Ion Cyclotron Resonance Spectroscopy in Structure Determination. II. Propyl Ions[1]

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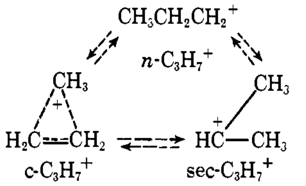
Received April 29, 1971

Abstract: Conflicting postulations have been made for the structures of $C_3H_7^+$ ions found in the mass spectra of various organic compounds; similar discrepancies are found in radiolysis and theoretical studies of these ions. In this study ion cyclotron resonance (icr) spectroscopy is used to examine proton–deuteron transfer and other ion–molecule reactions of specifically labeled propyl ions from a variety of precursors. Nondecomposing *sec*-propyl ions are found to undergo little (<20%) isomerization in the time required for icr reactions (*ca.* 10^{-3} sec). Almost no (<3%) n-$C_3H_7^+$ ions retain their structure; most (80–100%) isomerize to *sec*-$C_3H_7^+$. Protonation of cyclopropane produces propyl ions whose reactivity toward methanol is identical with the unique reactivity of *sec*-$C_3H_7^+$. This result indicates either that ΔH_f(c-$C_3H_7^+$) is significantly higher than ΔH_f(*sec*-$C_3H_7^+$) (*ca.* 7 kcal/mol), or that c-$C_3H_7^+$ isomerizes to *sec*-$C_3H_7^+$.

Extensive experimental investigations have been carried out on the structures of $C_3H_7^+$ ions in both the gas phase[3–5] and in solution.[6] Complementary theoretical studies utilizing molecular orbital calculations have also been reported.[7] Despite rapid progress in several areas, many anomalies remain; in particular this is true of the ubiquitous $C_3H_7^+$ ions found in the mass spectra of organic compounds.[3d,3e,8] Very recent results provide extensive new, although conflicting, evidence on the behavior of gaseous $C_3H_7^+$ ions generated by high energy radiation and by electron impact[4f,5b] and on the energies of possible isomeric structures.[7f]

Three main types of structures have been proposed for these ions: n-propyl, isopropyl (*sec*-$C_3H_7^+$), and protonated cyclopropane (c-$C_3H_7^+$),[9] which may be



interconvertible under particular circumstances. The first evidence for the structures of such ions in mass spectra was based on their heats of formation (ΔH_f) calculated from appearance potential measurements. As originally pointed out by Stevenson,[3a] ΔH_f values found for $C_3H_7^+$ ions from a number of alkanes and substituted alkanes[3a] indicate that these ions are formed as the *sec*-$C_3H_7^+$ structure; their ΔH_f values agree closely[3b,d] with that derived from the direct ionization of the isopropyl radical (192 kcal/mol; ΔH_f of n-$C_3H_7^+$ is 208 kcal/mol).[3b,f,10] For $C_3H_7^+$ ion formation from n-alkanes, isomerization thus provides a lower energy pathway for decomposition. However, at electron energies only a few electron volts above threshold, this pathway appears to be of little relative importance;[5b,11] in the 70-eV spectrum of $CD_3CH_2CH_2CD_3$ 94% of the propyl ions are $C_3H_4D_3^+$, consistent with their formation as the n-$C_3H_7^+$ structure.[5b] Dissociative charge-exchange reactions of rare gas ions with $CH_3CD_2CH_3$,[4c] as well as its 30-eV mass spectrum,[5b] indicate that n- as well as *sec*-propyl ions are formed at higher energies. The ΔH_f values found for $C_3H_7^+$ ions from some n-alkyl derivatives,[3b,d] such as the n-propyl halides,[3c] indicate that n-$C_3H_7^+$ ions can be formed without rearrangement even at threshold energies.[12] Some experiments indi-

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[1] Part I: M. L. Gross and F. W. McLafferty, *J. Amer. Chem. Soc.*, **93**, 1267 (1971).

[2] (a) Taken in part from the Ph.D. thesis of D. J. McAdoo, Cornell University, 1971; (b) NIH Predoctoral Fellow, 1969–1970.

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[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

[9] A very recent calculation favors the corner-protonated structure as the most stable form of c-$C_3H_7^+$.[7f]

[10] Metastable decompositions of $CH_3CD_2CH_3$ show only loss of D, not H, also indicating only *sec*-propyl ion formation in these threshold reactions.[4d]

[11] R. Liardon and T. Gaumann, *Helv. Chim. Acta*, **52**, 528, 1042 (1969).

[12] This is not conclusive evidence; ions are formed at energies below that required for the formation of n-$C_3H_7^+$ + X. Although these low-energy ions may be n-$C_3H_7^+$ ions formed with X^- in an ion-

cate that the initially formed *n*-$C_3H_7^+$ ions of low as well as higher energies rearrange in $<10^{-5}$ sec to a more stable structure; $C_3H_7^+$ ions from 1-bromopropane undergo collision-induced[4e] and unimolecular metastable[14] decompositions which are identical with those of $C_3H_7^+$ ions from 2-bromopropane. However, Gross observes wide differences in the ion–molecule reactivities of ions formed as *n*- and *sec*-$C_3H_7^+$, indicating that "two, and perhaps three, propyl ions are produced in mass spectral fragmentations."[4f]

It has been proposed that the *sec*-$C_3H_7^+$ ions also can isomerize to a more stable structure. Meyerson and coworkers[4a,b] point out that the c-$C_3H_7^+$ structure provides an explanation for the scrambling of isotopic labels indicated by the methyl ion abundances in ^{13}C and ^2H labeled propanes. The c-$C_3H_7^+$ structure is analogous to the other cationated cyclopropane structures used by these authors to provide a "unified interpretation" of similar structural data of other aliphatic and aromatic hydrocarbons.[4b] In contrast, Ottinger[4d] reports evidence for nonscrambled structures from decompositions of labeled *sec*-$C_3H_7^+$ ions in the metastable drift region by reaction 1. The molecular hydrogen lost from $CH_3C^+DCH_3$ formed from $CH_3CD_2CH_3$ showed $[-HD]/[-H_2] < 0.04$, while that from $CD_3C^+HCD_3$ formed from CD_3CHDCD_3 showed $[-HD]/[-D_2] = 1.0$. Ottinger concluded that $CH_3C^+DCH_3$ is formed from $CH_3CD_2CH_3$ and decomposes from only the secondary structure, but that both $CD_3CHDCD_2^+$ and $CD_3C^+HCD_3$ are formed from CD_3CHDCD_3 and undergo metastable decompositions. However, this apparent lack of H/D scrambling in the *sec*-propyl ions undergoing decomposition is surprising in view of the internal energies of those ions. Heats of formation of 226 kcal/mol[3g] for $C_3H_5^+$ and 192 kcal/mol for *sec*-$C_3H_7^+$ and a minimum reverse activation energy for reaction 1 of 4.6 kcal/mol[4e] gives 38.6 kcal/mol as the minimum activation energy for reaction 1. For the decomposition of *n*-$C_3H_7^+$ to take place without isomerization to the *sec*-$C_3H_7^+$ structure, an activation energy for the isomerization reaction of at least 23 kcal is required, much higher than that thought to be required in solution.[6d]

$$C_3H_7^+ \longrightarrow C_3H_5^+ + H_2 \qquad (1)$$

Evidence has been presented to support the formation of all three isomeric ions in gas-phase radiolysis reactions.[15] The stability of protonated cyclopropane in the gas phase is shown by the reaction of He^3H^+ with cyclopropane;[5a] the tritiated C_3 product recovered was largely cyclopropane, indicating initial addition of ^3H to form the tritiated cyclopropane ion followed by loss of ^1H without ring opening. In a very recent comprehensive report, Ausloos and coworkers[5b] conclude that *n*-$C_3H_7^+$ ions formed by radiolysis rearrange within 10^{-10} sec to *sec*- and c-$C_3H_7^+$ ions, with the proportion of the secondary isomer favored and increasing with increasing energy of the precursor ion. A small, but appreciable, reverse isomerism also occurs; the extent of *sec*-$C_3H_7^+ \rightarrow$ *n*-$C_3H_7^+$ increases with increasing energy of the precursor ions.

In solution c-$C_3H_7^+$ has been demonstrated to arise from the protonation of cyclopropane,[6a] and to act as an intermediate in some reactions of the *n*-propyl ion.[6b] Deno and coworkers[6a] found the order of stability of the possible ions in solution to be *sec*-$C_3H_7^+ >$ c-$C_3H_7^+ >$ *n*-$C_3H_7^+$. *sec*-$C_3H_7^+$, not c-$C_3H_7^+$, is observed in solution by nmr,[6d,e] although slow equilibration of ^{13}C in that ion occurs at $-60°$ in "magic acid."[6e] Similarly, substituted cyclopropane ions play an insignificant role in the reactions of 1-butyl and 1-pentyl ions.[6c] However, the order of stability of $C_3H_7^+$ ions found in solution is not compelling evidence against isomerization to the c-$C_3H_7^+$ structure in the gas phase; the relative acidities of a series of aliphatic alcohols are reversed in going from solution to the gas phase.[16]

In the most recent of several studies[7] of the $C_3H_7^+$ ions utilizing molecular orbital methods, Radom, Pople, Buss, and Schleyer[7f] report *ab initio* calculations using geometry optimization and an extended basis set which indicate that *sec*-$C_3H_7^+$ is the lowest energy structure; forms of both *n*- and c-$C_3H_7^+$ structures of rather unexpected geometries were found to be of nearly the same energy, approximately 17 kcal above that of *sec*-$C_3H_7^+$. Previous conclusions are in striking contrast;[7b–e] Kollmar and Smith[7d] report CNDO calculations indicating that c-$C_3H_7^+$ is 14 kcal/mol *more* stable than *sec*-$C_3H_7^+$ and 39 kcal/mol more stable than *n*-$C_3H_7^+$. Previous calculations indicated that c-$C_3H_7^+$ was even more stable relative to *sec*-$C_3H_7^+$, but it was emphasized that such semiempirical methods give less reliable data for the relative energy differences between open-chain and cyclic ion structures.[7e]

Clarification of the structure or structures of the gaseous $C_3H_7^+$ ions formed by electron impact should thus be useful for comparison of solution and gas-phase ion chemistry and for testing of theoretical predictions, as well as for increasing our basic understanding of electron impact reactions, such as the scrambling of hydrogen atoms in alkyl ions.[3e,8] To minimize the possibility of isomerization, we felt it necessary to study ions of low internal energy; a promising new technique of this kind utilizes ion–molecule reactions in the ion cyclotron resonance (icr) spectrometer.[17] Recent icr studies proved to be very successful in elucidating the structure of the $C_3H_6O^+$ ions formed by the single and double γ-hydrogen rearrangement of alkanones,[18] and of $C_2H_5O^{+}$[19] and $C_3H_6^{+}$[1] ions from a variety of sources. Recently we have learned of two other icr investigations of $C_3H_7^+$ ions.[4f,20] The results of these,

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pair process, alternative explanations involving *sec*-$C_3H_7^+$ formation from isomerized $C_3H_7X\cdot^+$ ions are possible. Note, however, that such an isomerization reaction should have a tight activated complex,[13] and thus its rate should increase much more slowly with increasing internal energy than a loose complex reaction such as the direct cleavage formation of *n*-$C_3H_7^+$, favoring the latter at higher ion internal energies.

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(15) However, conclusions of a previous report [P. Ausloos, R. E. Rebbert, and S. G. Lias, *J. Amer. Chem. Soc.*, **90**, 5031 (1968)] concerning the apparent stability of *n*-$C_3H_7^+$ and the absence of the *sec*-$C_3H_7^+ \rightarrow$ *n*-$C_3H_7^+$ isomerization have been withdrawn recently by the authors in light of further results.[5b]

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which have led to conflicting interpretations, will be discussed below.

Results and Discussion

Unimolecular Metastable Decompositions of Labeled $C_3H_7^+$ Ions. Labeled 1- and 2-bromopropanes were used to produce $CH_3CH_2C^+HD$, $CH_3C^+DCH_3$, and $CD_3C^+HCD_3$ ions for a reexamination of reaction 1 occurring in the metastable drift region. The results, along with those of Ottinger,[4d] are shown in Table I.

Table I. Metastable Decompositions of $C_3(H,D)_7^+ \rightarrow C_3(H,D)_5^{+\,a}$

Precursor	Ion initially formed	$[-HD]/[-H_2]$	$[-HD]/[-D_2]$
CH_3CH_2CHDBr	$CH_3CH_2C^+CHD$	0.148 ± 0.005	
$CH_3CDBrCH_3$	$CH_3C^+DCH_3$	0.138 ± 0.005	
$CD_3CHBrCD_3$	$CD_3C^+HCD_3$		0.86 ± 0.05
$CH_3CD_2CH_3{}^b$	$CH_3C^+DCH_3$	<0.04	
$CD_3CHDCD_3{}^b$	$CD_3C^+HCD_3$		1.0

[a] All data obtained at an electron energy of 30 eV. [b] Data from ref 4d.

The similarity of the values for $CH_3CH_2C^+HD$ and $CH_3C^+DCH_3$ indicates that the H and D atoms are lost with complete scrambling. The statistically predicted ratios for both $[-HD]/[-H_2]$ from $C_3H_6D^+$ and $[-HD]/[-D_2]$ from $C_3HD_6^+$ are 0.40; this is consistent with the values found for $CH_3CH_2C^+HD$, $CH_3C^+DCH_3$, and $CD_3C^+HCD_3$ if isotope effects of 2.7, 2.9, and 2.2, respectively, favoring the loss of H over D are assumed. Similarly large isotope effects have been reported previously for metastable ion decompositions.[21] Despite the experimental uncertainty involved, the hydrogen atoms must have lost nearly all of their positional identity before or during decomposition. Ottinger's value for $C_3HD_6^+$ from CD_3CHDCD_3 yields an isotope effect of 2.5, consistent with our values. We are unable to explain the disagreement in the data for $CH_3C^+DCH_3$; however, the ratio derived from the $CH_3CD_2CH_3$ precursor[4d] is clearly inconsistent with the other values of Table I. We conclude that isomerization of *sec*- and *n*-$C_3H_7^+$ ions accompanies reaction 1, as expected from its high activation energy. This emphasizes the importance of using ions of low internal energy for any characterization study.

Ion Cyclotron Resonance Studies of Labeled $C_3H_7^+$ Ions. As part of another icr study, Kriemler has recently observed[20] by icr techniques that $C_3H_6D^+$ ions generated from $(CH_3)_2CDNO_2$ show exclusive transfer of H^+ to neutral molecules of $(CH_3)_2CDNO_2$. Barring a large isotope effect, some D^+ transfer should have been noted if the hydrogen atoms in $C_3H_6D^+$ had rearranged their positions to a substantial extent prior to reaction. Kriemler also observed[20] reaction 2 from

$$C_3H_7^+ + CH_3CH_2CH_2NO_2 \longrightarrow C_6H_{14}NO_2^+ \qquad (2)$$

$C_3H_7^+$ derived from diisopropyl and di-*n*-propyl ether, 1- and 2-chloropropane, and iso- and *n*-butane, but not from $C_3H_7^+$ generated from 1-nitropropane.[22] He concluded, therefore, that $C_3H_7^+$ generated from 1-nitropropane has either a different structure[23] or a higher internal energy than $C_3H_7^+$ generated from the other sources. Gross has recently observed[4f] substantially different reactivities of $C_3H_7^+$ ions from a variety of sources; $C_3H_7^+$ from 1-chloropropane is unique in producing no $C_7H_{11}O^+$ in reaction with furan. The contrasting rates are interpreted as arising from the reactions of two (or possibly three) propyl ion structures, presumably *n*- as well as *sec*-$C_3H_7^+$. However, Beauchamp and Dunbar have reported that $CH_3CH{=}OH^+$ ions show a substantial variation of reactivity with internal energy.[19]

We first sought to differentiate between the possible $C_3H_7^+$ ion structures utilizing proton transfer reactions similar to those used by Kriemler.[20] A molecule N with a proton affinity higher than that of propene should undergo reaction 3; there should be a higher tendency to abstract a primary rather than a secondary hydrogen atom (reaction 4) from *sec*-$C_3H_7^+$ because of the greater

$$CH_3C^+HCH_3 + N \longrightarrow NH^+ + CH_3CH{=}CH_2 \qquad (3)$$

$$\not\longrightarrow NH^+ + CH_3\ddot{C}CH_3 \qquad (4)$$

$$CH_3CH_2C^+H_2 + N \longrightarrow NH^+ + CH_3CH{=}CH_2 \qquad (5)$$

stability of the C_3H_6 product formed. In the same way the *n*-$C_3H_7^+$ should undergo abstraction of a secondary hydrogen atom (reaction 5) if the reaction takes place before isomerization of the *n*-$C_3H_7^+$. Finally, abstraction of hydrogen from any c-$C_3H_7^+$ formed by isomerization of *n*- or *sec*-$C_3H_7^+$ should be random (except for isotope effects) under the assumption that the exchange of H atoms within the ion is rapid.[4-6]

To avoid ambiguities due to isotope effects, the labeled ions, *sec*-$C_3H_4D_3^+$, $CD_3C^+HCD_3$, $CH_3C^+DCH_3$, $CH_3C^+HCH_2D$, $CH_3CD_2C^+H_2$, and $CH_3CH_2C^+D_2$, were studied. The corresponding 1- and 2-bromopropanes were used as precursors because they yield abundant propyl ions whose heats of formation (215 and 194 kcal/mol, respectively[3b]) are indicative of initial *n*- and *sec*-$C_3H_7^+$ structures (*vide supra*). Double resonance studies were used, as interfering ion–molecule reactions were present in most single resonance spectra. Data for the rate of transfer of protons *vs.* deuterons using neutral reagents with a variety of proton affinities are shown in Table II.

Primary Isotope Effect. 2-Bromopropane was prepared in which the six terminal hydrogen atoms had been statistically equilibrated with deuterium. The primary H and D atoms of the $C(H,D)_3C^+HC(H,D)_3$ ion of *m/e* 46 $(C_3H_4D_3)^+$ should thus be equivalent. If proton abstraction occurs by eq 3 (*vide infra*), the relative abundances of NH^+ and ND^+ produced by irradiation of *m/e* 46 should be a direct measure of the primary isotope effect.[24] This yields an average k_H/k_D value of 1.5.[25]

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(20) Private communication, H. P. Kriemler, Varian Associates, Palo Alto, Calif., Aug 1969. We are indebted to Dr. Kriemler for communication of these results prior to publication and for helpful discussions.

(21) C. Lifshitz and R. Sternberg, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 303 (1969); F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfeld, *J. Amer. Chem. Soc.*, **93**, 3720 (1971).

(22) The occurrence of reaction 2 in a mixture of 2-bromopropane and 1-nitropropane and its absence in 1-nitropropane alone have been confirmed in our laboratory.

(23) The heat of formation found for $C_3H_7^+$ from 1-nitropropane is 214 kcal/mol.[3b]

(24) Note that this measurement will include any isotope effect on the relative double resonance signals.

(25) Proton abstraction from an equimolar mixture of $C_3H_7^+$ and $C_3D_7^+$ yielded uncorrected isotope effect values of 1.7 and 2.3 for single and double resonance measurements, respectively; these values should be lowered by corrections due to the large difference (43 : 50) in the masses of the precursor ions (footnote 19 in ref 19 and personal communi-

Table II. Double Resonance Signals for Proton and Deuteron Transfer from Labeled Propyl Ions

		Predicted value		Observed value[b]			
				Neutral reagent			
Precursor	Initial ion	Not isomerized	Isomerized	Acetone	1-Propanol	Propanal	Methanol
$C_2H_3D_3CHBr$[a]	$C_2H_3D_3C^+H$			0.68	0.67	0.69	
$CD_3CHBrCD_3$	$CD_3C^+HCD_3$	0.00[d]	0.25[d]	0.04[d]	0.06[d]	0.03[d]	0.41 (0.74)[c,e]
$CH_3CDBrCH_3$	$CH_3C^+DCH_3$	0.00	0.11	0.00	0.00	0.00	≤0.06 (0.04)[c]
$CH_3CHBrCH_2D$	$CH_3C^+HCH_2D$	0.13	0.11	0.11	0.16	0.13	0.39 (0.33)[c]
CH_3CH_2CHDBr	$CH_3CH_2C^+HD$	0.00	0.13[h]	0.14	0.15	0.15	0.41 (0.55)[c]
$CH_3CH_2CHDNO_2$	$CH_3CH_2C^+CHD$	0.00	0.13[h]	0.13[f]	0.16[g]	*g*	0.43
$CH_3CD_2CH_2Br$	$CH_3CD_2C^+H_2$	∞	0.13[h]	0.15	0.14	0.13	
$CH_3CH_2CD_2Br$	$CH_3CH_2C^+D_2$	0.00	0.33[h]	0.25	0.26	0.27	

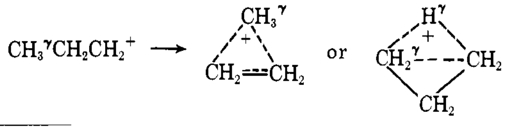
[a] 2-Bromopropane in which three of the six primary H atoms have been statistically replaced by D. [b] $[ND^+]/[NH^+]$ from reaction 3 or 5, unless noted otherwise; deviation ±0.02 for values <0.2, ±10% of the value for higher values. Ionizing electron energy = 11.0 eV. [c] Data from single resonance spectra. [d] $[NH^+]/[ND^+]$; ±0.04 (impurity contribution subtracted). [e] $[CH_4DO^+]/[CH_3D_2O^+]$. [f] Data are for the reaction with CD_3COCD_3. [g] Interference from the reaction $C_3H_6D^+ + CH_3CH_2CHDNO_2 \rightarrow C_3H_6 + C_3H_5D_2O^+$. [h] Assuming isomerization through eq 6; complete scrambling (such as eq 7) should give 0.11 for $C_3H_6D^+$ and 0.27 for $C_3H_5D_2^+$.

***sec*-$C_3H_7^+$ Ions.** If the *sec*-$C_3H_7^+$ ions undergo isomerization so that the hydrogen atoms lose their original positional identity, the rate of proton transfer relative to deuteron transfer from the $CD_3^+CHCD_3$ ion, or of deuteron relative to proton transfer ($[ND^+]/[NH^+]$) from the $CH_3C^+DCH_3$ ion, should be 0.25 and 0.11, respectively, after correction for the isotope effect; if only reaction 3 occurs, both values should be zero. The data for the reactions with acetone, 1-propanol, and propanal show that the extent of isomerization is small (<20%).[26] As will be discussed later, the reactions of methanol and 2-propanol are also consistent with this.[27] We conclude that the *sec*-$C_3H_7^+$ ions of low internal energy are stable in terms of the relatively long times (millisecond half-lives) required for reaction in the icr spectrometer. The data also show that reaction 3 is strongly favored over reaction 4, as predicted.

***n*-$C_3H_7^+$ Ions.** The data for the *n*-$C_3H_7^+$ ions, however, are consistent with nearly complete isomerization before the ion–molecule reaction takes place. The mechanism of eq 5 predicts only D abstraction from $CH_3CD_2C^+H_2$; thus its $[ND^+]/[NH^+]$ value (Table II) shows that at least 80% of the *n*-$C_3H_7^+$ ions have isomerized. The true proportion will obviously be larger if the isomerized product ion can form ND^+.

Isomerization of *n*-$C_3H_7^+$ to *sec*-$C_3H_7^+$ and c-$C_3H_7^+$ could proceed through eq 6 and 7. Although the identity of the proton abstracted from c-$C_3H_7^+$ should depend on the isomer produced, the rapid exchange of H atoms in c-$C_3H_7^+$ [4–6] should make all of the H and D atoms equivalent. $[ND^+]/[NH^+]$ values for $CH_3CD_2C^+H_2$ and $CH_3CH_2C^+D_2$ predicted by eq 7 are both 0.27; the data of Table II are clearly more consistent with the mechanism of eq 6, which predicts values of 0.13 and 0.33, respectively. Isomerization of $CH_3CD_2C^+H_2$ by eq 6 produces $CH_3C^+DCH_2D$, which should give a $[ND^+]/[NH^+]$ value by eq 3 which is identical with that from $CH_3C^+HCH_2D$. This is true within experimental error, and indicates that <3% of the original *n*-$C_3H_7^+$ ions remain to react by eq 5. The results for $CH_3CD_2C^+H_2$ also indicate that the *n*-propyl ions isomerize by eq 7 (or by other pathways involving scrambling, such as *n*-$C_3H_7^+ \rightarrow$ *sec*-$C_3H_7^+ \rightarrow$ *n*-$C_3H_7^+$) only 10 ± 10%[27] of the time.[28] This would predict a value of $[ND^+]/[NH^+] = 0.32$ for $CH_3CH_2C^+D_2$; an isotope effect of 1.8 would account better for the observed value. This altered isotope effect would make the $CH_3CD_2C^+H_2$ results consistent with 20 ± 10%[27] isomerization through eq 7. These relative proportions of 10–20% for *k*(eq 7)/*k*(eq 6) are consistent with the radiolysis results of Ausloos and coworkers.[5b]

$$CH_3CH_2{}^{\beta}CH_2{}^+ \longrightarrow CH_3C^+H^{\beta}CH_2H^{\beta} \qquad (6)$$



(7)

Very similar values result using ions from either the 1-bromo- or 1-nitropropane precursors, supporting the conclusion that the difference in reactivity of these ions found by Kriemler[20] is due to a difference of internal energy, not structure. The data of Table II also indicate that the difference in the reactivity of propyl ions from 1- and 2-halopropanes[4f] arises from energetic, not structural, differences.

No proton transfer was observed to H_2S from the $C_3H_7^+$ ions generated from either $CH_3CHBrCH_3$ or $CH_3CH_2CH_2NO_2$; this is consistent with the *sec*-$C_3H_7^+$ structure, as the reported proton affinities of H_2S and propene are 170[29] and 179 ±2 kcal/mol, respectively.[30] The heat of formation of *n*-$C_3H_7^+$ is 16 kcal/mol higher than that of *sec*-$C_3H_7^+$, so that 16 kcal/mol less energy should be required to abstract a proton from *n*-$C_3H_7^+$, making its reaction with H_2S quite favorable. Failure to observe this reaction with the propyl ions from $CH_3CH_2CH_2NO_2$ gives further evidence of the ready isomerization by eq 6.

Reaction with Methanol (Eq 8). The reaction of CH_3OH with $CD_3C^+HCD_3$ yields more $CH_3O^+D_2$ than

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cation, J. L. Beauchamp, March 1971). As will be discussed, the results for $CH_3CH_2CD_2^+$ are consistent with $k_H/k_D = 1.8$.

(26) Isomerization to a cyclopropyl structure in which the original secondary hydrogen occupies a unique (*e.g.*, bridging) position is highly unlikely on the basis of the known facile interchange of hydrogens in the c-$C_3H_7^+$ structure.[5,6] Further, this would demand that this unique hydrogen is *less* reactive than the other hydrogen atoms of the ion.

(27) Proton abstraction by methanol and 2-propanol is accompanied by exchange between the hydroxyl hydrogen and the primary hydrogens of *sec*-$C_3H_7^+$ (*vide infra*). If this occurs to an appreciable extent in the other proton abstraction reactions, it would also lead to isotopic scrambling of the *sec*-propyl ions, making the true extent of isomerization even less.

(28) Previous evidence could be interpreted[12] to indicate that part of the *sec*-$C_3H_7^+$ ions formed from *n*-C_3H_7Br arises from initial isomerization of the molecular ion, *n*-$C_3H_7Br^{\cdot+} \rightarrow$ *sec*-$C_3H_7Br^{\cdot+}$. To be consistent with these data, such isomerization must also be accompanied by minimal scrambling.

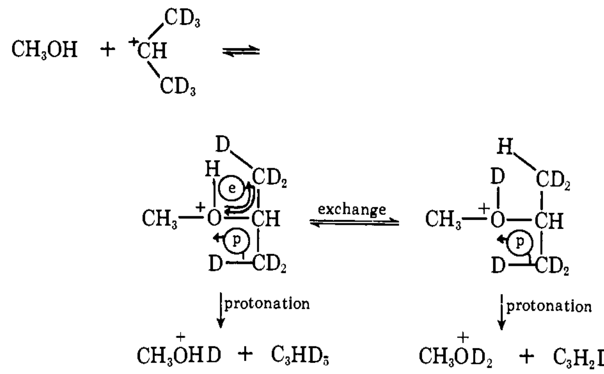
(29) M. Haney and J. L. Franklin, *J. Phys. Chem.*, 73, 4328 (1969).

(30) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1967.

$$sec\text{-}C_3H_7^+ + CH_3OH \rightleftharpoons CH_3CH{=}CH_2 + CH_3O^+H_2 \quad (8)$$

CH_3O^+HD (Table II); exchange must be taking place between the propyl D atoms and the hydroxyl H (no $CH_2D_3O^+$ was observed). The unusually large $[ND^+]/[NH^+]$ ratios found for the other methanol reactions are also consistent with an analogous exchange. The $CH_3C^+DCH_3$ shows little D exchange, however, supporting the conclusion that there is little (<20%) isomerization of $sec\text{-}C_3H_7^+$.

An examination of the methanol–propene system shows negative double resonance signals corresponding to the occurrence of eq 8 in both directions. This is consistent with the near equality of the reported proton affinities of methanol (180 kcal/mol[19]) and propene (179 ± 2 kcal/mol[30]) and suggests that the collision complex has a sufficient lifetime to permit the exchange to take place (eq 9). In support of this $C_3H_3D_4^+$ and



(9)

$C_3H_2D_5^+$ are also observed in the reaction of CH_3OH and $CD_3CHBrCD_3$.

The exchange mechanism is shown as a four-center unimolecular reaction; thus the reaction order for the formation of either CH_3O^+HD or $CH_3O^+D_2$ in eq 9 should be the same. Figure 1 shows that the dependence on the pressure of methanol is nearly identical for the reactions leading to CH_3O^+HD and to $CH_3O^+D_2$.

Table III. Effect of Ionizing Electron Energy on $[CH_3O^+HD]/[CH_3O^+D_2]$ from the Reaction of CH_3OH and $CD_3C^+HCD_3$ Produced from $CD_3CHBrCD_3$

Electron energy, eV	Double resonance	Single resonance
11.0	0.41 ± 0.03	0.74 ± 0.03
12.0	0.41 ± 0.03	0.82 ± 0.03
20		1.12 ± 0.02
40	0.81 ± 0.10	
50	0.95 ± 0.10	1.54 ± 0.02

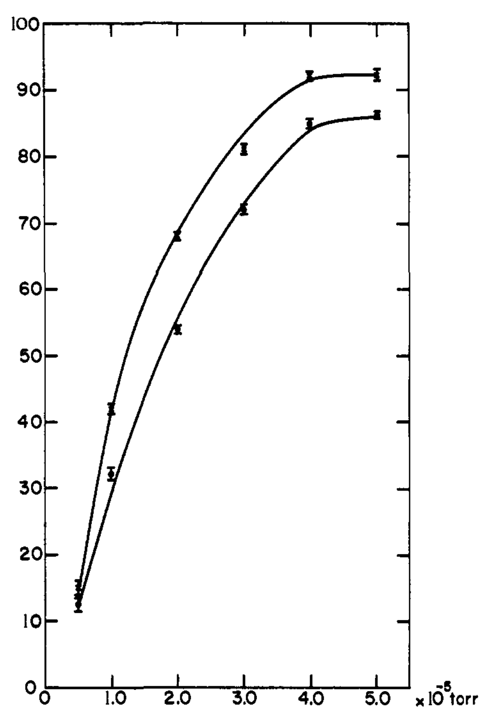


Figure 1. The dependence of single-resonance product ion abundance on the pressure of methanol for the reactions (●) $CD_3C^+HCD_3 + CH_3OH \rightarrow CH_3ODH^+$ and (X) $CD_3C^+HCD_3 + CH_3OH \rightarrow CH_3OD_2^+$.

The $[CH_3O^+HD]/(CH_3O^+D_2]$ ratio increases with increasing electron energy (Table III), indicating that the protonation reaction is favored over the exchange reaction with increasing ion internal energy. This is consistent with the postulation of eq 9 that the exchange reaction has more stringent steric requirements (a tighter activated complex[13]). The close agreement of the $[CH_3O^+HD]/[CH_3O^+D_2]$ (or $[CH_3O^+HD]/[CH_3O^+H_2]$) values of Table II with that of 0.40 predicted for the equilibration of 1 H and 6 D (or 1 D and 6 H) atoms before decomposition is probably fortuitous. Although the value of $[CH_3O^+HD]/[CH_3O^+D_2]$ was found to be the same (0.41) within experimental error for double resonance irradiating oscillator power levels of 0.010–0.048 V/cm, an abundance ratio of 0.76 ± 0.05 was obtained by increasing this to 0.26 V/cm. This approaches "ion ejection"[31] conditions, so that this value should be a more reliable measurement of the actual ion concentrations. This value is confirmed by one of 0.82 ± 0.03 from a single resonance determination under the same conditions (ionizing electron energy = 12.0 eV); double resonance signals indicative of alternative reaction pathways to CH_3O^+HD and $CH_3O^+D_2$ could not be found.

Lampe, Franklin, and Field have suggested[32] that whenever the reaction complex formed in an ion–molecule reaction can be written as a stable ionic species, products of the reaction should resemble the products of the unimolecular decomposition of that species, if the species are prepared with comparable internal energies. As a further test of the mechanism depicted by eq 9, the proposed intermediate ionic species was prepared independently by the protonation of $CH_3OCH(CD_3)_2$. The single resonance icr spectrum at 25-eV electron energy of this compound exhibited an increase in the abundances of the *m/e* 35 and 48 peaks (presumably $CH_3OD_2^+$ and $C_3H_2D_5^+$) in increasing the pressure from 3 × 10^{-7} to 1 × 10^{-5} Torr. Unfortunately, the origin of these ions could not be established by double resonance experiments. At 17 eV the *m/e* 35 peak from a 1.0 × 10^{-5} Torr sample of $CH_3OCH(CD_3)_2$ was barely observable; addition of 1.0 × 10^{-5} Torr C_2H_5I to provide $C_2H_5^+$ and $C_2H_5I^+$ as protonating agents gave [*m/e* 34]/[*m/e* 35] = 0.76 ± 0.10, but again the origin of the CH_3O^+HD and $CH_3O^+D_2$ could not be

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(31) J. M. S. Henis, *J. Chem. Phys.*, **52**, 282 (1970).

(32) F. W. Lampe, J. L. Franklin, and F. H. Field, *Progr. React. Kinet.*, **1**, 67 (1961).

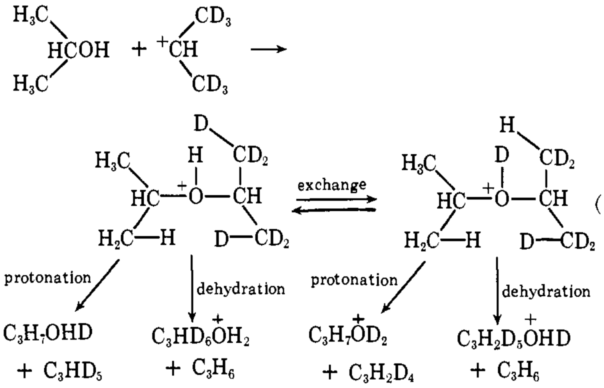
Table IV. Double Resonance Signals from the Reaction of Labeled Propyl Ions with 2-Propanol at 11 eV

Ion precursor	Reaction			Relative abundance
$CD_3CHBrCD_3$	$CD_3C^+HCD_3 + CH_3CHOHCH_3$	→	$CH_3CH(O^+H_2)CH_3$	0.04
		→	$CH_3CH(O^+HD)CH_3$	0.70
		→	$CH_3CH(O^+D_2)CH_3$	0.10
		→	$CD_3CH(O^+H_2)CD_3$	0.17
		→	$CD_3CH(O^+HD)CHD_2$	
$CH_3CDBrCH_3$	$CH_3C^+DCH_3 + CH_3CHOHCH_3$	→	$CH_3CH(O^+H_2)CH_3$	0.84
		→	$CH_3CD(O^+H_2)CH_3$	0.16
$CH_3CHBrCH_2D$	$CH_3C^+HCH_2D + CD_3CHOHCD_3$	→	$CD_3CH(O^+H_2)CD_3$	0.90
		→	$CH_3CH(O^+HD)CH_2D$	0.10[a]
$CH_3CH_2CHDNO_2$	$C_3H_6D^+ + CD_3CHOHCD_3$	→	$CD_3CH(O^+H_2)CD_3$	0.83
		→	$CH_3CH(O^+HD)CH_2D$	0.17

[a] Deviation ±0.07; other values *ca.* ± 0.03.

established by double resonance experiments. Similar efforts to investigate the ion origins using protonation with $CH_3CH{=}O^+H$ from 2-propanol and $C_2H_3^+$ from C_2H_4 were also unsuccessful.

Reaction with 2-Propanol. Proton abstraction from $CD_3C^+HCD_3$ by 2-propanol (Table IV) is low, again indicating little isomerization of *sec*-$C_3H_7^+$ before reaction. However, the reaction of this and other *sec*-$C_3H_7^+$ ions with 2-propanol also exhibits products corresponding to dehydration of the alcohol by the ion (Table IV). A mechanistic scheme similar to that of the CH_3OH–$C_3H_7^+$ reaction (eq 9) is possible, wherein 2-propanol produces a symmetrical intermediate (eq 10). From such a protonated diisopropyl

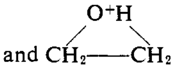


(10)

ether intermediate the two possible losses of propene should be equivalent (barring isotope effects), while the data indicate that protonation is several times as important as dehydration. Thus the intermediate formed in the reaction with 2-propanol is apparently of shorter half-life than that formed from methanol.

Within the limits of experimental error the propyl ion from $CH_3CH_2CHDNO_2$ exhibits the same proportion of protonation and dehydration reactions as the *sec*-$C_3H_7^+$ ions, again indicating that initially formed *n*-$C_3H_7^+$ ions isomerize to *sec*-$C_3H_7^+$ ions.

It is interesting to note that Beauchamp[33] has reported dehydrations of 2-propanol by ions such as

$CH_3CH{=}O^+H$ and

$\overset{O^+H}{CH_2{-}CH_2}$

which contain a "labile proton on oxygen." Thus *sec*-$C_3H_7^+$ represents another type of ion capable of abstracting H_2O.

Protonated Cyclopropane. Scrambling of the hydrogen atoms in c-$C_3H_7^+$ should be rapid on the time scale of icr experiments, obviating the usefulness of labeling as a structural probe. To compare the reactivities of c-$C_3H_7^+$ with those of *sec*- and *n*-$C_3H_7^+$ described above, c-$C_3H_7^+$ was generated by the protonation of cyclopropane.

Determination of the proton affinity (PA) of cyclopropane should provide a measurement of the heat of formation (ΔH_f) of c-$C_3H_7^+$ from the relationship of eq 11.[17] No double resonance signals could be detected corresponding to the protonation of H_2S (PA = 170 kcal/mol)[29] by the $C_3H_7^+$ ions formed in a mixture of H_2S and cyclopropane. A mixture of cyclopropane and methanol gave negative double resonance signals corresponding both to the formation of $C_3H_7^+$ from $CH_3O^+H_2$ and to the formation of $CH_3O^+H_2$ from $C_3H_7^+$. This indicates that the proton affinity of these $C_3H_7^+$ ions is nearly the same as that of methanol, 180 kcal/mol,[19] which corresponds to $\Delta H_f(\text{c-}C_3H_7^+)$ = 199 kcal/mol.[34] However, this proton transfer in both directions duplicates the unique behavior of the *sec*-$C_3H_7^+$ and $CH_3O^+H_2$ ions from methanol and propene, and strongly suggests that the reacting $C_3H_7^+$ ions formed by the protonation of cyclopropane have actually isomerized to the *sec*-$C_3H_7^+$ structure. The alternative explanation of identical proton affinities also indicates that c-$C_3H_7^+$ is of higher energy than *sec*-$C_3H_7^+$ (ΔH_f = 192 kcal/mol).[3f] This conclusion that *sec*-$C_3H_7^+$ represents the lowest energy form of the propyl ion is consistent with the observation (noted both above and in radiolysis studies)[5c] that the isomerization of *n*-$C_3H_7^+$ yields mainly *sec*-$C_3H_7^+$, and with the latest theoretical calculations.[7f]

$$PA(M) = \Delta H_f(M) + \Delta H_f(H^+) - \Delta H_f(MH^+) \quad (11)$$

Experimental Section

The icr spectrometer used in this study was a standard Varian V-5903 instrument with a dual inlet sample introduction system. The experimental techniques used were similar to those previously described.[17-19] Pertinent icr spectra are given in ref 2a. Unless otherwise indicated, the pressure of the species acting as the source of the propyl ion was nominally 2.0 × 10^{-5} Torr and that of the neutral reagent molecule was 1.0 × 10^{-5} Torr; pressures were determined from the ion pump meter current. An electron energy of 11.0 eV, as measured directly with a voltmeter, was used unless otherwise specified. The filament emission current was never allowed to exceed 1.0 μA, nor the total ion current 1.0 × 10^{-11} A.

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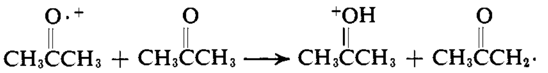
(33) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969).

(34) Based on ΔH_f(cyclopropane) = 12.7 kcal/mol and $\Delta H_f(H^+)$ = 366 kcal/mol.[3b]

Drift voltages of 0.75 V across both the source and analyzer regions were employed throughout.

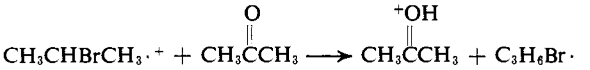
Single resonance spectra were recorded by magnetic field modulation with an amplitude of 20 G. In the pulsed double resonance experiments, an irradiating field of 0.035 V cm^{-1} was applied to the analyzer region of the cell to obtain the given data. However, all of the signals reported were examined down to 0.010 V cm^{-1} to ensure that they were not artifacts. The ratios observed in Table II did not change appreciably with this change of irradiating field.

No ion–molecule reactions were observed at 11.0 eV when pure propyl bromides were admitted to the instrument. However, the neutral molecules (N) used to accept protons from the propyl ions all formed NH$^+$ species when admitted singly to the instrument, for example, eq 12. Other interfering reactions were transfer of



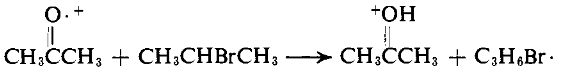
$$\mathrm{CH_3\overset{\overset{O\cdot^{+}}{\|}}{C}CH_3 + CH_3\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{^{+}OH}{\|}}{C}CH_3 + CH_3\overset{\overset{O}{\|}}{C}CH_2\cdot} \quad (12)$$

protons from the molecular ions of the bromides to the neutral reagents (eq 13) and abstractions of hydrogen atoms from neutral



$$\mathrm{CH_3CHBrCH_3\cdot^{+} + CH_3\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow CH_3\overset{\overset{^{+}OH}{\|}}{C}CH_3 + C_3H_6Br\cdot} \quad (13)$$

bromides (eq 14). At electron energies above 11.0 eV in the propyl



$$\mathrm{CH_3\overset{\overset{O\cdot^{+}}{\|}}{C}CH_3 + CH_3CHBrCH_3 \longrightarrow CH_3\overset{\overset{^{+}OH}{\|}}{C}CH_3 + C_3H_6Br\cdot} \quad (14)$$

bromides and 13.0 eV in 1-nitropropane, species other than propyl and molecular ions were present which also underwent proton transfer to the reagent molecules. All reported data are corrected for ^{13}C contributions. No attempt was made to correct for instrumental effects.[17,25]

Metastable ion intensities were recorded by the Major modification of the Barber–Elliott defocusing technique at 70 and 30 eV on an Hitachi RMU-7 mass spectrometer.[35]

Preparation of Materials.[2a] 1-Propanol-*1*-d_1 was prepared by the reduction of propanal with LiAlD$_4$ (Merck Sharp and Dohme, Ltd., minimum 99 atom % D). This was then converted to 1-bromopropane-*1*-d_1 (98% d_1) by slow distillation from an HBr—H$_2$SO$_4$ mixture. Reduction of acetic anhydride with LiAlD$_4$ in dry diglyme gave ethanol-*1,1*-d_2, which was converted to 1-bromoethane-*1,1*-d_2 in a similar fashion. Reaction of the corresponding Grignard reagent with gaseous CH$_2$O generated from paraformaldehyde yielded 1-propanol-*2,2*-d_2; 1-propanol-*1,1*-d_2 was prepared by LiAlD$_4$ reduction of propionic acid; both were converted to the corresponding bromides with PBr$_3$. 2-Bromopropane-*2*-d_1 (98% d_1) was prepared by the reduction of acetone with LiAlD$_4$ followed by slow distillation of the resulting 2-propanol-*2*-d_1 from 49% HBr. 2-Propanol-*1,1,1,3,3,3*-d_6 and -d_7, and 2-bromopropane-*1,1,1,3,3,3*-d_6 (95% d_6) and -d_7 were prepared from acetone-d_6 in similar fashion. 2-Bromopropane-*1*-d_1 (98% d_1) was prepared by the reduction of 1,2-epoxypropane with lithium aluminum deuteride[36] and conversion of the alcohol to the bromide. 1-Nitropropane-*1*-d_1 (96% d_1) was prepared from 1-bromopropane-*1*-d_1 and silver nitrate.[37] (CD$_3$)$_2$CHOCH$_3$ was prepared from 2-bromopropane-*1,1,1,3,3,3*-d_6 and methanol by the Williamson synthesis. All of these compounds were purified by gas chromatography prior to introduction into the spectrometer. The isotopic purities given were derived from the mass spectra of the compounds obtained on the icr spectrometer.

The acetone, propanol, methanol, and 1-propanol used were Mallinckrodt analytical reagent grade. These were used without further purification as no impurities were detected by either gas chromatography or mass spectrometry. The hydrogen sulfide and ammonia employed were Fisher high purity grade and were used without further purification. The ethylene, propylene, and cyclopropane used were from Matheson. All liquid samples were degassed by freeze–pump–thaw cycles on the instrument inlet.

Acknowledgment. The authors are indebted to Drs. M. L. Gross and T. Wachs for stimulating discussions. Dr. Wachs also synthesized some of the labeled compounds used in this study. Financial support was provided by the National Institutes of Health, Grant GM-16575.

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(35) F. W. McLafferty, J. Okamoto, H. Tsuyama, T. Nakajima, and H. W. Major, *Org. Mass. Spectrom.*, **2**, 751 (1969).

(36) We are indebted to Professor R. A. Caldwell for suggesting this synthesis and for providing the 1,2-epoxypropane.

(37) N. Kornblum, B. Taub, and H. E. Ungnade, *J. Amer. Chem. Soc.*, **76**, 3209 (1954).