Dehydration Reactions Involving Major Rearrangements. Comparison of Ordinary Mass Spectral Fragmentation to Ion–Molecule Reaction Processes

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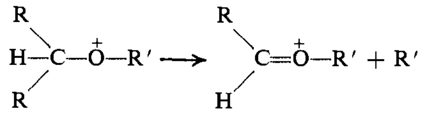
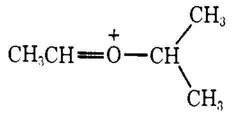
Abstract: Most prominent among the ionic species generated by mass spectral fragmentation processes of aliphatic ethers are α-cleavage products. These fragment ions further decompose by two pathways. The first involves the widely studied and facile rearrangement loss of an alkene to yield a protonated aldehyde or ketone. The second involves a more extensive rearrangement resulting in loss of water. Through the use of ion–molecule reactions it is possible to generate precursor ions, identical with those derived by α-cleavage processes from aliphatic ethers, with internal energy sufficient to observe and study only the thermodynamically more favored dehydration process. The low internal energy mitigates against scrambling of hydrogen, permitting an assessment of the mechanism of the dehydration reaction utilizing labeled reactants.

Among the products of fragmentation of ethers on electron impact, one of the most important is that caused by α cleavage to form a "new bond"[2] to oxygen.



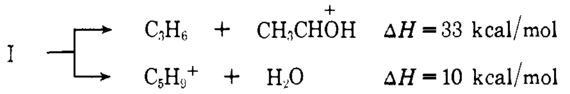
$$\mathrm{H{-}C(R)(R){-}\overset{+}{O}{-}R' \longrightarrow (R)(H)C{=}\overset{+}{O}{-}R' + R'} \qquad (1)$$

This product itself can undergo further decomposition if it has enough internal energy.[3–5] Since it is an even-electron ion, the favored decompositions are to even-electron ions;[2] in the case of 2-propyl ether, eq 2 and 3[6] are the observed processes which fit this rule.



$$\mathrm{CH_3CH{=}\overset{+}{O}{-}CH(CH_3)_2}$$

I



$$\mathrm{I} \longrightarrow \mathrm{C_3H_6} + \mathrm{CH_3\overset{+}{C}HOH} \qquad \Delta H = 33\ \mathrm{kcal/mol} \qquad (2)$$

$$\mathrm{I} \longrightarrow \mathrm{C_5H_9^+} + \mathrm{H_2O} \qquad \Delta H = 10\ \mathrm{kcal/mol} \qquad (3)$$

Both decompositions 2 and 3 are endothermic. When their precursor is generated from 2-propyl ether by electron impact with sufficiently high internal excitation, process 2 apparently dominates, involving a simpler and kinetically more favorable rearrangement. The data of Smith and Williams[3] make this entirely clear (Table I). Of particular interest is the ratio of products for processes 2 and 3 determined for precursors of relatively low internal energies from metastable ion intensities in the first field-free region of a double-focusing instrument. The process by which loss of water occurs in reaction 3 has received the attention of several investigators; no definitive evidence has been presented for the mechanism of this rearrangement process.

Table I. Variation with Electron Energy of the Relative Abundance of $C_2H_2O^+$ and $C_5H_9{}^+$ in the Mass Spectrum of 2-Propyl Ether[a]

Electron energy, eV	$C_2H_5O^+/C_5H_9{}^+$
70	32
16	8.4
14	1.9
b	0.034

[a] Data from ref 3. [b] Ratio of metastable ion intensities observed in first field-free region of double-focusing instrument. Electron energy unspecified but presumably 70 eV.

The gas-phase ion chemistry of 2-propanol has been reported as part of a recent study of $C_2H_5O^+$ isomeric ion structures. The ion chemistry of 2-propanol is consistent with the formulation of the *m/e* 45 ion as protonated acetaldehyde (eq 4). Among the products

$$\mathrm{(CH_3)_2CHOH + e \longrightarrow CH_3CHOH^+ + CH_3 + 2e} \qquad (4)$$

formed from the reactions 5–8 of CH_3CHOH^+ with 2-propanol are ions of *m/e* 87 ($C_5H_{11}O^+$) and 69 ($C_5H_9{}^+$), for which Beauchamp and Dunbar[7] suggested the reactions 5 and 6. It was further reasoned in analogy with process 3 that retention of internal excitation in the

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[1] (a) Research Fellow of the Alfred P. Sloan Foundation, 1969–1971; (b) Research Fellow of the Alfred P. Sloan Foundation, 1968–1970; (c) Contribution No. 4204.

[2] F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 100.

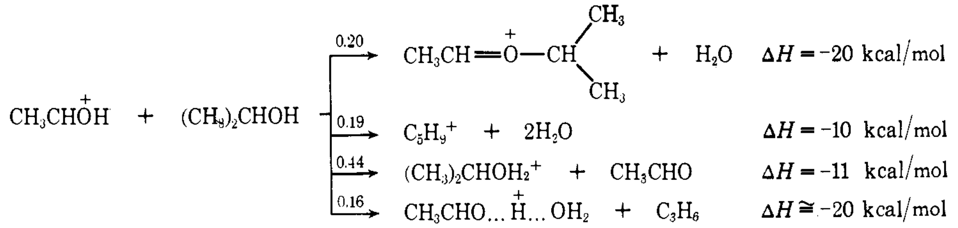
[3] G. A. Smith and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 5254 (1969).

[4] C. W. Tsang and A. G. Harrison, *Org. Mass Spectrom.*, **3**, 647 (1970).

[5] W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, **89**, 6164 (1967).

[6] Ionic heats of formation were taken from "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. Values utilized (kcal/mol) are: CH_3CHOH^+, 143; $CH_3CHOCH(CH_3)_2{}^+$, 115 (author's estimate based on additivity relations); $C_5H_9{}^+$, 183.

[7] J. L. Beauchamp and R. C. Dunbar, *J. Amer. Chem. Soc.*, **92**, 1477 (1970).



$$\mathrm{CH_3CH\overset{+}{O}H} + \mathrm{(CH_3)_2CHOH} \xrightarrow{0.20} \mathrm{CH_3CH{=}\overset{+}{O}{-}CH(CH_3)_2} + \mathrm{H_2O} \quad \Delta H = -20\ \mathrm{kcal/mol} \qquad (5)$$

$$\xrightarrow{0.19} \mathrm{C_5H_9^+} + 2\mathrm{H_2O} \quad \Delta H = -10\ \mathrm{kcal/mol} \qquad (6)$$

$$\xrightarrow{0.44} \mathrm{(CH_3)_2CHOH_2^+} + \mathrm{CH_3CHO} \quad \Delta H = -11\ \mathrm{kcal/mol} \qquad (7)$$

$$\xrightarrow{0.16} \mathrm{CH_3CHO\ldots\overset{+}{H}\ldots OH_2} + \mathrm{C_3H_6} \quad \Delta H \cong -20\ \mathrm{kcal/mol} \qquad (8)$$

$$\begin{array}{lccccccccc}
 & \mathrm{CD_3CHOH^+} & + & \mathrm{CD_3CHOHCD_3} & \longrightarrow & \mathrm{HOH} & + & \mathrm{C_5H_2D_{11}O^+} \longrightarrow & \mathrm{C_5H_2D_7^+} & + \mathrm{DOD} \\
m/e & 48 & & & & & & 96 & 76 & \\
\text{mass} & & & 66 & & 18 & & & & 20
\end{array} \qquad (9)$$

$$\begin{array}{lccccccccc}
 & \mathrm{CH_3CDOH^+} & + & \mathrm{CH_3CDOHCH_3} & \longrightarrow & \mathrm{HOH} & + & \mathrm{C_5H_9D_2O^+} \longrightarrow & \mathrm{C_5H_7D_2^+} & + \mathrm{HOH} \\
m/e & 46 & & & & & & 89 & 71 & \\
\text{mass} & & & 61 & & 18 & & & & 18
\end{array} \qquad (10)$$

product of reaction 5 led to further decomposition, yielding the observed $C_5H_9^+$ product. This conjectured sequence of events, if correct, can be studied to advantage in understanding the mechanism by which dehydration process 3 occurs. Reaction 5 yields $C_5H_{11}O^+$ with internal excitation sufficiently low to exclude the more facile but energetically unfavorable rearrangement process 2. Indeed the occurrence of this reaction would result in the overall removal of water from 2-propanol, a process endothermic by 13 kcal/mol.

We therefore undertook a reexamination of the ion chemistry of 2-propanol using labeled reactants in order to interpret the mechanism of the reactions which result in the formation of the $C_5H_{11}O^+$ and $C_5H_9^+$ products. We thought it of particular interest to explore the formation of these species as a commentary on the unimolecular reactivity of ethers on electron impact.

Results and Discussion

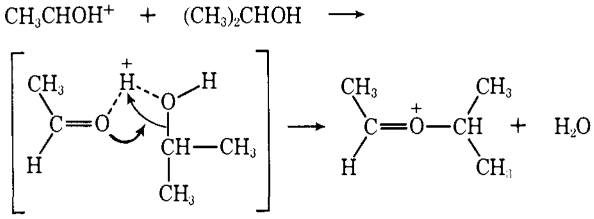
In order to unravel the mechanism of formation of the single and double dehydration products (reactions 5 and 6), we have studied several deuterium-labeled 2-propanols. The ion with only one water molecule expelled, *m/e* 87 in the unlabeled compound, is shifted to *m/e* 94 (6%), 95 (9%), and 96 (85%) in the spectrum of 2-propanol-*1,1,1,3,3,3-d*$_6$. The ion with two molecules of water expelled is shifted to *m/e* 75 (15%) and 76 (85%). Double-resonance studies on *m/e* 76 reveal its origin from *m/e* 48 and, when N_2 is admitted as a neutral diluent gas,[8] from the collision-induced decomposition of *m/e* 96. These observations are consistent with eq 9. The major doubly dehydrated ion arises at least in part from the major singly dehydrated ion.

In the spectrum of 2-propanol-*2-d*, the hydrocarbon ion appears at *m/e* 70 (13%) and 71 (87%); the singly dehydrated ion is found at *m/e* 88 (11%) and 89 (89%). Thus, in the major reaction forming $C_5H_9^+$, the H atom bound to C-2 of 2-propanol is not lost from either the reactant molecule or the reactant ion of eq 1. Double-resonance studies of *m/e* 71 indicate formation from *m/e* 46 and, in the presence of N_2 as a collision gas, by the collision-induced decomposition of *m/e* 89. These observations are consistent with eq 10, and the combination of data from eq 9 and 10 requires that the loss of two water molecules involve the two hydroxyl hydrogen atoms as well as two hydrogen atoms from the methyl groups of the original propanol molecules. Since two hydroxyl hydrogens are involved, both the ionic fragment and the neutral 2-propanol contribute their hydroxyl hydrogens to the water molecules, but we cannot yet say whether the source of methyl hydrogens is the neutral C_3H_8O molecule, the $C_2H_5O^+$ ion, or both.

In the icr spectrum of 2-propanol-*1,1,1,2-d*$_4$, the protonated acetaldehyde ion is divided between *m/e* 46 (45%) and 49 (55%), corresponding to the species CH_3CDOH^+ and CD_3CDOH^+. Subsequent reaction of these species with 2-propanol-*1,1,1,2-d*$_4$ results in the formation of ions at *m/e* 72–77 (summarized in Table II), owing to possible loss of HOH, HOD, or DOD. Reactions leading to the predominant formation of *m/e* 73 and 76 are favored, suggesting the operation of a highly specific mechanism for the loss of two molecules of water. In keeping with this specificity, the singly dehydrated ion appears as indicated in Table III predominately at *m/e* 92 and 95.

If one assumes that the *m/e* 45 ion (observed in the undeuterated alcohol) has the protonated acetaldehyde form,[7] then the reaction of *m/e* 45 with neutral 2-propanol can follow any of several courses.

The proton affinities of acetaldehyde and 2-propanol are 182 and 193 kcal/mol, respectively. Hence the transfer of the labile proton from protonated acetaldehyde to the more basic site in the formation of the collision complex would be expected to precede the nucleophilic displacement reaction detailed in eq 11. This mechanism is consistent with the generalized behavior detailed recently by one of us for nucleophilic displacement reactions.[9] Equation 11 is analogous to the condensation reaction of protonated alcohol dimers[10] and protonated heterodimers with hydrogen bonding between carbonyl oxygen and alcohol oxygen[11] in that both hydrogen atoms originate from hydroxyl protons. This mechanism has been suggested by one of us before,[7] and is consistent with all of the labeling results pre-



(11)

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[8] F. Kaplan, *J. Amer. Chem. Soc.*, 90, 4483 (1968).

[9] D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *ibid.*, 92, 7484 (1970).

[10] (a) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, 45, 1062 (1966); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, 89, 4569 (1967) (c) J. M. S. Henis, *ibid.*, 90, 844 (1968).

[11] T. A. Lehman, T. A. Elwood, M. K. Hoffman, and M. M. Bursey, *J. Chem. Soc. B*, 1717 (1970).

Table II. Isotopic Distribution of $C_5H_9^+$ Ions in 2-Propanol-*1,1,1,2-d*$_4$

m/e	Observed ion intensity	Possible origins	Calcd for eq 14	Calcd for eq 15	Calcd for scrambling[a]
72	0.060 ± 0.003	*m/e* 110 − HOH, DOD *m/e* 110 − DOH, DOH	0.000	0.225	0.15
73	0.31 ± 0.002	*m/e* 110 − HOH, HOD *m/e* 113 − DOD, DOD	0.34	0.00	0.24
74	0.093 ± 0.002	*m/e* 110 − HOH, HOH *m/e* 113 − HOD, HOH	0.11	0.225	0.26
75	0.144 ± 0.002	*m/e* 113 − HOH, DOD *m/e* 113 − HOD, HOD	0.14	0.275	0.19
76	0.38 ± 0.01	*m/e* 113 − HOD, HOH	0.41	0.00	0.08
77	0.039 ± 0.003	*m/e* 113 − HOH, HOH	0.00	0.275	0.01

[a] Complete scrambling of all 13 hydrogen atoms in the collision complex. Also *m/e* 70 = 0.01, *m/e* 71 = 0.06 for scrambling, but these were not observed.

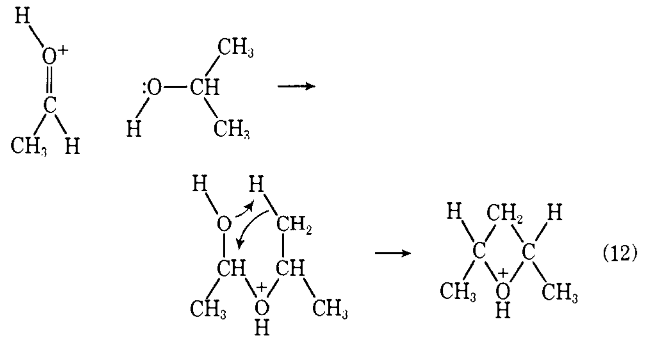
Table III. Isotopic Distribution of $C_6H_{11}O^+$ Ions in 2-Propanol-*1,1,1,2-d*$_4$

m/e	Ion intensity	Possible origins	Calcd for eq 11	Calcd for eq 12	Calcd for scrambling[a]
90	0.00	*m/e* 110 − DOD	0.00	0.00	0.07
91	0.072 ± 0.004	*m/e* 110 − HOD	0.000	0.225	0.21
92	0.34 ± 0.01	*m/e* 110 − HOH	0.45	0.225	0.17
93	0.052 ± 0.003	*m/e* 113 − DOD	0.000	0.000	0.21
94	0.084 ± 0.005	*m/e* 113 − HOD	0.000	0.275	0.26
95	0.44 ± 0.01	*m/e* 113 − HOH	0.55	0.275	0.08

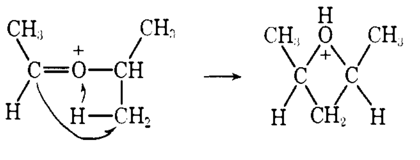
[a] Complete scrambling of all 13 hydrogens in the collision complex.

sented so far as the mechanism for the production of the major singly dehydrated ion. The structure of the product is similar to that proposed for the (M − 15) peak of 2-propanol ether.[7]

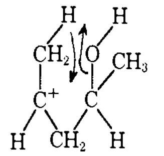
Alternatively, a mechanism assuming no proton transfer can be written which calls for a six-membered cyclic activated complex for the first dehydration (eq 12). In it CH_3CHOH^+ would be subject to nucleophilic attack at the substituted carbonium ion center. This mechanism requires that one of the hydrogen atoms lost in the water molecule originate from a methyl carbon. The distribution of ion intensities in the d_6 alcohol suggests that the maximum extent to which this mechanism can operate is about 9%. A further example is afforded by the d_4 alcohol, in which the four-center mechanism predicts single-dehydration peaks at *m/e* 92 and 95, and the six-center mechanism predicts peaks at *m/e* 91, 92, 94, and 95. Repeated scans of the spectrum of the d_4 compound in this region gave the labeling distribution shown in Table II. The calculated values are based on the distribution of primary ions reported above (45:55) and an absence of an isotope effect. In addition to the expected peaks, there is again a peak at *m/e* 93, which points to the intervention of yet another mechanism and which we ascribe to scrambling to avoid proliferation of hypotheses. Again, although peaks expected for the six-membered complex are present, it is clear that the four-membered complex predominates and the reaction is similar to other condensation reactions.


(12)

The second dehydration step requires the formation of a carbon–carbon bond, as in the second step of eq 12, where a protonated dimethyloxetane is formed.[12] This oxetane structure can also be formed from the product of eq 8 by a cyclization process.


(13)

If this strained ion loses water by first cleaving on either side of the oxygen atom and then passing through a six-membered complex (eq 14), a $C_5H_9^+$ ion is formed with


$\longrightarrow C_5H_9^+ + HOH$ (14)

an isotopic distribution in accord with predicted results for the protonated oxetane structure (Table II), with the same assumptions as before. It should be noted that the hydrogen transferred to oxygen in eq 13 is the same as that transferred to oxygen in eq 12; consequently, after the second loss of water, the mechanisms of loss of the first water molecule are indistinguishable.

Again, one can consider the simultaneous operation of a 1,2 elimination, which would have the superficially

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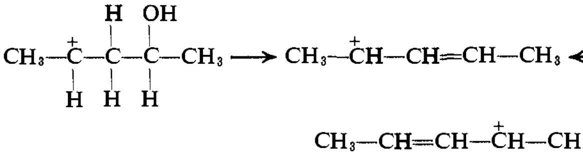
(12) When trimethylene oxide is protonated in a highly exothermic process, it decomposes to lose H_2O. Presumably this involves ring opening and 1,2 elimination: J. L. Beauchamp, Ph.D. dissertation, Harvard University, 1967.

attractive features of producing a stable dimethylallyl cation directly (eq 15) and of explaining the presence of



$$\mathrm{CH_3{-}\overset{+}{C}H{-}CH(H){-}CH(OH){-}CH_3 \longrightarrow CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}CH_3 \longleftrightarrow CH_3{-}CH{=}CH{-}\overset{+}{C}H{-}CH_3} \quad (15)$$

m/e 72 and 77 cations. On the other hand, the experimental results can be fit nearly as well by a combination of production through eq 14 and scrambling as by a combination of 85% production through eq 14 and 15% production through eq 15. Consequently, about 85% of the reaction is consistent with the mechanism proposed in eq 11.

A further check on the operation of the oxetane mechanism was made with the analysis of $C_5H_9^+$ ion intensities produced in the spectrum of an approximately 1:1 mixture of ordinary 2-propanol and 2-propanol-*1,1,1,3,3,3*-d_6. In this spectrum, peaks appear at all the masses from *m/e* 69 to 76 in the ratio shown in Table IV.

Table IV. Isotopic Distribution of $C_5H_9^+$ Ions in a 1:1 Mixture of $CH_3CHOHCH_3$ and $CD_3CHOHCD_3$

m/e	Obsd intensity	Calcd for eq 11	Calcd for scrambling	*m/e*, precursor Calcd	*m/e*, precursor Obsd
69	0.24 ± 0.003	0.250	0.26	45	45
70	0.035 ± 0.002	0.000	0.04		
71	0.11 ± 0.002	0.125	0.12	48	48
72	0.18 ± 0.003	0.125	0.14	48	48
73	0.13 ± 0.003	0.125	0.09	45	45
74	0.10 ± 0.003	0.125	0.07	45	45
75	0.046 ± 0.004	0.000	0.02		
76	0.17 ± 0.003	0.250	0.25	48	48

Again, some scrambling is occurring; none of the mechanisms predicts the appearance of *m/e* 70 or 75. The calculated distribution for the operation of eq 11 and 14 is in reasonable agreement with the results, but the specific mechanism does not give calculated results very different from those for scrambling in the activated complex. Here again calculated results are based on the assumption of no isotope effect, and also on the assumption that the mole ratio of undeuterated and deuterated reactants is 1.00. The results are not so useful as those of Tables II and III, but they cannot be taken as evidence against the mechanism.

Double-resonance studies on the $C_5H_9^+$ ions in the d_4 alcohol (Table V) and the mixture of d_0 and d_6 alcohols (Table IV) confirm the origin of these ions from the appropriate protonated acetaldehyde species as eq 14 predicts. Experiments to determine the $C_5H_{11}O^+$ ions giving rise to the $C_5H_9^+$ ions by collision-induced decompositions are also reported in Table V. The absence of detectable resonances from 91 and 94 as predicted by the operation of eq 12 and 14 most probably reflects the low intensity of these ions in the icr spectrum. Therefore the problem remains of identifying the nature of the first dehydration of ions which go on to dehydrate a second time. This problem is not solved by elucidation of the mechanism of dehydration of those ions which are observed as singly dehydrated species, for it is possible that ions of another, less stable form go on to form the doubly dehydrated species which are observed.

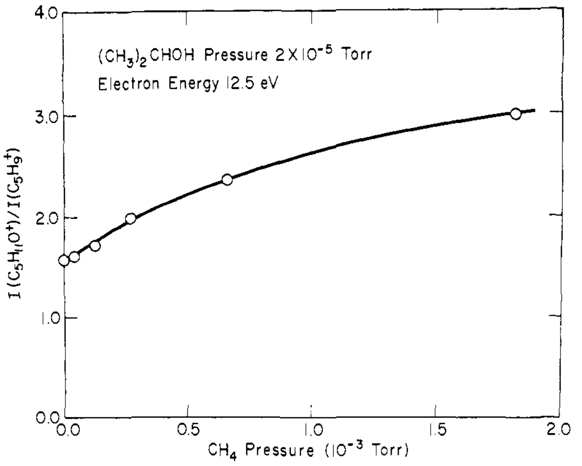


Figure 1. Variation of the $[87^+]/[69^+]$ intensity ratio with pressure of added methane collision gas.

In this regard the most valuable experiment is the observation of the singly dehydrated ion stabilized by addition of a collision gas at the expense of the doubly dehydrated ion. In the course of examining the pressure dependence of the ion abundances for 2-propanol at low electron energies it was noted that the ratio of *m/e* 87 ($C_5H_{11}O^+$) to *m/e* 69 ($C_5H_9^+$) increased with increasing pressure. This might be accounted for by collisional stabilization of the product of eq 11 prior to further decomposition in eq 3. Since the ratio could also be changing as a result of the two products reacting further with 2-propanol, we sought to confirm in the present work the sequential nature of the decomposition reaction by collisionally stabilizing the product of eq 3 with a nonreactive neutral buffer gas. While nitrogen was found to be relatively ineffectual for this purpose, methane provided the anticipated result. With a fixed pressure of 2-propanol (2 × 10^{-5} Torr), methane was admitted at an electron energy (12.5 eV) sufficiently low to avoid ionization of the buffer. The principal change noted in the spectrum was an increase in the *m/e* 87 ion intensity at the expense of the *m/e* 69 ion intensity. As shown in Figure 1, the ratio of single-resonance intensities for these two species increased by a factor of 2 over the range of methane pressures accessible. Collisional broadening of the absorption lines prevented examining the stabilization above the 2 × 10^{-3} Torr. The product of eq 11 undoubtedly possesses a distribution of internal excitation ranging up to 20

Table V. Predicted and Observed Icdr Signals for Formation of $C_5H_9^+$ in $CD_3CDOHCH_3$

m/e, product	*m/e*, precursor: Predicted by eq 11, 13, 14	*m/e*, precursor: Predicted by eq 12, 14	*m/e*, precursor: Observed
72			46[a]
73	46, 92	46, 91, 92	46, 92
74	46, 92	46, 92	46, 92
75	49, 94	49, 94	49, 94
76	49, 94	49, 94, 95	49, 94
77			49[a]

[a] These results are in accord with eq 15.

kcal/mol. The data in Figure 1 suggest that it is possible to stabilize only a fraction of the product ions, probably those which barely possess sufficient internal energies to promote eq 3.[13]

Conclusions

The combined experimental results are strong evidence in favor of eq 11, 13, and 14 as the preferred mechanism for the formation of $C_5H_{11}O^+$ and $C_5H_9^+$ from the reaction of CH_3CHOH^+ with 2-propanol. Our results are therefore directly applicable to the interpretation of the unimolecular decomposition of 2-propyl ether and provide another example of a four-center mechanism for secondary decomposition complementing those discussed by Tsang and Harrison.[4] The decomposition of $C_5H_{11}O^+$ formed by α cleavage of 2-propyl ether proceeds through a symmetrical protonated oxetane which opens to eliminate water in a 1,4 mechanism reminiscent of the dehydration of alcohols.[14] The operation of such a mechanism for dehydration in an ion where the charge is formally placed principally on a carbonium ion site at a distance from the oxygen function suggests that processes involving 1,4 elimination of water are not necessarily "triggered" by the charge or radical site on ionized oxygen.

It is not intended to imply that the present results are of general applicability. In the more general process, both the ring size formed upon cyclization (eq 13) and the site specificity of water loss (eq 14) will vary with the structure of the α-cleavage product undergoing dehydration.

Ion-molecule reactions may have general application as a means of generating reactants with controlled internal energy for studies of unimolecular decomposition processes. The present studies benefit from the ability to generate reactant ions in abundance with internal energy sufficient to observe only the process of interest. The low internal energy in the reactant ions mitigates against scrambling of hydrogen, permitting an assessment of reaction mechanisms utilizing labeled reactants.

Experimental Section

Spectra. The icr spectra were obtained with a Varian ICR-9 spectrometer; pulsed double-resonance experiments were performed in the usual fashion,[10,15,16] employing irradiating field strengths in the range of 50 mV in a cell 1.01 cm high. The observing oscillator level was below the limit of detection of the meter supplied with the commercial instrument. Cell voltages for a typical spectrum were: trap, 0.66 V; analyzer,[17] 0.06 and 0.09 V; source,[17] 0.07 and 0.15 V. The electron energy of 13 eV is obtained from the potential difference between the filament and the trapping plates. Pressure was monitored by the ion pump control. Samples were degassed by freeze-thaw cycling before use.

Data reported in tables and in the text are uncorrected for isotopic impurities of H in D (purity of all deuterated samples exceeded 99%), but are corrected for impurities of ^{13}C in ^{12}C by the usual assumption of distribution of naturally occurring isotopes. The data are also corrected for the expected mass discrimination for secondary ions by dividing by the square of the mean.[18] Where error figures are quoted, these represent the precision of five to seven replicate slow scans in both directions across a narrow mass range encompassing the total isotopic distribution; the numbers are standard deviations of the fraction of corrected ion current carried by ions of the composition $^{12}C_5H_nD_{9-n}^+$ or $^{12}C_5H_nD_{11-n}O^+$

Compounds. 2-Propanol was taken from a freshly opened bottle of Baker reagent grade 2-propanol; no impurities were detected by glc.

2-Propanol-*1,1,1,3,3,3-d*$_6$ was obtained from Merck Sharp and Dohme of Canada; no impurities were detected by glc.

2-Propanol-*2-d*. To 1.0 g of $LiAlD_4$ in 50 ml of ether was added a solution of 4.1 g of acetone (Baker reagent grade) in 20 ml of anhydrous ether over 30 min. After refluxing 1 hr, the cooled reaction mixture was decomposed by the addition of 4 ml of water, then 3 ml of 20% NaOH, and finally sufficient water to make the inorganic solids filterable.[19] The solid residue was washed several times with ether and the ethereal solutions were concentrated after drying by distillation of the ether. The alcohol was purified *via* glc and contained no impurities >0.1%.

2-Propanol-*1,1,1,2-d*$_4$. A solution of 5 g of acetaldehyde-d_4 (Stohler Isotope Chemicals Co.) in *ca.* 20 ml of anhydrous ether was added over 1 hr to a cooled solution of 50 ml of 3 *M* $CH_3MgBr-Et_2O$ (Columbia Organic Chemicals Co., Inc.). The reaction mixture was poured over 50 g of crushed ice. After the addition of 25 ml of 15% H_2SO_4, the ethereal layer was separated, the aqueous phase was extracted several times with ether, the ethereal extracts were combined and dried, and the alcohol was purified by distillation. Glc showed <0.5% impurity.

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(13) Collisional stabilization by methane of the adduct of the reactants in eq 11 was not observed in these experiments.

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