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Butyl Cations and Their Gas-Phase Dissociation Chemistry: Uniting Experiments with Theory

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The results of extensive mass spectrometric experiments have been interpreted with the aid of recent high-level ab initio theoretical calculations. The dissociative ionization of species containing formal n-C_4H_9 and i-C_4H_9 groups leads only to mixtures of s-$C_4H_9^+$ and t-$C_4H_9^+$, irrespective of the precursors' internal energy. Experimental distinction between s-$C_4H_9^+$ and t-$C_4H_9^+$ ions rests upon the much larger kinetic energy release observed when s-$C_4H_9^+$ are collisionally excited by O_2 to lose $CH_3^\bullet$ (500 meV) relative to t-$C_4H_9^+$ (90 meV). This distinction is lost when He is the target gas. Target gas behavior was shown to most strongly depend on its polarizability, and it is proposed that, in contrast to vertical excitation in the case of collision with He, small polarizable targets allow structural change during the collisional excitation. The $C_3H_6^{\bullet+}$ fragment ions produced from collisionally activated $C_4H_9^+$ ions only have the [propene]$^{\bullet+}$ structure. The $C_3H_5^+$ fragment ion resulting from the metastable loss of CH_4, a process common to all $C_4H_9^+$ isomers, has the 2-propenyl cation structure, not allyl as earlier concluded. Metastable $C_4H_9^+$ ions also lose C_2H_4 yielding the nonclassical ethyl cation. The structure leading to this dissociation is proposed to be a proton-bridged tetramethylene ion, shown by theory to occupy a potential energy well.

Introduction

Ever since the pioneering work of H. Meerwein, who some 76 years ago proposed the participation of carbocations to explain his observations on the rearrangement of camphene hydrochloride to isobornyl chloride,[1] the importance of organic ionic species in chemical reactions has been well established.[2] To study their individual properties, carbocations have been generated in solution in superacidic media[3] and in the gas phase by dissociative ionization and extensive mass spectrometric experiments.[4] Both in solution and in the gas phase the isomeric butyl cations have stimulated considerable interest. In these ions the charge may formally be located at two primary, a secondary, or a tertiary carbon producing the four isomers: $CH_3CH_2CH_2CH_2^+$ (n-$C_4H_9^+$), $(CH_3)_2CHCH_2^+$ (i-$C_4H_9^+$), $CH_3CH_2CH^+CH_3$ (s-$C_4H_9^+$), $(CH_3)_3C^+$ (t-$C_4H_9^+$).

The t-$C_4H_9^+$ ion was the first alkyl cation to be observed directly in solution.[5] Shortly thereafter, other alkyl cations were obtained by dissolving the corresponding alkyl fluoride in excess SbF_5.[6] The order of thermochemical stability for these cations is well established: tertiary > secondary > primary. In solution, the primary cations rearrange completely to the most stable isomer,[6] t-$C_4H_9^+$, whereas s-$C_4H_9^+$ can be generated quantitatively *only* at low temperature and under well-defined experimental conditions.[7] The enthalpy of rearrangement of s-$C_4H_9^+$ to t-$C_4H_9^+$ was measured by solution calorimetry to be -14.5 ± 0.5 kcal/mol.[7]

In the gas phase, $C_4H_9^+$ cations are easily generated by dissociative ionization of the corresponding C_4H_9X compounds[8] (for example, where X = halogen or CO_2R and R = alkyl), and they have also been generated from gas-phase radiolysis of the appropriate alkanes.[9] However, the structural identification of the $C_4H_9^+$ produced is not straightforward and is discussed below.

The currently accepted[10] experimental values for the heats of formation ($\Delta_f H°$) of t- and s-$C_4H_9^+$ are 170[11] and 183 kcal mol^{-1}, respectively, an enthalpy difference in agreement with the above-measured condensed-phase value. The ionization energies of the thermally generated n-C_4H_9 and i-C_4H_9 radicals have been measured,[10] leading to $\Delta_f H°$ values of 203 and 201 kcal mol^{-1} for the corresponding cations. Considerably lower $\Delta_f H°$ values are obtained from the appearance energies[12] of the $C_4H_9^+$ ions from n- and i-C_4H_9 containing precursor molecules (X = I, Br), showing that they spontaneously rearrange to the more stable isomers, and so definitive values for their $\Delta_f H°$ are unavailable from such measurements. The values obtained from the ionization energies of the radicals are in sound agreement with the results of high-level ab initio molecular orbital theory calculations by Sieber et al.[13] They showed that the primary cations had no minima on the hypersurface and represented only transition structures for their collapse to more stable configurations. Thus, these ions must be inaccessible via dissociative ionization of appropriate molecules. Theory has provided a value for the barrier to the isomerization t-$C_4H_9^+ \rightarrow s$-$C_4H_9^+$ of 33 kcal mol^{-1}.[13] This rearrangement can therefore take place below the dissociation limit of lowest energy requirement, methane loss (ca. 44 kcal mol^{-1} above t-$C_4H_9^+$). These calculations identified only four isomeric species that occupied potential wells, the t- and s-$C_4H_9^+$ ions, a protonated tetramethylene (PTM), and a corner protonated methylcyclopropane (PMC). The current energy diagram for the $C_4H_9^+$ system is shown in Figure 1and will be referred to in detail later.

Irrespective of their origin (i.e., from any C_4H_9 containing precursor molecule), metastable $C_4H_9^+$ ions dissociate almost exclusively by loss of methane.[8]

$$C_4H_9^+ \rightarrow C_3H_5^+ + CH_4 \qquad (1)$$

Davis et al.[8] showed that the shape of the metastable peak for

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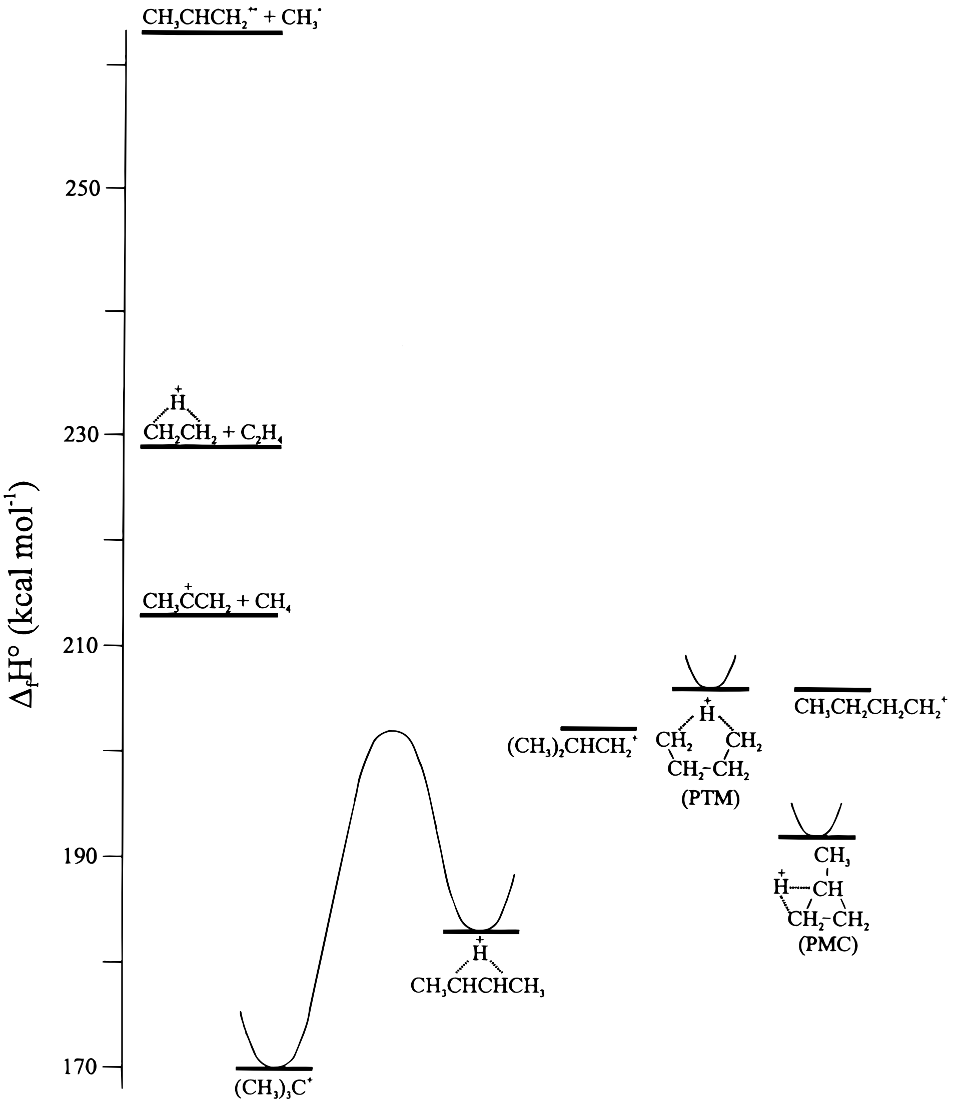

Figure 1. Potential energy surface for $C_4H_9^+$ species from Sieber et al.[13] anchored to $\Delta_fH°[t\text{-}C_4H_9^+] = 170$ kcal mol^{-1}.[11]

this methane loss, observed in the normal mass spectrum, was independent of the structure of the C_4H_9X precursor molecule, suggesting that all $C_4H_9^+$ ions rearrange completely to the same structure or mixture of structures prior to this dissociation. As supporting evidence, they showed by isotopic labeling experiments that all $C_4H_9^+$ undergo complete scrambling of both the hydrogen and the carbon atoms before dissociating. However, closer investigation of the (composite) metastable peak shapes showed subtle differences[14] for $C_4H_9^+$ ions from isomeric precursor molecules. A second reaction of metastable $C_4H_9^+$ ions, about 100 times less abundant than the CH_4 elimination, is the loss of ethene, and moreover, this process appeared to be at least in part collision induced.[15]

The collision-induced dissociation (CID) mass spectra of the $C_4H_9^+$ species are almost indistinguishable, as is the norm for even electron hydrocarbon ions.[16] Distinction between $C_4H_9^+$ species produced from dissociative ionization of simple precursor molecules containing a butyl function has thus heavily relied on thermochemical measurements, where the threshold appearance energy of the $C_4H_9^+$ fragment can be assigned to the production of the *s*- or *t*-$C_4H_9^+$ cation.[12,17]

Maquestiau et al.[18] reinvestigated the possibility of distinguishing between butyl cations by a careful examination of their helium CID mass spectra. The $C_4H_9^+$ ions were produced in the ion source and also from metastable ionized precursor molecules. Thus, the collision behavior of $C_4H_9^+$ ions with and without sufficient internal energy to fragment could independently be compared. A wide range of precursor molecules, containing all four C_4H_9 structures, were examined. From the sum of the peak abundances of the $C_3H_n^+$ fragment ions relative to those of the $C_2H_m^+$ fragment ions, they concluded that *s*- and *t*-$C_4H_9^+$ could be distinguished. In addition, they proposed that *n*-$C_4H_9^+$ isomerized to *s*-$C_4H_9^+$ whereas *i*-$C_4H_9^+$ isomerized to precursor-dependent mixtures of *s*- and *t*-$C_4H_9^+$.

Upon collisional activation,[18] both *s*- and *t*-$C_4H_9^+$ ions eliminate a methyl group to generate a $C_3H_6^{\bullet+}$ ion, the latter giving a much greater yield than the former. A possible rationale for this observation is that a simple bond cleavage in a *t*-$C_4H_9^+$ cation could directly yield the dimethylcarbene radical cation, $(CH_3)_2C^{\bullet+}$, a stable species that we have very recently characterized.[19] The lower yield of $C_3H_6^{\bullet+}$ from the *s*-$C_4H_9^+$ cation is unexpected, considering that a formal simple bond cleavage should yield the more stable propene molecular ion. Thus, our initial interest in this problem was to investigate the chemistry of the butyl cations with particular reference to the above dissociation and, further, to relate the results, so far as possible, with the potential energy surface described by theory.[13]

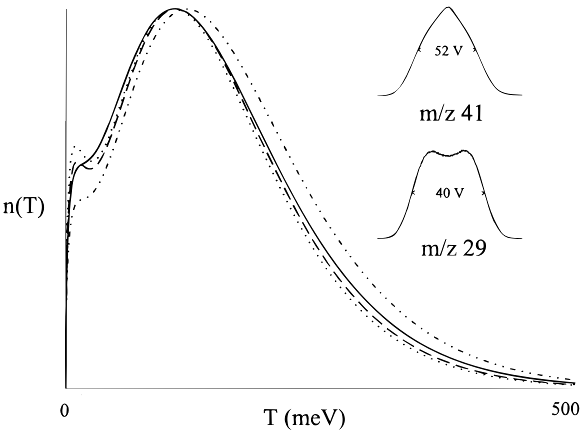

Figure 2. Kinetic energy release distribution associated with the metastable $C_4H_9^+ \rightarrow C_3H_5^+$ dissociation, for $C_4H_9^+$ ions produced from $(CH_3)_3CSCH_3^{\bullet+}$ (—), $(CH_3)_2CHCH_2I^{\bullet+}$ (– –), $CH_3(CH_2)_3CH_3^{\bullet+}$ (· · ·), and $CH_3(CH_2)_2CH_2I^{\bullet+}$ (· · –). Inset are the metastable peak shapes, $C_4H_9^+ \rightarrow C_3H_5^+$ (*m/z* 41) and $C_4H_9^+ \rightarrow C_2H_5^+$ (*m/z* 29).

Experimental Methods

All mass spectra were recorded on a modified VG ZAB-2F mass spectrometer of BEE geometry which has been described in detail elsewhere.[20] Kinetic energy release values, $T_{0.5}$, were obtained from the peak widths at half-height and evaluated by established methods.[21] Energy resolution was such that the half-height width of the main ion beam was ca. 4 V. For the collision-induced dissociation (CID) and charge-stripping (CS) experiments,[22] the target gas pressure used was sufficient to reduce the main ion beam by 15% (i.e., approximately single collision conditions). For experiments involving source ions, corrections for the contribution of the ^{13}C overlap from the adjacent ions of lower mass were carried out by measuring both the mass spectra of the ion of interest (*m/z* 57) and of the preceding peak (*m/z* 56). The required correction was made according to a procedure described elsewhere.[19] In the case of metastably generated ions, no correction was needed because any potentially interfering signals were too weak. In the neutralization–reionization (NR) experiments[22] Xe and O_2 were used for neutralization and reionization, respectively. Their pressures were adjusted to give a main beam transmission of 85% at each stage. All unlabeled compounds were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification. Research grade propene and cyclopropane were obtained from Phillips Petroleum Co. (Bartlesville, OK) and Matheson of Canada (Whitby, ON), respectively. Pentane-d_{12} was purchased from Cambridge Isotope Laboratories (Andover, MA) whereas 2-bromo-2-methylpropane-d_9 and propyl-d_7 alcohol were obtained from CDN Isotopes (Pointe-Claire, QC).

Results and Discussion

Metastable $C_4H_9^+$ Ions Reviewed; Fragment Ion Structures. The molecules t-$C_4H_9SCH_3$, n-C_5H_{12}, $(CH_3)_2CHCH_2I$, and n-C_4H_9I were selected as precursor molecules for *t*-, *s*-, *i*-, and n-$C_4H_9^+$ ions, respectively, and a detailed justification for their use is given below under “Choice of Precursor Molecules”.

We have carefully repeated the measurements[14] on the composite metastable peak for methane loss and conclude that, irrespective of the butyl cation precursor, the peaks are very closely similar (Figure 2), containing a narrow and a broad component with a clear discontinuity at their junction. However, the minor differences in the abundance of the small kinetic energy release component and overall kinetic energy release distributions are reproducible (Figure 2). A two-component metastable peak can arise from a single dissociating ion structure producing two isomeric fragment ions (via appropriate transition states) or two dissociating ion structures producing the same or isomeric fragment ion structures. The dissociation of metastable *m/z* 57 ions generated from ionized n-C_4H_9I shows a most probable kinetic energy release that is slightly but significantly larger than that observed for *m/z* 57 ions generated from t-$C_4H_9SCH_3$, n-C_5H_{12}, and $(CH_3)_2CHCH_2I$ precursor molecules. It is worth adding here that this composite peak is only weakly collision sensitive; e.g., the peak only increased by ca. 50% under single-collision conditions with helium, indicating that the reacting configurations for methane loss are only accessed at energies close to the dissociation limit. At these energies, the four $C_4H_9^+$ isomers can interconvert,[8] but the observed minor differences in the kinetic energy release distributions show that the mixture of dissociating structures depends (weakly) on the origin (precursor molecule) of the $C_4H_9^+$ ions.

To investigate the $C_3H_5^+$ fragment ion structure, narrow segments of the composite peak, about 5 V in width, were transmitted from the second to the third field-free region of the mass spectrometer, and their CID mass spectra were recorded. The $C_3H_5^+$ isomers have been identified by the *m/z* 27:26 ratio in their CID mass spectra.[23] The ratios for the allyl and 2-propenyl cations are 1.5 and 0.48, respectively.[23] The observed ratio here was 0.48 ± 0.02, independent of the segment selected and is that for the 2-propenyl cation, $[CH_3CCH_2]^+$. Thus there was no evidence for the cogeneration of the more stable allyl isomer, $[CH_2CHCH_2]^+$, in either component of the peak. Under single-collision conditions (He) in the second field-free region, however, the *m/z* 27:26 ratio for the *mixed* collision and metastably generated *m/z* 41 peak segments increased slightly but significantly to 0.58 ± 0.03, showing the likely minor coproduction of $[CH_2CHCH_2]^+$, for which the *m/z* 27:26 ratio is ca. 1.5 at a similar ion translational kinetic energy. We conclude that there are two transition states for a 1,2 methane elimination leading to the 2-propenyl product ion, one having an energy barrier greater than the other. Without a sure knowledge of the reacting configurations (i.e., the formal $C_4H_9^+$ structures which lead to these transition states) little more can be concluded. However, because neither PTM nor PMC can produce the $[CH_3CCH_2]^+$ ion without prior rearrangement, it is attractive to propose that the major (broad) component is associated with the t-$C_4H_9^+$ structure and the minor with the formal s-$C_4H_9^+$ species, these being the two isomers which exist in potential energy wells of significant depth; see Figure 1. Given the relative energies of these isomers, the t-$C_4H_9^+$ cation would provide the greater density of states among the metastably dissociating species.

It is noteworthy that it has long been assumed that the allyl cation (the most stable $C_3H_5^+$ isomer) was generated in this dissociation.[24] Indeed, in an earlier thermochemical study from this laboratory,[14] where the appearance energy of $C_3H_5^+$ ions from pyrolytically generated butyl radicals was measured, it was concluded that the allyl cation *was* the threshold energy product. However, the then available ancillary thermochemical data for the butyl radicals have since changed, and recalculation using present data[10,25] shows that the thresholds indeed corresponded to the generation of the 2-propenyl cation, the $\Delta_f H°$ for the $C_3H_5^+$ product ion lying between 230 and 235 kcal mol^{-1}, $\Delta_f H°[CH_2CHCH_2^+] = 226$ kcal mol^{-1}, and $\Delta_f H°[CH_3CCH_2^+] = 231$ kcal mol^{-1}.[25]

The weakly abundant metastable peak for the production of *m*/*z* 29, $C_2H_5^+$, from the *m*/*z* 57 ion produced by the dissociative ionization of *n*-C_4H_9I, is also shown in Figure 2. It is clearly a broad, dished peak and has a $T_{0.5}$ value of 50 ± 3 meV. The metastable *m*/*z* 57 ions from the other precursors had similar but *significantly* lower $T_{0.5}$ values, 45, 43, and 36 meV for *n*-C_5H_{12}, $CH_3CH(CH_3)CH_2I$, and *t*-$C_4H_9SCH_3$, respectively. However, all these peaks were extremely collision sensitive; the latter three increased by about a factor of 50 in going from the second field-free region background pressure to single-collision conditions with He as target gas. The ions from *n*-C_4H_9I had only half the collision sensitivity. Under the same background pressures in the field-free region and identical instrument parameters, the ratio of the metastable peak heights *m*/*z* 41:29 was ca. 60:1 for *m*/*z* 57 ions from metastable ionized *n*-C_4H_9I and ca. 100:1 for the other three *m*/*z* 57 species. At the lowest attainable second field-free region pressures (measured to be $<1 \times 10^{-8}$ Torr), all the *m*/*z* 29 peaks were dished but rapidly assumed Gaussian profiles with little increase in half-height width as the target gas was admitted to the collision cell. We conclude that the *m*/*z* 29 peak is largely but not wholly collision induced.

At the bottom of its potential energy well, the ethyl cation is of nonclassical form,[26] a H^+-bridged ethene. The classical structure is not a minimum and was calculated to be some 6−8 kcal mol^{-1} above the nonclassical form.[27] The *neutral* H atom bridged ethene molecule is predicted to be unstable, lying 46 kcal mol^{-1} above the classical ethyl radical,[28] an energy 10 kcal mol^{-1} *above* the dissociation limit to $C_2H_4 + H^{\bullet}$. Therefore, vertical neutralization of near-ground-state ethyl cations could not generate a stable $C_2H_5^{\bullet}$ species.[29] Note that $C_2H_5^{\bullet}$ radicals with kiloelectronvolt translational kinetic energies yield $C_2H_5^+$ as base peak when ionized by collision with O_2.[29] The Xe/O_2 neutralization−reionization mass spectra (NRMS) of the $C_2H_5^+$ ions generated from the metastable $C_4H_9^+$ ions (i.e., in the absence of added collision gas) were found to show only a very weak $C_2H_5^+$ recovery signal. The peaks *m*/*z* 25, 26, 27, 28, and 29 had relative abundances of 9:31:24:33:3. The $C_2H_5^+$ ions produced under single-collision (He) conditions showed a significantly larger recovery signal (8:29:25:32:6). The above results indeed indicate that the majority of the $C_2H_5^+$ produced from metastable butyl cations have the ground-state nonclassical structure.

Which $C_4H_9^+$ structure leads to the ethyl cations? In view of the great sensitivity of the reaction to collisional excitation, it is attractive to propose that the PTM isomer is responsible, being the only stable $C_4H_9^+$ ion from which $C_2H_5^+$ production requires no rearrangement.

Choice of Precursor Molecules for Specific $C_4H_9^+$ Structures. To study the collision-induced dissociation of *specific* $C_4H_9^+$ ion structures, it was necessary to produce such ions as close as possible to the bottom of their potential energy wells. For *t*- and *s*-$C_4H_9^+$ ions this can be achieved by producing them from appropriate metastable ionized precursors. The dissociation must take place at or near to the thermochemical minimum for a stable $C_4H_9^+$ ion. The kinetic energy release accompanying the metastable precursor ion's fragmentation should be small, showing that a reverse energy barrier is not involved. These conditions were met for the following cases: (1) *t*-$C_4H_9^+$ from $(CH_3)_3CCO^+$ from ionized methyl pivalate[18] ($T_{0.5}$ for the CO loss = 8 meV) and from *t*-$C_4H_9SCH_3$ ($T_{0.5}$ for the loss of $CH_3S^{\bullet}$ = 7 meV); (2) *s*-$C_4H_9^+$ from ionized pentane ($T_{0.5}$ for the $CH_3^{\bullet}$ loss = 14 meV), where the threshold energy has been shown to be that for the secondary cation;[17] (3) "*n*-$C_4H_9^+$" from ionized $CH_3CH_2CH_2CH_2I$ ($T_{0.5}$ for the I loss = 16 meV), where $C_4H_9^+$ is the only peak in the MI mass spectrum; (4) "*i*-$C_4H_9^+$" from ionized $(CH_3)_2CHCH_2I$ ($T_{0.5}$ for the I loss = 26 meV), where $C_4H_9^+$ is the only peak in the MI mass spectrum. Note that in principle attempts to make *n*- and *i*-$C_4H_9^+$ ions will result in their rearrangement to mixtures of *s*- and *t*-$C_4H_9^+$ ions (see Introduction). It was noted that *m*/*z* 57 ions generated in the ion source from ionized $CH_3CH_2CH_2CH_2CO_2CH_3$, $(CH_3)_2CHCH_2CO_2CH_3$, and $CH_3CH_2CH(CH_3)CO_2CH_3$ were all contaminated with minor $C_3H_5O^+$ components and so were rejected for further study. These precursors were used by Maquestiau et al.[18] for the expected generation of *n*-, *i*-, and *s*-$C_4H_9^+$ cations.

TABLE 1: Peak Widths ($w_{1/2}$) for *m*/*z* 41 and *m*/*z* 42 Ions Generated in He and O_2 Collision-Induced Dissociation of Metastably Produced and Ion Source $C_4H_9^+$ Species (All $w_{1/2}$ Are Reported for a Translational Kinetic Energy of 6333 V)

	metastably generated $C_4H_9^+$ $w_{1/2}$ 41:$w_{1/2}$ 42 (± 2 V)		source $C_4H_9^+$ $w_{1/2}$ 41:$w_{1/2}$ 42 (±2 V)	
type of ion	He	O_2	He	O_2
s-$C_4H_9^+$	49:35	50:100	45:43	45:72
t-$C_4H_9^+$	45:36	45:36	47:36	47:42
"*n*-$C_4H_9^+$"	47:34	48:58	49:44	50:93
"*i*-$C_4H_9^+$"	51:35	51:50	50:47	50:50[a]

[a] Composite peak.

Fragment Ion Structures and Phenomenology in the Collision-Induced Dissociation of Structurally Distinct $C_4H_9^+$ Ions. *t-$C_4H_9^+$ and s-$C_4H_9^+$.* In addition to the He CID mass spectra of the metastably generated ions, the experiment was also carried out using O_2 as collision gas. Overall, the results with He were in good agreement with those reported by Maquestiau et al.[18] for the same metastable precursor ions, and indeed *t*-$C_4H_9^+$ ions generated more *m*/*z* 42 fragment ions than did *s*-$C_4H_9^+$. This effect was enhanced when O_2 was used as collision gas. An attempt was made to use the *m*/*z* 41:42 abundance ratio to differentiate between the two isomers, but even though these ratios differ considerably for *t*- and *s*-$C_4H_9^+$ ions, they cannot reliably be used as a structure indicative tool because the ratios are themselves precursor molecule dependent; i.e., *t*-$C_4H_9^+$ ions generated from two different metastable precursor molecular ions produce different *m*/*z* 41:42 abundance ratios. Although not discussed in their paper, Maquestiau's results also showed such variations. This is not a translational kinetic energy effect because the *m*/*z* 41:42 ratio for a selected ion varied only slightly over energies ranging from 6 to 3 kV. The variation in the *m*/*z* 41:42 ratio with precursor molecule is ascribed to the internal energy distribution of the ions in the low-energy region of the potential energy wells, being dependent in turn upon the origin of the $C_4H_9^+$ ions, i.e., the precursor species.

We have however noted a structure sensitive phenomenon when O_2 is used as collision gas. In the case of the *s*-$C_4H_9^+$ isomer *only*, the half-height width ($w_{1/2}$) of the *m*/*z* 42 peak was much greater with O_2 than with He (Table 1). In sharp contrast, the $w_{1/2}$ for the *m*/*z* 42 ions generated from the t- isomer remained unchanged when O_2 replaced He. The peak shape of the *m*/*z* 42 ion generated from *s*-$C_4H_9^+$ changed from a Gaussian profile (He) to a flat-topped peak (O_2); see Figure 3. Therefore, a good structure distinguishing feature is the width of the *m*/*z* 42 peak generated by collision with O_2.

In recent literature,[30] it has been reported that in some ionic systems high-energy collisions with oxygen promoted new reaction pathways, a sharp increase in certain dissociation routes being observed when O_2 rather than He was the collision gas.

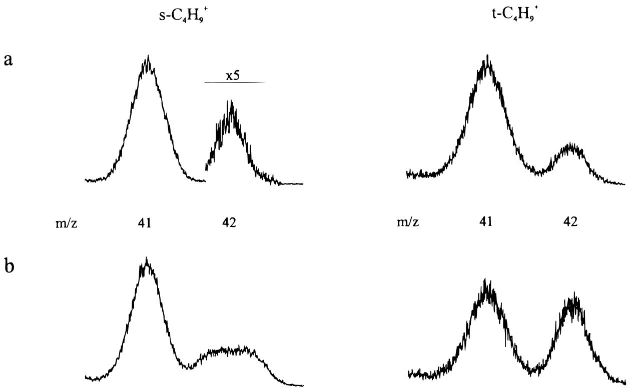

Figure 3. Peaks at *m/z* 41 and 42 in the collision-induced dissociations of *s*-$C_4H_9^+$ and *t*-$C_4H_9^+$ ions generated from metastable precursor molecules: (a) He collisions and (b) O_2 collisions.

TABLE 2: Effect of the Nature of the Collision Gas on Collision-Induced Dissociation of Metastably Generated *s*-$C_4H_9^+$ Ions

target gas	CID peak width $w_{1/2}$ 41:$w_{1/2}$ 42 (±2 V)	CID peak int[a] 41:42	polarizability[31] (10^{-24} cm^3)
He	49:42	10:1	0.205
H_2	50:73	10:1	0.804
H_2O	51:82	5.6:1	1.45
O_2	51:99	1.6:1	1.58
N_2	49:77	8.8:1	1.74
CO	51:80	8.1:1	1.95
CH_4	52:61	23:1	2.59
CO_2	52:65	13:1	2.91
NO_2	49:86	3.3:1	3.02
Xe	51:90	14:1	4.04
CS_2	51:98	4.7:1	8.74

[a] Peak intensities are calculated using the product of the peak height and peak $w_{1/2}$.

For the $C_4H_9^+$ species, O_2 noticeably increased the relative intensity of the *m/z* 42 ions, but more striking was the pronounced peak shape change observed for *s*-$C_4H_9^+$ ions. It would appear then that when O_2 is the target gas, a reaction channel for *s*-$C_4H_9^+$ to *m/z* 42 ions which involves a reverse energy barrier is accessed. Note that this peak shape was only observed for $C_4H_9^+$ ions of low internal energy and therefore singular structure. For source $C_4H_9^+$ ions from ionized pentane, the CID *m/z* 42 peak was less broadened (Table 1), in keeping with *source* ions being a mixture of structures.

As a general rule, it is assumed that the nature of the collision gas does not greatly affect CID mass spectra although it is usual to observe minor differences in relative fragment ion abundances when comparing oxygen and helium. These differences are rationalized on the basis of the different physicochemical properties of the two gases, such as their polarizability and ground electronic state. To try to identify a target gas property responsible for the observed peak shape differences, metastably generated *s*-$C_4H_9^+$ ions were excited using a wide variety of collision gases. The results are shown in Table 2. For all collision gases, broadening of the *m/z* 42 peak relative to its width in the helium CID was observed. However, only in the experiments with H_2O, O_2, NO_2, Xe, and CS_2 was the *m/z* 42 peak flat-topped. The yield of *m/z* 42 ion, relative to *m/z* 41, was also greater with these target gases, with the exception of Xe. It should be emphasized that the *m/z* 41 peak shape was always independent of the target gas. No simple correlation was evident between the intensity or the shape of the *m/z* 42 peak relative to *m/z* 41 and a single characteristic of a target gas, although the polarizability of the target gas appears to be important for observing the peak broadening. Furthermore, there was no evidence to indicate that the ground electronic state of the target gas is a determinant, the broadening being observed with collision gases having singlet, doublet, and triplet ground electronic states, namely, H_2O, NO_2, or O_2, respectively (Table 2). It is noteworthy that *no* broadening of the *m/z* 42 peak from *t*-$C_4H_9^+$ ions was observed, irrespective of the collision gas used.

The flat-topped *m/z* 42 peak ($T_{0.5} \cong 0.5$ V) observed with the more polarizable target gases indicates that the loss of $CH_3^{\bullet}$ from the *s*-$C_4H_9^+$ ions involves a reverse activation energy; i.e., the transition state for the process lies above the thermochemical minimum. Note that the ground-state geometry of *s*-$C_4H_9^+$ was calculated to be far from the classical form, being closer to a symmetrically protonated but-2-ene.[13] Thus, an appreciable geometry change may be needed to reach a transition state having a product-like configuration.

This effect of the polarizable gases is quite unusual and deserves discussion. Metastable peaks arise from dissociations that take place with rate constants in the range 10^4-10^7 s^{-1}. When the fragmentation takes place at the thermochemical minimum, the excess internal energy required to achieve these rate constants is small, and this in turn is reflected by small KER values. Such peaks have Gaussian profiles, corresponding to a Boltzmann distribution of released energies. The observation of a flat-topped peak accompanied by much larger KER values has long been accepted as arising from the fragmentation having a reverse energy barrier.[32] The KER distribution is now displaced toward higher energies, with only minor contributions from small KER values. Under collisional excitation, a flat-topped peak may become Gaussian in profile with no significant overall broadening of the signal. Thus, the higher energy ions with shorter lifetimes show *less* partitioning of internal energy into translational degrees of freedom. We propose that the flat-topped O_2 collision peak arose from *s*-$C_4H_9^+$ ion fragmentations taking place predominantly near the dissociation threshold, the reaction having a reverse energy barrier. The He collision peak was Gaussian and significantly narrower, in keeping with only higher energy species being involved. This picture is sustainable if the He excitation is essentially vertical whereas the O_2 collision, a longer range process, allows the geometry of the ion to change during the activation.

The structure of the *m/z* 42 ions collisionally produced from (a) structurally pure *s*- and *t*-$C_4H_9^+$ ions (the metastably generated species) and (b) the $C_4H_9^+$ ion mixtures produced in the ion source were therefore investigated. The isomeric $C_3H_6^{\bullet+}$ ions, $[CH_3CHCH_2]^{\bullet+}$, $[cy\text{-}CH_2CH_2CH_2]^{\bullet+}$, and $[(CH_3)_2C]^{\bullet+}$, can only be identified by means of their charge stripping (CS) mass spectra.[19]

For metastably generated *s*-$C_4H_9^+$, the CS mass spectrum of the $C_3H_6^{\bullet+}$ species was too weak to measure, but for *t*-$C_4H_9^+$ ions, it proved possible to accumulate sufficient data with O_2 as CS target gas. The *m/z* 20:20.5 ratio, 1.6 ± 0.2, indicated that ionized propene was generated (Table 3). The absence of a detectable signal at *m/z* 21 rules out any significant generation of $[(CH_3)_2C]^{\bullet+}$.

The CS mass spectra of $C_3H_6^{\bullet+}$ ions collisionally produced from *source* generated $C_4H_9^+$ ions were measured using the perdeuterated analogues, to eliminate any ^{13}C contribution from peaks of lower mass. For $C_4D_9^+$ ions from ionized *t*-C_4D_9Br, the O_2 CS mass spectrum of the He or O_2 collisionally generated $C_3D_6^{\bullet+}$ was closely similar to that of [propene-d_6]$^{\bullet+}$ (Table 3). The O_2 CS mass spectrum of the $C_3D_6^{\bullet+}$ ions from $C_4D_9^+$ generated from ionized C_5D_{12} was different from that of ground-state [propene-d_6]$^{\bullet+}$ because of the absence of a $C_3D_6^{2+}$ ion but was not like that for [cyclopropane-d_6]$^{\bullet+}$ (Table 3). This

TABLE 3: O_2 Charge Stripping Mass Spectra of $C_3D_6^{\bullet+}$ and $C_3H_6^{\bullet+}$ Species (All Spectra Were Obtained at a Translational Kinetic Energy Close to 5 kV)

$C_3D_6^{\bullet+}$	*m/z* 20:21:22:23:24	$C_3H_6^{\bullet+}$	*m/z* 19:19.5:20:20.5:21
$CD_3CDCD_2^{\bullet+}$ [a]	18:14:33:27:8	$CH_3CHCH_2^{\bullet+}$ [c]	16:13:26:28:7
$CD_2CD_2CD_2^{\bullet+}$	17:10:53:19:0	$[CH_3CHCH_2^{+}]$[d]	18:20:38:22:1
$C_3D_6^{\bullet+}$from *t*-$C_4D_9^+$	22:16:30:22:9		
$C_3D_6^{\bullet+}$from *s*-$C_4D_9^+$	20:19:30:31:0		

[a] Propene-d_6 produced from the metastable dissociation of $C_5D_{12}^{\bullet+}$. [b]Cyclopropane-d_6 produced from the metastable dissociation of $C_3D_7OH^{\bullet+}$. [c]Propene produced from the metastable dissociation of $C_5H_{12}^{\bullet+}$. [d]Propene produced from CID of $C_3H_7Cl^{\bullet+}$.[33]

observation may result from the $C_3D_6^{\bullet+}$ ions having only elevated internal energies, such that electron loss did not produce a stable $C_3D_6^{2+}$ ion. To investigate this, the O_2 CS mass spectra of ground-state (metastably generated from ionized pentane) and excited-state (collisionally generated from ionized 1-chloropropane[33]) [propene]$^{\bullet+}$ ions were compared. The results showed that the excited species yielded fewer $C_3H_6^{2+}$ ions and proportionately more fragment ions (Table 3). We therefore propose that CID of source-generated *s*-$C_4D_9^{\bullet+}$ ions produce [propene-d_6]$^{\bullet+}$ with high internal energies. These CS results do not provide *any* evidence for the generation of ionized cyclopropane, which could in principle be produced from the PMC isomer.

A comment on the observation of $C_3H_6^{2+}$ ions from collisionally excited low internal energy ionized propene is appropriate here because theory[34] has predicted that [propene]$^{2+}$ has no significant potential energy well. We suggested that $CH_3CHCH_2^{\bullet+}$ ions, when collisionally excited with O_2, communicate with the $(CH_3)_2C^{\bullet+}$ surface prior to or concomitant with electron loss, thus allowing for the small yield of $C_3H_6^{2+}$ ions. Higher energy [propene]$^{\bullet+}$ ions do not so communicate. These observations were not repeated with He as target gas, no $C_3H_6^{2+}$ ions being observed under any conditions. This too exemplifies the different behavior of O_2 as target gas.

Neutralization−reionization mass spectra (NRMS), using Xe as neutralizing target and O_2 for reionization, were studied for the low-energy *t*- and *s*-$C_4H_9^+$ isomers. The NR mass spectra were very closely similar but with the *t*-$C_4H_9^+$ ion giving a significantly larger recovery signal. The recovered *m/z* 57 ions had sufficient internal energy to be metastable with respect to CH_4 loss and so must consist of mixtures of $C_4H_9^+$ structures.

n-$C_4H_9^+$ and i-$C_4H_9^+$. Maquestiau's[18] observations led him to conclude that *n*-C_4H_9 containing precursors generated *s*-$C_4H_9^+$ fragment ions and that *i*-C_4H_9 analogues produced precursor molecule-dependent mixtures of *s*- and *t*-$C_4H_9^+$ ions with the former predominating. Oliveira et al.,[12] using photoelectron photoionization coincidence mass spectrometry, concluded from the dissociation onsets for the *n*- and *i*-bromo- and iodobutanes that H atom rearrangement caused the four isomeric species to produce only two $C_4H_9^+$ fragment ion structures; *n*- and *i*-C_4H_9 precursor molecules yielded *s*- and *t*-$C_4H_9^+$ fragment ions, respectively. It is noteworthy that the measured appearance energies[12] for the *m/z* 57 ion from *n*- and *i*-C_4H_9I showed that the *s*- and *t*-$C_4H_9^+$ fragment ions were not produced at their respective thermochemical thresholds; i.e., the fragment ions were generated with excess internal energy.

Using the relative *m/z* 41:42 peak widths (Table 1) as a structure identifier, we conclude instead that both metastable *n*- and *i*-C_4H_9I precursor molecules produced *mixtures* of *s*- and *t*-$C_4H_9^+$ fragment ions; i.e., in both cases, significant broadening of the *m/z* 42 peak was observed when O_2 replaced He in the CID experiment. The results indicated a major yield of *t*-$C_4H_9^+$ ions rather than *s*-$C_4H_9^+$, because the *m/z* 42 peaks were not greatly broadened and also that the mixture produced from *n*-C_4H_9I contained more *s*-$C_4H_9^+$ than that obtained from *i*-C_4H_9I. It is noteworthy that, for $C_4H_9^+$ ions generated in the ion source from *n*-C_4H_9I, the results were consistent with the ions being essentially *s*-$C_4H_9^+$ in nature. For ions similarly produced from *i*-C_4H_9I, the *m/z* 42 peak was clearly composite, representing the production of the same fragment ion, [propene]$^{\bullet+}$, but from two different precursors, i.e., methyl loss from the *s*- and *t*-$C_4H_9^+$ isomers.

Conclusions

We have shown that structurally pure *s*-$C_4H_9^+$ and *t*-$C_4H_9^+$ ions of low internal energy can be clearly distinguished via collisional excitation. The distinction rests upon the characteristically much larger kinetic energy release when *s*-$C_4H_9^+$ ions are activated by O_2 to lose $CH_3^{\bullet}$ (500 meV) relative to *t*-$C_4H_9^+$ (90 meV). The resulting $C_3H_6^{\bullet+}$ fragment ions only have the [propene]$^{\bullet+}$ structure. The dissociative ionization of species containing formal *n*-C_4H_9 and *i*-C_4H_9 groups lead only to mixtures of *s*- and *t*-$C_4H_9^+$ ions, in keeping with predictions from theory.

Metastable $C_4H_9^+$ ions clearly interconvert between a number of structures. Thus, the shape of the composite metastable peak for CH_4 loss is largely structure independent. The fragment ion is $[CH_3CCH_2]^+$. The only other metastable dissociation, C_2H_4 loss, is a minor process, yielding low internal energy (nonclassical) $C_2H_5^+$ ions. The $C_4H_9^+$ structure leading to this dissociation is proposed to be the proton-bridged tetramethylene structure (PTM), an isomer found by theory to occupy a potential energy well. The corner protonated methylcyclopropane (PMC) ion, also predicted to be stable, could not be allied to any dissociation characteristic of $C_4H_9^+$ ions.

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