9^+ + C_2H_5 \cdot & (7) \\ & m/z\ 105 \end{cases}$$

acyclic was used for the source of $[C_6H_6]^+ \cdot$, the results were more complicated. For example, using acyclic C_6H_6 isomers (1,5-hexadiyne, 1,4-hexadiyne, and 1,3-hexadien-5-yne), ion–molecule product ions were found at m/z 119 ($C_9H_{11}^+$), 105 ($C_8H_9^+$), and 95 ($C_7H_{11}^+$) which, according to pulsed double resonance, arise exclusively from $[C_4H_8]^+ \cdot$ (1-butene or 2-butene; see eq 8–10).

$$C_4H_8^+ \cdot \ + \ C_6H_6 \ \longrightarrow \ [C_{10}H_{14}^{+} \cdot]^* \ \begin{cases} \longrightarrow C_9H_{11}^+ + CH_3 \cdot & (8) \\ \longrightarrow C_8H_9^+ + C_2H_5 \cdot & (9) \\ \longrightarrow C_7H_{11}^+ + C_3H_3 \cdot & (10) \end{cases}$$
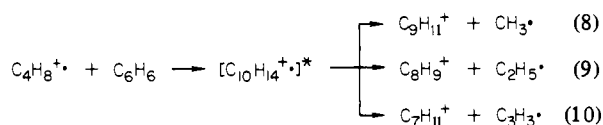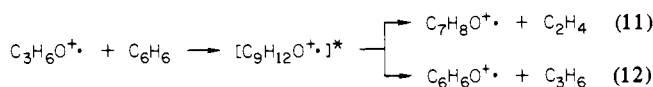
On the other hand, in mixtures of 2,4-hexadiyne with 1-butene, the same ion–molecule products were found (eq 8–10), but pulsed double resonance experiments show these secondary ions originate from *both* $[C_4H_8]^+ \cdot$ and $[C_6H_6]^+ \cdot$.
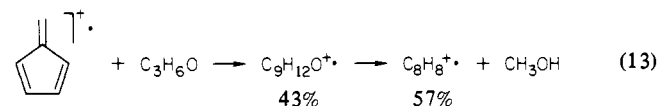
Results similar to those of the C_6H_6/butene system are observed with other alkenes (the isomeric pentenes, cyclopentene, cyclopentadiene, and cyclohexene). That is, secondary ions are observed which correspond to loss of CH_3, C_2H_4, C_3H_4, and C_3H_7 from the collision complex. For each of the $[C_6H_6]^+ \cdot$ sources, the secondary ions are formed both from molecular ions of the C_6H_6 source and of the alkene as verified by double resonance.

It is not easy to establish whether these differences in ion–molecule reactivity arise because of structural differences or internal energy effects. Therefore, we chose to continue the search for reagent neutrals which could be employed to resolve whether ionized fulvene had isomerized to a ring-opened structure. This is preferred in lieu of exhaustive ion ejection studies or isotopic labeling which may have given ambigous results.

Reactions with Methyl Vinyl Ether. Methyl vinyl ether was chosen as the first reagent neutral candidate. In a mixture of this compound and acyclic $[C_6H_6]^+ \cdot$ sources, no secondary ions, which can be attributed to $[C_6H_6]^+ \cdot$, were found. Small amounts of m/z 108 ($C_7H_8O^+ \cdot$) and 94 ($C_6H_6O^+ \cdot$) were observed to arise from the methyl vinyl ether molecular ion reacting with neutral acyclic C_6H_6 isomers as verified by pulsed double resonance (eq 11).

$$C_3H_6O^+ \cdot \ + \ C_6H_6 \ \longrightarrow \ [C_9H_{12}O^+ \cdot]^* \ \begin{cases} \longrightarrow C_7H_8O^+ \cdot + C_2H_4 & (11) \\ \longrightarrow C_6H_6O^+ \cdot + C_3H_6 & (12) \end{cases}$$

These results are in sharp contrast to the reactivity of ionized fulvene with methyl vinyl ether. Now, the collision complex (m/z 136) and $C_8H_8^+ \cdot$ are observed (eq 13). These product ions arise exclusively from $[C_6H_6]^+ \cdot$ as showed by pulsed double resonance.

$$\text{(fulvene)}^{+\cdot} + C_3H_6O \longrightarrow \underset{43\%}{C_9H_{12}O^+ \cdot} \longrightarrow \underset{57\%}{C_8H_8^+ \cdot} + CH_3OH \quad (13)$$

Based on these results, we conclude that isomerization of ionized fulvene and various acyclic C_6H_6 ions, in particular 1,5-hexadiyne, 2,4-hexadiyne, or 1,3-hexadien-5-yne, does not occur for low energy species. Because the ion–molecule chemistry does not change signficantly as the ionizing energy is increased from 10 to 17 eV, the conclusion also holds for the distribution of ions formed between the ionization threshold and the dissociation barrier. Strictly speaking, isomerization of the fulvene ions and some untested acyclic form is not precluded; however, this possibility is quite remote because all the acyclic isomers studied thus far exhibit quite similar ion chemistry.[2a]

The heats of formation of the radical cations of fulvene and various acyclic isomers are certainly in accord with the lack of
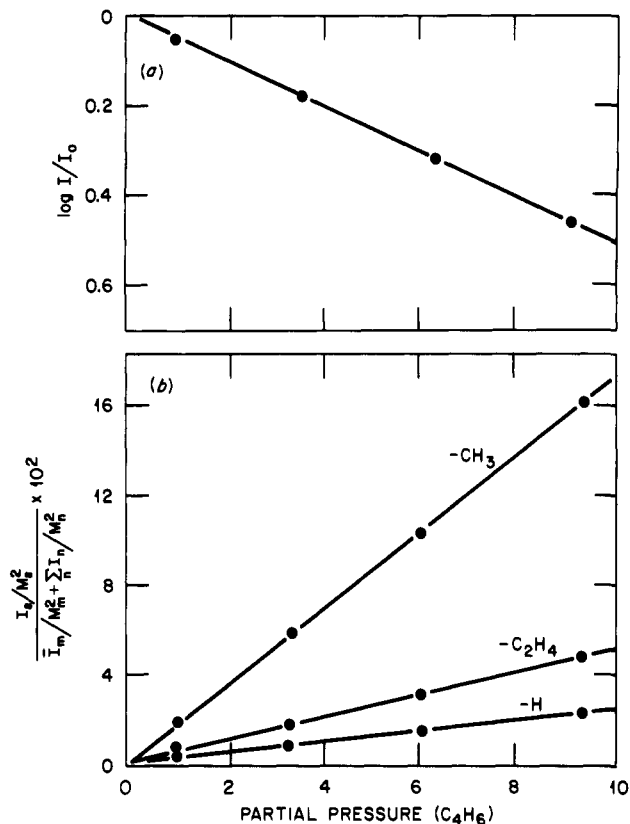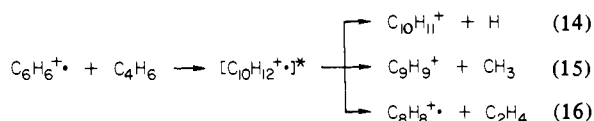

Figure 1. Kinetic plots for the reaction of ionized fulvene and 1,3-butadiene at 11 eV of ionizing energy: (a) disappearance of $[C_6H_6]^+$; (b) appearance of products from dissociation of the intermediate $[C_{10}H_{12}]^+$.

ring opening of fulvene upon removal of an electron.[12] The *minimum* barrier height, assuming no reverse activation energy, would be ~60 kcal/mol. There must be a reverse activation energy because no isomerization of the acyclic isomers to fulvene can be detected. Therefore, the benzene, fulvene, and the isomeric acyclic C_6H_6 radical cations exist in potential energy wells. Their chemical and physical properties can be explored provided that they are not activated to decompose. The energy onset for interconversion must be approximately that of a dissociation threshold.[17,18]

Ion–Molecule Reaction Chemistry of Ionized Fulvene and Neutral 1,3-Butadiene. The ion–molecule chemistry of fulvene and neutral 1,3-butadiene is of particular interest to us because this system is a likely candidate for a cycloaddition reaction mechanism. In fact, ionized fulvene is quite reactive with neutral 1,3-butadiene; three products are formed in bimolecular reactions (eq 14–16) as verified by the observation of the pressure depen-

$$C_6H_6^+ \cdot \ + \ C_4H_6 \ \longrightarrow \ [C_{10}H_{12}^{+} \cdot]^* \ \begin{cases} \longrightarrow C_{10}H_{11}^+ + H & (14) \\ \longrightarrow C_9H_9^+ + CH_3 & (15) \\ \longrightarrow C_8H_8^+ \cdot + C_2H_4 & (16) \end{cases}$$

dence of their relative intensities (see Figure 1). Pulsed double resonance experiments, performed to establish unambiguously the reacting precursor, show that $C_9H_9^+$ and $[C_8H_8]^+ \cdot$ are formed exclusively from $[C_6H_6]^+ \cdot$ while $C_{10}H_{11}^+$ is formed competitively from $[C_4H_6]^+ \cdot$ reacting with neutral C_6H_6 and $[C_6H_6]^+ \cdot$ with neutral 1,3-butadiene. The relative contribution from reactant $[C_6H_6]^+ \cdot$ to produce $C_{10}H_{11}^+$ was estimated by ion ejection studies.[19] A value of 30 ± 10% was obtained for equal partial

(17) Addition studies have revealed characteristic ion–molecule reaction chemistry for the molecular ion of 3,4-dimethylenecyclobutene. This establishes that the fulvene ion and the 3,4-dimethylenecyclobutene ion do not interconvert or ring open on the ICR time scale, i.e., ~10^{-3} s. See Russell, D. H. Ph.D. Thesis, University of Nebraska, 1978.

(18) See ref 2a and references cited therein.

Table II. Comparison of the Experimental Rate Constant for Product Ion Formation with the Calculated Collision Frequency[a]

compds	exptl[b]	calcd
fulvene + 1,3-butadiene	1.0×10^{-9}	1.3×10^{-9}

[a] Units of cm^3 molecule^{-1} s^{-1}. Expressed as the sum of the three reaction channels (eq 14–16). [b] Ionizing energy = 11.0 eV. Relative standard deviation of replicate measurements ±3%.

Table III. Isotopic Distribution for the Reaction of Fulvene with Deuterium Labeled 1,3-Butadiene[a]

neutral product	rel intensity	
	1,3-butadiene-1,1,4,4-d_4	1,3-butadiene-d_6
CH_3	32 (25)[b]	20 (9)
CH_2D	38 (51)	31 (41)
CHD_2	26 (22)	31 (41)
CD_3	4 (2)	18 (9)
C_2H_4	16 (14)	8 (3)
C_2H_3D	25 (45)	18 (24)
$C_2H_2D_2$	47 (34)	36 (46)
C_2HD_3	12 (6)	23 (24)
C_2D_4	0 (1)	15 (3)

[a] Ionizing energy = 11.0 eV. [b] Numbers in parentheses are the calculated values assuming statistical distribution.

Table IV. Isotopic Distribution for the Reaction of Fulvene with ^{13}C-Labeled 1,3-Butadiene[a]

neutral lost	*I*	
	1,3-butadiene-1-^{13}C	1,3-butadiene-2,3-$^{13}C_2$
CH_3	76 (90)[b]	68 (80)
$^{13}CH_3$	24 (10)	32 (20)
$^{12}C_2H_4$	60 (90)	51 (62)
$^{12}C^{13}CH_4$	40 (10)	38 (36)
$^{13}C_2H_4$		11 (02)

[a] Ionizing energy = 11.0 eV. [b] Numbers in parentheses are the calculated values expected for a statistical distribution.

pressures of neutrals and equal ion intensities for m/z 78 and 121.

To assess the efficiency of the reaction of ionized fulvene with neutral 1,3-butadiene, the absolute rate constants for formation of secondary product ions were measured and these values compared with the collision frequency calculated using the Langevin equation[20] (see Table II). If we assume that the collision frequency obtained from the Langevin calculation is the best estimate of the collision frequency, we conclude that the reaction is very efficient; ~80% of the ion–neutral collisions lead to product formation.

Results of ^2H and ^{13}C Isotopic Labeling

In order to examine in detail the reaction mechanism for product ion formation in a mixture of ionized fulvene and 1,3-butadiene, we have utilized ^2H- and ^{13}C-labeled 1,3-butadienes. With deuterium substitution, extensive, but incomplete, randomization of the H/D is observed to occur in the collison complex. Nonetheless, subtle features are discernible. For example with 1,3-butadiene-1,1,4,4-d_4, the loss of CH_3 is significantly larger than is expected for complete H/D randomization (see Table III). Moreover, with 1,3-butadiene-d_6 both CH_3 and CD_3 losses exceed the statistical value.

Because of the rather extensive isotopic randomization associated with the experimental results for ^2H labeling, an unambiguous assignment of the reaction mechanism is not possible. However, the intense loss of CD_3 when 1,3-butadiene-d_6 is used as a neutral may be in accord with a mechanism whereby a significant fraction of the methyl loss involves the original atoms of the butadiene moiety. This possibility can be addressed by employing ^{13}C-labeled 1,3-butadiene (see Table IV).

Based on the ^{13}C-labeling results, it is confirmed that a large fraction of the methyl loss originates from the original butadiene moiety. For example, the isotopic distribution for ionized fulvene reacting with neutral 1,3-butadiene-1-^{13}C is 24% loss of $^{13}CH_3$ and 76% loss of $^{12}CH_3$. Owing to the symmetry of the butadiene molecule, the measured intensity for loss of $^{13}CH_3$ can be multiplied by a factor of 2 to obtain the label distribution if 1,3-butadiene-1,4-$^{13}C_2$ were the reacting neutral. This shows that ~50% of the methyl loss originates from the original butadiene termini.

To investigate the internal carbons of 1,3-butadiene, 1,3-butadiene-2,3-$^{13}C_2$ was employed as the neutral. Now, 32% loss of the labeled methyl is observed. Thus, in the collision complex formed in the reaction of ionized fulvene with 1,3-butadiene,

~80% of the methyl loss incorporates the original butadiene carbon atoms.

The results obtained for 1,3-butadiene-2,3-$^{13}C_2$ are of key importance in understanding the mechanism for the ion–molecule reaction of ionized fulvene and 1,3-butadiene. Although the loss of $^{13}CH_3$ from the complex formed when 1,3-butadiene-1-^{13}C is employed does not allow a distinction to be drawn between a cyclic or acyclic intermediate, $^{13}CH_3$ loss with the 1,3-butadiene-2,3-$^{13}C_2$ constitutes proof that at least a fraction of the $[C_{10}H_{12}]^{+\cdot}$ intermediates must possess a cyclic structure or must pass through a cyclic transition state enroute to loss of methyl. Only in this way can an internal carbon of the butadiene moiety be expelled as a methyl group.

For the loss of ethene, the C-13-labeling results reveal that the neutral originates primarily from the butadiene moiety. The principal evidence for this is with 1,3-butadiene-1-^{13}C as the neutral; 40% of the expelled ethene contains a C-13. Multiplying by a factor of 2, we see that 80% of the departing ethenes contain a terminal carbon from the butadiene neutral. If only the butadiene carbons are involved, we would predict that 80% of the collision complexes formed with 1,3-butadiene-2,3-$^{13}C_2$ would lose $^{12}C^{13}CH_4$. Clearly, this is not the case (see Table IV). In fact, only 38% do. Thus, at least one fulvene carbon atom must be incorporated in 42% of the ethene loss.

Approximately 10% of the collision complexes expel ethene which originates from the center carbons of butadiene (see results with 1,3-butadiene-2,3-$^{13}C_2$). This loss is possible only if both terminal carbons of the butadiene are bound to the fulvene in the collision complex. As for the methyl loss from the 2 and 3 positions of the butadiene, also, this is possible only if a fraction of the reaction pathways involve a cycloadduct as an intermediate.

Structural Assignment of the Reaction Intermediate. The C-13 results clearly are in accord with a cycloaddition reaction mechanism. Although a number of mechanistic possibilities could be summed to explain the labeling results, a single mechanism is preferable if it can accommodate all of the results. Because of the bifunctional nature of fulvene (possesses both ene and diene character), it may be difficult to settle on a single process. Nevertheless, we will consider a number of possible intermediates making use of the evidence that the reaction proceeds, at least in part, as a cycloaddition, and using the isotopic patterns for methyl and ethene losses from the collision complex to decide the contribution of the various cycloaddition pathways.

[4 + 2] Cycloaddition. Neutral fulvene can serve as a diene or a dienophile in [4 + 2] cycloadditions. The structures **3** and **4** are formed if this mechanism pertains to the ionic reaction (the


3   4
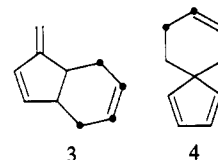
darkened atoms represent the original butadiene). However, these structures are ruled out based on the the large fraction of $^{12}C_2H_4$ lost (~50%) when 1,3-butadiene-2,3-$^{1,3}C_2$ is employed (see Table IV). If these structures represent the intermediate, ratios of $^{12}C_2H_4$:$^{12}C^{13}CH_4$:$^{13}C_2H_4$ losses would be 0:2:1 for **3** and 1:2:1 for

(19) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.
(20) Gioumousis, G.; Stevenson, D. P. *J. Chem. Phys.* **1958**, *29*, 294.

4 assuming all nonbridgehead carbons in the cyclohexenyl ring can participate equally. The observed ratio of 5:4:1 is clearly not consistent. Even invoking preferential losses from the substituted cyclohexenyl ring, no agreement can be found.

The structures **5** and **6** can arise via [4 + 2] cycloadditions in
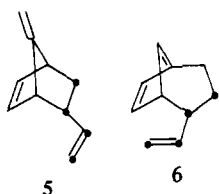

which fulvene reacts as a cis and trans diene, respectively. Both structures can be dismissed immediately because it is impossible to lose $^{13}C_2H_4$ when 1,3-butadiene-$2,3$-$^{13}C_2$ is employed. Moreover, the bridgehead double bond in structure **6** is sterically unfavorable.

[4 + 4] Cycloaddition. There are two possible structures for an ionic analogy of a [4 + 4] cycloaddition reaction mechanism: **7** and **8**. These structures are subject to the same inconsistencies
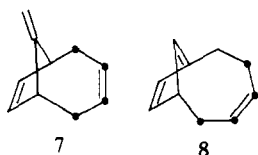

as the [4 + 2] structures; that is, it is not possible to account for the preference for $^{12}C_2H_4$ loss when 1,3-butadiene-$2,3$-$^{13}C_2$ is the reacting neutral. For example the predicted ratios for $^{12}C_2H_4$, $^{12}C^{13}CH_4$ and $^{13}C_2H_4$ losses, of 0:2:1 for **7** and 1:2:1 for **8** do not agree with measured of 5:4:1, $^{12}C_2H_4$:$^{12}C^{13}CH_4$:$^{13}C_2H_4$. Preferential loss of ethylene containing one fulvene carbon and a terminal carbon from the 1,3-butadiene, however, could account for the large loss of $^{12}C_2H_4$. However, the bridgehead double bond in structure **8** is sterically unfavorable.

[6 + 4] Cycloaddition. We propose that the experimental results can be best understood in terms of a single intermediate, structure **9**, which can arise by a stepwise or synchronous process analogous to a [6 + 4] cycloaddition for neutrals (eq 17–18). It is recognized
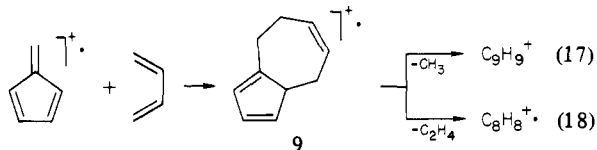
that one π electron is missing from the fulvene molecule and, as a result, the designation should be [5 + 4]. Nevertheless, the designation of a neutral reaction is maintained for the sake of familiarity.

All of the measured isotopic distributions from the ^{13}C labeling are consistent with structure **9**. For example, we expect that, for loss of methyl, each of the five carbons in the seven-member ring would participate about equally owing to the mobility of the double bond. The observed values (as depicted below) agree with the expected value of 20% per carbon with an error of ±4% absolute.
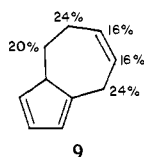
The [6 + 4] cycloadduct is also consistent with the C-13 distribution for ethene loss. Double-bond migration in the seven-membered ring can lead to a set of three structures which can undergo cycloreversion reactions (Scheme I). The initially formed intermediate **9a** or a structurally degenerate isomer in the absence of C-13 labeling formed by migration of the double bond, **9b**, can both cyclorevert to return to starting materials (fulvene and

Scheme I. Cycloreversion Reactions of the Intermediate Complex Produced in Reaction of Ionized Fulvene and 1,3-Butadiene
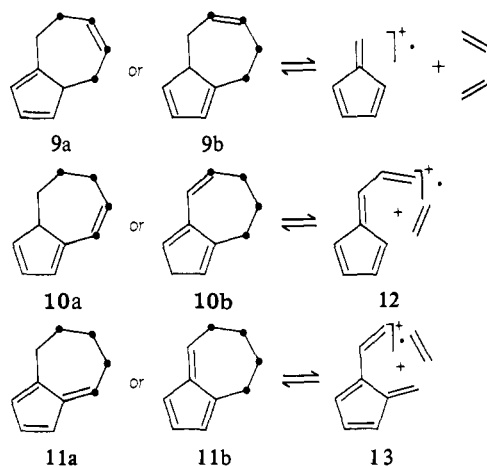

Table V. Comparison of Predicted and Observed Isotopic Distribution (Percent) for Ethene Loss in the Reaction of Fulvene and 1,3-Butadiene

loss, neutral	1,3-butadiene^a-$1,4$-$^{13}C_2$		1,3-butadiene-$2,3$-$^{13}C_2$	
	predicted	obsd	predicted	obsd
C_2H_4	10	20	40	51
$^{13}CCH_4$	90	80	50	38
$^{13}C_2H_4$			10	11

^{a} 1,3-Butadiene-$1,4$-$^{13}C_2$ was not employed. These results were predicted based on the data for the reaction of fulvene and 1,3-butadiene-1-^{13}C.

1,3-butadiene). An additional double-bond migration for **9a** and **9b** gives **10a** and **10b**, respectively, which can now cyclorevert to give ethene and **12**. A final double-bond migration takes **10a** and **10b** to **11a** and **11b**, and these structures may also undergo a cycloreversion to expel ethene and produce **13**. The neutral counterparts of the reactions of **10a**, **10b**, **11a**, and **11b** are [8 + 2] cycloreversions which are thermally allowed.

To explain the C-13 isotopic distribution for ethene loss, it is necessary to favor a more facile cycloreversion of structures **10a** and **10b**. Although this is difficult to justify a priori, one would expect structures **10** and **11** to exhibit different but competitive reactivities. Assuming that a cycloreversion to expel ethene occurs 80% of the time from **10a** and **10b** and 20% from **11a** and **11b**, theoretical isotopic distributions for reaction with butadiene-$1,4$-$^{13}C_2$ and butadiene-$2,3$-$^{13}C_2$ can be predicted and compared with the experimental values (see Table V).

Although the agreement is not perfect, we believe that it is satisfactory. The ethene loss patterns, taken alone, are not convincing support for the mechanism. This is because there is no independent evidence to verify the greater propensity of structures **10a** and **10b** to cyclorevert. However, it must be pointed out that only this cycloadduct allows us to understand both the methyl and ethene losses. It serves as a single and reasonable intermediate capable of accommodating all the results obtained thus far.

Cycloaddition Chemistry of Neutral Fulvene. While we could designate the ion–molecule reaction chemistry of fulvene and butadiene as a [3 + 4] reaction (based on the number of carbons involved), it is formally a [6 + 4] concerted reaction of the corresponding neutrals. Although this is not a common mode of reaction of neutral fulvenes, it appears to become important when the fulvene LUMO-diene HOMO interaction becomes strong as has been suggested by Houk and co-workers.[21a] An example is

(21) (a) Houk, K. N.; George, J. K.; Duke, R. E., Jr. *Tetrahedron* **1974**, *30*, 523. (b) Dunn, L. C.; Chang, Y.-M.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 7095.

Chart I
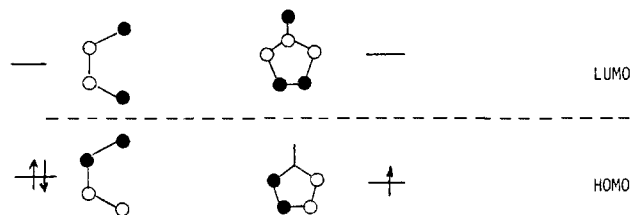
LUMO

HOMO

the [6 + 4] cycloaddition of diethylamino-1,3-butadiene to substituted fulvenes.[21b]

For the ionic counterpart, we propose that the important molecular orbital interaction is the LUMO of fulvene and the HOMO of butadiene because it is a two-electron interaction (Chart I). There is another interaction unique to radical ions, and that is the three-electron HOMO/HOMO; however, it is the two-electron interactions which principally direct the cycloaddition that is observed. Furthermore, we have estimated the charge distribution of the fulvene radical cation using the Hückel MO approach and find that the major fraction of the charge is located at the reacting positions 2 (or 5) and 6 (27 and 38%, respectively). This reinforces the MO interaction leading to the incredibly facile cycloaddition that occurs on about three of four collisions of ion and neutral.

Experimental Section

The apparatus used was a Varian ICR-9 spectrometer equipped with a duel inlet and a three-section standard flat cell. Single resonance spectra were obtained in the field modulation mode, typically at 153 kHz. For mass measurements >140 amu, a frequency of 123 kHz was used. Typical drift fields for the source and analyzer were 0.15–0.10 V cm^{-1} with trapping fields of ~0.4 V. All ionizing energies were nominal values with emission currents of ~0.1 μA. Double-resonance measurements were made in the pulsed mode. All studies were conducted at ambient temperature.

Relative rate constant measurements were made by introducing a degased sample of fulvene to a pressure of ~4–6 × 10^{-6} Torr and allowing the cell to equilibrate. The butadiene was admitted via the second inlet and the partial pressure controlled with a variable leak valve using the total ion current monitor as a reference for relative pressure changes. The relative rate constants for product ion appearance, i.e., $C_{10}H_{11}^+$ (m/z 131), $C_9H_9^+$ (m/z 117), and $C_8H_8^{+\cdot}$ (m/z 104), were calculated from the least-squares slopes of the plot of $(i_s/m_s^2)/(i_p/m_p + \Sigma_i i_s/m_s^2)$ vs. partial pressure of 1,3-butadiene. The rate of disappearance of the fulvene molecular ion was determined from a plot of log (i/i_0) vs. the partial pressure of 1,3-butadiene where i_0 is the intensity of the m/z 78 signal without added 1,3-butadiene and i is the corresponding intensity with the reactant neutral present.

The absolute rate constant for the reaction of the fulvene molecular ion with neutral 1,3-butadiene was obtained using the rate constant for production of CH_5^+ in methane as a reference. This strategy was em-

ployed because of the uncertainty in the calculation of residence times ions in the cell. To circumvent this uncertainty, plots of the rates of appearance for product ions in the fulvene/butadiene mixture and of CH_5^+ in methane were made from 10 back-to-back experiments. For each case, the absolute pressures were measured using a Datametrics Barocel Electronic Manometer Model 1173. The ion pump was calibrated at pressures in the range of 5 to 20 × 10^{-5} torr. Pressures in the low 10^{-5}-torr region were obtained by extrapolation of the linear calibration plots. The absolute rate constant for the fulvene–butadiene reaction was calculated from the ratio of slopes of the product ion appearance curves using a rate constant of 1.2 × 10^{-9} cm^3 molecule^{-1} s^{-1} for the production of CH_5 in methane.[5] The relative precision for this determination was ±10% for six determinations on different days.

The samples of reagent gases were obtained from standard commercial sources and their purity was checked by mass spectrometry. The samples of 1,3-butadiene-*1,1,4,4-d$_4$*, 1,3-butadiene-*d$_6$*, and 1,3-butadiene-*1-^{13}C$_1$* were obtained from Merck, Inc. Isotopes: 90 atom % for each.

Fulvene was synthesized by the method of Wentrup and Miller[22] by pyrolysis of α-coumaranone in a vacuum flow apparatus consisting of pre-oven at 80 °C, a quartz reactor tube held at 750 ± 50 °C in a muffle furnace and a liquid nitrogen cold trap. A 1.0-g sample of starting material required 6–7 h. The products (fulvene and benzene) were collected in the cold trap, transferred to gas-sample tube, and stored at –20 °C. Prior to ICR experiments, the fulvene was purified using gas chromatography (6.1 m × 0.64 cm column of SE-30 at 50 °C) with a flow rate of 60 cm^3 min^{-1}. The ^{1}H NMR spectrum showed multiplets at τ 5.72, 6.23, and 6.34 in agreement with the literature.[23]

The 1,3-butadiene-*2,3-^{13}C$_2$* was prepared from 3.25 g of 1,2-dibromoethane-*1,2-^{13}C$_2$* which was dissolved in 7 mL of 100% ethanol and added to a refluxing solution of 2.08 g of KCN in 2 mL of water. After 3.5 h, an additional 1.0 g of KCN was added and reflux was continued for 20 h. Excess KCN was removed by addition of cold sulfuric acid and ethanol followed by 12 h of reflux. After cooling, the mixture was continuously extracted with ethyl ether for 38 h.[24] The resulting diethyl succinate was reduced with LiAlH$_4$ to give 1,4-butanediol-*2,3-^{13}C$_2$* which in turn was converted into the dibromide. Dehydrohalogenation was effected by dropwise addition to a suspension of 2.5 g of sodium hydride in DMF in a reaction vessel connected to an acetone–dry ice cold trap. The volatiles were continuously swept with dry nitrogen at a rate of 2–5 cm^3 s^{-1} into the cold trap. The product (40% yield overall) was purified by a low-temperature distillation and analyzed by mass spectrometry at low ionizing energy (10.5 eV). The isotopic composition was found to be 78% ^{13}C$_2$, 16% ^{13}C$_1$, 6% ^{13}C$_0$.

(22) Wentrup, C.; Muller, P. *Tetrahedron Lett.* **1973**, No. 31, 2915.

(23) Coller, B. A. W.; Heffernan, M. L.; Jones, A. J. *Aust. J. Chem.* **1968**, *21*, 1807, and references cited therin.

(24) This is a modified version of the preparation described by Vogel, A. I. "Practical Organic Chemistry"; Longman Group Ltd.: London, 1972; p 761.