termining this angle is the exchange repulsion.

The reaction of two closed-shell systems is exemplified by the nucleophilic attack of methyl fluoride by fluoride ion. As noted above, the VSCC of carbon in methyl fluoride exhibits a region of charge depletion in the face opposite the fluorine and the Laplacian thus dictates that the F⁻ ion approach this face along the threefold symmetry axis. One anticipates that HOMO will be the 2p orbital on F⁻ directed along the symmetry axis and LUMO the antibonding C–F orbital on $CH_3F$. This is found to be the case when the reactants are 2.1 Å apart. Both orbitals are of $a_1$ symmetry and hence the lowest energy excited state and the associated transition density (Figure 3) are also of $A_1$ symmetry. The transition density does not show a simple transfer of charge from one reactant to the other as found for the addition reactions discussed above. Instead charge is transferred to the approaching F as well as to carbon and the departing fluorine. In addition, a region of charge removal is formed between the carbon and the approaching fluorine. Such a rearrangement of charge is similar to that found for the approach of two helium atoms[30] and is as anticipated for the approach of two closed-shell systems in general.

The charge relaxation in the neighborhood of the fluorine nucleus initially bonded to carbon is such as to draw this nucleus away from carbon. The relaxation of charge in the vicinity of the carbon and the approaching fluorine is such as to draw the nuclei of these two atoms together. Thus the lowest energy transition density exerts forces on the nuclei as required for a nucleophilic displacement. This reaction has been previously shown[18b] to possess a symmetrical transition state 7 kcal/mol less stable than the reactants, a result which is consistent with gas-phase experimental measurements.[31] The transition density pictured in Figure 3 changes to $A_2''$ symmetry in the transition state as originally predicted.[2] It was there pointed out that such a transition density could exert forces on the protons as required to achieve inversion about the carbon nucleus in the reaction. One notes in Figure 3 that even at 2 Å the charge relaxation in the vicinity of the protons is such as to lead to both inversion and to an initial shortening of the C–H bonds. The previous theoretical calculations show that the C–H bonds do indeed shorten by ≈0.04

Å in the formation of the transition state.[18b]

The examples given in this paper illustrate that the relative approach of reactants as determined by aligning regions of charge concentration with regions of charge depletion in their Laplacian distributions leads to the formation of an initial complex in which the most facile relaxation of the charge density is one which leads to further motion along the reaction coordinate initiated by this approach. In these examples the local concentrations of charge present in the Laplacian of the base coincide with the properties associated with the HOMO orbital. Similarly, the local regions of charge depletion in the Laplacian of the acid or electrophile coincide with the properties associated with the LUMO orbital. Perhaps the most important information contained in the state function to be sacrificed in its reduction to the charge density is the information regarding its phase. In the orbital approximation, the relative phases of the orbitals determine their symmetry properties and their effective overlap. The Laplacian of a charge distribution, by recovering predictions based upon orbital phase information, provides not only a bridge between the density and orbital approaches but a step toward the development of a theory of reactivity based solely on the properties of the charge density.

Parr and co-workers[32,33] have already shown that the principal ideas of frontier orbital theory can be related, in a formal manner, to density functional theory. They relate reactivity to a function, called the Fukui function, which determines the local contributions to the change in the electronic chemical potential. They argue that attack occurs where the Fukui function is largest and that this function can be approximated by HOMO, by LUMO, and by their average respectively in electrophilic, nucleophilic, and radical attack. Clearly, the Laplacian of the electronic charge density and the Fukui function of density functional theory contain similar information. It is possible that a pursual of the connection between these two functions will facilitate the development of a density-based theory of chemical reactivity.

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# The Ring Opening of Gas-Phase Cyclopropane Radical Cations

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**Abstract:** The possibilities of isomerization of gas-phase cyclopropane radical cations to propene or of ring opening to the trimethylene radical cation are addressed. Structural information was obtained by collisionally ionizing various $C_3H_6$ radical cations formed over a range of ionizing energies to give $C_3H_6{}^{2+}$ which fragments to give distinctive spectra of product ions. Confirmation of the conclusions drawn from these studies was found by measuring the reactivity of the $C_3H_6$ radical cations in ion–molecule reactions studied with use of Fourier transform mass spectrometry. The neutral reagents which react selectively with $C_3H_6$ radical cations are ammonia, propene-$d_6$, and carbon disulfide. Collisionally stabilized adducts were delineated by obtaining their collisionally activated decomposition spectra with a tandem mass spectrometer. On the basis of the ammonia reaction studied here and by others, a structural change of activated cyclopropane radical cations can be clearly established. Structural isomerization to the propene radical cation can be ruled out, however, on the basis of several pieces of evidence: reactivity with propene-$d_6$ and carbon disulfide, the structure of the cyclopropane–$CS_2$ adduct radical cation, and the collisional ionization spectra. Ring opening to the trimethylene radical cation is consistent with the results of these studies, and this process is entirely analogous to the structural change of cyclopropane radical cations in condensed phases.

There is considerable evidence that small (3–5 carbon) cyclo-alkane radical cations isomerize in the gas phase to yield acyclic

structures prior to dissociating.[1] The ring opening of the simplest cycloalkane radical cation, cyclopropane, has been extensively

studied with both experimental[2-14] and theoretical[15,16] methods, yet it is still imperfectly understood because of conflicting interpretations.

Because it is not possible to distinguish between cyclopropane and propene on the basis of their conventional mass spectra,[2] it has been necessary to turn to other tools to characterize better the ions. The first reactivity comparisons of the $C_3H_6$ radical cations formed from propene and cyclopropane were made by Ausloos and Lias[3] and Sieck and Futrell.[4] Evidence that the two ions are distinguishable was presented in the latter paper.[4]
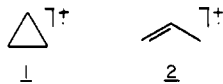


The first direct evidence for the intact cyclopropane radical cation was based on its reactivity with $NH_3$ to form $CH_2NH_2^{+}$[5] and the distonic ion $\dot{C}H_2NH_3^{+}$.[6] Propene radical cations do not exhibit this property but react exclusively by transferring a proton to $NH_3$.[7] The reaction of cyclopropane radical cations with ammonia is energy dependent; ions formed near the ionization threshold remain cyclic, whereas at higher ionizing energies, a significant fraction of the ions exhibit propene-like reactivity.

Recently Lias and Buckley[8] have shown that ionized cyclopropane reacts with other nucleophiles besides $NH_3$ and that there is an onset of 1.3–1.6 eV before the cyclopropane-derived $C_3H_6^{+}$ ions begin to react by proton transfer. They concluded that cyclopropane ions can also isomerize to propene by a low energy bimolecular process.

Unimolecular or metastable decompositions of the two isomeric $C_3H_6$ radical cations cannot be used to distinguish them.[9] Conventional collision activated dissociations (CAD) of the two ions are also indistinguishable.[1f,10] These results may be taken to indicate that cyclopropane ions isomerize to the propene structure prior to decomposition. However, distinctive features are produced when the ions are subjected to collisional ionization.[11] The dif-

ferences in the spectra of doubly charged product ions are independent of ionizing energy over the range of 17 to 70 eV.[12] Thus, the barrier for isomerization of cyclopropane to propene radical cations was interpreted to be higher in energy ($>1.6$ eV) than the threshold for H· loss.[12c] No evidence could be found for other $C_3H_6^{+}$ ions such as the trimethylene radical cation, **3**. If trimethylene radical cations are formed, it was surmised that they convert to **2**.



On the basis of the photodissociation spectra of cyclopropane and propene radical cations, two different ion populations of cyclopropane are thought to be formed by 16-eV electron ionization.[13] Furthermore, the isomerization of **1** to **2** was postulated to explain that the photodissociation spectrum of the reactive fraction of cyclopropane ions formed at 16 eV resembles that of propene ions. However, at 12 eV, the cyclopropane ions still remain cyclic on the basis of evidence from proton affinity measurements.[14]

There is agreement among theoretical studies that the most stable form of cyclic $C_3H_6^{+}$ is a long-bonded isosceles[15] or a scalene triangle.[16] Other cycloalkane radical cations are also predicted to have long-bonded structures.[15c,17] In addition, the long-bonded form is expected to be the trimethylene radical cation in the limit of extreme vibrational excitation.[16]

From these reports, it is clear that there are three reasonable possibilities for the structures of gas-phase $C_3H_6$ radical cations. Conflicting interpretations have been presented for the existence of both **1** and **2** from cyclopropane at high ionizing energies. It is possible, however, that the conflict may be resolved if a third structure is formed which, according to the theoretical work, is the trimethylene radical cation, **3**. The "trimethylene radical cation" may not be a unique chemical species existing on a separate minimum on a potential energy surface; rather, the term may refer to a species with an enlarged C–C–C bond angle which is made by ionizing and adding additional energy to cyclopropane.

In this paper, a search for the existence of the trimethylene radical cation in the gas phase is reported. The experimental strategy is as follows. Firstly, collisional ionization spectra of $C_3H_6^{+}$ ions formed at lower ionizing energies than previously used were obtained in order to see if changes are apparent near the isomerization threshold. Secondly, different specific ion–molecule reactions were devised for measuring the reactivities of the propene and cyclopropane radical cations as a function of internal energy. These experiments were conducted by using both a triple sector tandem mass spectrometer and a Fourier transform (FT) mass spectrometer,[18] a combination which has proven to be useful for determining structures of gas-phase ions.[19]

## Experimental Section

The CAD spectra were acquired by using a triple sector Kratos MS-50 TA mass spectrometer of EBE geometry.[20] Ion beams were accelerated to 8 kV, selected at a mass resolution of $>12\,000$ (10% valley definition)[21] by using MS-I (comprised of the first electrostatic sector and the magnet), and activated in the third field-free region by collisions with neutral

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*The Ring Opening of Cyclopropane Radical Cations*

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He or $N_2$. A CAD spectrum was obtained by scanning the second ESA voltage from 0 V to the main beam voltage. The collision gas pressures were adjusted to reduce the main beam by 50%.

Collisional ionization spectra were obtained in a similar way except that the collision gas pressure was adjusted to give a 75% suppression of the main beam; at this pressure, approximately 50% of the collision events are single collisions, 30% are double collisions, and 20% are higher order. The ESA voltage was scanned only over the mass range of $m/z$ 18 to 22 to obtain the spectrum of the double charged ions resulting from collisional ionization of $C_3H_6^+$ ions. The reported values are the averages of 3–4 runs of 50 scans each.

Low-energy electron ionization of the $C_3H_6^+$ ions was effected in a standard Kratos EI source which had been modified to exhibit greater sensitivity at low electron energies.[22] Charge exchange (CE) and high-pressure ion–molecule reactions were conducted in a Kratos chemical ionization (CI) source by using 280-eV electrons for ionization. For the CE reactions, a trace of the $C_3H_6$ was added with $CS_2$ or $N_2$ to a source pressure of 0.5 torr. High-pressure ion–molecule reactions were typically conducted with a 1:1 mixture of the two reagent gases and a tenfold excess of buffer gas (COS or $CS_2$) to give a total source pressure of 0.1–0.5 torr. CE and buffer gases were admitted via an all-metal reagent gas inlet. Sample gases were admitted through either an all-glass heated (150 °C) inlet or an ambient temperature glass reservoir probe. Source pressures were measured by using an ion gauge which had been calibrated with a probe-mounted Hastings gauge interfaced directly to the ion source.

Low-pressure ion–molecule reactions were carried out with a FT mass spectrometer which consisted of a Nicolet Analytical Instruments FTMS-1000 console interfaced to a custom-built spectrometer.[23] A 5.08-cm cubic cell located in a 1.2-T magnetic field was used for all experiments. The trap voltage was maintained at 1 V. Electron beam duration and current were varied in order to maintain reasonable signals at low ionizing energies; typical parameters were a duration of 15 ms and a current of 500 nA. Reactants for static reactions were admitted as 1:1 molar mixtures to a total pressure of $1 \times 10^{-6}$ torr via all-metal leak valves maintained at 50 °C.

Studies of consecutive ion–molecule reactions in the FT mass spectrometer were facilitated by using a pulse valve inlet.[23,24] The neutral $C_3H_6$ was admitted to a static pressure of $0.5–5 \times 10^{-7}$ torr. The CE reagent was then introduced via a pulse valve to a peak pressure of over $10^{-5}$ torr, ionized, and allowed to react with the neutral $C_3H_6$ for 1 s. The excess reagent ions and unwanted fragment ions were then ejected by swept double resonance pulses (21.7 V p-p, 100 Hz/μs) to isolate the $C_3H_6^+$ ions. The diagnostic neutral reagent gas was then pulsed into the cell and allowed to react with the trapped $C_3H_6^+$ ion for 0.5–1 s. Reagent gases were introduced to the pulse valves from stainless steel reservoirs pressurized to ca. 1 torr.

Research grade cyclopropane (Matheson) and propene (Phillips) were used without further purification. Their purity was established by using IR and mass spectrometry. The $^{13}CS_2$ and propene-$d_6$ were obtained from MSD Isotopes and were verified to be >99% pure with mass spectrometry. Pyrazoline was synthesized according to the method of Crawford et al.[25] All other chemicals were obtained from commercial sources and used without further purification.

## Results and Discussion

**Collisional Ionization Mass Spectrometry.** If the cyclopropane radical cation isomerizes to propene with increasing facility as internal energy is increased, a mixture of ions will form whose chemical and physical properties should become more propene-like. This has been the interpretation given in investigations of the reactivity of $C_3H_6^+$ with $NH_3$ and in ion photodissociation studies but is not true for collisional ionization studies. However, in the previous studies of collisionally ionized $C_3H_6^+$ ions, only ions formed with relatively energetic (>17 eV) electrons were considered. These ions cannot be considered ground-state cyclopropane ions; a fraction have energies above the reported isomerization threshold of 1.3–1.6 eV.[8]

Therefore, collisional ionization spectra of more nearly ground-state cyclic $C_3H_6^+$ ions were obtained as part of this study (see Table I). It is evident that the relative abundance of the

**Table I.** Collisional Ionization Spectra of $C_3H_6^+$ Ions

| precursor | eV | m/z | | | | | 19/20.5 |
| | | 19 | 19.5 | 20 | 20.5 | 21 | |
|---|---|---|---|---|---|---|---|
| propene | 50 | 32.6 | 20.7 | 33.7 | 12.2 | 0.8 | 2.7 |
| | 20 | 34.0 | 20.2 | 34.1 | 11.2 | 0.6 | 3.0 |
| | 15 | 32.1 | 20.4 | 34.6 | 12.1 | 0.7 | 2.7 |
| | 12.5 | 33.5 | 20.3 | 34.3 | 11.6 | 0.5 | 2.9 |
| cyclopropane | 50 | 37.2 | 22.5 | 35.7 | 4.3 | 0.1 | 8.7 |
| | 20 | 36.3 | 22.5 | 36.4 | 4.6 | 0.2 | 7.9 |
| | 15 | 36.5 | 22.5 | 35.8 | 5.0 | 0.2 | 7.3 |
| | 12.5 | 35.3 | 21.3 | 36.4 | 6.0 | 0.1 | 5.9 |

[a] Abundances relative to the sum of all fragments. [b] The values are the means of at least three measurements. [c] The precision is better than 5% relative standard deviation for all peaks except for $m/z$ 21, which is 10%.

$C_3H_5^{2+}$ fragment ($m/z$ 20.5) decreases for cyclopropane as the ionizing energy is increased. The ion abundance ratio $m/z$ 19/20.5 increases with internal energy, while the corresponding ratio for propene radical cations remains constant. This is *not* the expected result if the cyclopropane radical cation is isomerizing to propene and the extent of isomerization is increasing as the ionizing energy is raised.

Collisional ionization of the $C_3H_6^+$ ions derived from pyrazoline and tetrahydrofuran yielded spectra identical with that of cyclopropane ions formed at the lowest ionizing energy. This is in accord with results from earlier ICR studies.[5b]

A sharper energy distribution of near-ground-state cyclopropane radical cations can be prepared by using low-energy charge exchange (CE) in lieu of EI. Moreover, by choosing appropriate high-energy CE, excess energy can be sharply deposited in cyclopropane such that most of the initially formed ions possess greater than the proposed isomerization energy of 1.3–1.6 eV. Furthermore, if the pressure of the CE gas is high enough, the activated ions will be stabilized by undergoing collisions with neutral gas molecules.

Collisional ionization spectra were obtained of propene [IE = 9.74 eV[25]] and cyclopropane [IE = 9.86 eV[8]] molecular ions formed by CE with $CS_2^+$ (recombination energy = 10.08 eV)[26] and $N_2^+$ (recombination energy = 15.58 eV).[26] For propene, the ion abundance ratios for $m/z$ 19/20.5 were identical with those found when the ions were made by EI (2.8 ± 0.1). For cyclopropane ionized by $CS_2^+$, the ratio was 2.5 ± 0.1, a value fortuitously similar to those obtained for propene. Ionization of cyclopropane by $N_2^+$ gave $C_3H_6^+$ which yielded a ratio of 3.4 ± 0.1 which indicates that the collisional stabilization was incomplete. Ionization of cyclopropane by CE with $N_2^+$ should produce most of the ions above the isomerization threshold.[8,12c]

It appears that, as the internal energy of the cyclopropane radical cation is increased, the ion does *not* isomerize to propene, but to some other structure, possibly **3**, as predicted by theoretical calculations.[15–17] Moreover, the abundance ratio $m/z$ 19/20.5 for nearly ground-state $c$-$C_3H_6^+$ is fortuitously similar to and probably smaller than the corresponding ratio for propene radical cations. This was not apparent from the measurements of EI-produced ions which still possessed, under the experimental conditions used here, sufficient activation to permit ring opening of a fraction of the ions.

These conclusions are based on small differences in the collisional ionization spectra. Although the differences may be interpreted in terms of different structures, exact structural assignments are difficult to make because only relatively uninformative fragments (losses of H, $H_2$, ...) are observed for these doubly charged ions. Thus, it is desirable to take another experimental approach to obtain corroborative structural evidence. Measurements of reactivity in specific ion–molecule reactions were chosen as the additional source of structural information.

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**Table II.** Product Distributions in the Reaction of Cyclopropane Radical Cations with Ammonia[a,b]

| ionization method | IE or RE (eV) | $CH_2NH_2^+$ | $NH_4^+$ |
|---|---|---|---|
| electrons | 10 | 0.79 | 0.21 |
| electrons | 11 | 0.52 | 0.48 |
| electrons | 12 | 0.30 | 0.70 |
| electrons | 13 | 0.25 | 0.75 |
| electrons | 14 | 0.22 | 0.78 |
| electrons | 15 | 0.20 | 0.80 |
| electrons | 20 | 0.18 | 0.82 |
| electrons | 50 | 0.21 | 0.79 |
| *c* | 10.08 ($CS_2$) | 0.87 | 0.52 |
| *c* | 11.18 (COS) | 0.48 | 0.52 |
| *c* | 15.58 ($N_2$) | 0.29 | 0.71 |

[a] All values as $i/\sum i$. [b] Ammonia pulsed into the cell to ca. $10^{-6}$ torr. [c] Pulsed charge exchange, see Experimental.

**Table III.** Product Abundance Ratios[a] in the Reaction of $C_3H_6^+\cdot$ with $C_3D_6$

| | | ratio $C_2/C_1$ | |
|---|---|---|---|
| expt | IE or RE (eV) | △ | ◁ |
| *b* | 10 | 2.7 | 1.2 |
| *b* | 15 | 3.6 | 1.3 |
| *b* | 25 | 3.8 | 1.4 |
| *c* | 10 | 3.1 | 1.1 |
| *c* | 15 | 2.9 | 1.3 |
| *c* | 20 | 2.9 | 1.5 |
| *c* | 50 | 2.9 | 1.5 |
| *d* | 10.08 ($CS_2$) | 2.7 | 1.4 |
| *d* | 11.18 (COS) | 2.4 | 1.2 |
| *d* | 15.58 ($N_2$) | 2.4 | 1.2 |
| *c* | 50 | 3.0 | 1.5 |

[a] All values ± 0.1. [b] Static experiment; compounds admitted in 1:1 ratio to total pressure of $1 \times 10^{-6}$ torr. [c] Static $C_3H_6$ ($1 \times 10^{-7}$ torr), pulsed $C_3D_6$. [d] Static $C_3H_6$ ($1 \times 10^{-7}$ torr), pulsed CE, pulsed $C_3D_6$.
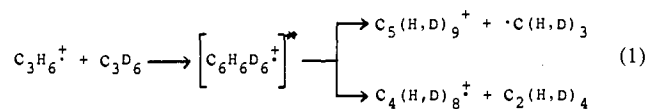
**Reaction with Ammonia.** The established reaction of cyclopropane radical cations with $NH_3$ was examined first by using the FT mass spectrometer to verify the earlier results obtained by using ICR spectrometry. The reactions of both EI and pulsed-CE formed $C_3H_6^+\cdot$ ions with $NH_3$ (also pulsed for some experiments) were monitored as a function of ionization or recombination energy (see Table II). In all cases, the $C_3H_6^+\cdot$ ions were "isolated" prior to the pulse of ammonia by ejecting all other ions.

The changes in reactivity follow the same trends as previously reported;[7,8] that is, as ionizing energy is increased, the protonation of $NH_3$ becomes a more favored pathway. Furthermore, charge exchange by $CS_2^+\cdot$ produces exclusively the cyclic ions in accord with the conclusion of Lias and Buckley.[8] Thus, the surprising similarity of the collisional ionization spectra of propene and cyclopropane radical cations formed by $CS_2$ CE is verified to be fortuitous. The change in the proportion of propene-like ions was observed to be more gradual than reported in previous papers[8] probably because increments in internal energy are achieved gradually when using electron ionization.

**Reaction with Propene-$d_6$.** The changes of reactivity with ammonia as ionizing energy is increased serve to establish that the cyclopropane radical cation is undergoing a structural change either to propene or to some other species which reacts in a similar way to propene. One was to distinguish these possibilities is to examine other specific ion–molecule reactions of $C_3H_6^+\cdot$.

Propene-$d_6$ was chosen as a second specific reagent neutral for two reasons. Firstly, cyclopropane and propene radical cations react with propene-$d_6$ to give different product ion distributions.[27] Secondly, the deuterium-labeled $C_3D_6^+\cdot$ can be ejected so that the observed chemistry is a result of only the reaction of the test ion and neutral propene-$d_6$.

When either propene or cyclopropane radical cations are allowed to react with propene-$d_6$ introduced into the FT mass spectrometer at a pressure equal to that of the ion precursor, two characteristic sets of product ions are produced by losses of various deuterated forms of methyl and ethene (see eq 1) from the adduct.[28] The

$$C_3H_6^+ + C_3D_6 \longrightarrow \left[C_6H_6D_6^+\cdot\right]^* \begin{array}{c} \nearrow C_{5}(H,D)_9^+ + \cdot C(H,D)_3 \\ \searrow C_4(H,D)_8^+ + C_2(H,D)_4 \end{array} \quad (1)$$

isotopic distributions of the two sets of ions are characteristically different for cyclopropane and propene formed by 10-eV EI, in accord with work of Bowers et al.[27] Most notably, the loss of $C_2H_4$ from the adduct derived from cyclopropane occurs much more readily than loss of $C_2H_2D_2$, whereas for the adduct derived from propene the opposite is true. Moreover, large differences in the

(27) Bowers, M. T.; Aue, D. H.; Elleman, D. D. *J. Am. Chem. Soc.* **1972**, *92*, 4255.

(28) The ion–molecule reaction adduct is not observed in the low-pressure FTMS cell due to the exothermicity of the reaction and the lack of stabilizing collisions.

(29) The peak cell pressure has been estimated to be approximately two orders of magnitude greater than the peak pressure measured at the ion gauge during the pulse valve experiment.

overall relative abundances of the two sets of ions [adduct – $C_2(H,D)_4$] vs. [adduct – $\cdot C(H,D)_3$] were also observed. Cyclopropane ions formed at lowest energies react with propene-$d_6$ to form possibly adduct **4** which loses $C_2(H,D)_4$ more readily than the adduct derived from propene, **5**.
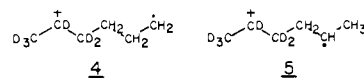


These differences were then monitored as a function of ionizing energy to determine the extent of isomerization (if any) of cyclopropane radical cations to the propene structure. The experimental steps consisted of forming $C_3H_6^+\cdot$ ions from cyclopropane and propene by using either EI or pulsed CE ionization in the FT mass spectrometer. The $m/z$ 42 ions were then "isolated" in the cell by ion ejection and allowed to react with either static or pulsed pressure of propene-$d_6$. The extent of isomerization as a function of ionizing energy was established by measuring the abundance ratios of the ions formed from both various ethene losses ($m/z$ 58–62) and methyl losses ($m/z$ 72–75) (defined as $C_2/C_1$).
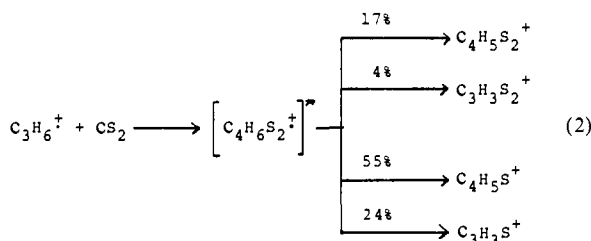
The differences (Table III) can be attributed to different structures of the reacting $C_3H_6^+\cdot$ ions. As the internal energy of the cyclopropane ions is increased, the ratio $C_2/C_1$ either increases, as in the static experiment, or remains relatively constant. Both outcomes are *not* consistent with isomerization to the propene radical cation, which yields smaller, more constant ratios over the energy range covered. The increase of the ratio with internal energy of the cyclopropane radical cation in the static experiment indicates that a significant proportion of $C_3H_6^+\cdot$ ions formed above 15 eV exhibit chemical properties that are clearly different than those of either propene or ground-state cyclopropane radical cations.

The corresponding ratios from the pulse valve experiments do not increase, but remain relatively constant as the internal energy of the $C_3H_6^+\cdot$ is increased. This is interpreted to indicate that the cyclopropane radical cation opens to form the trimethylene species, undergoes collisional stabilization because of the high local pressures[29] during the pulse of $C_3D_6$, and returns to its cyclic form. To test this hypothesis, the ratio of $C_2/C_1$ was monitored as a function of the $C_3D_6$ pulse pressure. As the pulse pressure was increased from 0.2 to $1 \times 10^{-6}$ torr (measured at the ion gauge), the ratio of $C_2/C_1$ decreased linearly with the rate of $-3.4/10^{-6}$ torr$^{-1}$. Thus, it appears that collisional stabilization is occurring and that the ratio $C_2/C_1$ is sensitive to small variations in the pulse pressures. The small variation in the two sets of pulse valve data obtained for 50-eV-produced cyclopropane ions (see Table III) may be accounted for in terms of this sensitivity to pressure.

On the basis of the reaction of $C_3H_6^+\cdot$ with propene-$d_6$, it is concluded that cyclopropane radical cations do not isomerize to the propene structure to any appreciable extent. The differences in the product ion abundances depend markedly on the internal excitation of the cyclopropane and propene radical cations. The reactivity trends exhibited by cyclopropane radical cations can

be accounted for by invoking ring opening to give the trimethylene radical cation, **3**.

**Reaction with CS$_2$.** CS$_2$ has been used in this and other work[8,22] as a CE agent to form cyclopropane radical cations near the ionization threshold. In addition, the C$_3$H$_6^+\cdot$ ions from cyclopropane react with neutral CS$_2$ in the cell of the FT mass spectrometer to form an array of products (see eq 2), while propene radical cations are largely unreactive. Careful investigation of

$$C_3H_6^+ + CS_2 \longrightarrow \left[C_4H_6S_2^{+\cdot}\right]^* \begin{cases} \xrightarrow{17\%} C_4H_5S_2^+ \\ \xrightarrow{4\%} C_3H_3S_2^+ \\ \xrightarrow{55\%} C_4H_5S^+ \\ \xrightarrow{24\%} C_3H_3S^+ \end{cases} \quad (2)$$

this reaction by using ion ejection techniques revealed that the observed products resulted from reactions of both CS$_2^+\cdot$ and C$_3$H$_6^+\cdot$ ions, yet the product distributions from the two reactions are identical. Nevertheless, all subsequent experiments involving this reaction were conducted while continuously ejecting the CS$_2^+\cdot$ ions from the cell.

The reaction of two isomeric ions with the same neutral molecule may be expected to proceed by different rates. The rates of disappearance ($k_d$) for both propene and cyclopropane radical cations reacting with CS$_2$ were monitored as a function of ionizing energy. Each reactant was admitted to a partial pressure of 5 × 10$^{-7}$ torr, and the reactions were followed to approximately 90% completion ($\sim$1000 ms). The $k_d$'s were corrected for any contribution from the competing reactions of the C$_3$H$_6^+\cdot$ ions with their neutral precursors.

For the reaction of cyclopropane radical cations with CS$_2$, $k_d$ is constant ($\pm$5%) over eight measurements (six spanning the range of 10–15 eV and two at 20 and 50 eV) and is three times larger than the rate constant for cyclopropane radical cations reacting with neutral cyclopropane. Furthermore, the product distribution from the reaction (see eq 2) is also constant from 10–15 eV ($\pm$5%). The corresponding $k_d$ for reaction of propene radical cations is also energy independent but more than 8 times less than the $k_d$ for cyclopropane radical cations and 10 times smaller than the $k_d$ for reaction of propene ions with neutral propene. Under these static conditions, no product ions were observed for the reaction of propene radical cations and CS$_2$. The energy independence of the rate constants and product distributions for the reaction of cyclopropane radical cations and CS$_2$ is additional evidence that cyclopropane radical cations do *not* isomerize to propene ions under these experimental conditions.

The distribution of products from the reaction of only C$_3$H$_6^+\cdot$ with neutral CS$_2$ was remeasured by pulsing the CS$_2$ into the cell after the C$_3$H$_6^+\cdot$ was formed and "isolated". The propene radical cations now form detectable, low-abundance products with the pulsed CS$_2$. However, their relative abundances are substantially different than those of product ions formed in reactions of cyclopropane radical cations at the various ionizing energies. The distribution of products at 1000 ms is relatively independent of ionizing energy for cyclopropane (within $\pm$10%), while for propene, the distributions vary considerably. For example, the relative abundances of both $m/z$ 85 and 103 increase with ionizing energy by a factor of 1.8 over the range 10–20 eV and the abundance of $m/z$ 71 decreases by a factor of 1.3 over the same ionizing energy range. Again, there is no evidence that the cyclopropane ions are isomerizing to propene. The distributions of products formed in this or in any of the other experiments do not converge as one might expect if propene were formed as a consequence of high-energy ionization of cyclopropane.

Since the reaction of cyclopropane ions with CS$_2$ has not been reported before, we sought to characterize better the nature of this reaction by investigating the product ions formed by reacting a 1:1 mixture of CS$_2$:C$_3$H$_6$ in the CI source of a tandem mass spectrometer.

**Table IV.** Product Distribution from the Reaction of C$_3$H$_6$ and CS$_2$ in a High-Pressure Ion Source

| $m/z$ | △ | ⌁ | $m/z$ | △ | ⌁ |
|---|---|---|---|---|---|
| 41 | 8.1 | 3.7 | 84 | 2.3 | 4.6 |
| 42 | 28.4 | 100.0 | 85 | 100.0 | 1.4 |
| 43 | 0.8 | 14.6 | 86 | 4.6 | <1.0 |
| 55 | 4.0 | 10.2 | 87 | 4.2 | <1.0 |
| 56 | 5.9 | 29.5 | 103 | 12.6 | 3.0 |
| 69 | 1.0 | 19.6 | 117 | 39.7 | <1.0 |
| 71 | 89.7 | <1.0 | 118 | 30.7 | 12.0 |
| 72 | 3.8 | <1.0 | 119 | 3.9 | <1.0 |
| 73 | 3.9 | <1.0 | 120 | 2.5 | <1.0 |

$^a$Source pressure ca. 0.1 torr. $^b$Peaks due to the CS$_2$ at $m/z$ 64, 76, 77, 78, and 108 are omitted for clarity.

**Table V.** CAD Spectra of C$_3$H$_6$ + CS$_2$ Ion–Molecule Reaction Adducts

| $m/z$ | △ | ⌁ | $m/z$ | △ | ⌁ |
|---|---|---|---|---|---|
| 117 | 100.0 | 1.9 | 59 | sh | 3.7 |
| 103 | 4.4 | 7.7 | 58 | 42.9 | 4.8 |
| 90 | 1.0 | – | 51 | 1.6 | – |
| 85 | 82.5 | 2.9 | 50 | 1.6 | – |
| 77 | 15.1 | <1.0 | 45 | 31.7 | 8.7 |
| 76 | 23.8 | 34.6 | 42 | 52.4 | 100.0 |
| 73 | 5.6 | – | 41 | 27.8 | 11.5 |
| 72 | – | 7.6 | 39 | 12.7 | 7.6 |
| 71 | 99.2 | 7.8 | 32 | 3.2 | <1.0 |
| 69 | 11.1 | 3.8 | 27 | 4.8 | 1.9 |
| 64 | 6.3 | <1.0 | | | |

$^a$Shoulder, probably C$_4$H$_6$S$_2^{2+}$.

The distributions of products resulting from the reactions of cyclopropane and propene ions with CS$_2$ and with their respective neutrals are quite different (see Table IV). The distribution of products formed when cyclopropane ions react at low pressure in the FT mass spectrometer is similar to that observed at the higher source pressure used with the tandem MS; thus, the mechanisms must be the same. As at low pressure, the high-pressure reaction for cyclopropane yields a spectrum of products of which ca. 90% are due to the reaction of CS$_2$ and cyclopropane. For propene, on the other hand, less than 9% of the products result from reactions of CS$_2$ and C$_3$H$_6$. It is noteworthy that at these higher pressures, the intact adducts, $m/z$ 118, were detectable because they were stabilized by collisions with neutral molecules. It also must be pointed out that it is not possible to distinguish which ions (C$_3$H$_6$ or CS$_2$) are responsible for product formation.

To characterize the stabilized adducts and their decomposition products, CAD spectra were obtained. The spectra (see Table V) of the adducts of cyclopropane and propene with CS$_2$ are different; consequently, the adducts must have different structures. On the basis of the dominant $m/z$ 42 and 76 ions seen in the CAD spectrum of the propene-derived adduct, it is concluded that the propene–CS$_2$ forms a weakly-bound collision complex which simply reverts to the starting materials upon collisional activation.

The stabilized cyclopropane–CS$_2$ adduct exhibits the properties of a covalently bound collision complex because reversion to starting materials is minimal. The differences in the fragmentation of the two adducts are consistent with the other observations that the rate for the reaction of cyclopropane radical cations with CS$_2$ is nearly an order of magnitude greater than that for propene and that the reaction of propene ion with CS$_2$ produces few, if any, products in the FT mass spectrometer.

The fragmentations of the cyclopropane–CS$_2$ adduct are expected for the product of a reaction of either cyclopropane or trimethylene radical cation or both and neutral CS$_2$. The FTMS spectrum of the reaction products and the CAD spectrum of the adduct are similar which is taken as evidence that the decomposing, short-lived adduct at low pressure is the same as that stabilized in the higher-pressure CI source. The cyclic or distonic ion structures proposed for the adduct shown in Scheme I should show minimal CH$_3$ loss and considerable losses of CH$_3$S and C$_2$H$_4$S to give $m/z$ 71 and 58, respectively (see table V). Furthermore,
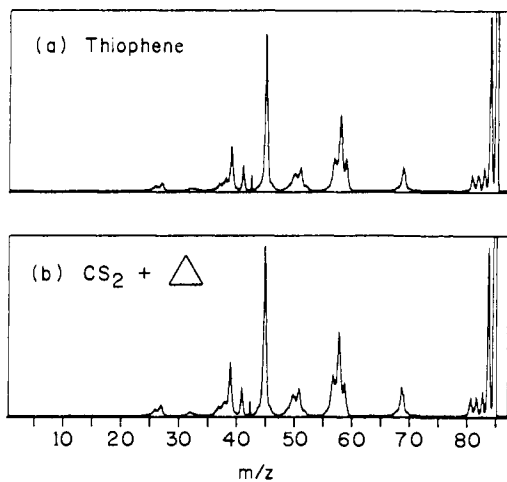
**Figure 1.** CAD spectra of protonated thiophene (a) and of the $m/z$ 85 fragment from the adduct of cyclopropane ion and $CS_2$ (b).

**Scheme I**
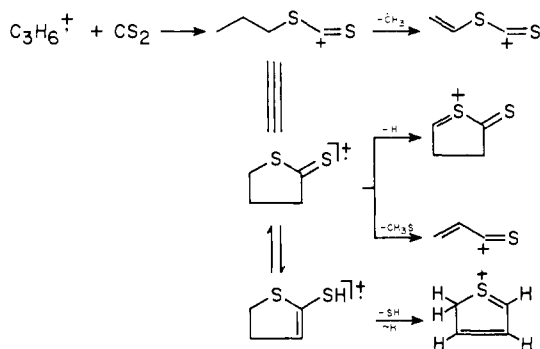


the small loss of $C_2H_4$ (absent in the CAD spectrum of the propene–$CS_2$ adduct) is also in accord with the proposed mechanism. Following cyclization and tautomerization, the adduct loses SH, and the product ($m/z$ 85), after hydrogen rearrangement, adopts the protonated thiophene structure. The CAD spectrum of $m/z$ 85 is nearly identical with that of authentic thiophene protonated in the high pressure or CI source (see Figure 1). These fragmentations are viewed as necessary but not sufficient proof of structure for the adduct.

The $m/z$ 71 product ion is proposed to arise from hydrogen transfer followed by loss of $CH_3S\cdot$ to yield a highly unsaturated $C_3H_3S^+$ ion. This pathway was verified by investigating the reaction of cyclopropane radical cations with $^{13}CS_2$ in the FT mass spectrometer. All of the product ions were cleanly shifted 1 amu higher, which proves that the carbon atom provided by the $CS_2$ is retained in the charged fragments. The result is consistent with the proposal that the collision complex adopts a cyclic structure prior to decomposing.

The CAD spectra of the other major product ions $m/z$ 117, 103, 85, and 71 were also obtained. Spectra of products from the cyclopropane reaction were clearly different than those of products from the propene reaction.

### Structure of the Cyclopropane Radical Cation

The only consistent explanation for the results presented here and elsewhere[2–10,12–17] is that the cyclopropane ion undergoes bond stretching with increases in internal energy to yield eventually an acyclic trimethylene radical cation (see equ 3). Cyclic $C_3H_6^+\cdot$
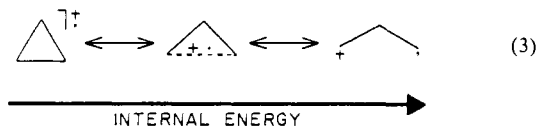


ions do not readily isomerize to the propene structure[7,8,13] because *no* propene-like behavior is exhibited by the cyclopropane radical

cation as its internal energy is increased. On the other hand, the formation of the trimethylene radical cation is consistent with the structural change manifested by cyclopropane radical cations in the ammonia reaction, since protonation of $NH_3$ by the trimethylene radical cation would not yield the cyclopropyl radical but the stable allyl radical as would proton transfer from the propene radical cation. Thus, the proton-transfer reaction is only indicative of a structural change and cannot be taken as proof of structure for the propene radical cation.

The photodissociation results[13] may also be rationalized by the formation of a trimethylene radical cation. The photodissociation of $C_3H_6^+\cdot$ ions formed by 16-eV electron ionization of cyclopropane was interpreted in terms of the presence of two structures: the cyclopropane radical cation and a more reactive isomer which was proposed to be the propene radical cation. However, the spectroscopic properties of the propene and trimethylene radical cations may be similar. It is reasonable to expect that both would absorb at higher energy than the cyclopropane radical cation because the trimethylene species has an unpaired electron in a nonbonding orbital on carbon whereas cyclopropane can absorb by $\sigma-\sigma^*$ transitions.

Cyclopropane radical cations exhibit analogous behavior in condensed phases. From NMR[30] and ESR[31] studies, it is revealed that the most stable form of $C_3H_6^+\cdot$ ions derived from cyclopropane is indeed the long-bonded or trimethylene species rather than a propene isomer. Furthermore, the thermal chemistry of cyclopropane is dominated by the formation of the 1,3-diradical intermediate,[32] from which the rate of recombination to form cyclopropane is at least 20 times the rate of isomerization to propene.[33]

Since the trimethylene radical cation is simply a high-energy form of the cyclopropane radical cation, it should be possible to remove some of its excess energy and return the trimethylene ion to its ground-state cyclic form. Cyclopropane was ionized by electrons in the FT mass spectrometer in the presence of $NH_3$, and the trapped ions were subjected to a burst of methane[34] which should collisionally stabilize the $C_3H_6^+\cdot$ ions prior to their reaction with $NH_3$. At higher ionizing energies (>15 eV) the proportion of $C_3H_6^+\cdot$ ions which reacts to form the $m/z$ 30, $CH_2NH_2^+$, should increase in the pulsed $CH_4$ mode, while at low ionizing energies (<10 eV) the relative increase would be smaller due to the reduced proportion of trimethylene ions which could be stabilized. Furthermore, as the pressure of $NH_3$ is reduced, an increase in the amount of stabilization should occur because the $C_3H_6^+\cdot$ ions experience more stabilizing collisions with $CH_4$ prior to the reactive collisions with $NH_3$. This was indeed the case, as it was possible to stabilize nearly 15% of the $C_3H_6^+\cdot$ ions at 25 eV and $1 \times 10^{-7}$ torr of $NH_3$ while at 10 eV no increase in the proportion of cyclopropane-like ions was observed. As the $NH_3$ pressure was increased, the degree of collisional stabilization also decreased to 10% at $5 \times 10^{-7}$ torr and $\sim 0\%$ at $9 \times 10^{-7}$ torr. At the latter pressure, the reaction with $NH_3$ now occurs more rapidly than collisional stabilization.

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(34) Methane was chosen as it has nearly the same vibrational modes as cyclopropane and would be expected to extract energy more efficiently than, say, COS.