(15) M. L. Gross, D. H. Russell, and P.-H. Lin, unpublished results.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. Kochl, *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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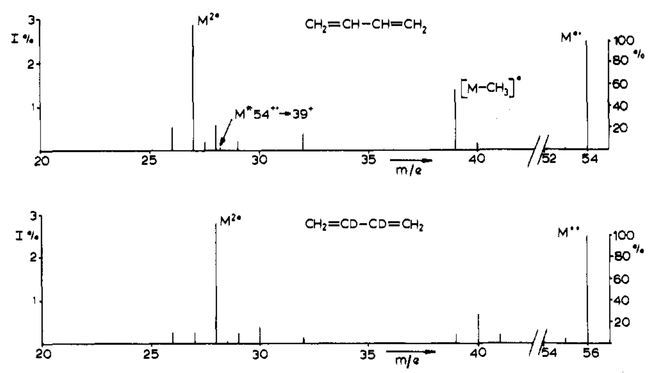


Figure 1. Field ionization mass spectra of 1,3-butadiene and 1,3-butadiene-*2,3-d*$_2$.

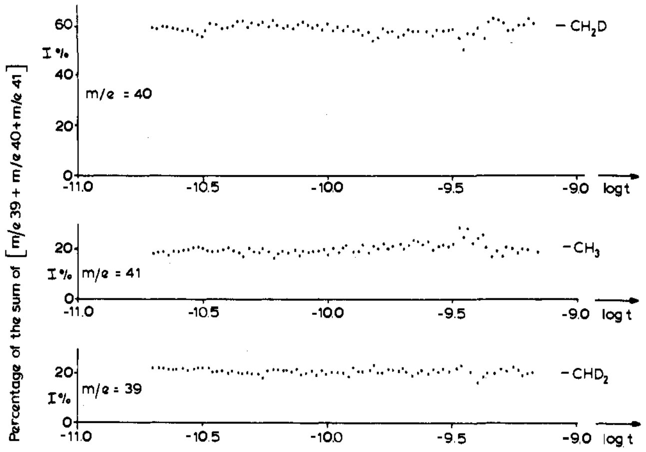


Figure 2. Time dependence for loss of methyl from 1,3-butadiene-*2,3-d*$_2$ molecular ion.

ionization spectra obtained for 1,3-butadiene and 1,3-butadiene-*2,3-d*$_2$ using the University of Amsterdam mass spectrometer.[8] As can be seen, the only fragmentation of note is the loss of methyl to yield $C_3H_3^+$ (*m/e* 39). Confirmation of the process is obtained by observation of the appropriate metastable ion at $39^2/54$ = *m/e* 28.2. The spectrum of 1,3-butadiene-*2,3-d*$_2$ shows that the loss of methyl is accompanied by complete H/D randomization: the ratio for loss of CH_3:CH_2D:CHD_2 is 1:3:1, which is statistical.

In order to examine the time dependence for the H/D randomization, the distributions of isotopic label in the (M − methyl) ions from deuterated 1,3-butadiene were viewed at discrete times from $10^{-10.7}$ to 10^{-9} s (see Figure 2). These observations were made using the technique of field ionization kinetics (FIK)[2] by which selected ion lifetimes can be observed by varying the field ionization emitter potential on a double-focusing mass spectrometer. Compared to other systems examined by FIK, we find that the hydrogen atom randomization is complete at the shortest times accessible on the Amsterdam instrument. An identical conclusion can be drawn from results for 1,3-butadiene-*1,1,4,4-d*$_4$. For comparison, FIK studies of the C_4H_8 molecule ions[9] (specifically 1-butene and isobutene) show that hydrogen randomization is not complete until greater than 10^{-10} s.

The hydrogen-atom randomization can occur by a variety of mechanisms such as 1,2 or 1,3 hydrogen shifts on an intact carbon skeleton or by the skeletal rearrangements which would accompany ring formation. To assess whether skeletal rearrangements have occurred and, if so, whether the mechanism is that for hydrogen-atom interconversions, FIK results were obtained for 1,3-butadiene-*1*-^{13}C (see Figure 3a). Based on the symmetry of the molecule, the probability for methyl loss from the terminal carbons is simply twice that of $^{13}CH_3$ loss (ignoring isotope effects). In Figure 3b, we show the probability of terminal carbon atom participation in the methyl loss.

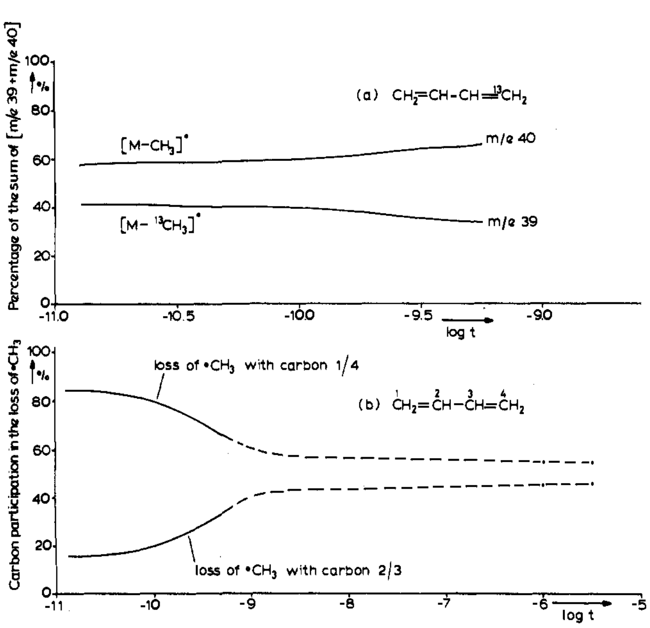


Figure 3. Time dependence for loss of methyl from 2,3-butadiene-*1*-^{13}C molecular ion: 3a (upper), actual data; 3b (lower), calculation of the percent terminal vs. internal carbon loss from 1,3-butadiene.

Clearly, there is a definite specificity for terminal carbon involvement in the dissociation reaction at short times. At approximately 10^{-11} s, 85% of the departing methyl originates from either the 1 or the 4 position. As time is prolonged, there is a slow but definite loss in specificity. Comparing Figures 2b and 3a leads us to the conclusion that there are separate mechanisms for carbon-atom interchange and hydrogen randomization.

2. Mass-Analyzed Ion Kinetic Energy (MIKES) Studies. Low-energy unimolecular or collisionally induced dissociations can be studied readily with a reversed geometry double focusing mass spectrometer.[3] The technique, known as MIKES (mass-analyzed ion kinetic energy spectrometry) or DADI (direct analysis of daughter ions), involves mass analyzing the ion of interest using the magnetic field analyzer. Following that, unimolecular decompositions in the field-free region between the magnet and the electrostatic analyzer (ESA) can be observed by scanning the ESA field. Data were taken with the University of Nebraska double-focusing Hitachi RMU-6D mass spectrometer, which has been modified recently to operate in the MIKES mode.[10] The chief advantage for the MIKES method in studies of this nature is that, by separating the isotopically labeled molecular ions by mass analysis, interferences from partial isotopic substitution are avoided. In addition, kinetic energy released in the dissociation reaction can be readily measured. Typical scans are presented in Figure 4.

Measurement of the peak heights shown in Figure 4 yields the results in Table I. The results tell us that the molecule ion has undergone nearly complete carbon and hydrogen interchanges within 10^{-5} s, which is the time required for $[C_4H_6]^{+\bullet}$ to reach the second field-free region of the spectrometer. Of course, the pattern for methyl loss from the 1,3-butadiene-*1,1,4,4-d*$_4$ is not surprising in view of the fact that a statistical result is observed at the shortest times in the FIK experiment. On the other hand, carbon interchange is not quite statistical; there is still a vestige of specificity for methyl loss involving the

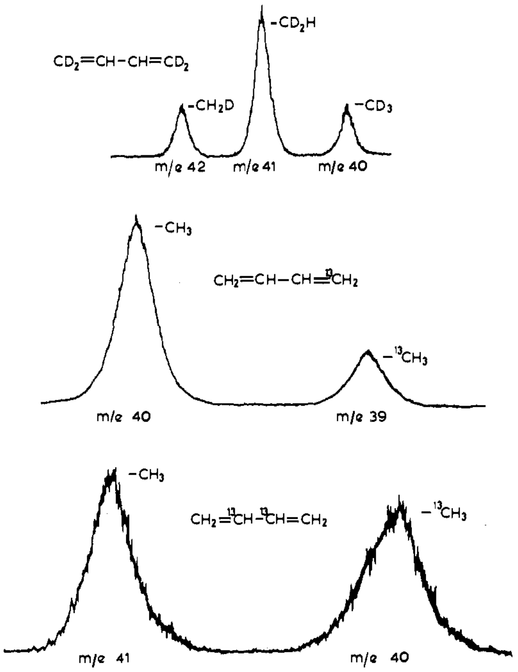


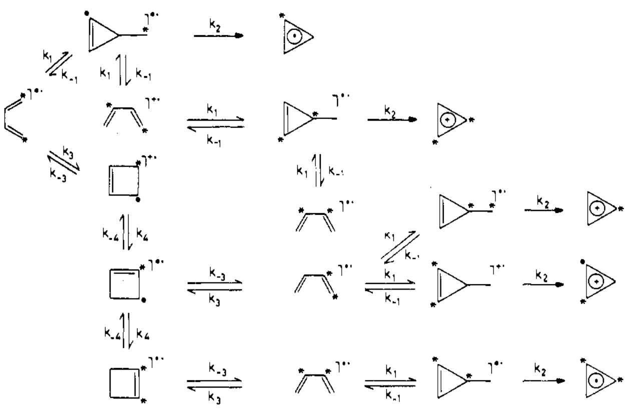
Figure 4. Loss of methyl from various isotopically labeled 1,3-butadienes observed in the MIKES mode (i.e., 10^{-5} s after ion formation). The peak broadening at lower mass is due to a nonlinear scan function.

Table I. Isotopic Distribution (%) for Methyl Loss for Various Isotopically Enriched 1,3-Butadienes as Measured by MIKES

	loss of				
precursor	$^{12}CH_3$	$^{13}CH_3$	CD_3	CD_2H	CDH_2
1,3-butadiene-*1*-^{13}C	77 (75)	23 (25)			
1,3-butadiene-*2,3*-^{13}C	53 (50)	46 (50)			
1,3-butadiene-*1,1,4,4*-d_4			20 (20)	60 (60)	20 (20)

[a] Precision of eight separate measurements is ±1% absolute. [b] Values in parentheses are calculated for statistical losses.

Scheme I. Mechanism for Decomposition of the 1,3-Butadiene Radical Cation



terminal carbons even on the metastable time scale. The broken lines in Figure 3b show the extrapolation from the FIK to the metastable (MIKES) time frame.

In addition to the studies of isotopically labeled 1,3-butadienes, the relative intensities and the kinetic energy release were measured for all the unimolecular decompositions of C_4H_6 radical cations formed from a variety of sources (see Tables II and III). It should be noted that the metastable decomposition branching ratios (Table II) are not a consequence of collisional processes (collisional activation) because the measurements were made in the second field-free region of the MIKE spectrometer at pressures below 1×10^{-6} Torr in this region. Moreover, the branching ratios are independent of pressure in the 10^{-6} Torr range.

Close examination of the branching ratios (Table II) reveals that they are approximately equal for ionized 1,3-butadiene, cyclobutene, 3-methylcyclopropene, and 1-butyne. The precision of the measurements is better than ±10% relative and the agreement in branching ratios for decompositions of approximately 2% relative abundance for the four compounds is better than ±20% (relative standard deviation). However, C_4H_6 ions produced from 2-butyne and 1,2-butadiene show a significant attenuation in the relative abundance for methyl loss and corresponding increases for the losses of H through $2H_2$ and for losses of C_2H_2, C_2H_3, and C_2H_4 (the percentages are increased by a factor of approximately 4 on the average).

Discussion

In the previous paper, it has been shown that the "stable" (nondecomposing) cyclobutene radical cation converts to 1,3-butadiene. From the results in Table II, we know with certainty that the C_4H_6 ions formed from 1,3-butadiene, cyclobutene, 3-methylcyclopropene, and 1-butyne are rapidly equilibrating provided that they have been activated above the decomposition threshold.

The situation is less certain for ionized 2-butyne and 1,2-butadiene because of their decreased propensity to dissociate by loss of methyl. The question which must be answered is, "Are the differences observed for branching ratios to be ascribed to structural differences or are they manifestations of internal energy effects?" Turning to the amounts of kinetic energy released for slow (metastable) decomposing ions (Table III), we find some variations but no trend as observed for the branching ratios. We conclude that the kinetic energy release data support a mixture of equilibrating C_4H_6 ions independent of their neutral precursor. This is identical with the conclusion of Werner and Baer[5] which is based on their rate measurements for methyl loss from energy-selected C_4H_6 ions. Thus, the variations found for the branching ratios must reflect internal energy differences only.[11]

Because of the different rates for carbon and hydrogen interchange, a detailed picture of the possible routes for the decomposing C_4H_6 ions can be formulated (see Scheme I). The starting point for understanding the decomposing ions is the mechanism proposed by Chesnavich and Bowers,[7] which involves a rate-determining isomerization (k_1) to 3-methylcyclopropene (or other structure of similar energy) followed by simple cleavage (k_2).

For simplicity we do not consider isomerization of the 1,3-butadiene ion to form 1,2-butadiene, 1-butyne, or 2-butyne. Certainly, these isomerizations occur very rapidly and serve to give a statistical distribution of hydrogen atoms on the intact carbon skeleton. In fact, at higher internal energies, it has been proven using deuterium labeling that ionized 1-butyne undergoes direct methyl loss in competition with isomerization.[12] Nevertheless, we consider only processes which can lead to skeletal isomerization.

From the previous paper,[2a] we surmise that interconversion of 1,3-butadiene and cyclobutene ions is a facile process for C_4H_6 ions which are activated above the decomposition threshold. However, the rate constants for hydrogen shifts in the cyclobutene structure (k_4 and k_{-4}) must be smaller than for electrocyclic ring opening (k_{-3}) and for decomposition to give $C_3H_3^+$ (k_2). This is because little carbon interchange can be observed at 10^{-10}–10^{-11} s. Therefore, the rate for ring formation (k_1) must be a rate-determining step for the fast decomposing C_4H_6 ions observed in the FIK experiments.

Table II. Relative Metastable Intensities for Decomposing C_4H_6 Radical Cations[a]

	metastable reaction loss of							
$C_4H_6^{+\cdot}$ source	H	H_2	$H_2 + H$	$H_2 + H_2$	CH_3	C_2H_2	C_2H_3	C_2H_4
1,3-butadiene	13	1.7	0.8	0.6	81	0.8	1.7	0.4
cyclobutene	13	1.9	1.2	0.7	81	0.8	1.4	0.2
3-methylcyclopropene	13	1.4	0.7	0.5	81	0.8	1.9	0.6
1-butyne	10	1.8	1.8	1.4	81	0.9	2.2	0.2
2-butyne	25	8.9	5.7	3.8	49	1.3	4.6	1.3
1,2-butadiene	21	6.4	7.1	3.6	51	3.6	5.7	1.4

[a] Integrated peak areas for signals measured by MIKES.

Table III. Comparison of the Metastable Kinetic Energy Release (meV) for Decomposing C_4H_6 Radical Cations[a]

	metastable reaction loss of							
$C_4H_6^{+\cdot}$ source	H	H_2	$H_2 + H$	$H_2 + H_2$	CH_3	C_2H_2	C_2H_3	C_2H_4
1,3-butadiene	130	320	370	160	10	10	11	12
cyclobutene	190	390	340	200	8	10	10	13
3-methylcyclopropene	130	320	365	160	8	11	11	12
1-butyne	150	430	380	260	6	10	11	11
2-butyne	180	340	370	220	7	11	8	13
1,2-butadiene	240	490	370	160	8	12	13	11

[a] Measured from peak widths at half-height.

Chesnavich and Bowers[7] have postulated that this is true for ions decomposing within 10^{-5}–10^{-6} s. From the FIK results, we suggest that this mechanism is true for the more rapid fragmenting ions.

Turning to the effect of increasing the lifetime of the fragmenting ions, we note that the rate for carbon interchange is competitive with the dissociation to $C_3H_3^+$. Actually, at the shortest ion lifetimes, the dissociation rate constant (k_2) is slightly larger than carbon interchange because some methyl loss involving the internal carbons of the original 1,3-butadiene is observed (15%). At $10^{-9.3}$ s, 34% of the methyl loss originates from the internal carbon atoms, and by 10^{-5} s the value has increased to 46%. These data indicate that there are different but similar transition states for carbon isomerization and dissociation, and that the height of the isomerization activation barrier is slightly less than the dissociation barrier. Because the dissociation reaction is favored at short times, its transition state can be described as somewhat less "tight" than the isomerization transition state.

To make the arguments more explicit, a schematic two-dimensional potential surface is presented in Figure 5. The energies of the various structures shown are taken from the work of Werner and Baer[5] and Chesnavich and Bowers.[7] For their theoretical calculations, Chesnavich and Bowers[7] estimated the ionization potential of 3-methylcyclopropene to be 9.62 eV. The activation energy necessary for elimination of methyl was taken to be 0.35 eV (the well depth of the 3-methylcyclopropene radical cation) plus 0.20 eV, a quantity of energy which gave satisfactory agreement between the calculated and observed rate curves. We have measured the ionization potential of 3-methylcyclopropene both by ion cyclotron resonance spectrometry (Amsterdam) and by conventional mass spectrometry (Nebraska) and obtained values of 9.11 and 9.18 eV, which are considerably lower than the Chesnavich and Bowers estimate.[7] The corresponding appearance potentials for $C_3H_3^+$ were found to be 9.77 and 9.70 eV. Using the Chesnavich and Bowers estimate for the ΔH_f of neutral 3-methylcyclopropene of 2.59 eV, we obtain values of 12.36 and 12.30 eV for the ΔH_f of the activated complex. These values agree satisfactorily with 12.51 eV, which was determined by Werner and Baer.[5] The barrier height for ring opening to cyclobutene was estimated in the preceding paper.[2a] Because the fast decomposing C_4H_6 ions must be more highly activated than the ions observed in the MIKES experiments, two arbitrary energy levels, representing the fast (E) and slow (E') decomposing ions, will be considered.

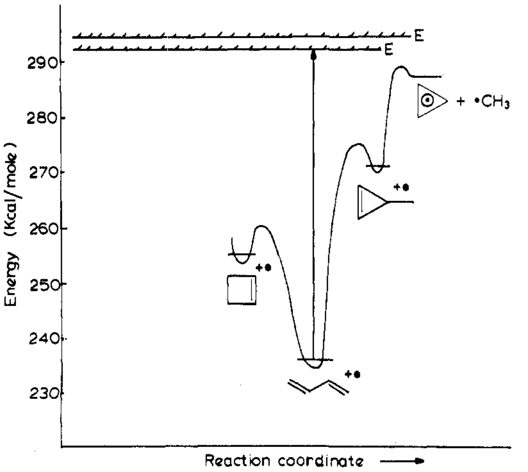


Figure 5. Schematic potential energy surface for loss of methyl from 1,3-butadiene radical cation.

As the internal energy is lowered from E to E', k_2 and k_{-1} must decrease. Because the barrier height for ring opening is lower than for dissociation, and because both processes involve similar transition states, i.e., simple C–C bond cleavage, k_{-1} is less strongly affected than k_2. Thus, lower energy, longer lived C_4H_6 ions undergo carbon scrambling via processes represented by k_1 and k_{-1}. Once ring opening occurs, a hydrogen transfer is necessary to re-form the 1,3-butadiene ion. We postulate that this transfer is rapid by citing the evidence for complete H/D randomization at the shortest times observed in the FIK experiments.

Although we prefer this explanation for the competitive carbon atom randomization, we cannot rule out double-bond isomerization in the cyclobutene ion (processes represented by k_4 and k_{-4}), which would also lead to loss of the internal carbons of the 1,3-butadiene. However, based on the low barrier height for the electrocyclic ring opening (k_{-3}), we suggest that the cyclobutene intermediate is a transient species for highly activated C_4H_6 ions. When it forms, it rapidly ring opens to re-form the 1,3-butadiene cation. The rate for hydrogen shifts (represented by k_4 and k_{-4}) on the cyclobutene nucleus cannot compete with the rapid electrocyclic ring opening; consequently we postulate that skeletal isomerization does not occur by this mechanism. This is consistent with many observations in mass spectrometry that H/D randomization is slow when put in competition with a simple cleavage reaction.[13] The statement is not at odds with the observation of fast H/D randomization for decomposing C_4H_6 ions because, in this case, the competition is with a skeletal isomerization to give the 3-methylcyclopropene or similar intermediate rather than a direct cleavage reaction. Moreover, the activation energy required for dissociation to $C_3H_3^+$ is much greater than for interconversion of the various acyclic C_4H_6 ions.

Conclusion

The observation that decomposition of $[C_4H_6]^{+\cdot}$ from 1,3-butadiene to give $C_3H_3^+$ is more rapid than carbon-atom randomization at short ion lifetimes (10^{-9}–10^{-11} s) is interpreted to show rate-determining ring formation of 3-methylcyclopropene or similar structure in this time frame. This kinetic scheme has been proposed by Chesnavich and Bowers,[7] but it is true only for highly energized C_4H_6 radical cations. As longer lived ions are sampled by employing the MIKES method, the carbon skeletal isomerization becomes competitive and ultimately dominates. In other words, at internal energies close to the dissociation threshold, k_1 and k_{-1} become greater than k_2, and the 1,3-butadiene and 3-methylcyclopropene radical cations are in equilibrium. The rate-determining step is no longer formation of the 3-methylcyclopropene structure (as postulated by Chesnavich and Bowers[7]) but formation of $C_3H_3^+$ as was originally assumed by Werner and Baer.[5] We have learned recently that Baer[14] has augmented his study of C_4H_6 ions by including 3-methylcyclopropene. Lifetime measurements show that the 3-methylcyclopropene ions near the threshold for dissociation do indeed isomerize to the 1,3-butadiene ion more rapidly than directly decompose to give $C_3H_3^+$ (i.e., for threshold energies $k_{-1} > k_2$ as we have postulated).

Moreover, the results appear to show that hydrogen randomization cannot compete with the facile electrocyclic ring opening of the cyclobutene ion, but does compete very well with dissociation of C_4H_6 radical cations to give $C_3H_3^+$.

Experimental Section

FIK experiments were performed on a Varian MAT 711 double-focusing mass spectrometer as described earlier.[15] The metastable kinetic energy release measurements were performed on an Hitachi RMU-6D double-focusing mass spectrometer modified for mass-analyzed ion kinetic energy spectroscopy (MIKES).[10] In this mode the second field-free region metastables are analyzed by electric sector scans.[3] The source was maintained at 150 °C with a nominal ionizing electron energy of 70 eV and an electron current (total emission) of 100 μA. The slits were adjusted to give an energy spread of the main ion beam of less than 0.15 V, which normally corresponds to approximately 0.2-mm slit widths. The kinetic energy release values were corrected for the normal energy spread of the ion beam by subtracting the half-height width of the main ion beam from the deserved metastable peak width at half-height. The ionization and appearance potentials were determined by the semilogarithmic method.

The samples of 1,3-butadiene (Matheson Co.), 1,2-butadiene, 1-butyne, and 2-butyne (Chemical Samples Co.) were analyzed by mass spectrometry and found to be pure. The deuterium-labeled 1,3-butadienes, 1,3-butadiene-*2,3*-d_2 and 1,3-butadiene-*1,1,4,4*-d_4, and 1,3-butadiene-*1*-^{13}C were obtained from Merck and Co. Isotopes (minimum isotopic purity 90 atom %) and were used without further purification. The cyclobutene was prepared as described previously.[1]

The sample of 1,3-butadiene-*2,3*-$^{13}C_2$ was prepared in the following manner.[16,17] 1,2-Dibromoethane-*1,2*-$^{13}C_2$ (3.25 g) was dissolved in 7 mL of 100% methanol and added slowly (period of 1.25 h) to a refluxing solution of 2.08 g of KCN in 2.0 mL of water. After 3.5 h of reflux, an additional 1 g of KCN was added. Reflux was continued for an additional 20 h. The excess KCN was removed by the addition of 7 mL of cold sulfuric acid and 7 mL of cold ethanol. The mixture was refluxed for 12 h and then cooled and continuously extracted with ethyl ether for 48 h. The resulting diethyl succinate was reduced with $LiAlH_4$ to give 1,3-butanediol-*2,3*-$^{13}C_2$. The 1,4-butanediol-*2,3*-$^{13}C_2$ was then converted to 1,4-dibromobutane-*2,3*-$^{13}C_2$ by adding the reactant dropwise to a suspension of sodium hydride (2.5 g) in dimethylformamide (20 mL) maintained at 80 °C. The 1,3-butadiene-*2,3*-$^{13}C_2$ was collected in a cold trap maintained at −78 °C (acetone/dry ice) by sweeping the reaction vessel with a slow stream of dry nitrogen (2–5 cm^3 min^{-1}). The product was distilled at −78 °C and 0.25 mmHg into a gas sample tube. The sample was then analyzed by low-voltage mass spectrometry (10.5 eV) to determine the isotopic purity (78% $^{13}C_2$, 16% $^{13}C_1$, 6% $^{13}C_6$) and used without further purification. The overall yield of this synthesis, as determined by the measured gas volume using an oil manometer, was approximately 40% of the theoretical.

The 3-methylcyclopropene was synthesized from crotyl chloride and lithium amide as has been described in the literature.[18]

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References and Notes

(1) (a) Department of Chemistry; (b) Laboratory for Organic Chemistry; University of Amsterdam.
(2) (a) M. L. Gross and D. H. Russell, *J. Am. Chem. Soc.*, preceding paper in this issue. (b) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *Ibid.*, **94**, 6794 (1972), and references cited therein.
(3) R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973.
(4) M. L. Vestal in "Fundamental Processes in Radiation Chemistry", P. Ausloos, Ed., Interscience, New York, 1968, p 59.
(5) A. S. Werner and T. Baer, *J. Chem. Phys.*, **62**, 2960 (1975).
(6) Wendell Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973, pp 15–28.
(7) W. J. Chesnavich and M. T. Bowers, *J. Am. Chem. Soc.*, **99**, 1705 (1977).
(8) P. Wolkoff, J. VanderGref, and N. M. M. Nibbering, *J. Am. Chem. Soc.*, **100**, 541 (1978).
(9) P. J. Derrick and A. L. Burlingame, *Acc. Chem. Res.*, **7**, 328 (1974); R. P. Morgan, P. J. Derrick, and A. G. Harrison, *J. Am. Chem. Soc.*, **99**, 4189 (1977).
(10) T. Wachs, P. F. Bente, III, and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.*, **9**, 333 (1972).
(11) In an earlier, detailed analysis of metastable decomposition intensity ratios, A. N. H. Yeo and D. H. Williams, *J. Am. Chem. Soc.*, **93**, 395 (1971), have concluded that small variations in metastable ratios (factors of 5 approximately) are *not* proof of different structures.
(12) Z. Dolejsek, V. Hanus, and K. Vokac, *Adv. Mass Spectrom.*, **3**, 503 (1966).
(13) J. van der Greef, F. A. Pinkse, C. W. F. Kort, and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.*, **25**, 315 (1977).
(14) T. Baer, *J. Electron Spectrosc. Relat. Phenom.*, in press.
(15) This has been clearly established by FIK. For leading references, see ref 9.
(16) This is a modified version of the preparation described by A. I. Vogel, "Practical Organic Chemistry", Longman, London, 1972, p 761.
(17) Reference 16, p 280.
(18) R. Köster, S. Arora, and P. Binger, *Justus Liebigs Ann. Chem.*, 1219 (1973).