the experimental value of the V ← N band maximum of 54,550 cm^{-1}.

Conclusions

In conclusion, several aspects of the results of the comparative method are summarized. (1) The initial large destabilization of the π orbital energy of ethylene on chlorine substitution is present in the chlorofluoroethylenes. (2) The initial large stabilization of the π^* orbital energy observed in the chloroethylenes is not present in the chlorofluoroethylenes. (3) There is a relatively strong π^* destabilizing effect present when halogen substitution occurs cis to a halogen present in the parent molecule (*i.e.*, the relatively large values of X_i for i = 3, 5, 7, and 8). This suggests a geometry effect in the V state. This effect is observed in the chlorofluoroethylenes as well as in the chloro- and fluoroethylenes. (4) The effects that halogen substitution exerts on the π and π^* orbital energies appear to be dependent on the kind of halogen substituted and on the positions, relative to the substituent, occupied by other halogens. The specific halogens present in the parent molecule do not appear to be a dominant factor.

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Ion–Molecule Reactions of 2-Butanol by Ion Cyclotron Resonance Spectroscopy

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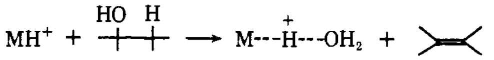
Abstract: The reactions of 2-butanol with fragment ions generated from 2-butanol on electron impact have been studied by ion cyclotron resonance techniques. The reaction sequences involved are formulated from evidence obtained from double resonance experiments, the use of deuterium-labeled alcohols, and the measurement of single resonance ion intensities at 13 and 70 eV over a range of sample pressures (10^{-7}–10^{-3} Torr). The gas-phase ion chemistry of 2-butanol, methanol, ethanol, 2-propanol, and *tert*-butyl alcohol is compared and reveals a remarkably systematic behavior characteristic of the hydroxyl functional group.

The gas-phase ion chemistry of several alcohols has been investigated by means of ion cyclotron resonance spectroscopy (icr) and high-pressure mass spectrometry.[3–11] The reactions of methanol,[3,9–12] ethanol,[10,11] 2-propanol,[5] and *tert*-butyl alcohol[4,6] have been reported in some detail, and some important similarities and differences in the ion chemistry of these alcohols have been noted. The present work describes the ion chemistry of 2-butanol which, from preliminary studies, indicated a sequence of reactions related to those observed for 2-propanol[5] and *tert*-butyl alcohol.[4,6] Of particular interest is the dehydration of alcohols induced by ions possessing a labile proton (eq 1). This



(1)

reaction, while not observed for methanol or ethanol, is prominent in the ion chemistry of secondary and tertiary alcohols.[4–6] A major objective of the present work was to investigate the dehydration reaction of eq 1 using deuterium-labeled 2-butanols in order to determine the relative yields of the various isomeric hydrocarbon products.

A second objective was to investigate the condensation reactions of 2-butanol. Reactions of this type are important in the ion chemistry of methanol and higher molecular weight alcohols and involve the elimination of one and sometimes two molecules of water from reaction intermediates. A pertinent example is the reaction of protonated acetaldehyde with 2-propanol as indicated in eq 2.[5,8] The condensation reactions of labeled and unlabeled 2-butanols were examined in the present study in order to determine the possible structures of the reactant and product ions and to evaluate the nature of the processes by which the products are formed. Before discussing these reactions further, a

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[6] J. L. Beauchamp and M. C. Caserio, unpublished results.

[7] T. B. McMahon and J. L. Beauchamp, unpublished results.

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[12] S. K. Gupta, E. G. Jones, A. G. Harrison, and J. J. Myher, *Can. J. Chem.*, 45, 3107 (1967).

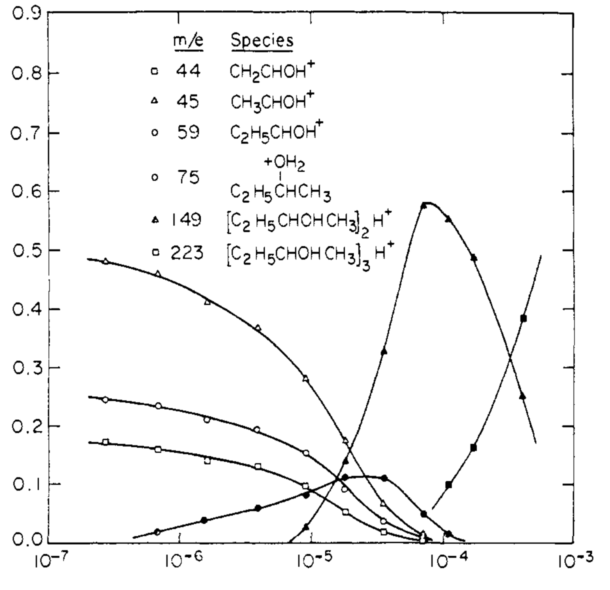
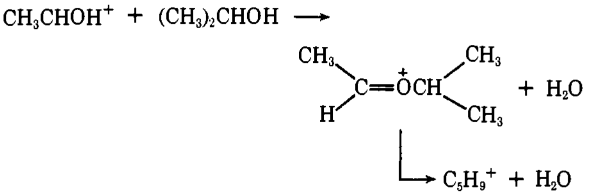


Figure 1. Variation of single resonance intensities with pressure for the major ionic species in 2-butanol at 13 eV.

general summary of the ion chemistry of 2-butanol is given.

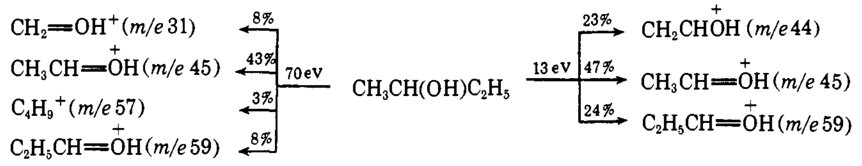


(2)

Ion–Molecule Reactions of 2-Butanol

The principal fragments observed in the spectrum of 2-butanol at low pressures and electron energies of 13 eV and higher are the α-cleavage products, CH_3CHOH^+ (*m/e* 45) and $C_2H_5CHOH^+$ (*m/e* 59), representing protonated acetaldehyde and propionaldehyde, respectively. Other fragment ions include CH_2OH^+ (*m/e* 31), $C_4H_9^+$ (*m/e* 57), and $CH_2CHOH\cdot^+$ (*m/e* 44). Whereas the fragment $CH_2CHOH\cdot^+$ is observed mainly at 13 eV, the CH_2OH^+ and $C_4H_9^+$ fragments become relatively important only at 70 eV. The principal fragmentation products are listed in Scheme I, along with their abundance at 70 and 13 eV, given as per cent of the total ionization. The variation in single resonance intensity of the major ionic species with increasing sample pressure at 13 eV (Figure 1) indicates that the ions produced by direct electron impact decrease in intensity as the result of their subsequent reactions with 2-butanol.

Scheme I



Confirmation of the structures assigned to the fragment ions was obtained from a study of several labeled 2-butanols, including $CH_3CD(OH)CH_2CH_3$, $CH_3CH(OH)CHDCH_3$, $CH_3CH(OH)CD_2CH_3$, $CD_3CH(OH)CH_2CH_3$, and $CD_3CH(OH)CD_2CH_3$. The changes in ion intensity in the mass spectrum of 2-butanol at 13 eV with deuterium substitution are consistent with the changes expected on the basis of the structures assigned to the major fragments.

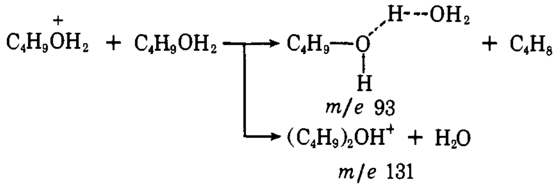
The product ions generated directly and indirectly from the major fragments *m/e* 45 and 59 are summarized in Figure 2. Double resonance techniques were employed to identify the ionic precursors to each of the product ions listed, and the variation of single resonance intensities for the major and minor reactant and product ions at 13 eV is illustrated in the pressure–intensity plots of Figures 1 and 3. These may be used effectively to assess the relative importance of each of the ionic species indicated in Figure 2 over the range of pressures studied.

The protonated parent alcohol, *m/e* 75, is formed in simple proton transfer reactions (eq 3) involving all the

$$MH^+ + C_4H_9OH \longrightarrow C_4H_9OH_2^+ + M \qquad (3)$$

fragments listed in Scheme I possessing a labile proton. The proton affinities of methanol and ethanol are 180 and 186 kcal/mol,[13,14] corresponding to hydrogen affinities of 117 and 114 kcal/mol, respectively. Assuming a hydrogen affinity of ~116 kcal/mol for 2-butanol yields an estimated proton affinity of 197 kcal/mol.[15] These data are summarized in Table I along with the thermochemical properties of other ionic species pertinent to the ensuing discussion.

The decrease in intensity of *m/e* 75 at higher pressures (Figure 1) is principally the result of its reaction with 2-butanol to form sequentially the proton-bound dimer (*m/e* 149) and trimer (*m/e* 223) as indicated in Figure 2. There are two other processes which lead to the decay of *m/e* 75. The first involves dehydration of 2-butanol as generalized in eq 1, to give *m/e* 93, with the eliminated water molecule remaining associated with the protonated alcohol through the agency of the labile proton (eq 4). The second involves a condensation reaction (eq 5) leading to protonated 2-butyl ether (*m/e* 131) which combines with another molecule of alcohol at



(4)

(5)

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(13) For a general discussion of proton affinity studies, see J. L. Beauchamp and S. E. Buttrill, Jr., *J. Chem. Phys.*, **48**, 1783 (1968).

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

(15) The assumption that hydrogen affinities are independent of alkyl substitution for a homologous series serves to correlate measured proton affinities. Note in Table I, for example, that while proton affinities vary over a wide range, the hydrogen affinities of aldehydes and ketones are very nearly equal.

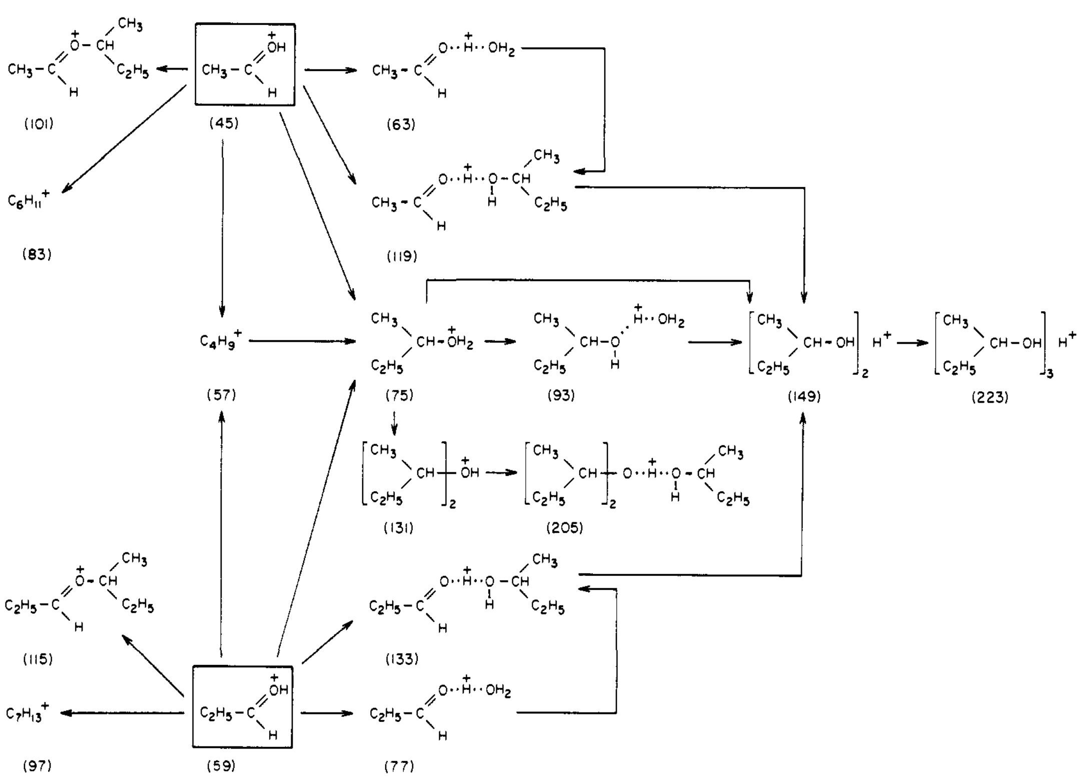


Figure 2. Reaction sequence initiated in 2-butanol by the two α-cleavage products, CH_3CHOH^+ (*m/e* 45) and $C_2H_5CHOH^+$ (*m/e* 59). Each step involves 2-butanol as the neutral reactant. All reactions indicated were identified by ion cyclotron double resonance techniques. The importance of the various reaction pathways may be assessed in Figures 1 and 3.

higher pressures to give the cluster ion observed at *m/e* 205 (Figure 2).

Table I. Summary of Thermochemical Data Useful for Describing Ion–Molecule Reactions of Aliphatic Alcohols[a]

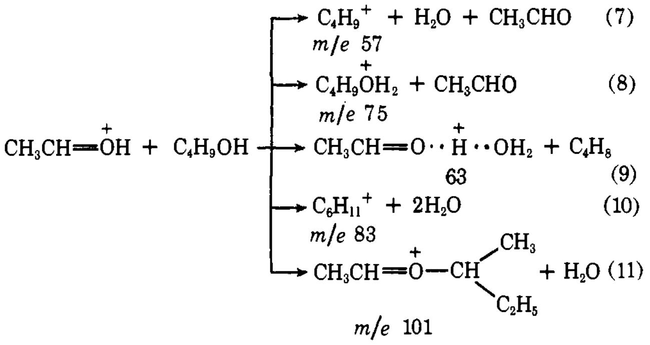
Species (M)	ΔH_f(M)[b]	IP(M)[b]	ΔH_f(MH^+)[b]	PA(M)[c]	HA(M^+)[d]
Methanol	−48.1	10.85	138	180[e]	117
Ethanol	−56.2	10.48	124	186[e]	114
2-Propanol	−65.2	10.17	106	195	(116)[f]
2-Butanol	−69.8	10.1	99	197	(116)[f]
tert-Butyl alcohol	−74.7	9.70	85	206	(116)[f]
Formaldehyde	−27.7	10.87	172[g]	166	103
Acetaldehyde	−39.7	10.20	143[g]	183	105
Propionaldehyde	−45.6	9.98	133[h]	187	104
Acetone	−51.8	9.65	124[g,h]	190	99
Ethylene	12.50	10.45	219[i]	160	87
Propylene	4.88	9.73	192[i]	179	90
trans-2-Butene	−2.67	9.13	183[i,j]	180	77
cis-2-Butene	−1.67	9.13	183[i,j]	181	78
1-Butene	−0.03	9.58	183[i,j]	183	90
Isobutylene	−4.04	9.23	167[i]	195	94

[a] All thermochemical data except ionization potentials are given in kcal/mol at 298°K. Ionization potentials are given in eV. [b] Except as noted ionization potentials and ionic heats of formation are from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. Neutral heats of formation are from the compilation of S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). [c] PA(M) = proton affinity of M, defined as the negative of the enthalpy change for the process $M + H^+ \rightarrow MH^+$. [d] $HA(M)^+$ = hydrogen affinity of M^+, defined as the negative of the enthalpy change for the process $M^+ + H \rightarrow MH^+$. [e] Proton affinity data from M. A. Haney and J. L. Franklin, *J. Phys. Chem.*, **73**, 4328 (1969). [f] Hydrogen affinity of 116 kcal/mol assumed. $\Delta H_f(MH^+)$ and PA(M) are calculated on this basis. [g] K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, **48**, 5205 (1968). [h] A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966). [i] F. P. Lossing and G. P. Semeluk, *ibid.*, **48**, 955 (1970). [j] MH^+ assumed to be the *sec*-butyl cation.

The low abundance of $C_4H_9^+$ (*m/e* 57) at 13 eV (Figure 3b) contrasts with the observed behavior at 70 eV where $C_4H_9^+$ is not only a primary reactant ion but also the most abundant product ion at intermediate pressures (10^{-5} Torr). Similar behavior has been previously noted for 2-propanol[5] and *tert*-butyl alcohol.[6] Apparently at high electron energies the major fragment ions are generated with high internal excitation. This is partially transmitted to the protonated parent ion which subsequently dissociates to $C_4H_9^+$ and H_2O (eq 6).[16]

$$[C_4H_9OH_2^+]^* \longrightarrow C_4H_9^+ + H_2O \quad (6)$$

The α-cleavage products *m/e* 45 and 59 also participate in dehydration, condensation, and clustering reactions with 2-butanol. These processes are illustrated by considering the sequence initiated by protonated acetaldehyde, *m/e* 45 (eq 7–12).[17] Product ions attributable to reactions of *m/e* 45 with 2-butanol appear with increasing pressure at *m/e* 63, 83, and 101. The product at *m/e* 63 from the dehydration of 2-butanol by protonated acetaldehyde (eq 9) reacts further to yield the proton-bound cluster of acetaldehyde with 2-butanol (*m/e* 119, eq 12). The latter may also be formed by clustering of *m/e* 45 with 2-butanol. In turn, acetaldehyde may be displaced from *m/e* 119 by 2-butanol to give the proton-bound dimer (*m/e* 149, eq 13).

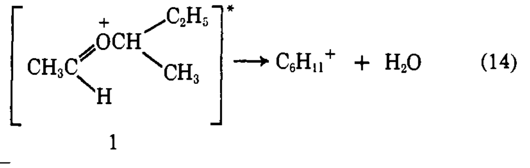


$$CH_3CH{=}\overset{+}{O}H + C_4H_9OH \longrightarrow \underset{m/e\ 57}{C_4H_9^+} + H_2O + CH_3CHO \quad (7)$$
$$\longrightarrow \underset{m/e\ 75}{C_4H_9\overset{+}{O}H_2} + CH_3CHO \quad (8)$$
$$\longrightarrow \underset{63}{CH_3CH{=}O\cdot\cdot\overset{+}{H}\cdot\cdot OH_2} + C_4H_8 \quad (9)$$
$$\longrightarrow \underset{m/e\ 83}{C_6H_{11}^+} + 2H_2O \quad (10)$$
$$\longrightarrow \underset{m/e\ 101}{CH_3CH{=}\overset{+}{O}{-}CH(CH_3)(C_2H_5)} + H_2O \quad (11)$$

$$CH_3CHO{\cdots}\overset{+}{H}{\cdots}OH_2 + C_4H_9OH \longrightarrow \underset{m/e\ 119}{CH_3CHO{\cdots}\overset{+}{H}{\cdots}\underset{H}{O}{-}C_4H_9} + H_2O \quad (12)$$

$$CH_3CHO\cdot\cdot\overset{+}{H}\cdot\cdot\underset{H}{O}{-}C_4H_9 + C_4H_9OH \longrightarrow \underset{149}{(C_4H_9OH)_2H^+} + CH_3CHO \quad (13)$$

The remaining product ions of interest are *m/e* 101 and 83, which differ from *m/e* 119 in the loss of one and two water molecules, respectively (eq 11 and 10). By analogy with the related reaction sequence for 2-propanol[5,8] (eq 2), an appreciable fraction of product ions **1** (*m/e* 101) formed by H_2O elimination (eq 11) are assumed to retain sufficient internal excitation to decompose further, eliminating a second water molecule as indicated in eq 14. Supporting evidence for the process of eq 14 may be found in Figure 3a which shows that formation of *m/e* 83 roughly parallels that of *m/e* 101 up to a pressure of ~2 × 10^{-5} Torr. At this pressure the intensity of *m/e* 101 increases relative to the intensity of *m/e* 83, possibly indicating collisional stabilization of *m/e* 101 prior to further decomposition. In addition, double resonance techniques indicate that *m/e* 83 is generated by the collision-induced decomposition of *m/e* 101.[18] There is also considerable precedent for the elimination of water from oxonium ions analogous to *m/e* 101.[19–22] Further discussion of the process of eq 14 is given in a later section.



$$\left[CH_3CH{=}\overset{+}{O}CH(C_2H_5)CH_3\right]^* \longrightarrow C_6H_{11}^+ + H_2O \quad (14)$$

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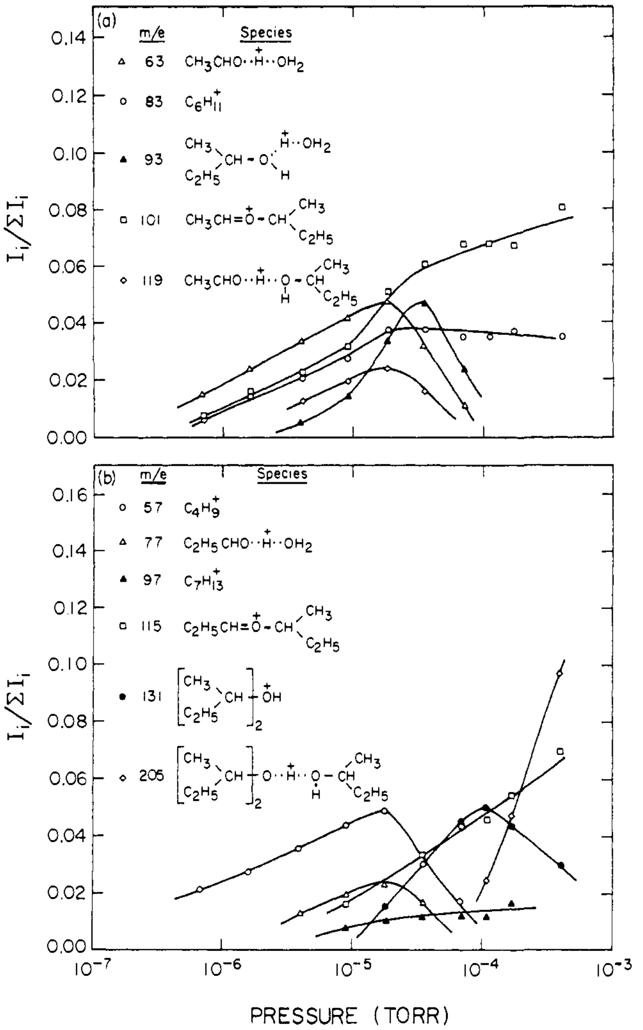

Figure 3. Variation of single resonance intensities with pressure for the minor ionic species in 2-butanol at 13 eV: (a) product ions from CH_3CHOH^+ (*m/e* 45); (b) product ions from $C_2H_5CHOH^+$ (*m/e* 59). Major ionic species are displayed in Figure 1.

The variation with electron energy of the product distribution from the reaction of CH_3CHOH^+ with 2-butanol is illustrated in Figure 4. Below an electron energy of 12.0 eV the butyl cation is not observed as a reaction product. This threshold occurs ~1.6 eV above the appearance potential of CH_3CHOH^+ from 2-butanol and corresponds to a maximum internal ex-

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[16] Reaction 6 is endothermic by 26 kcal/mol for protonated 2-butanol dissociating in its ground state. From the thermochemical data in Table I it may be calculated that only proton transfer from CH_2OH^+ to 2-butanol can generate ions with sufficient internal excitation to dissociate to $C_4H_9^+$ and H_2O. However, double resonance results at 70 eV indicate that *m/e* 31, 44, 45, and 59 all participate in the formation of $C_4H_9^+$, indicating that the latter three reactant ions possess an internal energy of at least 7, 12, and 16 kcal/mol, respectively.

[17] Entirely comparable reactions were observed for *m/e* 59.

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

[19] W. Carpenter, A. M. Duffield, and C. Djerassi, *ibid.*, **89**, 6165 (1967).

[20] F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

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

[22] W. H. McFadden, J. Wasserman, J. Corse, R. E. Landin, and R. Teranishi, *Anal. Chem.*, **36**, 1031 (1964).

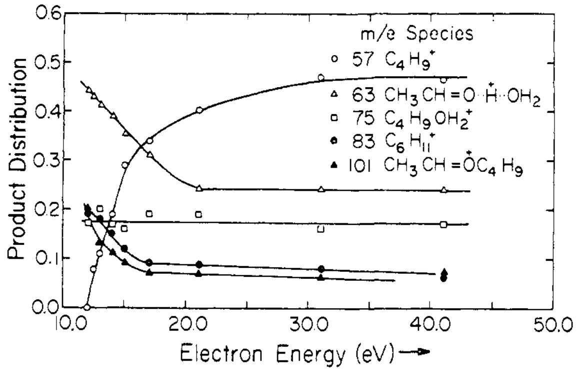


Figure 4. Variation with electron energy of the product distribution from the reaction of CH_3CHOH^+ with 2-butanol. The total product distribution is normalized to unity at each electron energy. The electron energy scale is calibrated against the known appearance potential of CH_3CHOH^+ from 2-butanol.

citation of 37 kcal/mol in the reactant ion. This is more than sufficient to overcome the calculated endothermicity of 12 kcal/mol for its reaction with 2-butanol to give $C_4H_9^+$. The abundance of the protonated parent ion is relatively constant. It appears that the formation of $C_4H_9^+$ occurs at the expense of the processes of eq 9–11. These results are entirely consistent with observations of the variation of reactivity of CH_3CHOH^+ with 2-propanol[5] and $(CH_3)_2COH^+$ with *tert*-butyl alcohol.[6] The possible implications of this variation of reactivity with electron energy have been previously discussed.[5]

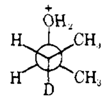
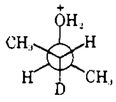
The reaction sequence initiated by *m/e* 44 is analogous to that of *m/e* 45 to a limited extent only. In addition to proton transfer (eq 3), dehydration of 2-butanol is observed (eq 15). The product of reaction 15 then re-acts in the same manner as *m/e* 45 (eq 12 and 13) to eventually yield the proton-bound dimer. Interestingly, *m/e* 44 does not participate in condensation processes analogous to those represented in eq 2, 10, and 11.

$$\cdot CH_2CH{=}\overset{+}{O}H + C_4H_9OH \longrightarrow \cdot CH_2CH{=}O\cdot\cdot\overset{+}{H}\cdot\cdot OH_2 + C_4H_8 \quad (15)$$

Ionic Dehydration of 2-Butanol. Distribution of Neutral Products. Although double resonance techniques establish that ions of *m/e* 44, 45, 59, and 75 participate in the dehydration of 2-butanol to give *m/e* 62, 63, 77, and 93, respectively, no information can be obtained directly from the icr spectrum of 2-butanol as to the structure of the C_4H_8 neutral hydrocarbon product. In order to obtain this information and to probe the mechanism of dehydration, the icr spectra of deuterium-labeled 2-butanols were examined. The distribution of product ions observed in dehydration of $CH_3CD(OH)CH_2CH_3$, $CD_3CH(OH)CHDCH_3$, $CH_3CH(OH)CD_2CH_3$, $CD_3CH(OH)CH_2CH_3$, and $CD_3CH(OH)CD_2CH_3$ by the protonated parent ion ROH_2^+ is given in Table II. Entirely comparable results were obtained for the reactant ions corresponding to *m/e* 45 and 59 in unlabeled 2-butanol.

A full interpretation of the data of Table II requires knowledge of the isotope effect to be expected for the dehydration reaction. This has been determined independently from a related study of the dehydration of 2-propanol-*1,1,1,2-d*$_4$.[23] The α-cleavage product CD_3CDOH^+ (*m/e* 49) was observed to lead to the ionic dehydration products *m/e* 67 and 68, corresponding to the elimination of H_2O and HDO, respectively, in the ratio 1.7:1. The same ratio is obtained in dehydration effected by the protonated parent ion. *Hence in dehydration reactions involving 1,2 elimination of water it is expected that, under otherwise identical conditions, H transfer will be preferred over D transfer from the β carbon by a factor of roughly 1.7.*

Table II. Distribution of Isotopic Products in the Dehydration of Labeled 2-Butanols by the Corresponding Protonated Parent Ion[a]

Reactant ion + (ROH_2)	*m/e*	Product ion	*m/e*	Product ion distribution[b]
$CH_3CH_2CH(CH_3)^+OH_2$	75	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	93	1.00
$CH_3CH_2CD(CH_3)^+OH_2$	76	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	94	1.00
$CH_3CH_2CH(CD_3)^+OH_2$	78	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	96	0.84
		$ROH\cdot\cdot H^+\cdot\cdot OHD$	97	0.16
$CH_3CD_2CH(CD_3)^+OH_2$	80	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	98	0.18
		$ROH\cdot\cdot H^+\cdot\cdot OHD$	99	0.63
		$ROH\cdot\cdot H^+\cdot\cdot OD_2$	100	0.19
$CH_3CD_2CH(CH_3)^+OH_2$	77	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	95	0.31
		$ROH\cdot\cdot H^+\cdot\cdot OHD$	96	0.54
		$ROH\cdot\cdot H^+\cdot\cdot OD_2$	97	0.15
	76	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	94	0.63
		$ROH\cdot\cdot H^+\cdot\cdot OHD$	95	0.30
		$ROH\cdot\cdot H^+\cdot\cdot OD_2$[c]	96	0.07
	76	$ROH\cdot\cdot H^+\cdot\cdot OH_2$	94	0.61
		$ROH\cdot\cdot H^+\cdot\cdot OHD$	95	0.31
		$ROH\cdot\cdot H^+\cdot\cdot OD_2$[c]	96	0.08

[a] The product distributions derived from ions related to *m/e* 44, 45, and 59 were comparable to the distributions reported here for ROH_2^+ with ROH. [b] In each case the sum of the isotopic product distribution is normalized to unity. [c] Loss of D_2O implicates the participation of both reaction partners in the scrambling process (see text).

In the spectrum of $CH_3CD(OH)CH_2CH_3$ product ions of *m/e* 95 corresponding to the elimination of HDO were *not* evident from which we conclude that 1,1 elimination of water does not occur. This is consistent with previous findings concerning ionic dehydration of 2-propanol for which a simple 1,2 elimination of water was established.[5] Since the dominant product ion in the ionic dehydration of $CD_3CH(OH)CD_2CH_3$ is *m/e* 99 (Table II) corresponding to the elimination of HDO, we may conclude that dehydration of 2-butanol, like 2-propanol, occurs predominantly by 1,2 elimination of water. However, elimination of D_2O and H_2O also occurs to a significant extent in the case of the alcohol-*d*$_5$ (*m/e* 98 and 100, Table II). Loss of D_2O can be attributed to scrambling, the suggested mechanism for which is indicated in eq 16. The reversibility of the dehydration process shown in eq 16 involving the reactant ion CD_3CHOH^+ is evidenced by the observation of CD_3CHOD^+ as a minor reaction product in the spectrum of $CD_3CH(OH)CD_2CH_3$. Scrambling appears to involve only the 3-carbon in that D_2O elimination is not observed with $CD_3CH(OH)CH_2CH_3$. Attributing D_2O and HDO loss to the formation of butenes by 1,2 elimination in the case of alcohol-*d*$_5$, the remaining 18% H_2O elimination may possibly arise by 1,3 elimina-

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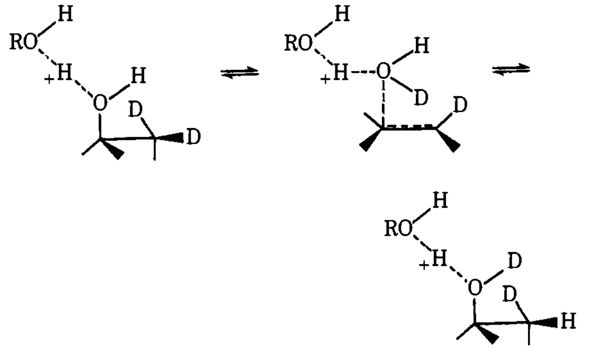
[23] We are indebted to Professor M. M. Bursey for generously supplying a sample of 2-propanol-*1,1,1,2-d*$_4$.

Table III, Distribution of Neutral Products in Dehydration of 2-Butanol

Product	Basis for conclusion	Conclusion	Approximate distribution[a]	Distribution for dehydration on Al_2O_3[a,b]
Methyl cyclopropane	$CD_3CH(OH)CD_2CH_3$	$\leqslant 0.18$	0.08	
1-Butene	$CD_3CH(OH)CH_2CH_3$	$\geqslant 0.16$	0.18	0.26
trans-2-Butene	$CH_3CH(OH)CD_2CH_3$	$\geqslant 0.35$	0.37	0.14
cis-2-Butene	$CH_3CH(OH)OHDCH_3$[c]	$\geqslant 0.35$	0.37	0.60

[a] In each case the total product distribution is normalized to unity. [b] Reference 27. [c] Erythro and threo isomers indicated equal amounts of *cis*- and *trans*-2-butene.

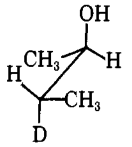
tion to give methylcyclopropane. The estimated 18% 1,3 elimination represents a *maximum* since correction for an isotope effect would reduce this figure. Similarly, from the product distribution for the alcohol-d_3



(16)

a *minimum* of 16% 1,2 elimination occurs to give 1-butene. From the alcohol-d_2 a minimum of 69% 1,2 elimination to give 2-butene is observed. These conclusions are summarized in Table III.

A further point of interest concerning ionic dehydration of 2-butanol is the distribution of *cis*- and *trans*-2-butenes formed. To obtain a measure of this distribution, the diastereomeric alcohols of 2-butanol-*3*-d_1, **2** and **3**, were prepared. Surprisingly, the icr spectra



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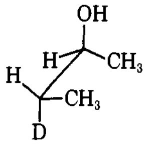

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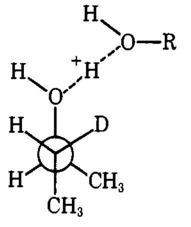
of **2** and **3** were virtually identical, and the ratio of ion intensities at *m/e* 94 and 95 (Table II) indicates that each isomer has a 2:1 preference for H_2O elimination over HDO elimination on dehydration.

A plausible explanation of these results is based on a preferred transition state for dehydration involving cis 1,2 elimination from an intermediate complex of the reactant ion and the neutral alcohol such as **4** or **5**. It is further suggested that the rotational conformations related to **4** or **5** are equally populated and lead equally to dehydration. The 2:1 preference for H_2O over HDO elimination must then partly reflect elimination to give 1-butene and methylcyclopropane and partly reflect operation of the isotope effect in the formation of 2-butenes. Equivalent conformations of the reactants for unlabeled 2-butanol would necessarily give equal amounts of *cis*- and *trans*-2-butene by this mechanism.[24]



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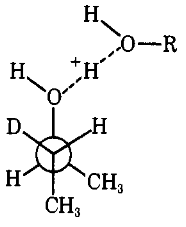

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In summary, we may conclude with some confidence that dehydration of 2-butanol occurs largely to give 2-butene in a nonselective process leading to equal amounts of cis and trans isomers. The derivation of a quantitative product distribution for unlabeled 2-butanol is confused by the simultaneous operation of isotope effects, scrambling, and the competition of dehydration with other reactions of the protonated parent ion. We present in Table III a product distribution roughly consistent with both the derived limits and the expected isotope effects discussed above. We include in Table III related data on the dehydration of 2-butanol over an alumina catalyst.[25-27] Both ionic and basic dehydration are thought to be cis eliminations, yet there is no evident correspondence in their product distributions. For example, the distribution of *cis*- and *trans*-2-butenes is notably different and favors the cis isomer in the case of basic dehydration.

Condensation Reactions of 2-Butanol

The α-cleavage product *m/e* 45 reacts with 2-butanol to eliminate a molecule of water and generate the condensation product *m/e* 101 (eq 11). Although it has not been established with certainty, this species is presumed to have structure **1**. Further decomposition of *m/e* 101 results in the loss of a second water molecule to give *m/e* 83.[17] The process by which this occurs involves an extensive rearrangement since it necessitates the formation of a new carbon–carbon bond and cleavage of two carbon–oxygen bonds if the structure assigned to **1** is correct. The corresponding condensation reactions of labeled 2-butanols were studied, therefore, in the hope of clarifying the nature of the processes involved.

The product distributions observed for the labeled alcohols indicate that the first condensation step in each case predominately involves elimination of H_2O.[28]

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(24) The possibility of epimerization at C-3 to explain the identical behavior of **2** and **3** should also be considered. Epimerization could occur, for example, by the reversible dehydration of eq 16. This and related processes must be discounted, since label scrambling was far from complete at C-3.

(25) H. Knözinger, *Angew. Chem.*, 7, 791 (1968), and references contained therein.

(26) H. Pines and J. Manassen, *Advan. Catal. Relat. Subj.*, 16, 49 (1966).

(27) H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, 83, 2847 (1961).

(28) The maximum amount of HDO elimination observed was 12%, measured for the reaction of the d_5 alcohol with the fragment CD_3-$CHOH^+$. This may be attributed to the label scrambling discussed previously.

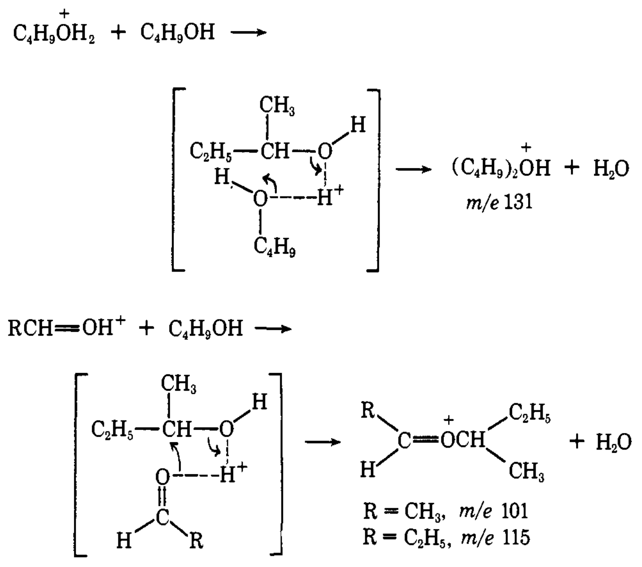
Table IV. Product Ions of Double Condensation Reactions[a]

Reactants	Products[b]	Product ion distribution[c]
$CH_3CH{=}O^+H$ (45) + $CH_3CH(OH)CH_2CH_3$	$C_6H_{11}^+$ (83) + H_2O + H_2O	1.00
$CH_3CD{=}O^+H$ (46) + $CH_3CD(OH)CH_2CH_3$	$C_6H_9D_2^+$ (85) + H_2O + H_2O	0.64
	$C_6H_{10}D^+$ (84) + H_2O + HDO	0.36
$CH_3CD{=}O^+H$ (46) + $CH_3CH(OH)CHDCH_3$[d]	$C_6H_{10}D^+$ (84) + H_2O + H_2O	0.69
	$C_6H_{11}^+$ (83) + H_2O + HDO	0.31
$CH_3CH{=}O^+H$ (45) + $CH_3CH(OH)CD_2CH_3$	$C_6H_9D_2^+$ (85) + H_2O + H_2O	0.46
	$C_6H_{10}D^+$ (84) + H_2O + HDO	0.54
$CH_3CD_2CH{=}O^+H$ (61) + $CH_3CH(OH)CD_2CH_3$	$C_7H_9D_4^+$ (101) + H_2O + H_2O	0.22
	$C_7H_{10}D_3^+$ (100) + H_2O + HDO	0.50
	$C_7H_{11}D_2^+$ (99) + H_2O + D_2O[e]	0.28
$CD_3CH{=}O^+H$ (48) + $CD_3CH(OH)CH_2CH_3$	$C_6H_5D_6^+$ (89) + H_2O + H_2O	0.44
	$C_6H_6D_5^+$ (88) + H_2O + HDO	0.43
	$C_6H_7D_4^+$ (87) + H_2O + D_2O[e]	0.13
$CD_3CH{=}O^+H$ (48) + $CD_3CH(OH)CD_2CH_3$	$C_6H_{13}D_8^+$ (91) + H_2O + H_2O	0.18
	$C_6H_4D_7^+$ (90) + H_2O + HDO	0.50
	$C_6H_5D_8^+$ (89) + H_2O + D_2O[e]	0.32

[a] The product distributions observed for *m/e* 59 and its labeled analogs were comparable to, but not identical with, the distribution reported here for *m/e* 45; their intensities were less than half those due to *m/e* 45 and could not be measured with comparable accuracy. Numbers in parentheses are *m/e* values of reactant and product ions. [b] Loss of water is stepwise, the first step being H_2O elimination (see text). [c] In each case the sum of the product distribution is normalized to unity. [d] Erythro and threo isomers yielded identical product distributions. [e] The elimination of H_2O and D_2O cannot be distinguished from the elimination of 2HDO (see discussion in the text).

Thus it appears that the protons in the first water molecule eliminated come from the hydroxylic groups of the reactant ion and parent neutral. The condensation reaction of interest is viewed, therefore, as the association of the reactant ion with the parent alcohol through the agency of a labile proton and the subsequent displacement of water as shown in Scheme II. The displaced water retains two of the protons originally bonded to oxygen in the reactants.[29] These processes conform to the postulated rules governing the occurrence of nucleophilic displacement reactions in the gas phase.[30]

Scheme II



The major fragment ions produced in the second condensation step are listed in Table IV for *m/e* 45 (and its labeled analogs) as the reactant ion. Clearly, loss of the second water molecule is more complicated than loss of the first since significant elimination of H_2O and HDO occurs for all the labeled alcohols studied. In the case of $CD_3CH(OH)C_2H_5$ and $CD_3CH(OH)CD_2CH_3$, loss of D_2O is also significant. Although the successive elimination of H_2O and D_2O cannot be distinguished from the elimination of 2HDO, the latter process is ruled out by the observed predominance of H_2O elimination in the first condensation step. A further point to note is the similarity in the product ion distributions observed for $CH_3CD(OH)C_2H_5$ and $CH_3CH(OH)CHDCH_3$, indicating the same relative amounts of H_2O and HDO elimination. This result suggests that the label distributions in the two alcohols may become equivalent prior to or during reaction, as would be the case if C-2 and C-3 become indistinguishable at some stage. It also appears certain that the water eliminated contains hydrogen atoms from both the reactant ion and the neutral alcohol. This may be assessed from the distribution of product ions obtained in the case of $CH_3CH(OH)CD_2CH_3$, the data from the labeled analog of *m/e* 59 being included in Table IV in this instance. The fact that relatively more HDO and D_2O eliminations occur for the reactant ion $CH_3CD_2CHOH^+$ than for CH_3CHOH^+ substantiates that to a certain extent hydrogen atoms eliminated with the second water molecule originate from the reactant ion.

When derived from electron impact induced fragmentation of ethers, the mode of decomposition of oxonium ions analogous to **1** generally involves transfer of hydrogen to oxygen with expulsion of a neutral alkene fragment.[8] There is insufficient energy in the intermediate **1** to allow for direct decomposition in the present case.[8,31] If, however, such a rearrangement

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(29) An alternate mechanism for the elimination of water in the reaction of *m/e* 45 with 2-butanol involves attack of the neutral alcohol on the carbonyl carbon of *m/e* 45 accompanied by cleavage of the C-O bond of *m/e* 45. By this mechanism the oxygen of the eliminated water originates from the reactant ion. However, recent experiments with ^{18}O-labeled *tert*-butyl alcohol show that the related condensation reaction involving *m/e* 59 results in loss of water having oxygen originating from the neutral alcohol (ref 6). This is consistent with the mechanism of Scheme II illustrated in the case of 2-butanol

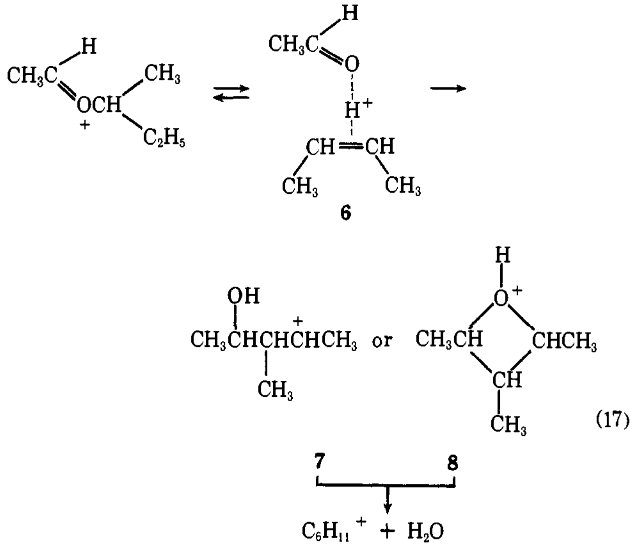
(30) D. Holtz, J. L. Beauchamp, and S. D. Woodgate, *J. Amer. Chem. Soc.*, 92, 7484 (1970).

Table V. Product Distribution (and Enthalpy Changes) for the Reactions of α-Cleavage Fragment Ions with Their Corresponding Parent Alcohols

		Process[b,c]				
Ionic reactant[a]	Neutral reactant	Proton transfer	Proton transfer followed by decomposition	Nucleophilic displacement	Nucleophilic displacement and decomposition	Dehydration[d]
CH_2OH^+	CH_3OH	1.00 (−14)	0.0 (50)	0.0 (−24)	0.0 (29)	0.0
CH_2OH^+	C_2H_5OH	1.00 (−20)	0.0 (17)	0.0 (−30)	0.0 (0)	0.0 (−24)
CH_3CHOH^+	C_2H_5OH	0.94 (−3)	0.0 (34)	0.06 (−20)	0.0 (0)	0.0 (−24)
CH_3CHOH^+	$(CH_3)_2CHOH$	0.44 (−12)	0.0[e] (16)	0.20 (−21)	0.19 (−11)	0.16 (−23)
CH_3CHOH^+	$CH_3CH(OH)C_2H_5$	0.20 (−14)	0.0[e] (12)	0.18 (−21)	0.14 (−24)	0.47 (−26)
$C_2H_5CHOH^+$	$CH_3CH(OH)C_2H_5$	0.24 (−10)	0.0[e] (16)	0.12 (−21)	0.18 (−24)	0.46 (−26)
$(CH_3)_2COH^+$	$(CH_3)_3COH$	$\leqslant$0.03[f] (−16)	$\leqslant$0.13[e,f] (8)	$\geqslant$0.42[f] (−17)	0.0 (−15)	$\geqslant$0.42[f] (−22)

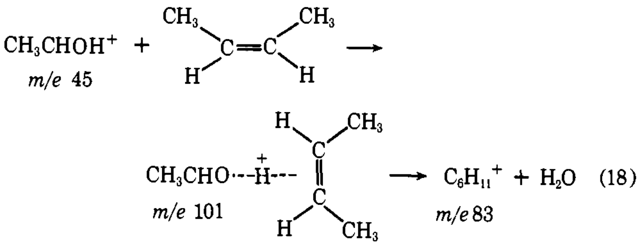
[a] Ionic reactant generated from corresponding neutral reactants by electron impact. [b] Product distribution measured at low electron energies, typically 1-2 eV in excess of the appearance potential of the reactant ion. In each case the sum of the product distribution is normalized to unity. [c] The numbers in parentheses represent the enthalpy change for the reaction in kcal/mol. Thermochemical data are taken from Table I and references contained therein. Several heats of formation were estimated with additivity methods. [d] For the dehydration reactions a proton bond strength, $D(R_1R_2C{=}O^+H\cdots OH_2)$, of 35 kcal/mol is assumed [J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969)]. [e] While this reaction channel is endothermic for ground-state reactants, it becomes important at higher electron energies where reactant ion internal excitation is appreciable (see text). [f] The indicated limits represent the trend of the product distribution if extrapolated to lower electron energies, where the endothermic channel involving proton transfer followed by decomposition would not be observed.

occurs with the protonated carbonyl species remaining bound to a butene fragment, then the resulting binding energy would more than suffice to make the rearrangement energetically feasible. Such a rearrangement process in the present case would be expected to yield the intermediate **6**. Dehydration of **6** would then involve nucleophilic addition to the carbonyl group followed by 1,2 or 1,4 elimination of water. Whether the proposed rearrangement of **6** gives the open-chain structure **7** or the protonated oxetane **8** cannot be determined from the present data. It is interesting to note, however, that the icr spectra of cyclic ethers show that proton transfer to give ions related to **8** is followed by dehydration, lending support to the scheme proposed in eq 17.[32] If the formation of **6** occurs reversibly, then C-2 and C-3 become equivalent which, as noted previously, is suggested by the labeling results.



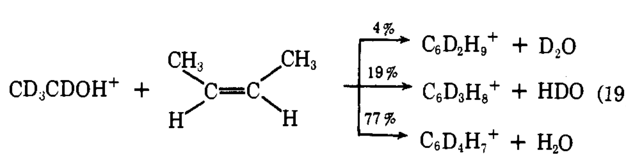
(17)

The intermediate **6** can be directly prepared by the reaction of protonated acetaldehyde with *cis*-2-butene. The first component, *cis*-2-butene, was admitted through one sample inlet into the cell of the icr spectrometer and the spectrum recorded at 2 × 10^{-5} Torr. Then acetaldehyde was admitted to double the ion current at an electron energy of 70 eV. Product ions at *m/e* 83 and 101 were the major species to be observed which were not common to either *cis*-2-butene or acetaldehyde alone.[33] Double resonance identified *m/e* 45 as the precursor to both species, indicating reaction 18 with



(18)

the adduct analogous to **6** or its rearranged forms **7** and **8**, being directly observable at *m/e* 101. In a mixture of CD_3CDO with *cis*-2-butene, the reactions of CD_3CDOH^+ and CD_3CDOD^+ were observed to lead to the approximate (±5%) product distributions indicated in eq 19 and 20. Apparently, loss of the hydrogen



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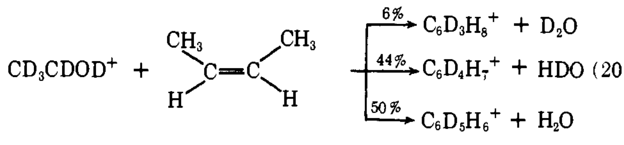

(20)

bound to oxygen in the reactant ion is prominent but not exclusive in the eliminated water molecule. This suggests that the rearrangement leading to the intermediate **6** occurs reversibly.

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(31) Such a decomposition would result in the dehydration of 2-butanol, a process which is calculated to be endothermic by 9 kcal/mol.

(32) J. L. Beauchamp, Ph.D. Thesis, Harvard University, 1968.

(33) The ion chemistry of *cis*-2-butene is reported to yield *m/e* 83 as a minor production [F. Abramson and J. H. Futrell, *J. Phys. Chem.*, **72**, 1994 (1968)]. We did not observe this ion in the icr spectrum of *cis*-2-butene over the range of pressure studied.

General Discussion of the Ion Chemistry of Alcohols

An examination of the gas-phase ion–molecule chemistry of methanol, ethanol, 2-propanol, 2-butanol, and *tert*-butyl alcohol reveals a remarkably systematic behavior. In each case the protonated parent ion is generated in abundance and reacts with the parent neutral to generate proton bound dimers and trimers. The proton-bound dimer eliminates water to yield the corresponding protonated dialkyl ether. In addition to undergoing proton transfer to the parent alcohol, the prominent α-cleavage fragments initiate a series of more complex reactions. Summarized in Table V are the product distributions for the reactions of α-cleavage fragment ions with the neutral alcohol from which they were formed. Proton transfer decreases in importance in proceeding from methanol to *tert*-butyl alcohol. Thus, while protonated formaldehyde reacts entirely by proton transfer with methanol, protonated acetone is observed to make only a minor contribution to protonated *tert*-butyl alcohol. Dehydration and condensation reactions become increasingly important in proceeding from methanol to *tert*-butyl alcohol. Interestingly, dehydration of ethanol is not observed. Perhaps the intrinsic activation energy for this process is less than the chemical activation energy provided by the formation of the strong hydrogen bond in the interaction of acidic species with ethanol.

In summary, because of the abundance of α-cleavage fragments, the interaction of protonated aldehydes and ketones with alcohols initiate the reaction sequences important in describing the ion chemistry of aliphatic alcohols. This interaction can be formulated as involving the binding of the two reactants through the agency of a labile proton. This provides a chemical activation energy in the range 30–40 kcal/mol. In the case of the lower alcohols, the lifetime of the intermediate is limited and dissociation occurs along the hydrogen bond with the labile proton remaining bound to the more basic site in the intermediate. An increasing number of degrees of freedom in the higher alcohols leads to a correspondingly longer lifetime for the intermediate and hence higher probability that rearrangement and condensation processes occur. These processes include dehydration of secondary and tertiary but not primary alcohols and nucleophilic displacement reactions involving elimination of one and sometimes two molecules of water from the reaction intermediate. The product distributions depend markedly on the internal energy content of the reactant ion and hence vary with electron energy. Higher internal energies in the intermediate lead not unexpectedly to the decreased importance of condensation and rearrangement processes.

Experimental Section

A standard Varian V-5900 series ion cyclotron resonance mass spectrometer equipped with a dual inlet system was utilized in the studies reported herein. The instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been described in detail.[5,13,34,35] All icr experiments were performed at ambient temperature. Product distributions were determined from single resonance peak intensities and source ion ejection experiments using previously described methods of analysis.[35] The spectrometer was thoroughly baked prior to performing the reported studies. With the filament operational, the total pressure of residual gas in the ion pumped system was $\leq 10^{-8}$ Torr prior to admitting reactant gas. Thus, at the higher pressures employed to observe ion–molecule reactions, the participation of impurities (particularly H_2O) in the proposed reaction schemes can be discounted.

The deuterium-labeled compounds utilized in the synthesis of the variously labeled 2-butanols included methyl-d_3 iodide and ethyl-*1,1*-d_2 alcohol (99 atom % D, Stohler Isotope Co.), lithium aluminum deuteride (99 atom % D, Metal Hydrides Corp.), and deuterium oxide (99.8 atom % D, International Chemical and Nuclear Corp.).

In all cases, the 2-butanols prepared were purified by preparative glpc and subsequently analyzed for isotopic purity by nmr and mass spectrometry.

2-Butanol-*2-d* was prepared by the reduction of 2-butanone with lithium aluminum deuteride in dry ether. For the synthesis of **2-butanol-*1,1,1*-d_3**, a solution of methyl-d_3-magnesium iodide was prepared from methyl-d_3 iodide and magnesium turnings in dry ether and was allowed to react with a solution of freshly distilled propionaldehyde in ether. 2-Butanol-*3,3*-d_2 was prepared from the reaction of ethyl-*1,1*-d_2-magnesium iodide with freshly distilled acetaldehyde in ether. The ethyl-d_2-magnesium iodide required for this preparation was obtained from ethyl-*1,1*-d_2 iodide and magnesium in dry ether. The ethyl-*1,1*-d_2 iodide was in turn obtained from the reaction of ethyl-*1,1*-d_2 alcohol with potassium iodide in phosphoric acid.[36]

2-Butanol-*1,1,1,3,3*-d_5 was prepared by the reduction of 2-butanone-*1,1,1,3,3*-d_5 with lithium aluminum hydride. The ketone-d_5 was obtained from 2-butanone by repetitive exchange with deuterium oxide in the presence of catalytic amounts of sodium deuterioxide. Initially, a 20-g sample of 2-butanone was refluxed with 100 ml of basic deuterium oxide for 24 hr followed by continuous ether extraction. Two further treatments of the recovered 2-butanone with 100-ml samples of basic deuterium oxide gave 2-butanone-*1,1,1,3,3*-d_5 of 98% isotopic purity. This sample was used in the subsequent hydride reduction.

Diastereomeric alcohols, threo and erythro forms of 2-butanol-*3*-d_1, **3** and **2**, respectively, were prepared by lithium aluminum deuteride reduction of *cis*- and *trans*-2-butene oxides, respectively. The latter were obtained by stereospecific epoxidation of *cis*-2 butene (99%) and *trans*-2-butene (98%) with cumene hydroperoxide in toluene catalyzed with molybdenum hexacarbonyl.[37] Analysis by glpc showed the *cis*-2-butene oxide obtained to be 99% pure and the *trans*-2-butene oxide to be 95% pure, the contaminant in the case of the trans isomer being the cis isomer. Deuteride reduction of the respective oxides gave 2-butanol having similar but not identical nmr spectra. The major spectral difference was apparent in the chemical shift and splitting pattern of the proton at C-3. A shift of 0.12 ppm at 220 MHz was measured between the band centers for the resonances due to the proton at C-3 of the two alcohols as neat liquids at 17°. The resonance of the erythro isomer was downfield of the threo alcohol. Nmr analysis also showed that the threo alcohol was essentially pure, whereas the erythro alcohol contained no more than 5% of the threo alcohol.

Acknowledgment. The authors wish to express appreciation for the technical assistance given by Mr. John Tangney in the synthesis of the labeled alcohols. The use of the Varian 220-MHz high-resolution nmr spectrometer operated and maintained by the California Institute of Technology was made possible by the National Science Foundation.

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(34) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

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