(6) D. M. Lemal in "Nitrenes", W. Lwowski, Ed., Interscience, New York, 1970, Chapter 10; B. V. Ioffe and M. A. Kuznetsov, *Russ. Chem. Rev.* (*Engl. Transl.*), **41**, 131 (1972).
(7) C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Am. Chem. Soc.*, **79**, 6430 (1957); *ibid.*, **80**, 3009 (1958).
(8) C. G. Overberger, M. Valentine, and J-P. Anselme, *J. Am. Chem. Soc.*, **91**, 687 (1969).
(9) K. R. Kopecky and J. Soler, *Can. J. Chem.*, **52**, 2111 (1974).
(10) D. M. Lemal, T. W. Rave, and S. D. McGregor, *J. Am. Chem. Soc.*, **85**, 1943 (1963).
(11) W. D. Hinsberg, III, and P. B. Dervan, *J. Am. Chem. Soc.*, **100**, 1608 (1978).
(12) A. R. Jones, *Chem. Commun.*, 1042 (1971).
(13) P. B. Dervan, T. Uyehara, and D. S. Santilli, *J. Am. Chem. Soc.*, preceding paper in this issue.
(14) For the 2,5 isomers see: C. G. Overberger, L. C. Palmer, B. S. Marks, and N. R. Byrd, *J. Am. Chem. Soc.*, **77**, 4100 (1955).
(15) The contents of the pyrolysis tube containing the base and benzenesulfonamide are frozen and plunged in the constant temperature bath at 120 ± 2 °C. When the contents melt and react to generate the 1,1-diazene they may not have reached the 120 °C bath temperature. Therefore, we will consider the 1,1-diazene decompositions to be occurring at $\leq$120 °C.
(16) P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).
(17) C. Morse, California Institute of Technology, unpublished results.

Electrocyclic Ring Opening of the Cyclobutene Radical Cation

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Abstract: The electrocyclic ring opening of cyclobutene to give 1,3-butadiene is a well-understood chemical isomerization. The process occurs with a lower than anticipated activation energy presumably because it is an "allowed" reaction. In order to ascertain whether the electrocyclic ring opening occurs for the gas-phase cyclobutene radical cation, we have undertaken a comparative study of the chemical properties of ionized cyclobutene and 1,3-butadiene. Both ions exhibit nearly identical chemical reactivities with a variety of neutral molecules including methyl vinyl ether, furan, ethene, propene, isomeric butenes, and isomeric pentenes. The explanation proposed to account for these results is that the cyclobutene ion rapidly undergoes (within less than 2 ms) an electrocyclic isomerization to give the 1,3-butadiene ion. The maximum activation energy for this process is estimated to be less than 7 kcal/mol. The chemical properties of the molecular ions of 1,2-butadiene, 1-butyne, and 2-butyne were determined using the same reactant neutral molecules, and they differ considerably from the 1,3-butadiene and cyclobutene ions. The results are interpreted to exclude other isomeric [$C_4H_6^{+\cdot}$] species in the electrocyclic reaction.

The ring opening of cyclobutene to produce 1,3-butadiene serves as the classic example of the application of principles of orbital symmetry control to electrocyclic reactions.[1] It is now well established that the transformation occurs in a conrotatory manner for the thermal process. The activation energy for the ring opening of the neutral cyclobutene has been determined to be 33 kcal/mol, which is approximately 15 kcal/mol lower than a "some nonallowed pathway."[2] This latter quantity can be assigned as the energy advantage for the allowed process.

In this paper, we report a study of the 1,3-butadiene and the cyclobutene radical cations designed to establish whether the cyclobutene ion isomerizes to 1,3-butadiene and to estimate the activation energy required for the process. Obviously, these are the first pieces of information that are needed to test the applicability of various selection rules to the chemistry of isolated radical ions in the gas phase.

Mass spectrometric techniques are the methods of choice for investigating gas-phase ions, and we have chosen ion cyclotron resonance spectrometry for this study. The strategy is to develop highly specific reactions of the various C_4H_6 radical cations which can be employed as structural probes.

Various authors have considered the applicability of orbital symmetry rules for reactions of open-shell systems (radical cations) in a mass spectrometer source.[3-8] However, it is not clear what the effect of removal of one electron should be on orbital symmetry considerations. In fact, recent studies of various substituted cyclobutene radical cations are indicative of contradictory experimental results. Similarities found in ionic fragmentations for the isomeric cyclobutenedicarboxylic acids and the corresponding muconic acids have been interpreted to indicate electrocyclic interconversions via electronically excited states (a photochemical analogy).[8] The quantities of kinetic energy released in the decompositions of isomeric 1,2,3,4-tetramethylcyclobutenes have been compared to the 3,4-dimethyl-2,4-hexadienes, and a similar conclusion was reached.[9] However, the results of a study of the dimethyl esters of cyclobutenedicarboxylic acids and the corresponding ring-opened 1,3-butadienes show that *no* correlation exists between the behavior of the radical cations and the photochemical or thermal reactivities of the neutral molecules.[10] That is, the cyclobutene ions refrain from ring opening, and the 1,3-butadienes do not ring close even when the ions are sufficiently excited to decompose.

In a recent study, Werner and Baer[11] have investigated the unimolecular decompositions of energy-selected C_4H_6 ions from 1,3-butadiene, cyclobutene, and other isomers using the elegant technique of photoelectron-photoion coincidence spectroscopy. They conclude that all the isomeric C_4H_6 ions rearrange to a common structure prior to dissociation. Because these data were taken at energies above the dissociation limit for $[C_4H_6]^{+\cdot}$, they tell us nothing about isomerization at low internal energies, nor do they provide an answer to the question we have posed concerning the specific ring opening of the cyclobutene ion to give 1,3-butadiene.

Results and Discussion

To answer the question we have raised, it is necessary to compare the physical or chemical properties of ionized cyclobutene and 1,3-butadiene. As a strategy, we have chosen to determine the chemical reactivities of the various isomeric C_4H_6 radical cations which are prepared by direct ionization of 1,3-butadiene and cyclobutene. In addition, $[C_4H_6]^{+\cdot}$ will be generated from 1,2-butadiene, 1-butyne, and 2-butyne. Using the technique of ion cyclotron resonance spectrometry

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(ICR) to investigate low kinetic energy (approximately thermal) ion-molecule reactions, we have conducted a search for reactions of the stable (nondecomposing) C_4H_6 ions which will discriminate on the basis of ion structure. If the cyclobutene ion readily undergoes an electrocyclic ring opening, we would expect its bimolecular ion chemistry to match that of 1,3-butadiene. Moreover, if the chemistry of the other isomeric C_4H_6 ions from 1,2-butadiene, 1-butyne, and 2-butyne is different than that of the ionized 1,3-butadiene, a highly specific connection between ionized cyclobutene and 1,3-butadiene can be established.

The following sections contain a survey of the chemistry observed for the various C_4H_6 radical cations. No attempt will be made in this paper to explain the mechanisms of the reactions discovered nor will absolute rate constants be reported. Rather, the objective, as stated above, is to determine whether the biomolecular chemistry of the cyclobutene ion matches that of 1,3-butadiene, and in this way to establish a link between these two radical cations.

1. Reactions with Methyl Vinyl Ether. Based on work by Nibbering and Jennings,[12] who have found that 1,3-butadiene ion reacts with methyl vinyl ether to give an intermediate which undergoes loss of CH_3OH, we have chosen this molecule as our first candidate reagent neutral. Mixing 1,3-butadiene and methyl vinyl ether in the cell of the ICR leads to production of *m/e* 80 (presumably $C_6H_8^+$) in accord with the report of Nibbering and Jennings:

$$C_4H_6^{+\cdot} + CH_3OCH{=}CH_2 \rightarrow [C_7H_{12}O^{+\cdot}]^* \rightarrow C_6H_8^{+\cdot} + CH_4O \quad (1)$$

Pulsed double resonance experiments confirm that $[C_6H_8]^{+\cdot}$ is produced competitively from $[C_4H_6]^{+\cdot}$ (eq 1) and from the molecular ion of methyl vinyl ether reacting with neutral butadiene.

Similarly, ionized cyclobutene reacts with methyl vinyl ether to produce *m/e* 80 ($C_6H_8^{+\cdot}$). In order to make a quantitative comparison of the reactivities of these two C_4H_6 ions, the relative rate constants for disappearance of $C_4H_6^{+\cdot}$ were measured by plotting the logarithm of the normalized intensity of C_4H_6 vs. the partial pressure of methyl vinyl ether. In this way, the ratio of k_d (cyclobutene) to k_d (butadiene) was determined to be 0.85.

Mixtures of each of the remaining three isomeric C_4H_6 sources and methyl vinyl ether also were admitted to the cell, but no reaction with methyl vinyl ether could be detected. The upper limit for the rate constant for reaction with the ether is 0.02-0.04 that of 1,3-butadiene at 11 eV of ionizing energy. Increasing the ionizing energy to 20 eV has no effect. In addition, ionized 3-methylcyclopropene does not react with methyl vinyl ether,[12] and this may be interpreted to exclude isomerization of this stable ion to the 1,3-butadiene or cyclobutene structures.

2. Reactions with Furan. We have previously reported that ionized furan reacts with neutral 1,3-butadiene

$$C_4H_4O^{+\cdot} + C_4H_6 \rightarrow [C_8H_{10}O^{+\cdot}] \rightarrow C_7H_7O^+ + {\cdot}CH_3 \quad (2)$$

but the 1,3-butadiene ion is inert with neutral furan.[13] Ionized cyclobutene is found to be unreactive with neutral furan, nor does the reaction shown by eq 2 occur with neutral cyclobutene. As an aside, we note that the furan radical cation can be used to differentiate between neutral 1,3-butadiene and cyclobutene.

Unlike the ions produced in the direct ionization of 1,3-butadiene and cyclobutene, the C_4H_6 radical cations from 1,2-butadiene, 1-butyne, and 2-butyne react readily with neutral furan to produce *m/e* 107 and 93 (eq 3). The reactivity of the various ions is, to a first approximation, independent of the precursor C_4H_6 neutral; i.e., production of *m/e* 107 accounts for approximately 80% of the two pathways.

$$\begin{tikzcd}
{[C_4H_6]^{+\cdot} + C_4H_4O} \arrow[d] & \\
{[C_8H_{10}O^{+}\cdot]^*} \arrow[r] \arrow[dr] & C_7H_7O^+ + \cdot CH_3 \ (m/e\ 107) \\
 & m/e\ 93 + \cdot C_2H_5(CHO)
\end{tikzcd} \quad (3)$$

Table I. Isotopic Distribution for Methyl Loss for the Reaction of $[C_4H_6]^{+\cdot}$ and C_2D_4

source of $[C_4H_6]^{+\cdot}$	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
1,3-butadiene	27	44	26	3
cyclobutene	26	45	26	3
calcd[a]	17	50	30	3

[a] Based on complete statistical H/D isomerization.

Although no connective link between ionized 1,3-butadiene and cyclobutene can be established based on these data, the results do show that 1,2-butadiene, 1-butyne, and 2-butyne produce C_4H_6 ions which are separate and distinct from those of 1,3-butadiene and cyclobutene in terms of their bimolecular reaction properties.

3. Reactions with Ethene and Ethene-*d*$_4$. Because the reaction of 1,3-butadiene and ethene is the simplest candidate for a [4 + 2] cycloaddition, we have investigated the ion chemistry in great detail. In another paper,[13] we have reported that ionized 1,3-butadiene reacts with ethene according to the equation

$$C_4H_6^{+\cdot} + C_2H_4 \rightarrow [C_6H_{10}^{+\cdot}]^* \rightarrow C_5H_7^+ + CH_3 \quad (4)$$

Substitution of cyclobutene for 1,3-butadiene gives the same chemistry, whereas the other three acyclic sources produce an inert $[C_4H_6^{+\cdot}]$ according to eq 4.

The loss of methyl from the collision complex in eq 4 occurs with extensive H/D isomerizations when C_2D_4 is used in lieu of unlabeled ethene. In Table I, we compare the label distribution for methyl loss starting with ionized 1,3-butadiene and with cyclobutene. It can be seen clearly that not only does the ion chemistry coincide, but the mechanistic details for methyl loss are identical. Nearly statistical patterns are found, but both $[C_4H_6]^{+\cdot}$ sources show a slight preference for CH_3 loss. These data suggest that the $C_6H_{10}^{+\cdot}$ intermediate possesses an identical structure independent of the source of the reacting ion. A likely explanation for this is that the structures of the reactant ions are the same.

4. Reactions with Propene and Propene-*d*$_6$. The C_4H_6 radical cations from 1,3-butadiene and cyclobutene react with propene according to the equation

$$C_4H_6^{+\cdot} + C_3H_6 \rightarrow [C_7H_{12}^{+\cdot}]^* \rightarrow C_6H_9^+ + CH_3 \quad (5)$$

The relative rate constants for production of $C_6H_9^+$ are 1.0:0.9 for k(1,3-butadiene):k(cyclobutene) over a range of ionizing energies (10-17 eV). The $[C_4H_6]^{+\cdot}$ from 1,3-butadiene is somewhat more reactive presumably because of its lower internal energy content.[14] Under ICR conditions, very little collisional stabilization is possible; therefore, at minimum, the difference in the heats of formation of the cyclobutene ion ($\Delta H_f = 255$ kcal/mol) and the 1,3-butadiene ion ($\Delta H_f = 236$ kcal/mol) will be present as excess internal energy (approximately 19 kcal/mol) in the ring-opened cyclobutene ion.

A more detailed comparison can be obtained by examining the isotopic distribution for methyl loss when C_3D_6 is employed. These data are contained in Table II.

Table II. Isotopic Distribution for Methyl Loss of the Reaction of $[C_4H_6]^{+\cdot}$ and Propene-d_6

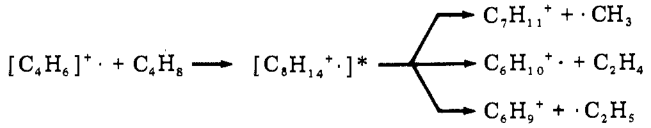
source of $[C_4H_6]^{+\cdot}$	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
1,3-butadiene	20	24	16	40
cyclobutene	21	23	16	40
calcd[a]	09	41	41	09

[a] Based on statistical H/D isomerization.

As was found for the reaction with deuterated ethene (Table I), the patterns for methyl loss are identical independent of whether 1,3-butadiene or cyclobutene serves as the source for $[C_4H_6]^{+\cdot}$. Moreover, the loss of methyl is preceded by considerable, but incomplete, H/D isomerization. Unlike the ethene reaction, definite preference for expulsion of CH_3 and CD_3 is found. These results are in accord with ^{13}C labeling of 1,3-butadiene, which shows that the carbon in the departing methyl originates from both reactants in the approximate ratio of 1:1.[15]

Employing 1,2-butadiene, 1-butyne, and 2-butyne as sources for $[C_4H_6]^{+\cdot}$, we obtain significantly different results. No loss of methyl, as denoted in eq 5, can be detected. Again, the data establish the identical nature of ionized cyclobutene and 1,3-butadiene and their distinct properties with respect to other $[C_4H_6]^{+\cdot}$ isomers. The maximum rate constants for reaction 5 for ionized 1,2-butadiene and the isomeric butynes are 0.05 of that for 1,3-butadiene.

5. Reactions with Isomeric Butenes. Both ionized 1,3-butadiene and cyclobutene react identically with the four isomeric butenes in a highly specific manner which is a function of the structure of the neutral butene. In fact, the C_4H_6 ion is a useful reagent to distinguish various butene isomers because of the different branching ratios found for the reaction (eq 6). The results are compiled in Table III.



$$[C_4H_6]^{+\cdot} + C_4H_8 \longrightarrow [C_8H_{14}{}^{+\cdot}]^* \longrightarrow \begin{cases} C_7H_{11}{}^+ + \cdot CH_3 \\ C_6H_{10}{}^{+\cdot} + C_2H_4 \\ C_6H_9{}^+ + \cdot C_2H_5 \end{cases} \quad (6)$$

These observations are in sharp contrast to those for the three other acyclic sources of $[C_4H_6]^{+\cdot}$. Although it is difficult to make quantitative comparisons because of the interfering reactions of $C_4H_8{}^{+\cdot}$ and neutral C_4H_6, nevertheless semiquantitative conclusions can be reached based on product intensities and double-resonance experiments.

First, both 1,2-butadiene and 2-butyne yield a $[C_4H_6]^{+\cdot}$ which reacts with all of the butenes to give methyl loss only (no C_2H_4 or C_2H_5 loss can be detected). Second, 1-butyne ion reacts with 1-butene and the 2-butenes to give a collision complex which undergoes methyl and ethyl loss but no dissociation to give $[C_6H_{10}]^{+\cdot}$ (C_2H_4 loss). A slight preference for C_2H_5 loss was found. With isobutene, dissociation of the collision complex by expulsion of CH_3 and C_2H_5 occurs, but the CH_3 loss is favored.

With the butenes, we see some selectivity exhibited by the C_4H_6 ions from 1,2-butadiene, 1-butyne, and 2-butyne. But the chemistry of these ions is significantly different than that of ionized 1,3-butadiene and cyclobutene. The latter sources give C_4H_6 ions which are nearly identical in terms of chemical reactivity with the neutral isomeric butenes (see Table III).

6. Reactions with Isomeric Pentenes. As a final comparison, we will report briefly on the chemistry of isomeric C_4H_6 radical cations and various pentenes. In a previous paper,[16] we have pointed out that the 1,3-butadiene ion reacts with 1-pentene, 3-methyl-1-butene, 2-methyl-1-butene, and *cis*- and *trans*-2-pentene to produce five ion–molecule products ($C_8H_{13}{}^+$, $C_7H_{12}{}^{+\cdot}$, $C_7H_{11}{}^+$, $C_6H_{10}{}^{+\cdot}$, and $C_6H_9{}^+$). Based on the specificity of these reactions, we have suggested that 1,3-butadiene ion may be a useful analytical reagent for isomeric olefins. We now report that ionized cyclobutene reacts in a nearly identical fashion with the 1- and 2-pentenes.

Table III. Reactive Product Abundance in the Reactions of $[C_4H_6]^{+\cdot}$ with Isomeric Butenes (12 eV Ionizing Energy)

	rel intensity of					
	$C_7H_{11}{}^+$		$C_6H_{10}{}^+$		$C_6H_9{}^+$	
neutral	1[a]	2[a]	1	2	1	2
1-butene	6	5	14	12	80	83
cis-2-butene	55	56	12	13	33	31
trans-2-butene	62	62	7	8	31	30
isobutene	55	54	20	18	25	28

[a] 1 refers to 1,3-butadiene; 2 refers to cyclobutene.

Ionization of 2-butyne, however, produces an entirely different $[C_4H_6]^{+\cdot}$. The ions react with 1-pentene to give only two products ($C_8H_{13}{}^+$ and $C_6H_{10}{}^{+\cdot}$) and with the 2-pentenes to give one ionic product ($C_8H_{13}{}^+$). The $[C_4H_6]^{+\cdot}$ from 1,2-butadiene does *not* react with any of the isomeric pentenes to produce the five products discussed above. Three ionic products, $C_8H_{13}{}^+$, $C_7H_{11}{}^+$, and $C_6H_9{}^+$, are found in approximately the same ratios for the reaction of ionized 1-butyne with 1-pentene or the 2-pentenes.

Again we see nearly identical chemical reactivities for 1,3-butadiene and cyclobutene ions which contrast sharply with the other sources of $C_4H_6{}^+$. It appears that, based on the different chemistry exhibited by ionized 1,2-butadiene, 1-butyne, and 2-butyne, the corresponding stable ions possess unique structures.

7. Ion Chemistry of 1,3-Dienes and Monoolefins. In the preceding sections, we have surveyed a large number of ion–molecule reactions which are postulated to be characteristic of 1,3-butadiene ion and have shown that ionized cyclobutene reacts identically in terms of product ion distributions and slightly more slowly in terms of rate. This latter fact can be ascribed to an internal energy effect.[15] Direct ionization of 1,2-butadiene, 1-butyne, 2-butyne, and 3-methylcyclopropene produces C_4H_6 radical cations which exhibit entirely different chemical properties. However, these $[C_4H_6]^{+\cdot}$ sources cannot undergo a smooth electrocyclic ring opening as can cyclobutene.

To establish firmly that the chemistry of ionized cyclobutene is characteristic of a 1,3-diene ion, we compared its reactivity with that of the *cis*-2-butene ion and the cyclopentene ion. The latter sources were chosen as models for simple olefin ions. As was pointed out in the first section, 1,3-butadiene reacts with methyl vinyl ether via a collision complex which undergoes loss of CH_3OH (eq 1). Ionized *cis*-2-butene and cyclopentene do *not* react with methyl vinyl ether to produce a collision complex which undergoes loss of CH_4O.[17] Therefore, we feel assured that the chemistry discussed above is indeed that of 1,3-diene ion and not of a cyclic olefin.

The stability of the cyclobutene ion compared to 1,3-butadiene is in accord with the hypothesis that it is the cyclobutene ion which undergoes the ring opening rather than the reverse ring closing of 1,3-butadiene ion. The latter process is endothermic by 19 kcal/mol [ΔH_f(cyclobutene ion) − ΔH_f(1,3-butadiene ion)]; therefore, the *minimum* activation energy for ring closure is 19 kcal/mol.

8. Estimate of the Activation Energy for Electrocyclic Ring Opening of the Cyclobutene Ion. Based on the above chemical data, we estimate that the nondecomposing cyclobutene ion has isomerized to 1,3-butadiene in the time frame available in a drift cell of the ion cyclotron resonance spectrometer. For our experiments, the time required for $[C_4H_6]^{+\cdot}$ to reach the center of the analyzer is approximately 2 ms. Accordingly, a conservative estimate of the half-life for the cyclobutene ion is 0.5 ms, which means that in a period of 2 ms greater than 90% of the ions will isomerize to 1,3-butadiene. Therefore, the minimum rate constant for ring opening is 1×10^3 s^{-1}.

Because the ionized cyclobutene exhibits the characteristic chemistry of the 1,3-butadiene at ionizing energies as low as 0.6 eV above threshold, we conclude that ions possessing internal excitation as low as 0.3 eV on the average will ring open with a rate constant of 1×10^3 s^{-1}. The value of 0.6 eV was obtained by assigning the threshold as the electron voltage at which the intensity of *m/e* 54 from cyclobutene had dropped to 0.1% of the intensity observed at 25 eV. To establish that the chemistry displayed by ionized cyclobutene at 0.6 eV above threshold is that of the 1,3-butadiene ion, we have obtained the rate constants for disappearance of $[C_4H_6]^+$ from cyclobutene and 1,3-butadiene. Even at this ionizing energy $[C_4H_6]^{+\cdot}$ from cyclobutene reacts with methyl vinyl ether at a rate 0.80 that of the 1,3-butadiene ion to produce *m/e* 80 ($C_6H_8^{+\cdot}$).

From these reasonable assumptions, we estimate the activation energy for ring opening to be less than 0.3 eV or 7 kcal/mol. According to the quasi-equilibrium theory of unimolecular decompositions,[18] the activation energy for a reaction that is observed to occur must be less than the internal energy content of the ion. On that basis the estimate of less than 7 kcal/mol is made.

Conclusion

By investigating the bimolecular reaction chemistry of ionized 1,3-butadiene and cyclobutene, we have demonstrated that these ions display identical chemical properties. Their characteristics are significantly different than those of $[C_4H_6]^{+\cdot}$ produced in the direct ionization of 1,2-butadiene, 1-butyne, and 2-butyne. These results strongly support the conclusion that the cyclobutene ion rapidly undergoes an electrocyclic ring opening to produce 1,3-butadiene. By all criteria available with our experimental approach, the ring opening is essentially complete within 2 ms for cyclobutene ions which possess less than a few tenths of an electron volt of internal excitation. These data allow us to estimate that the *minimum* activation energy for the electrocyclic ring opening is less than 7 kcal/mol.

In view of the well-established concept in mass spectrometry that simple cleavage reactions proceed with little or no activation energy, it may be argued that the proposed low-energy ring opening of cyclobutene is not surprising. However, the distinctive spectra of *cis-* and *trans*-dimethyl esters of cyclobutenedicarboxylic acids[10] compared to the corresponding 1,3-butadienes show that these compounds do not interconvert even as higher energy decomposing ions. Moreover, we have demonstrated that stable C_3H_6 radical cations from cyclopropane largely retain their cyclic structure for millisecond time periods.[19] Photoionization of cyclopropane at 0.7 eV above the ionization potential is required to produce a small population (approximately 15%) of ring-opened structures even though the ring opening for the ground-state cyclic ion is exothermic by 10 kcal/mol.[20] Increasing the ionizing energy to approximately 1.7 eV above threshold shifts the composition to nearly 50% ring-opened structures.[20] For cyclobutene ionization, we believe that the ring opening is essentially complete at less than 0.6 eV above threshold.

Based on these observations, we draw the tentative conclusion that there does exist an energy advantage for the electrocyclic reaction of ionized cyclobutene. For neutral cyclobutene, the activation energy of 33 kcal/mol has been estimated to be 15 kcal/mol less than a nonallowed ring opening. Removal of one bonding electron, presumably from a π molecular orbital, leads to an even larger reduction in the activation energy. The rapid ring opening precludes study of the properties of the cyclobutene radical cation using available techniques. An interesting question remains, and that is, what is the mode of ring opening of the cyclobutene ion? If the reaction of the radical cation is similar to that of the neutral, a conrotatory process is anticipated. Studies of substituted cyclobutenes are in progress in an attempt to generate the necessary data.

Experimental Section

All measurements were made using a Varian ICR-9 spectrometer equipped with a dual inlet. A flat drift cell was employed, and the spectra were taken in the field modulation mode with a marginal oscillator frequency of 153 kHz. The source and analyzer drift fields were 0.20 V/cm, the trapping voltage was 0.5 V, and the emission current was kept below 0.2 μA. A typical experiment involved admitting the degassed source of $[C_4H_6]^{+\cdot}$ to the cell to a pressure of $2–5 \times 10^{-6}$ Torr. The reactant neutral was admitted via the second inlet, and relative rate measurements were made by varying the partial pressure of this neutral. Confirmation of reaction pathways was achieved by pulsed double resonance at an oscillator level of approximately 0.04 V/cm.

The samples of 1,2-butadiene, 1-butyne, and 2-butyne were obtained from Chemical Samples Co. The sample purity was checked by mass spectrometry, and they were used without further purification. The cyclobutene was prepared according to the method of Bacha and Kochi.[21] The reaction was carried out as follows: 0.017 g of $Cu(OAc)_2 \cdot H_2O$ (0.535 mmol), 0.110 g of pyridine (1.39 mmol), and 2.75 g (2.8 mmol) of cyclobutenecarboxylic acid (Chemical Samples Co.) were added to 15 mL of benzene in a three-neck 50-mL round-bottom flask equipped with a screw condenser and magnetic stirring bar. The mixture was stirred for approximately 1 h. To the resulting solution were added 4.50 g of 97% $Pb(OAc)_4$ (9.86 mmol) and an additional 25 mL of benzene. The mixture was stirred for an additional 2 h. The condenser was then connected via Tygon tubing to a cold trap and cooled to −78 °C (acetone/dry ice). A light stream of dry nitrogen was passed through the reaction vessel at a rate of 2–3 mL/min, and the outgassing was continued while the reaction mixture was refluxed for 2 h. The cold trap was then removed and degassed at liquid nitrogen temperature. The cyclobutene was then vacuum distilled from the cold trap at −78 °C into an evacuated (approximately 10^{-4} Torr) gas manifold. The volume of gas collected was measured by an oil manometer in order to give an estimate of the percent yield (in this case approximately 75%). The cyclobutene was then condensed into gas sample tubes and was analyzed by mass spectrometry and ^1H NMR. The proton chemical shifts of δ 2.54 and 6.00 are in good agreement with the literature values of δ 2.54 and 5.97.[22]

All other materials were obtained from commercial sources and their purity was checked by mass spectrometry. They were used without additional purification.

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References and Notes

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(2) L. M. Stephenson, Jr., and J. I. Brauman, *Acc. Chem. Res.*, **7**, 65 (1974).
(3) R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc. C*, 1805 (1968).
(4) M. J. Bishop and I. Fleming, *J. Chem. Soc. C*, 1712 (1969).
(5) M. S. Baird and C. B. Reese, *Tetrahedron Lett.*, 2117 (1969).
(6) M. L. Gross and C. L. Wilkins, *Tetrahedron Lett.*, 3875 (1969).
(7) R. C. Dougherty, *J. Am. Chem. Soc.*, **90**, 5780, 5788 (1968).
(8) M. K. Hoffman, M. M. Bursey, and R. E. K. Winter, *J. Am. Chem. Soc.*, **92**, 727 (1970).
(9) M. E. Rennekamp and M. K. Hoffman, *Org. Mass Spectrom.*, **10**, 1067 (1975).
(10) A. Mandelbaum, S. Weinstein, M. E. Gil-Av, and J. H. Leftin, *Org. Mass Spectrom.*, **10**, 842 (1975).
(11) A. S. Werner and T. Baer, *J. Chem. Phys.*, **62**, 2900 (1975).
(12) R. van Doorn, N. M. M. Nibbering, A. J. V. Ferrer-Correia, and K. R. Jennings, *Org. Mass Spectrom.*, submitted.
(13) M. L. Gross, D. H. Russell, R. Phonbetchara, and P.-H. Lin, *Adv. Mass Spectrom.*, **7**, 129 (1977).
(14) W. A. Chupka and M. E. Russell, *J. Chem. Phys.*, **48**, 1527 (1968). M. L. Gross and Joseph Norbeck, *ibid.*, **54**, 3651 (1971).

(15) M. L. Gross, D. H. Russell, and P.-H. Lin, unpublished results.
(16) M. L. Gross, P.-H. Lin, and Stanley J. Franklin, *Anal. Chem.*, **44**, 974 (1972).
(17) N. M. M. Nibbering has informed us of a very slow reaction to eliminate CH_4O for ionized 2-butene and methyl vinyl ether. We were unable to detect this reaction.
(18) H. B. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci. U.S.A.*, **38**, 667 (1952). For a review, see M. L. Vestal, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, 1968.
(19) M. L. Gross, *J. Am. Chem. Soc.*, **94**, 3744 (1972); M. L. Gross and F. W. McLafferty, *ibid.*, **93**, 1267 (1971).
(20) L. W. Sieck, R. Gordon, Jr., and P. Ausloos, *J. Am. Chem. Soc.*, **94**, 7157 (1972).
(21) J. D. Bacha and J. K. Kochi, *Tetrahedron*, **24**, 2215 (1968).
(22) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

Decomposition of the 1,3-Butadiene Radical Cation on the Microsecond to Picosecond Time Scale

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Abstract: The decomposition of ionized 1,3-butadiene to give $C_3H_3^+$ and $\cdot CH_3$ has been studied over the time interval of approximately 10^{-11}–10^{-5} s using the complementary techniques of field ionization kinetics (FIK) and mass-analyzed ion kinetic energy spectroscopy (MIKES). By employing both carbon-13 and deuterium labeled 1,3-butadiene, it has been established that (1) hydrogen atom randomization takes place very rapidly and is complete by approximately 10^{-11} s, (2) carbon atom randomization occurs at a slower rate which is competitive with the decomposition reaction. The hydrogen atom randomization is postulated to take place by isomerization to other acyclic C_4H_6 ions without change in the carbon skeleton. The near lack of carbon atom interchange at short times (10^{-9}–10^{-11} s) is explained by invoking a high-energy formation of a methylcyclopropene which occurs as a rate-determining step. For more slowly decomposing (metastable) C_4H_6 ions, the ring-opening reaction of this intermediate to re-form the 1,3-butadiene cation becomes more competitive with dissociation, and this explains the nearly complete carbon atom randomization at longer times.

In the previous paper,[2a] we have shown that the cyclobutene radical cation smoothly undergoes an electrocyclic ring opening to produce exclusively the 1,3-butadiene radical cation. An estimate of the activation energy for this process is less than 7 kcal/mol. In this report, we examine highly activated 1,3-butadiene radical cations, which undergo loss of a methyl radical. The techniques of field ionization kinetics (FIK)[2b] and mass-analyzed ion kinetic energy spectrometry (MIKES)[3] are employed to observe rapidly decomposing C_4H_6 ions in the time span of 10^{-9}–10^{-11} s (FIK) and the more slowly fragmenting ions in the 10^{-5}–10^{-6}-s range (MIKES). Results are obtained for both deuterated and carbon-13 labeled 1,3-butadiene.

By making use of isotopically labeled 1,3-butadiene, we hope to gain information about the mechanisms of hydrogen atom randomization and carbon skeletal isomerizations. An understanding of the mechanisms will permit us to describe schematically the potential energy surface for various C_4H_6 radical cations. At this stage, we know that there is a low-energy requirement for the electrocyclic ring opening of the cyclobutene ion.[2a] But in addition to specific details concerning C_4H_6 radical cations, this study is directed at the broader question of isomerization vs. direct dissociation in highly activated chemical species, a subject of interest in the areas of unimolecular kinetics and mass spectrometry.

The decomposition reactions of C_4H_6 radical cations have been studied by other workers. The earlier work by Vestal[4] was interpreted in terms of complete equilibration of the $[C_4H_6]^{+\cdot}$ isomers prior to the dissociation to $C_3H_3^+$ and $\cdot CH_3$. More recently, Werner and Baer[5] have characterized the decomposing C_4H_6 ions from a variety of sources using the elegant technique of photoion-photoelectron coincidence spectroscopy. By this method, it is possible to examine decompositions from selected energy states of the fragmenting precursor ion. From the data, the energy dependence of the unimolecular rate constant can be assessed and compared with theory.[6] Werner and Baer[5] have calculated a k (E) curve for the methyl loss using RRKM theory, and they find that the calculated results are in disagreement with the experimental rate constant vs. energy curve. Specifically, the observed rate constants for loss of methyl from 1,3-butadiene, 1,2-butadiene, 1-butyne, 2-butyne, and cyclobutene are nearly equal for the same internal energy content, but the observed values are a factor of 10 or more greater than the RRKM calculated values. The independence of rate constant as a function of the neutral precursor was interpreted to indicate that the fragmenting ions had sampled a common potential energy surface; i.e., they had isomerized to a common structure or mixture of structures. However, from the lack of agreement between the calculated and experimental rate constants, it was suggested that statistical partitioning of energy was not complete.

Chesnavich and Bowers[7] have taken issue with this point based on their RRKM and phase-space calculations of this reaction. By modifying the Werner and Baer model[5] of the decomposition mechanism to include a rate-determining isomerization to the 3-methylcyclopropene structure, which has an energy below the dissociation limit, they have been able to match the experimental results. However, there is no experimental evidence to confirm that 3-methylcyclopropene or other three-membered ring intermediates exist on the potential surface for decomposing 1,3-butadiene.

In view of lack of experimental results, we deemed it urgent to study the methyl loss from ionized 1,3-butadiene over a wide time range in order to provide a foundation for future theoretical studies.

Results

1. Field-Ionization Studies. In Figure 1, we present the field

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