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Isomerization Barriers and Stabilities of $C_3H_6^{+\cdot}$ Isomers

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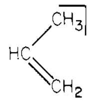
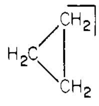
Abstract: The mass spectra formed by collisionally activated dissociation (CAD) of $C_3H_6^{+\cdot}$ using He, N_2, and O_2 as the collision gases show no evidence for the existence of stable isomers other than propene (a) and cyclopropane (b) ions. Ions initially formed as $\cdot CH_2CH_2CD_2^+$ or $\cdot CD_2CH_2CD_2^+$ isomerize to b, and ions initially formed as $(CH_3)_2C^{+\cdot}$ isomerize to a. Ionization of cyclopropane with either 15 or 70-eV electrons gives the same low proportion of a ions (much less than 35%). This indicates a high energy barrier for a ⇄ b, in contrast to conclusions from ion–molecule reaction studies.



a



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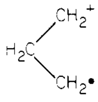
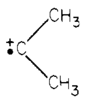


c



d

Isomers of the $C_3H_6^{+\cdot}$ radical cation, in particular a–c, have been studied extensively by both experimental[1-14] and theoretical[15,16] techniques. An attempt to construct an energy surface (Figure 1) representing these results for the $C_3H_6^{+\cdot}$ isomers is hampered by a paucity of information on isomers such as c and d and shows a serious disagreement in the predicted ease of the isomerization of cyclopropane ions (b) to propene ions (a).

The barrier a ⇄ b must be below that for the lowest energy decomposition (H loss),[17] as decompositions of metastable a and b ions proceed through a common intermediate, presumed to be a.[9] Both ^{13}C and ^2H labeling[1-3] indicate that extensive 1,3-H equilibration of a precedes decomposition, as is also observed for 2-hydroxypropene ions.[18] The $C_3H_6^{+\cdot}$ ions formed from tetrahydrofuran-*2,2,5,5-d*$_4$, which could initially have the trimethylene (c) structure $\cdot CH_2CH_2CD_2^+$, react with NH_3 and ND_3 to give products that show that their carbon atoms, but not their hydrogen atoms, have become equivalent before reaction; this suggests that the energy barrier for c → b is below that for b → a.[7] The difference in the proton affinities of a and b ions produced from propene and cyclopropane with ~12-eV ionizing electrons is cited as evidence that b does not ring-open under these conditions.[13] Very recent theoretical calculations of the energy surface of the cyclopropane cation predict a local energy minimum for the ground electronic state of b (but not of c) and for the first electronic excited state of c, with ionization energies of 9.8 and 11.1 eV,[16] consistent with the photoelectron spectrum of cyclopropane.[19] The mass spectra of doubly charged ions formed by collisionally activated dissociation (CAD)[20,21] of a and b are characteristically different,[10-12] and those of $C_3H_6^{+\cdot}$ ions from cyclopropane show no increase in the proportion of a ions on increasing the ionizing electron energy from 17 to 70 eV.[10,12]

In contrast, careful ion-molecule reaction studies indicate[8] that only those $C_3H_6^{+\cdot}$ ions formed by photoionization of cyclopropane near the ionization threshold have exclusively structure b. Ionization with photons whose energies are 0.7 and 1.8 eV above threshold (9.9 eV) yields 15% and 43%, respectively, of ions undergoing ion–molecule reactions identical with that of the a isomer. A recent study using ion cyclotron resonance (ICR)

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Table I. CAD Mass Spectra of $C_3H_6^{+}\cdot$ Ions

	N_2 collision gas[a]				O_2 collision gas	
	$CH_3CH=CH_2$		c-C_3H_6		$CH_3CH=CH_2$	c-C_3H_6
m/z	70 eV	15 eV	70 eV	15 eV	70 eV	70 eV
19	92	93	79	81	56	62
19.5	85	78	57	54	66	68
20	100	100	100	100	100	100
20.5	53	48	26	25	81	69
21	12	12	7	7	65	24

[a] Data rerun several months later showed some change in relative abundances, but for both c-C_3H_6 and $CH_3CH=CH_2$ the 70-eV and 15-eV CAD spectra agreed within ±5% on the basis of peak areas. Similar agreement was found between the spectra of $C_3H_6^{+}\cdot$ ions from 1,1-dimethylcyclopropane and propene run at this time.

Table II. CAD Mass Spectra of $C_3H_4D_2^{+}\cdot$ Ions[a]

	$CD_2=CHCH_3$			c-C_3H_6-*1,1-d*$_2$			γ-butyrolactone-*2,2-d*$_2$, 70 eV
m/z	70 eV	15 eV	calcd[a]	70 eV	15 eV	calcd[b]	
19	31	32	37	44	33	39	38
19.5	84	85	87	78	82	89	95
20	66	71	81	64	72	75	58
20.5	87	82	92	100	100	100	91
21	100	100	100	95	96	93	100
21.5	71	76	51	31	29	31	26
22	38	30	19	16	8	13	12

[a] Using N_2 as the collision gas. [b] Values calculated for complete H/D scrambling based on abundances of Table I assuming $k(H)/k(D) = 1.5$.

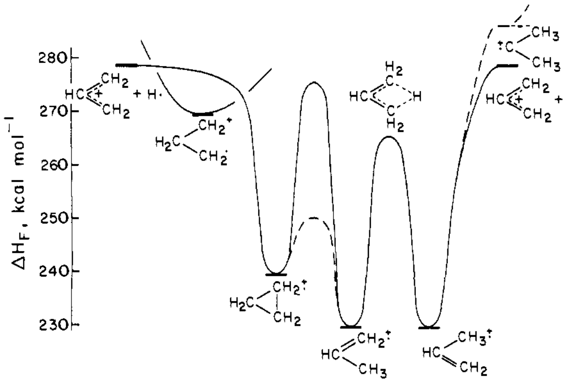

Figure 1. Potential energy surface for isomeric $C_3H_6^{+}\cdot$ ions.

spectroscopy reports that with electron ionization of cyclopropane at energies above 13 eV about 60% of the ions have the propene structure.[14] The characterization of CAD mass spectra of the isomers a and b is based on the higher abundance of $C_3H_5^{2+}$ found for a ions; even if the CAD of pure b gave *no* $C_3H_5^{2+}$ ions, which is unlikely, the maximum proportion of the a isomer which could be formed by ionizing cyclopropane with 70-eV electrons would be 57%,[10] 41%,[11] and 31%[12] based on these independent measurements.

To clarify these discrepancies we have sought CAD evidence for the additional $C_3H_6^{+}\cdot$ isomers, ionized trimethylene (c) and dimethylcarbene (d). To detect either of these when both a and b can be present requires an additional CAD peak sensitive to isomeric identity. Although using helium as the collision gas generally gives the highest cross section for the production of CAD *fragment* ions,[22,23] reports[24-27] indicate that the cross section for electron removal ("charge-stripping") is substantially higher for other collision gases.

Results and Discussion

The use of either N_2 or O_2 as the collision gas does give CAD mass spectra of the molecular ions of propene and cyclopropane showing usefully abundant $C_3H_6^{2+}$ ions from charge stripping (Table I). These CAD spectra differ significantly in the abundance of both m/z 20.5 and 21; a similar effect is seen for m/z 21.5 and 22 in the CAD spectra of $C_3H_4D_2^{+}\cdot$ ions from the corresponding dideuterio species of these molecules (Table II). Even if none of the $C_3(H,D)_5^{2+}$ and $C_3(H,D)_6^{2+}$ species are formed by CAD of *pure* b ions, the data (Tables I and II) show that the maximum proportion of a formed is 49% (N_2, d_0), 37% (O_2, d_0), and 43% (N_2, d_2), consistent with values of 31–57% from the earlier CAD data using helium as the collision gas.[10-12] The fact that the CAD spectra from both cyclopropane-d_0 and -d_2 (Tables I and II) are independent of ionizing energy is only explicable, in our opinion, by an energy requirement for the isomerization a $\rightleftarrows$ b which is sufficiently high so that most stable $C_3H_6^{+}\cdot$ ions formed with 70-eV electrons from cyclopropane have energies below this threshold (Figure 1). The photoelectron spectrum of cyclopropane[19] indicates that a substantial proportion of stable $C_3H_6^{+}\cdot$ ions formed by 70-eV electron ionization will have energies near the threshold for H loss.

It is conceivable that the ICR data for cyclopropane results from an isomerization of b to an isomer other than a, such as c or d. To study c the ions $C_3H_4D_2^{+}\cdot$ and $C_3H_2D_4^{+}\cdot$ were prepared by 70-eV electron-ionization of γ-butyrolactone-*2,2-d*$_2$ and -*2,2,4,4-d*$_4$, which should initially produce $\cdot CH_2CH_2CD_2^{+}$ (c′) and $\cdot CD_2CH_2CD_2^{+}$ (c″). Their CAD spectra of singly charged product ions[28] are not affected outside experimental error by lowering the energy of the ionizing electrons and are consistent with complete H/D scrambling. However, this is not indicative of the isomerization of c $\rightleftarrows$ b, as the CAD spectra (m/z 12–17) of $CH_2{=}CHCH_3$ and $CD_2{=}CHCH_3$ also indicate complete H/D scrambling in the CAD process.[28] In searching for more specific cleavages, C^{2+} (m/z 6) was the only one of the $C_1H_n^{2+}$ ions which could be observed in the CAD spectra of the initial c′ and c″ ions, and their $C_2H_n^{2+}$ ions were obscured by the CH_n^{+} peaks. The abundances of $C_3(H,D)_n^{2+}$ ions formed by CAD of initial c′ ions (Table II) are also consistent with complete H/D scrambling, but so are the $C_3(H,D)_n^{2+}$ abundances from cyclopropane-*1,1-d*$_2$. The c″ ions gave similar results, but of poorer reproducibility.[28] Although this does not rule out the formation of some stable c ions, this is

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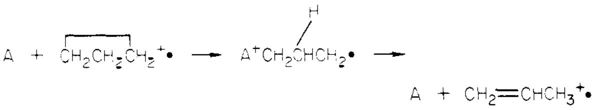
consistent with the conclusions concerning the facile isomerization c → b from the ICR studies of Gross.[7]

No evidence could be obtained either for isomer d.[29] Electron ionization of 1,1-dimethylcyclopropane followed by C_2H_4 loss should yield initially $C_3H_6^{+}\cdot$ ions having structure d.[30] However, those reaching the collision region are primarily the stable a; their CAD spectrum is identical within experimental error with that of a (Table I). Although prior isomerization of the molecular ion cannot be ruled out, the results suggest that d isomer is of relatively low stability.

Evidence from Ion–Molecule Reactions for the Low a ⇄ b Barrier. A significant proportion of ions which react like isomer a are produced by ionization of cyclopropane only 0.7 eV above threshold.[8] This appears to be well below the energy required for formation of c[7,16] or d, so that isomerization of b to these isomers, or any $C_3H_6^{+}\cdot$ isomer other than a does not appear to be a logical explanation for the ICR data.[8,14] However, such a low energy barrier appears to us to be totally inconsistent with the CAD data cited here, as well much previous evidence.[1-3,5-7,9-13,15,16,19] It is conceivable that the isomerization of excited b ions to a ions can proceed efficiently by an ion molecule reaction, such as (I), at



$$A + CH_2CH_2CH_2^{+}\cdot \rightarrow A^{+}CH_2CHCH_2\cdot \rightarrow A + CH_2{=}CHCH_3^{+}\cdot \quad (I)$$

lower energies than that required for unimolecular isomerization. Isomerization of $C_4H_9^{+}$ ions has been observed in the reaction complex $CH_3OH_2^{+}/2\text{-}C_4H_8$.[31] Resolution of this discrepancy is obviously important in terms of the past and future use of these techniques for the assay of isomeric ion mixtures.

Experimental Section

A triple analyzer MS/MS instrument consisting of a Hitachi RMH-2 double-focusing mass spectrometer as MS-I, a molecular beam collision region, and an electrostatic analyzer as MS-II was used to obtain the CAD spectra.[32] The temperature of the all-glass sample inlet and of the ion source were 50–150 and 150 °C, respectively, and the primary ion kinetic energy was 9.8 kV. A collision gas pressure was used sufficient to attenuate the primary ion beam to 25% of its original intensity. Degradation of diffusion pump oil can be severe with routine use of oxygen as the collision gas. The precursor $C_3H_6^{+}\cdot$ ions were separated from isobaric interferences such as $C_2H_2O^{+}\cdot$ by the high resolution MS-I. Particular care was necessary to obtain reproducible CAD spectra of the *m/z* 19–21 region, as this represents <0.5% of the total ion abundance of the $C_3H_6^{+}\cdot$ spectra. The CAD spectra (peak heights) are averages of 3–6 runs, each of approximately 20 scans; reproducibility of the $C_3H_6^{2+}$ abundances is somewhat less than that for other peaks because of the narrowness of this peak from charge-stripping. Measurements made at a nominal 15-eV ionizing-electron energy represent reduction of the primary ion beam intensity to 10% of its original value.

Cyclopropane-*1,1*-d_2 and propene-*1,1*-d_2 were purchased from Merck Sharp & Dohme. Other compounds, obtained commercially, were used without further purification. γ-Butyrolactone-*2,2*-d_2 was produced from butyrolactone by repeated deprotonation with lithium diisopropyl amide in tetrhydrofuran and quenching with D_2O. Cyclobutanone-*2,2,4,4*-d_4 was made from cyclobutanone by exchanges with D_3PO_4/D_2O and used to produce γ-butyrolactone-*2,2,4,4*-d_4 by Baeyer-Villager oxidation using *m*-chloroperbenzoic acid in CH_2Cl_2. Deuterium incorporation was confirmed by NMR and mass spectrometry.

Dr. Pierre Ausloos has informed us[33] that a charge transfer study[34] in his laboratory shows that 10.6-eV photoionization of cyclopropane yields 99% isomer b, in confirmation of our conclusions.

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Registry No. a, 34504-10-4; b, 34496-93-0; propene, 115-07-1; cyclopropane, 75-19-4; cyclopropane-*1,1*-d_2, 65146-94-3; propene-*1,1*-d_2, 1517-49-3.

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