

Collisional Studies of Some $C_3H_7O^+$ Ions*

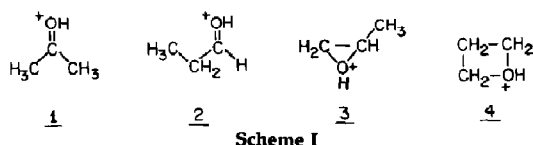
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The $C_3H_7O^+$ ions of nominal structures 1, 2, 3, and 4, produced by protonation of acetone, propanal, propylene oxide, and oxetan, respectively, have been studied by a variety of collisional techniques. The nominal isomers 2 and 3 give, within experimental error, identical high-energy collision-induced dissociation (CID) mass spectra. In addition, the breakdown graphs for the two isomers obtained from low, variable energy CID are identical, as are the neutralization-reionization mass spectra. The results are consistent with a facile isomerization of 3 to 2. By contrast, the ions of nominal structures 1 and 4 are shown by each technique to be distinct stable species in the gas phase. While the differences in the high-energy CID mass spectrum of 4 compared to 2 and 3 are relatively small, these differences are more pronounced in the low-energy CID mass spectra and become very large in the neutralization-reionization mass spectra. (*J Am Soc Mass Spectrom* 1990, 1, 301-307)

The $[C_nH_{2n+1}O]^+$ species are major fragment ions in the electron ionization (EI) mass spectra of many aliphatic alcohols and ethers. As a consequence, the chemistry of many of these species has seen extensive study (for a review, see Levsen [1]). Among the species that have been studied in detail are the $[C_3H_7O]^+$ isomers 1 and 2 (Scheme I) [2-12], produced mainly by electron impact. It has been clearly established, from both unimolecular fragmentation studies [7-9] and collision-induced dissociation (CID) studies [5, 12], that 1 and 2 are stable, noninterconverting species in the gas phase. By contrast, the chemistry of isomers 3 and 4, which cannot be prepared directly by EI, has been studied much less. McLafferty and Sakai [5] reported that ions of nominal structures 3 and 4, prepared by protonation (CH_4 chemical ionization) of propylene oxide and oxetan, respectively, gave high-energy CID mass spectra similar to the CID mass spectrum of 2, prepared by EI, implying isomerization of all three to a common structure or mixture of structures. A detailed CID study by Harrison et al. [12] showed that 2 and 3 gave very similar CID spectra, suggesting isomerization to a common structure or mixture of structures. However, the CID mass spectrum of the ion of nominal structure 4 showed some differences, especially when prepared by a protonation reaction gentler than protonation in CH_4 CI, suggesting that 4 might be a stable noninterconverting structure. In contrast with these results, Bowers et al. [13] reported that the ions of nominal structures 1-4, when prepared by self-protonation, give distinct CID mass spectra [14].

The present work reports a reinvestigation of the collisional mass spectra of the ions of nominal structures 1-4. In addition to studying the high-energy



CID mass spectra, we examined the low-energy collisional activation of these ions as a function of collision energy, the so-called energy-resolved mass spectral (ERMS) technique [15-17]. In addition, the technique of neutralization-reionization mass spectrometry (NRMS) [18-20] was used to explore the integrity of structures 1 to 4. All the results show that 2 and 3 form a common structure or mixture of structures, most likely 2, whereas 1 and 4 are distinct stable structures in the gas phase. This conclusion is most dramatically supported by the neutralization-reionization (NR) studies.

Experimental

All experimental work was carried out with a VG Analytical ZAB-2FQ mass spectrometer (VG Analytical Ltd., Manchester, England), which has been described in detail previously [21]. Briefly, the instrument is a reverse-geometry (BE) double-focusing mass spectrometer with a third stage consisting of a deceleration lens system, an rf-only quadrupole collision cell, and a quadrupole mass analyzer. This assembly permits collisional studies to be carried out in the low-energy regime. In addition, the instrument is equipped with dual collision cells and an intermediate deflector electrode in the field-free region between the magnetic (B) and electric (E) sectors, which provides the capability of studying collision processes in the kiloelectronvolt energy (laboratory-scale) range as well as studying NR processes.

For the high-energy CID experiments, the ions of interest were mass-selected by the magnetic sector and

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underwent collision, at 8 keV ion energy, with helium in the collision cell (CC2) located at the focal point between the magnetic and electric sectors. The ionic products were analyzed according to their kinetic energy by scanning the voltage applied to the electric sector, the so-called mass-analyzed ion kinetic energy spectroscopy (MIKES) technique [22]. The helium pressure was adjusted to give approximately 30% reduction of the main beam.

For the low-energy CID experiments, the ions of interest were mass-selected by the double-focusing BE mass spectrometer at 6 kV accelerating potential, decelerated to the required kinetic energy, and introduced into the rf-only quadrupole collision cell, where they underwent collision with N₂. The ionic dissociation products were detected by the final quadrupole mass analyzer. The N₂ pressure was adjusted to give approximately 30% reduction of the main beam at 50 eV (laboratory scale) collision energy. The CID mass spectra were determined as a function of collision energy over the range 5–150 eV (laboratory scale). The results are presented in the following as breakdown graphs, that is, plots of the percent fragment ion abundances as a function of collision energy. The uncertainty in the data is of the order of $\pm 3\%$.

In the NR experiments the ions of interest were mass-selected by the magnetic sector at 8 keV kinetic energy and underwent neutralization in collision cell 1 (CC1) by collision with either NO or NH₃; the fast neutral species were transmitted to CC2, with a voltage of 5 kV applied to the deflector electrode, and reionized by collision with O₂. The ionic species produced were analyzed according to their kinetic energy by scanning the electric sector voltage. The pressure of each gas was adjusted to give, for each, approximately 40% reduction of the main beam.

A significant problem in using collisional mass spectra to distinguish isomeric ion structures is the criterion one uses to decide that two spectra differ significantly and that therefore the two ion structures are likely different. Lay et al. [23] proposed that CID spectra be compared on the basis of similarity indices, where the similarity index (SI) for two spectra is given by

$$SI = \left(\frac{[(i - i_0)/i_0] \times 100}{N} \right)^{1/2} \quad (1)$$

In eq 1, $i - i_0$ is the difference in fractional ion intensities for a given ion signal, with i_0 the smaller intensity, and N is the total number of masses used in the comparison. As pointed out earlier [12], the problem still arises as to the value of the SI that one selects as indicating significantly different CID mass spectra. Lay et al. [23] proposed that if $SI \geq RSD_{\max}$ the spectra are nonidentical; RSD_{\max} is the maximum value of the relative standard deviation of the fractional ion intensity measurements, considering all ions in the spectrum. In the present work we calculated SI values for repeat determinations, on different days, of the CID

spectrum of the same ionic species and used as a criterion for nonidentity of spectra an SI value that is twice the SI_{mean} obtained in these repeat measurements. The SI_{mean} value reflects the variation of CID mass spectra arising from instrumental and other experimental variables from day to day.

The C₃H₇O⁺ ions of nominal structures 1–4 were prepared by protonation of the appropriate C₃H₆O compound in the CI source. A variety of protonation reactions were used. In some experiments, self-protonation was used to produce the C₃H₇O⁺ ions by introducing a high pressure of the C₃H₆O compound through the heated inlet system. In other experiments, CH₃OH CI was used by introducing a high pressure of methanol through the heated inlet system. Finally, a mixture of approximately 10% CH₃OH in CH₄, admitted through the normal CI reagent gas inlet, was used to effect protonation of the C₃H₆O compounds by reaction with CH₃OH₂⁺. The latter method proved to provide the most reproducible collisional mass spectra, particularly for the NRMS spectra, which appeared to be most sensitive to experimental conditions; this sensitivity to experimental conditions presumably reflects an effect of internal energy on the neutralization-reionization mass spectra. In all experiments the ionizing electron energy was 50 eV and the source temperature was 250 °C. All C₃H₆O isomers and reagent gases were commercially available and were used as received.

Results and Discussion

High-Energy Collision-Induced Dissociation Studies

The mass spectra obtained from the high-energy (8-keV) CID of the C₃H₇O⁺ ions of nominal structures 1–4 are presented in Table 1, and the relevant similarity indices are recorded in Table 2. The results in Table 1 represent the mean of four determinations on different days with the standard deviations indicated. The C₃H₇O⁺ ions were prepared by CH₃OH CI.

From comparison of the results for repeat determinations of the CID spectrum of the same species, we obtain $SI_{\text{mean}} = 22 \pm 14$. Clearly, from the SI values of Table 2, both 1 and 4 represent distinct structures or mixtures of structures, while 2 and 3 give indistinguishable CID mass spectra, suggesting isomerization to a common structure or mixture of structures for these two species. This latter conclusion is in agreement with the conclusions of earlier studies [12] indicating that ions of nominal structures 2 and 3 cannot be distinguished by means of their high-energy CID mass spectra. These conclusions also are in agreement with the low barrier estimated for isomerization of 3 to 2 [9, 10, 14]. However, the present CID results are in quantitative disagreement with respect to fractional ion intensities with the CID results reported earlier [12]. It should be noted that the present results were obtained under essentially single-collision conditions (30% beam

Table 1. 8-keV CID mass spectra of C₃H₇O⁺ ions (intensities as percent of total fragment ions)

<i>m/z</i>	Nominal ion structure			
	1	2	3	4
57	5.4 ± 0.3	37.8 ± 1.3	37.5 ± 1.1	52.5 ± 2.0
56		1.5 ± 0.2	1.3 ± 0.1	
55	1.9 ± 0.3	5.2 ± 0.3	4.7 ± 0.5	4.2 ± 0.3
53	0.8 ± 0.1	1.2 ± 0.2	1.3 ± 0.1	0.7 ± 0.1
44	6.3 ± 1.3	3.8 ± 0.5	3.7 ± 0.7	1.3 ± 0.6
43	47.0 ± 1.9	9.6 ± 0.7	11.9 ± 0.5	5.1 ± 0.4
42	13.2 ± 1.0	5.2 ± 0.2	5.4 ± 0.2	2.6 ± 0.2
40	2.6 ± 0.2	2.5 ± 0.1	2.8 ± 0.3	4.0 ± 0.2
39	12.0 ± 0.9	9.7 ± 0.5	9.9 ± 0.8	8.5 ± 0.4
38	3.4 ± 0.2	2.6 ± 0.2	2.8 ± 0.2	
37	2.0 ± 0.2	1.5 ± 0.2	1.6 ± 0.1	
30		2.8 ± 0.3	2.6 ± 0.4	3.3 ± 0.2
29	3.1 ± 0.2	8.7 ± 0.8	8.1 ± 0.9	8.4 ± 0.9
28		2.8 ± 0.3	2.9 ± 0.4	4.5 ± 0.5
27	1.7 ± 0.3	3.8 ± 0.5	3.7 ± 0.4	3.7 ± 0.3
26	0.7 ± 0.1	1.3 ± 0.2	1.4 ± 0.2	1.6 ± 0.5

attenuation), whereas the earlier results [12] were obtained under multiple-collision conditions (60% beam attenuation), where sequential activating collisions are more likely, thus emphasizing the formation of lower mass products. In the earlier study [12] the distinction of 4 from 2 and 3 was marginal at best; the present results show that the distinction is much more readily made when the CID mass spectra are recorded under single-collision conditions.

It has been reported [13] that ions of nominal structures 2 and 3 can be distinguished from each other when the ions are produced by self-protonation using the appropriate C₃H₆O isomer. In our hands, production of the C₃H₇O⁺ ions by self-protonation, followed by 8-keV collisional activation, gave CID mass spectra identical, within experimental error, to those reported in Table 1. Specifically, the nominal isomers 2 and 3 gave spectra that were indistinguishable on the basis of the similarity index.

Low-Energy Collision-Induced Dissociation

The low-energy CID mass spectra of the ions of nominal structures 1-4 are presented in Figures 1-4 in the form of breakdown graphs expressing the percent fragment ion abundance as a function of the collision energy (laboratory scale). The C₃H₇O⁺ ions were prepared by CH₃OH/CH₄ CI and showed negligible unimolecular metastable ion fragmentation; thus, the

breakdown graphs include the *m/z* 31 (CH₂OH⁺) and *m/z* 41 (C₃H₅⁺) ion signals. As expected, these two products dominate the breakdown graphs at low collision energies; however, a number of other fragment ions are observed at higher collision energies that are useful in distinguishing ion structures. The breakdown graph for 1 is clearly distinctive in that substantial yields of *m/z* 43 (C₂H₃O⁺) and *m/z* 15 (CH₃⁺) fragments are observed at higher collision energies; thus, the *m/z* 43 signal is approximately 25% of the total fragment ion signal at 40 eV collision energy for 1, whereas it never rises above 5% for the other ions. In the same vein, the yield of CH₃⁺ as a fragment ion is much greater for 1 than for any of the other nominal ion structures. Isomer 4 is clearly distinguishable from nominal structures 2 and 3 by the much greater abundance of *m/z* 31 (CH₂OH⁺) and much lower yields of *m/z* 44 and *m/z* 43 above 40 eV collision energy. The high yield of CH₂OH⁺ at higher collision energies is consistent with the H₂ CI mass spectral data [14], which also show an enhanced abundance of CH₂OH⁺ compared to the other isomers. The breakdown graphs for the ions of nominal structures 2 and 3 are identical within experimental error, indicating isomerization to the same structure or mixture of structures prior to fragmentation. The low-energy CID results are therefore in agreement with the high-energy CID results.

Neutralization-Reionization Studies

The NR mass spectra of the ions of nominal structures 1-4 determined with NO as neutralization gas and O₂ as reionization gas are presented in Table 3, and those obtained with NH₃ as neutralization gas and O₂ as reionization gas are presented in Table 4. In each case the spectra are the mean of four determinations (on different days) with the standard deviations shown. The C₃H₇O⁺ ions were prepared by CH₃OH/CH₄ CI of the

Table 2. Similarity indices for 8-keV CID mass spectra*

	1	2	3	4
1		220	204	408
2			9.6	73.5
3				77.8

* SI_{mean} = 22 ± 14.

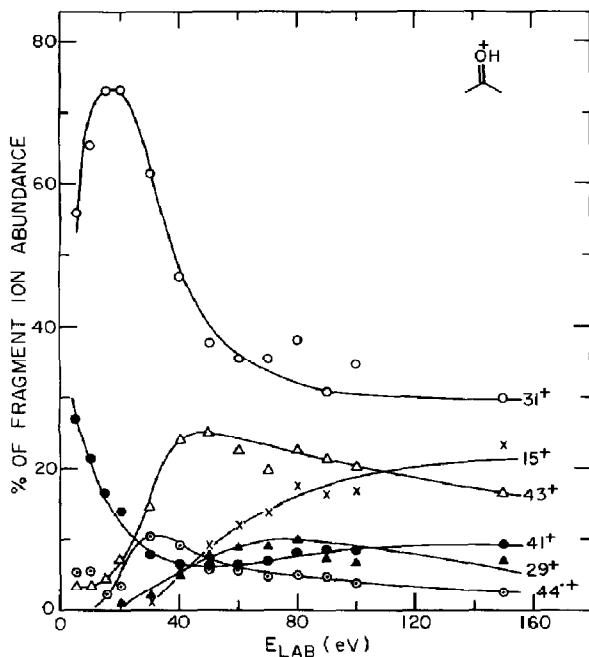


Figure 1. Breakdown graph for protonated acetone.

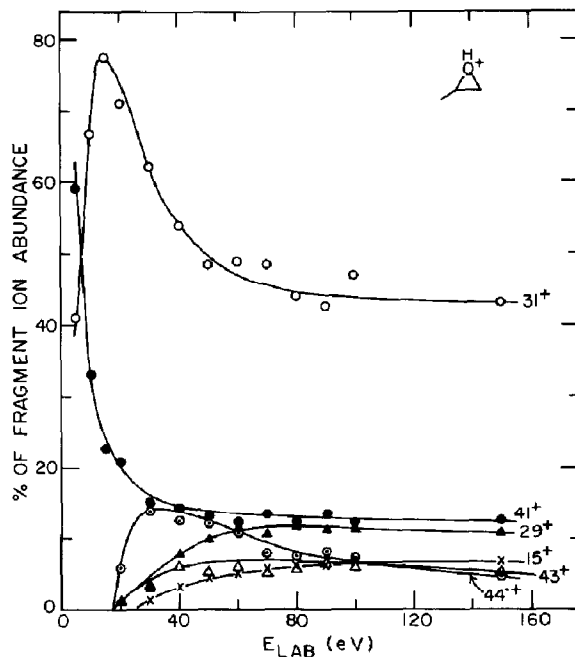


Figure 3. Breakdown graph for protonated propylene oxide.

appropriate C_3H_6O compound. The spectra obtained for each species with the two neutralization gases are very similar; in our experience the use of NH_3 gives stronger ion signals in the NR experiment.

The similarity indices for the NR experiments are given in Tables 5 and 6. The SI_{mean} for repeat determi-

nations in the NH_3/O_2 NR experiments was 20.4 ± 8.3 ; for the NO/O_2 NR experiments it was 17.0 ± 4.3 . Clearly, on the basis of this criterion, as well as by visual inspection, the NR mass spectra of the ions of nominal structures 2 and 3 are indistinguishable. In light of the CID experiments, we believe that this sim-

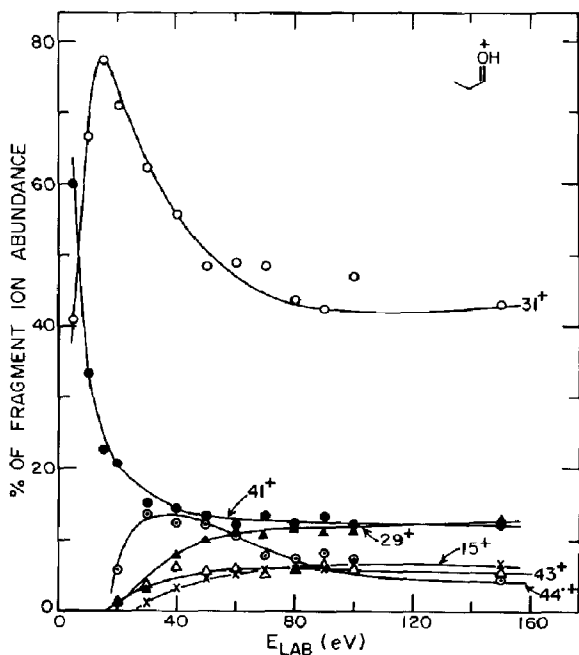


Figure 2. Breakdown graph for protonated propanal.

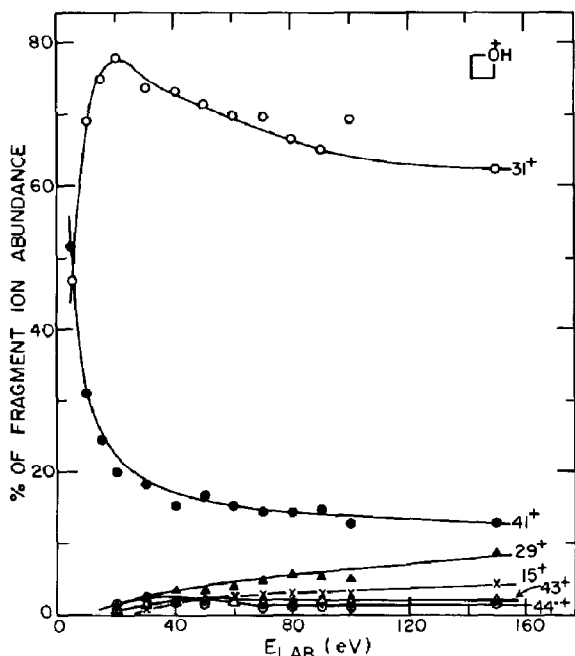


Figure 4. Breakdown graph for protonated oxetan.

Table 3. NO/O₂ NR mass spectra of $C_3H_7O^+$ ions (intensities as percent of total fragment ions)

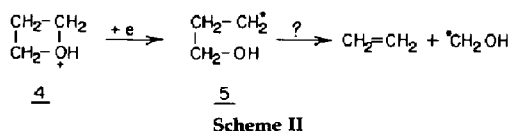
<i>m/z</i>	Nominal structure			
	1	2	3	4
59	28.2 ± 1.3	16.3 ± 1.7	13.3 ± 0.7	4.0 ± 0.7
58	6.4 ± 0.3	3.1 ± 0.3	3.1 ± 0.2	1.5 ± 0.5
57	1.5 ± 0.2	9.2 ± 0.3	7.0 ± 0.7	3.7 ± 0.4
56		0.6 ± 0.1	0.5 ± 0.1	
55	0.6 ± 0.1	1.7 ± 0.3	1.5 ± 0.2	1.1 ± 0.2
53		0.5 ± 0.1	0.5 ± 0.1	
44	2.7 ± 0.3	4.6 ± 0.2	5.4 ± 0.5	2.3 ± 0.3
43	22.6 ± 1.0	4.9 ± 0.4	7.1 ± 1.2	2.3 ± 0.4
42	8.9 ± 0.6	3.8 ± 0.3	4.7 ± 0.1	1.6 ± 0.3
41	4.0 ± 0.2	4.3 ± 0.3	4.2 ± 0.1	2.1 ± 0.2
40		1.3 ± 0.1		1.1 ± 0.1
39	5.4 ± 0.1	4.1 ± 0.2	4.3 ± 0.4	4.1 ± 0.1
38	2.7 ± 0.2	1.9 ± 0.1	2.2 ± 0.2	2.2 ± 0.3
37	2.3 ± 0.3	1.7 ± 0.1	1.9 ± 0.1	1.8 ± 0.2
31	2.1 ± 0.4	5.9 ± 0.5	4.7 ± 0.2	2.6 ± 0.3
30		2.0 ± 0.1	1.8 ± 0.2	3.5 ± 0.4
29	2.4 ± 0.1	8.9 ± 0.3	8.3 ± 0.2	8.6 ± 0.1
28	4.7 ± 0.8	10.9 ± 1.0	13.2 ± 0.9	30.3 ± 1.5
27	2.1 ± 0.3	6.4 ± 0.6	7.2 ± 0.4	12.4 ± 0.9
26	2.5 ± 0.4	5.9 ± 0.7	6.9 ± 0.3	11.8 ± 0.6
25	0.9 ± 0.1	1.8 ± 0.2	1.9 ± 0.1	2.7 ± 0.4

ilarity arises because of isomerization of the two ions to a common structure, most likely 2, prior to neutralization. Both from inspection of the data and from the similarity indices, it is clear that the ions of nominal structures 1 and 4 give distinct spectra. For 1 the major signals are the reionized parent $C_3H_7O^+$ and the frag-

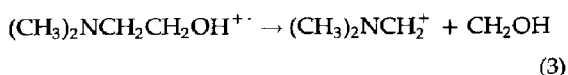
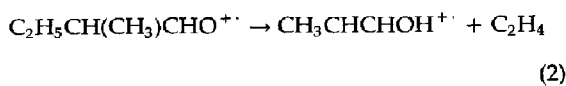
ment ion $C_2H_3O^+$ (*m/z* 43). For 4 the major ion signals are observed to be those of $C_2H_4^+$ (*m/z* 28), $C_2H_3^+$ (*m/z* 27), and $C_2H_2^+$ (*m/z* 26). The origin of the large $C_2H_4^+$ ion signal in the NR mass spectrum of 4 is not clear. It is likely that, on neutralization of 4, an open-chain radical 5 (Scheme II) is formed, and we considered the

Table 4. NH₃/O₂ NR mass spectra of $C_3H_7O^+$ ions (intensities as percent of total fragment ions)

<i>m/z</i>	Nominal structure			
	1	2	3	4
59	32.8 ± 1.2	19.8 ± 1.7	16.2 ± 1.8	4.1 ± 0.6
58	9.6 ± 0.6	4.6 ± 0.6	4.5 ± 0.5	2.2 ± 0.5
57	1.9 ± 0.3	12.7 ± 0.7	10.5 ± 1.1	5.3 ± 0.8
56		0.9 ± 0.1	0.8 ± 0.2	0.5 ± 0.3
55	0.5 ± 0.3	2.4 ± 0.1	2.3 ± 0.2	1.6 ± 0.3
53		0.7 ± 0.1	0.6 ± 0.3	
44	2.8 ± 0.2	7.3 ± 1.0	7.8 ± 0.7	2.6 ± 0.4
43	23.3 ± 1.2	6.9 ± 0.4	9.2 ± 0.7	2.6 ± 0.1
42	8.5 ± 0.3	4.6 ± 0.1	5.4 ± 0.2	1.9 ± 0.2
41	3.6 ± 0.1	4.0 ± 0.3	4.1 ± 0.2	2.3 ± 0.2
40		1.4 ± 0.1	1.5 ± 0.1	1.6 ± 0.3
39	5.1 ± 0.2	4.5 ± 0.3	5.0 ± 0.3	6.2 ± 0.6
38	2.6 ± 0.3	2.3 ± 0.3	2.4 ± 0.2	2.9 ± 0.3
37	1.9 ± 0.2	1.8 ± 0.3	1.8 ± 0.2	2.3 ± 0.1
31	1.2 ± 0.2	3.4 ± 0.2	2.8 ± 0.2	1.7 ± 0.2
30		1.4 ± 0.1	1.5 ± 0.1	2.6 ± 0.4
29	1.6 ± 0.9	5.4 ± 1.5	5.1 ± 0.4	5.6 ± 0.2
28	1.8 ± 0.9	7.8 ± 0.8	10.0 ± 0.9	32.4 ± 2.2
27	1.1 ± 0.2	4.0 ± 0.6	4.6 ± 0.4	11.8 ± 1.0
26	0.6 ± 0.3	3.4 ± 0.6	4.1 ± 0.3	9.4 ± 0.9
25		0.8 ± 0.3	0.9 ± 0.1	1.5 ± 0.3



possibility that this radical decomposed as shown in Scheme II to form C_2H_4 and CH_2OH . Such a fragmentation should yield approximately equal fluxes of the two neutral species entering the reionization collision cell, yet we see only a very low signal at m/z 31 corresponding to CH_2OH^+ . To test the possibility that fast C_2H_4 neutral fragments have a much larger CID cross section than fast CH_2OH neutral fragments, we prepared the two neutral species in separate experiments by the following metastable ion fragmentation reactions:



Collisional ionization of the two fast neutral species was achieved in CC2 using O_2 collision gas. Within experimental error, the signals for the collisionally ionized neutral species relative to the metastable ion signal were the same for C_2H_4 and CH_2OH . Clearly, decomposition of the radical species 5 as indicated in Scheme II cannot account for the observed results. Thus we conclude that the radical 5 is stable but that on collisional ionization it fragments primarily to form C_2H_4^+ rather than the more stable product CH_2OH^+ . The recovered signal at m/z 59 for 4 may represent a small amount of isomerization of 4 to 2 prior to neutralization, because ionization of the neutral 5 should not lead to a stable ionic species. In addition, it would not be expected that neutralization of either 3 or 4 would lead to stable neutral species in the absence of rearrangement.

Conclusions

The low-energy and high-energy CID studies, as well as the NR studies, are in agreement that $\text{C}_3\text{H}_7\text{O}^+$ ions

Table 5. Similarity indices for NO/O_2 NR mass spectra*

	1	2	3	4
1				
2		158	164	366
3			18.9	116
4				113

* $SI_{\text{mean}} = 17.0 \pm 4.3$.

Table 6. Similarity indices for NH_3/O_2 NR mass spectra*

	1	2	3	4
1				
2		257	265	684
3			16.0	154
4				135

* $SI_{\text{mean}} = 20.4 \pm 8.3$.

of nominal structures 1 and 4 are stable neutral species in the gas phase but that ions of nominal structures 2 and 3 isomerize to a common structure or mixture of structures. These results are in agreement with the potential energy surface for the $\text{C}_3\text{H}_7\text{O}^+$ system [9, 10, 14], from which it has been concluded that the barrier for isomerization of 3 to 2 is only about 20 kJ/mol, with 2 being more stable. By contrast, the barrier for isomerization of 4 to 2 is of the order of 90 kJ/mol, and it is clear that if 4 is prepared with low internal energy it represents a stable species with an energy higher than that of 2. This is most clearly shown by the NR study where the differences in the spectra of 4 compared to 2 are particularly striking. McLafferty and co-workers [24, 25] previously noted the utility of NR studies in distinguishing isomeric ion structures through neutralization to neutral species of differing structure that either fragment by different routes or fragment differently on reionization. In the present case the differing behavior of 4 appears to result from isomerization of the neutral species to a structure that shows a distinct spectrum on reionization.

Acknowledgments

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