Ion–Molecule Reactions of *tert*-Butyl Alcohol by Ion Cyclotron Resonance Spectroscopy
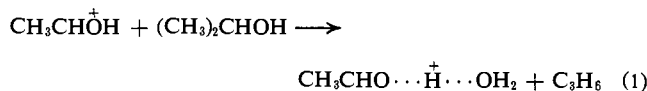
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Abstract: The gas phase ion chemistry of *tert*-butyl alcohol has been investigated using the techniques of ion cyclotron resonance spectroscopy. The reaction sequences involved are formulated from evidence obtained from double resonance experiments, the use of *tert*-butyl alcohol-^{18}O, and the measurement of single resonance intensities at 13 and 70 eV, over a range of sample pressures (10^{-7}–10^{-3} Torr). An investigation of sequential bimolecular reactions using trapped ion cyclotron resonance techniques at pressures near 10^{-6} Torr provides confirmatory information regarding the proposed reaction sequence and yields rate constants for the major processes important in describing the gas phase ion chemistry of *tert*-butyl alcohol. Trapped ion studies in mixtures of aliphatic alcohols demonstrate the feasibility of using bimolecular reaction sequences to generate and study proton bound dimers. The gas phase ion chemistry of *tert*-butyl alcohol is compared and contrasted to that of related alcohols.

The gas phase ion chemistry of methanol,[2-4] ethanol,[4] and more recently 2-propanol[5,6] and 2-butanol[7] has been studied in detail by a variety of techniques. The ion chemistry of 2-propanol and 2-butanol proved to be far richer than the ion chemistry of methanol and ethanol, the principal difference being in the reaction sequences initiated by the interaction of the α-cleavage products corresponding to protonated aldehydes with the parent alcohol.[7] One process observed, for instance, is the ionic dehydration reaction 1 according to which a water molecule is removed from 2-propanol and remains loosely bound to the reactant ion by the labile proton. The dehydration reaction 1

$$CH_3CH\overset{+}{O}H + (CH_3)_2CHOH \longrightarrow$$

$$CH_3CHO\cdots\overset{+}{H}\cdots OH_2 + C_3H_6 \quad (1)$$

was originally observed in an examination of the ion chemistry of *tert*-butyl alcohol,[8] the analogous process being reaction 2. In the present paper, a study of the

$$(CH_3)_2C\overset{+}{O}H + (CH_3)_3COH \longrightarrow$$

$$(CH_3)_2CO\cdots\overset{+}{H}\cdots OH_2 + C_4H_8 \quad (2)$$
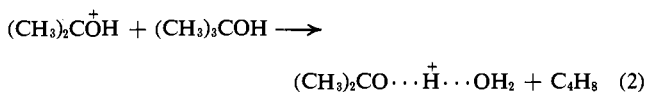
ion chemistry of *tert*-butyl alcohol, utilizing the techniques of ion cyclotron resonance spectroscopy,[9] is reported in detail and compared and contrasted to the ion chemistry of lower molecular weight aliphatic alcohols. The present study makes use of newly developed trapped ion cyclotron resonance techniques[10] to provide information regarding kinetics of sequential bimolecular reactions at low pressures. Mechanistic information is supplied by an examination of the reactions of ^{18}O-labeled *tert*-butyl alcohol. These mechanistic studies confirm earlier and somewhat controversial conjectures regarding the mechanism of condensation reactions which are important[5-7] in describing the ion chemistry of alcohols.

(1) (a) Dreyfus Teacher-Scholar, 1971–1976; (b) California Institute of Technology; (c) University of California, Irvine.

(2) M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 5313 (1965).

(3) J. M. S. Henis, *J. Amer. Chem. Soc.*, **90**, 844 (1968).

(4) L. W. Sieck, F. P. Abramson, and J. H. Futrell, *J. Chem. Phys.*, **45**, 2859 (1966); K. R. Ryan, L. W. Sieck, and J. H. Futrell, *J. Chem. Phys.*, **41**, 111 (1964).

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

(6) T. A. Lehman, T. A. Elwood, J. T. Bursey, M. M. Bursey, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **93**, 2108 (1971).

(7) J. L. Beauchamp and M. C. Caserio, *J. Amer. Chem. Soc.*, **94**, 2638 (1972).

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

(9) For a recent review, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

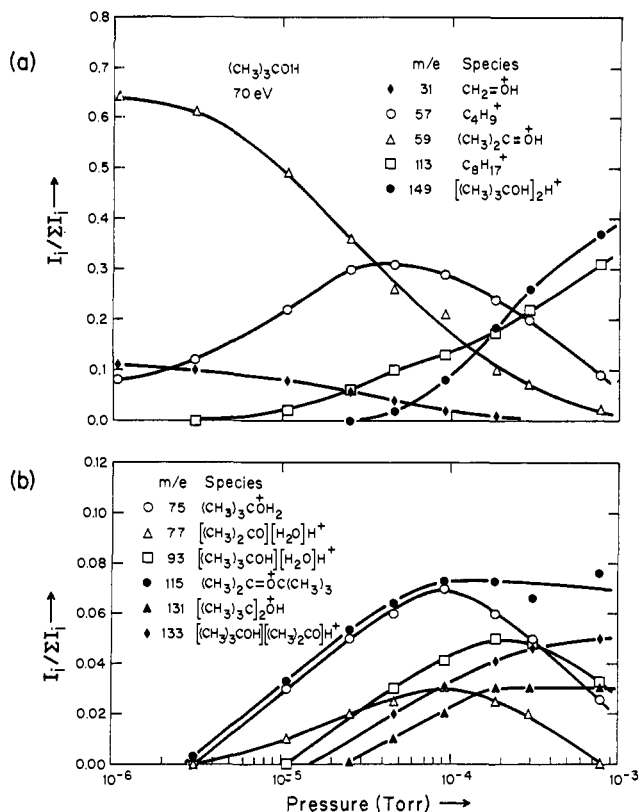(10) T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.*, **43**, 509 (1972).

Figure 1. Variation of single resonance intensities with pressure for ionic species in *tert*-butyl alcohol at 70 eV: (a) major ions; (b) minor ions.

Experimental Section

Two icr spectrometers were utilized in the present studies. Most of the results were obtained using a standard Varian V5900 ion cyclotron resonance mass spectrometer equipped with a 9-in. magnet system. Studies requiring higher mass resolution at elevated pressures utilized a second instrument, built in the instrument shops at Caltech. This instrument incorporates a 15-in. magnet system and is similar in other respects to the Varian spectrometer. Both spectrometers are equipped for routinely performing trapped ion experiments using circuitry which permits switching between trapped ion and drift modes of operations.[11] These and other aspects of the instrumentation and experimental techniques associated with ion cyclotron resonance spectroscopy have been previously described in detail.[9,10,12]

Electron energies were measured with a digital voltmeter, calibrated against the known appearance potential of N_2^+. Appearance potentials were determined by the extrapolated voltage difference method.[13] Pressures were determined using a Schulz-Phelp gauge calibrated against an MKS Model 90-H-1E capacitance manometer, as previously described.[12] All experiments were performed at ambient temperature ($\sim 25°$).

Gas chromatography indicated a purity of greater than 99.5% for *tert*-butyl alcohol prepared by vacuum distillation of reagent grade material. Labeled *tert*-butyl alcohol-^{18}O was prepared by the hydrolysis of *tert*-butyl chloride with normalized (deuterium free) ^{18}O-labeled water (42.05 atom per cent ^{18}O) in the presence of pyridine which served to solubilize the reagents and to neutralize the hydrochloric acid formed. The alcohol formed was isolated by glpc and the isotopic enrichment was estimated from the low-pressure icr spectrum to be $42.0 \pm 0.2\%$.

Results and Discussion

Identification of Reactions. The major ion m/e 59 derived from electron impact ionization of *tert*-butyl

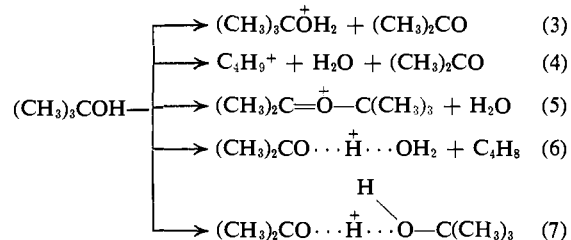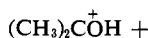(11) T. B. McMahon, Ph.D. Thesis, California Institute of Technology, 1973.

(12) T. B. McMahon, R. J. Blint, D. P. Ridge, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, **94**, 8934 (1972).

(13) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 169.

alcohol at all electron energies is the α-cleavage product corresponding to protonated acetone. At 70 eV a variety of fragment ions are present, with CH_2OH^+ being the second most prominent ion in the mass spectrum, but amounting to only 18% of the total ionization. The parent ion is almost undetectable except at the lowest electron energies.
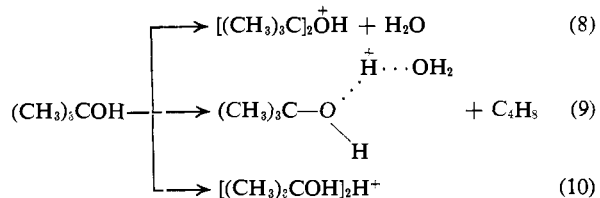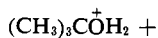
The variation with pressure at 70 eV of the single resonance intensities of the major ionic species in *tert*-butyl alcohol is illustrated in Figure 1. The m/e 59 ion, $(CH_3)_2COH^+$, decreases with increasing pressure as do the other fragments with the exception of $C_4H_9^+$ at m/e 57.

The minor fragments such as CH_2OH^+ react mainly by proton transfer to form the protonated parent ion, m/e 75, which may then subsequently decompose to form the butyl cation, m/e 57. The major fragment ion, m/e 59, initiates the most important reaction sequence. Five reaction products are identified utilizing the ion cyclotron double resonance technique. Proton transfer to form the protonated parent is observed, reaction 3, in addition to the subsequent decomposition of the

$$(CH_3)_2\overset{+}{C}OH +$$

$$
\begin{array}{ll}
\longrightarrow (CH_3)_3\overset{+}{C}OH_2 + (CH_3)_2CO & (3) \\
\longrightarrow C_4H_9^+ + H_2O + (CH_3)_2CO & (4) \\
(CH_3)_3COH \longrightarrow (CH_3)_2C\overset{+}{=}O—C(CH_3)_3 + H_2O & (5) \\
\longrightarrow (CH_3)_2CO\cdots\overset{+}{H}\cdots OH_2 + C_4H_8 & (6) \\
 \overset{\textstyle H}{\underset{\textstyle \diagdown}{}} \\
\longrightarrow (CH_3)_2CO\cdots\overset{+}{H}\cdots O—C(CH_3)_3 & (7)
\end{array}
$$

product of this process in which H_2O is lost (reaction 4). Reaction 5, corresponding to proton transfer followed by displacement of H_2O gives the product appearing at m/e 115. The dehydration product appears at m/e 77, and at sufficiently high pressures clustering of protonated acetone with the parent alcohol is probable (reactions 6 and 7, respectively). The product distribution, measured using cyclotron resonance ion ejection methods at a sufficiently low pressure to avoid the clustering process, is given in Table I.

The products of reactions 3-7 are responsible for the majority of the species appearing at pressures of 10^{-6} Torr and higher. The protonated parent undergoes the condensation process involving loss of H_2O, reaction 8,

$$(CH_3)_3\overset{+}{C}OH_2 +$$

$$
\begin{array}{ll}
\longrightarrow [(CH_3)_3C]_2\overset{+}{O}H + H_2O & (8) \\
 \overset{+}{H}\cdots OH_2 \\
(CH_3)_3COH \longrightarrow (CH_3)_3C—O + C_4H_8 & (9) \\
 \diagdown H \\
\longrightarrow [(CH_3)_3COH]_2H^+ & (10)
\end{array}
$$

in addition to the dehydration reaction 9, and the clustering process which generates the proton bound dimer, reaction 10. Reactions 8-10 are directly analogous to reactions 5-7, respectively, involving protonated acetone as the reactant ion.
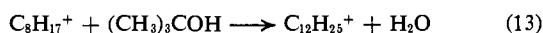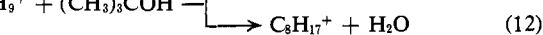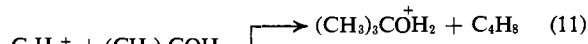
The single resonance intensity of the *tert*-butyl cation (m/e 57), which is produced both by direct electron impact and reaction 4, increases with increasing

Table I. Product Distribution for Reaction of Protonated Acetone ($C_3H_7O^+$, m/e 59) with *tert*-Butyl Alcohol

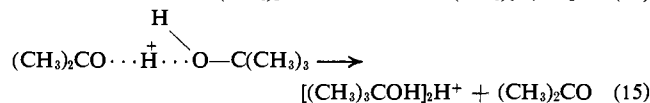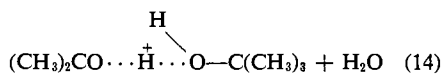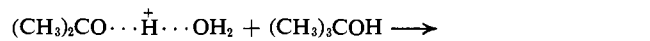| Reaction	ΔH,[a] kcal/mol	Product distribution[b] 11.4 eV	70 eV
$(CH_3)_2COH^+ + (CH_3)_3COH \longrightarrow$ $(CH_3)_3CO^+H_2 + (CH_3)_2CO$	-16	$0.03^{c,d}$	0.11^d
$\longrightarrow C_4H_9^+ + H_2O + (CH_3)_2CO$	8	0.13^c	0.60
$\longrightarrow (CH_3)_2C=O^+C(CH_3) + H_2O$	-17	0.42	0.14
$\longrightarrow (CH_3)_2CO\cdots H^+\cdots OH_2 + C_4H_8$	-22	0.42	0.14

[a] Thermochemical data from ref 7. [b] Total product yield is normalized to unity in each case. [c] At lower electron energies these two products extrapolate to zero abundance with concomitant increases in the remaining two products. [d] Secondary reactions involving $C_4H_9^+$ may make a small contribution to m/e 75 (protonated *tert*-butyl alcohol).

pressure, goes through a maximum, and then decreases (Figure 1). This species reacts by proton transfer, reaction 11, and in addition initiates the condensation

$$C_4H_9^+ + (CH_3)_3COH \longrightarrow (CH_3)_3CO^+H_2 + C_4H_8 \quad (11)$$
$$\longrightarrow C_8H_{17}^+ + H_2O \quad (12)$$

$$C_8H_{17}^+ + (CH_3)_3COH \longrightarrow C_{12}H_{25}^+ + H_2O \quad (13)$$

sequence involving reactions 12 and 13 which yields the alkyl cations at m/e 113 and 169.

As previously reported[8] *tert*-butyl alcohol displaces H_2O from the product of the ionic dehydration reaction 6 as indicated in reaction 14. The ionic dehydration

$$(CH_3)_2CO\cdots\overset{+}{H}\cdots OH_2 + (CH_3)_3COH \longrightarrow$$

$$\underset{\overset{|}{H}}{(CH_3)_2CO\cdots\overset{+}{H}\cdots O-C(CH_3)_3} + H_2O \quad (14)$$

$$\underset{\overset{|}{H}}{(CH_3)_2CO\cdots\overset{+}{H}\cdots O-C(CH_3)_3} \longrightarrow$$

$$[(CH_3)_3COH]_2H^+ + (CH_3)_2CO \quad (15)$$

product of reaction 9 reacts in a similar fashion. In both cases the proton bound dimer is eventually generated, with reaction 15 occurring as an intermediate step in the former instance.

The product of reaction 5 is apparently stable against further reaction, as is evidenced by the constant abundance of this species at the higher pressures illustrated in Figure 1. Since this species does not possess a labile proton it does not readily cluster with the parent alcohol. It is also of interest to note that the product of reaction 8, presumed to be protonated di-*tert*-butyl ether, does not cluster with the parent alcohol, even under conditions where the proton bound trimer of the parent alcohol is an abundant species. This may be due to steric effects of the butyl groups which prevent the close approach to the parent alcohol to the site of protonation. The major reaction pathways as initiated by the m/e 59 ion are summarized in Figure 2.

Variation of Reactivity with Electron Energy. At low electron energy (13.0 eV), the variation with pressure of the single resonance intensities shown in Figure 3 suggests an interesting variation of the reactivity of the m/e 59 ion with electron energy. The butyl cation, which is the most prominent reaction product apparent at 70 eV, appears only to a minor extent at 13.0 eV, amounting at most to 4% of the total ion abundance. The product distribution for reactions 3-7 measured at 11.4 eV (the lowest electron energy at which it could be recorded) is included in Table I for comparison to the results obtained at 70 eV. The full variation of the product distribution with electron energy is illustrated in Figure 4. Protonated *tert*-butyl alcohol (m/e 75) is
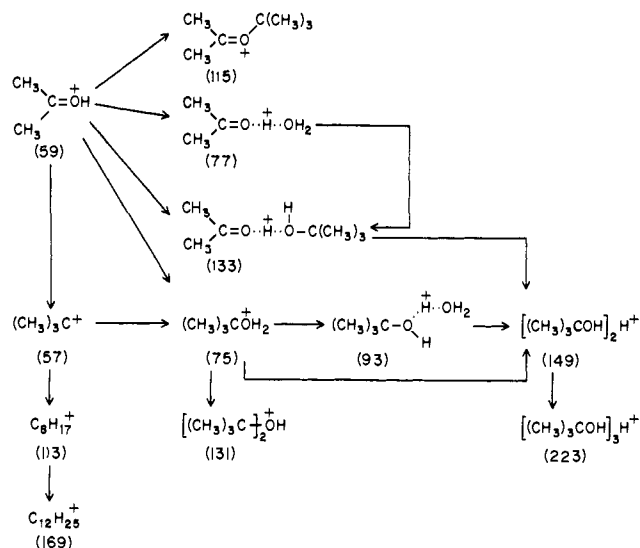

Figure 2. Reaction sequence initiated in *tert*-butyl alcohol by the α-cleavage product corresponding to protonated acetone [$(CH_3)_2COH^+$, m/e 59]. All reactions were identified by ion cyclotron double resonance techniques. Each step involves *tert*-butyl alcohol as the neutral reactant. The importance of the various reaction pathways may be assessed in Figures 1 and 3.

not included with the data shown in Figure 4. The extent to which this species is formed by direct reaction of m/e 59 is uncertain due to reaction 11. The total reaction rate did not vary by more than 10% over the full range of electron energies indicated in Figure 4. The m/e 59 ion has an appearance potential 10.1 ± 0.2 eV.[14] Only when this species is generated with electron energies above ~15 eV is the butyl cation an important reaction product, suggesting the requirement of excess internal energy in the reactant ion.

The proton affinity of tertiary butyl alcohol is 206 ± 5 kcal/mol.[7] Reaction 3 is thus exothermic by about 16 kcal/mol. The decomposition process 16 is 24 kcal/

$$(CH_3)_3CO^+H_2 \longrightarrow (CH_3)_3C^+ + H_2O \quad (16)$$
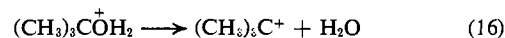
mol endothermic, making the overall reaction 4 endothermic by 8 kcal/mol, thus explaining the requirement of excess internal energy in the reactant ion to observe the process. Photoelectron spectroscopy reveals two low-lying excited states of *tert*-butyl alcohol parent ion, with onsets at approximately 10.7 and 11.6 eV.[15] Fragmentation from either of these states could produce the m/e 59 ion with sufficient internal excitation to observe reaction 4.

(14) Harrison reports a value of 10.2 eV for the appearance potential of m/e 59 (protonated acetone) from $(CH_3)_3COH$: A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).
(15) M. B. Robin and N. A. Kuebler, *J. Electron Spectrosc.*, **1**, 13 (1972).
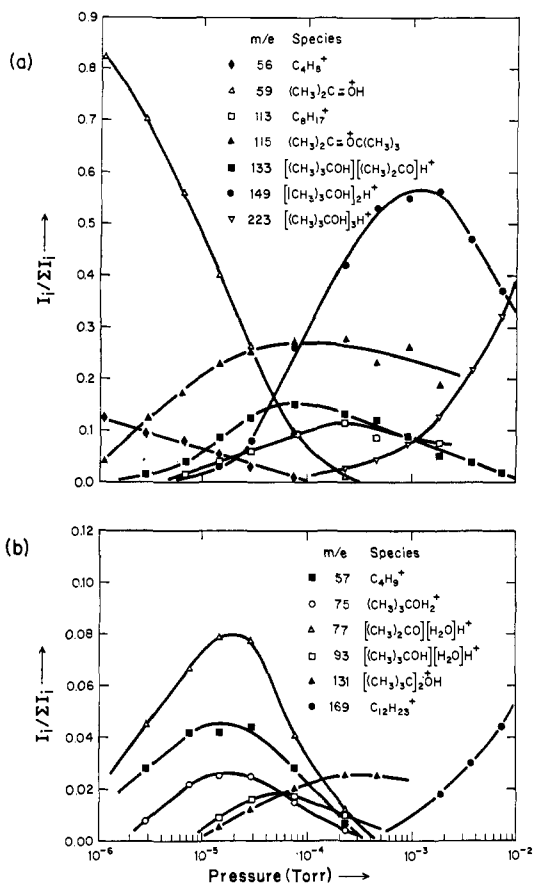
Figure 3. Variation of single resonance intensities with pressure for ionic species in *tert*-butyl alcohol at 13 eV: (a) major ions; (b) minor ions.
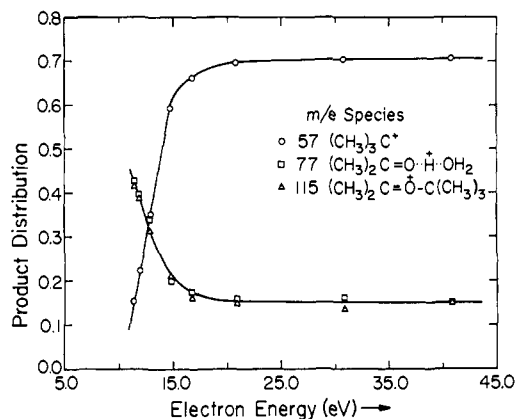

Figure 4. Variation with electron energy of the product distribution from the reaction of $(CH_3)_2COH^+$ with *tert*-butyl alcohol.

Investigation of Reaction Mechanisms with *tert*-Butyl Alcohol-^{18}O. Labeled *tert*-butyl alcohol-^{18}O containing 42 % ^{18}O permits the mechanisms of several of the reactions to be further elucidated. An examination of the gas phase ion chemistry of *tert*-butyl alcohol-^{18}O generally confirms the reaction pathways and product identifications as detailed above. For example, the hydrocarbon product at m/e 113 formed in reaction 12 appears as expected only at m/e 113 in the single resonance spectrum of the ^{18}O labeled alcohol. The distribution of isotopic products in reactions 5 and 6 are of mechanistic interest. Double resonance techniques for distinguishing mechanisms in similar circum-

stances have been described previously and applied to interpret reaction mechanisms of alkyl halides,[16,17] boron hydrides,[18] and acetonitrile.[19]

Two reasonable mechanisms may be proposed for reaction 5 in analogy with those proposed earlier for similar reactions in 2-propanol[5,6] and 2-butanol.[7] Mechanism I involves nucleophilic attack of the alcohol

Mechanism I

$(CH_3)_2COH^+ + (CH_3)_3COH \longrightarrow$
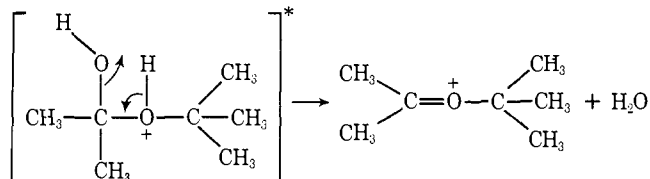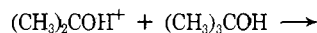
on the carbonium ion center in protonated acetone followed by elimination of H_2O from the chemically activated intermediate. The oxygen of H_2O lost in this mechanism comes exclusively from the reactant ion. In mechanism II it is proposed that, as the reactants

Mechanism II

$(CH_3)_2COH^+ + (CH_3)_3COH \longrightarrow$
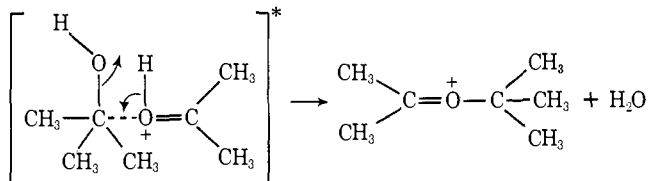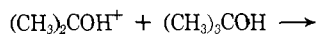
approach, the labile proton is transferred to the more basic site in the intermediate (alcohol oxygen) and the carbonyl group acts as a nucleophile, displacing H_2O from the protonated alcohol; the oxygen in H_2O lost in this process comes exclusively from the reactant neutral. Mechanism II also conforms to postulated rules for nucleophilic displacement reactions in the gas phase.[20]

In the case of reaction 5 with ^{18}O labeled alcohol, the reactant ion appears at m/e 59 and 61 and the product ion appears at m/e 113 and 115, the higher mass in each instance corresponding to ^{18}O and representing 42% of the isotopic abundance. Double resonance experiments indicate that only m/e 59 contributes to m/e 113 and similarly only m/e 61 contributes to m/e 115. Clearly these results are consistent only with mechanism II and the process must be considered a nucleophilic displacement reaction. Rules proposed for nucleophilic displacement reactions of the type related to mechanism II require that the proton affinity of *tert*-butyl alcohol be higher than acetone. Available thermochemical data suggest this to be the case, although the proton affinity of acetone remains controversial.[21] Thus as the reactants approach, the labile proton is effectively trans-

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

(17) J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, *J. Amer. Chem. Soc.*, **94**, 2798 (1972).

(18) R. C. Dunbar, *J. Amer. Chem. Soc.*, **90**, 5676 (1968).

(19) G. A. Gray, *J. Amer. Chem. Soc.*, **90**, 6002 (1968).

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

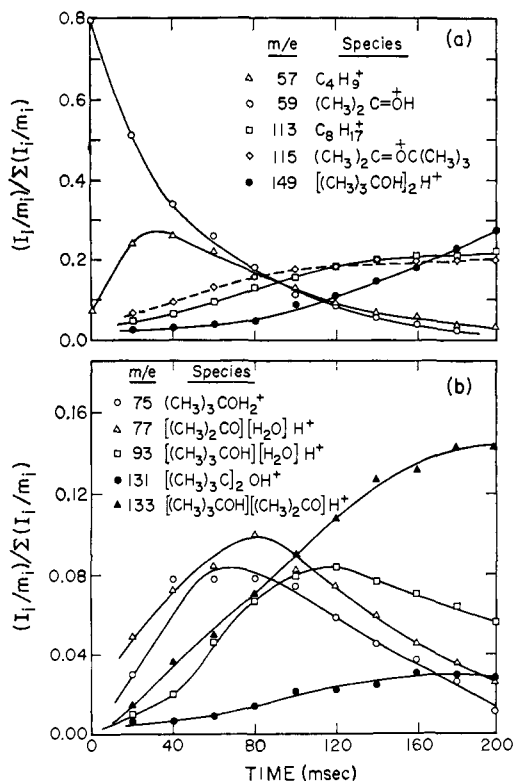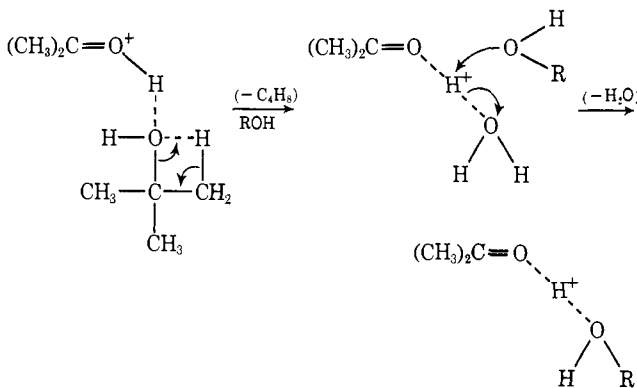(21) J. Long and B. Munson, *J. Amer. Chem. Soc.*, **95**, 2427 (1973)).

Figure 5. Variation of ion abundance with time for tert-butyl alcohol at 15 eV and 5.0 × 10⁻⁷ Torr: (a) major ions; (b) minor ions. An electron beam pulse of 10-msec duration was used to generate the primary reactant ions.

Figure 6. Variation of the log of ion abundance with time for major reactive ions displayed in Figure 5.

ferred to the neutral alcohol. Although ruled out in this instance, processes which occur in analogy with mechanism I have been documented in other systems.[22]

In the sequence of reactions 6 and 14 it is observed that only m/e 59 contributes (eventually) to m/e 133 and only m/e 61 contributes to m/e 137. This can be taken as evidence that the two oxygen atoms in the dehydration product of reaction 6 are nonequivalent, thus eliminating a protonated geminal diol or other symmetrical product ion structure. It also demonstrates that the O atom of H_2O which is lost in reaction 14 originates from the neutral in reaction 6. Likewise, the double resonance contributions of m/e 77, 79, and 81 to m/e 135 in reaction 14 indicate that the displaced H_2O comes exclusively from the reactant ion. The formulation of the dehydration products as strongly hydrogen bound dimers is further substantiated by these results, which are consistent with the mechanistic sequence shown below.

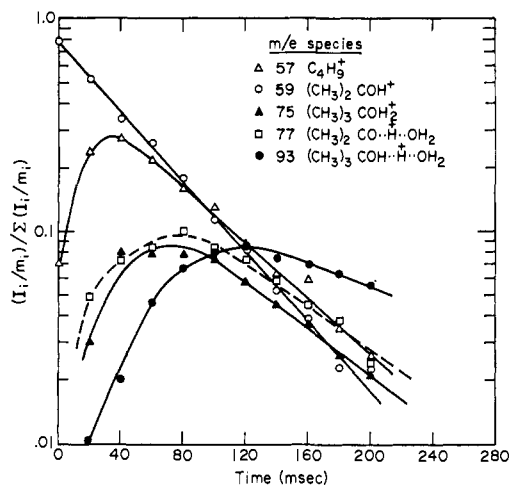(22) J. H. Cook and J. L. Beauchamp, J. Amer. Chem. Soc., in press.

Trapped Ion Cyclotron Resonance Investigation of Reaction Kinetics.

Trapped ion cyclotron resonance experiments facilitate the determination of kinetic parameters such as reaction rate constants, both for primary ions and for the intermediates involved in sequential bimolecular reaction processes.[10,23] Such experiments are generally conducted at relatively low pressures (typically 10⁻⁶ Torr) by pulsing the electron beam and storing ions for a predetermined delay or reaction time, following which they are sampled in a time short compared to the time between collisions. The results of such an experiment are illustrated in Figure 5 by the variation of ion abundance with time for tert-butyl alcohol at 15 eV and 1.1 × 10⁻⁶ Torr. It is apparent that the trapped ion data presented in Figure 5 are generally consistent with the reaction scheme summarized in Figure 2. Interestingly, even at pressures as low as 10⁻⁶ Torr, the proton-bound dimer is the most abundant species after 200 msec. While signal to noise problems precluded the accurate measurement of the intensities of minor ions at times longer than 200 msec, it was observed that the proton bound dimer increases to a constant fraction (~60%) of the total ionization at 500 msec and does not decay at longer times (up to 2.0 sec), indicating that the dimer is unreactive at this pressure. The production of the proton bound dimer in abundance under these circumstances is clearly the result of sequential bimolecular reactions and not due to the collisional stabilization of reaction intermediates.

Total reaction rate constants can be derived for the principal reactant ions indicated in Figure 5 from the limiting slopes for the variation of the log of the ion abundance with time (Figure 6). Rate constants determined in this fashion are summarized in Table II. The total rate constant for the reaction of m/e 59 is 11 ± 2 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹ (measured at 15.0 eV). Combined with the product distribution reported in Table I at low electron energy, this gives k = 4.6 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹ for the dehydration reaction 6, which is slightly higher than the value of 3.7 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹ determined from the variation of ion abundance with pressure and quoted earlier.[8]

Trapped Ion Studies of Proton Bound Dimer Forma-

(23) R. J. Blint, T. B. McMahon, and J. L. Beauchamp, J. Amer. Chem. Soc., 96, 1269 (1974).
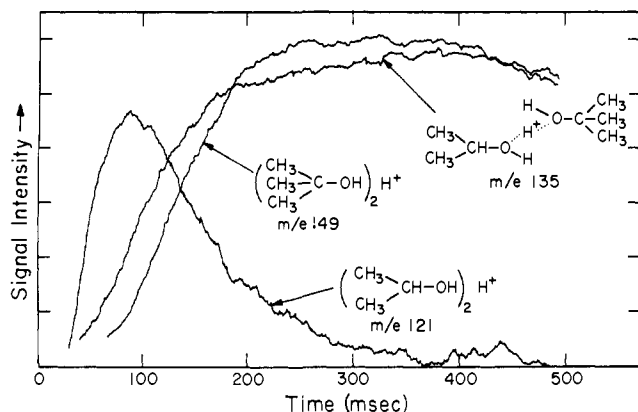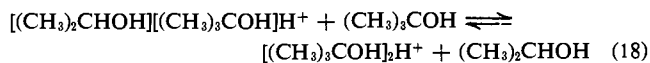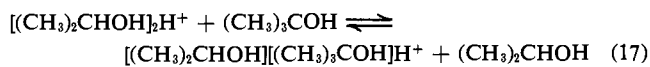
Figure 7. Variation of single resonance intensities with time for the three clusters observed in a 2:1 mixture of isopropyl and *tert*-butyl alcohol at a total pressure of 2.8 × 10⁻⁶ Torr and 17 eV.

Table II. Total Rate Constants for Disappearance of Reactant Ions in *tert*-Butyl Alcohol

m/e	Reactant ion	Disappearance rate constant,[a] 10^{-10} cm³ molecule⁻¹ sec⁻¹
57	$C_4H_9^+$	8.9
59	$(CH_3)_2COH^+$	11.0
75	$(CH_3)_3COH_2^+$	7.2
77	$(CH_3)_2CO\cdots H^+\cdots OH_2$	6.8
93	$(CH_3)_3COH\cdots H^+\cdots OH_2$	2.3

[a] Measured at 15 eV electron energy in trapped ion studies. Data are taken from limiting slopes of curves in Figure 6. Error estimated to be ±20% due to uncertainties in pressure measurement.

tion in Alcohol Mixtures. From the above results and from previous investigations it is clear that the bimolecular reaction sequences permit the formation of proton bound dimers at pressures below those where termolecular reactions lead to the generation of these species. In a mixture of alcohols (or an alcohol with an arbitrary n-donor base) it should be possible to study relative stabilities of dimers in trapped ion icr experiments. The feasibility of such studies is demonstrated by the data in Figure 7. In a 2:1 mixture of isopropyl with *tert*-butyl alcohol the three possible dimers are observed. With an excess of isopropyl alcohol the dimer of this species is observed to dominate at short times. This species decays with concomitant increase in the abundances of the remaining dimers. These changes are accounted for by reactions 17 and 18, identified in

$[(CH_3)_2CHOH]_2H^+ + (CH_3)_3COH \rightleftharpoons$

$[(CH_3)_2CHOH][(CH_3)_3COH]H^+ + (CH_3)_2CHOH$ (17)

$[(CH_3)_2CHOH][(CH_3)_3COH]H^+ + (CH_3)_3COH \rightleftharpoons$

$[(CH_3)_3COH]_2H^+ + (CH_3)_2CHOH$ (18)

double resonance experiments. Ejection of either the reactant or product ion in reaction 18 leads to the decay of the other, indicating that the reaction proceeds reversibly. From the decay of m/e 121 (proton bound dimer of isopropyl alcohol) a rate constant of 3.9 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹ is obtained for reaction 17. While the equilibrium in reaction 17 lies to the right ($-\Delta G \geqslant 3$ kcal/mol), observation of steady state ion abundances indicates an equilibrium constant of $K = 1.8$ for reaction 18, corresponding to a free

energy change $\Delta G = -0.3 \pm 0.1$ kcal/mol. Variation of the ratio of neutrals leads to the expected variation in dimer abundance at long times. Dimer stability appears in this case to be largely determined by the basicity of the monomers. The estimated proton affinities of isopropyl and *tert*-butyl alcohol are 195 and 206 kcal/mol, respectively.[17] The enthalpy change for addition of the second alcohol molecule is approximately 30 kcal/mol.[24] While protonation of *tert*-butyl alcohol is energetically favored, our results indicate that there is *little preference for isopropyl or tert-butyl alcohol in the interaction of a second alcohol molecule with protonated tert-butyl alcohol*. Related studies of the stability of proton bound dimers of n-donor bases have been reported by several investigators.[25]

Collisional Stabilization of Reaction Intermediates. Ion–molecule reaction sequences observed at low pressures can be markedly different under conventional radiolytic conditions, where interception and collisional stabilization of reaction intermediates is in general important. For example, the data in Figure 1 indicate proton bound trimer is formed in the pressure range between 10⁻⁴ and 10⁻² Torr, the higher pressure corresponding to 10³ collisions during the 1 msec ion residence time in the cell. The variation of ion abundance with time at 1.1 × 10⁻⁶ Torr (Figure 4) shows *no* trimer formation even after two seconds (corresponding to 200 collisions in the cell) under conditions where proton bound dimer formation results from sequential bimolecular reactions. At higher pressures it is likely that the ion chemistry is dominated entirely by cluster formation. To investigate certain aspects of these processes in the present study the possibility of stabilizing the intermediate in the reaction of m/e 59 with *tert*-butyl alcohol was considered. In these experiments there is an additional expectation dictated by the data in Figure 3 which demonstrates that internal excitation of m/e 59 causes a major change in the product distribution. Collisional relaxation of this internal excitation is expected to lead to an increase of the dehydration (m/e 77) and condensation (m/e 115) products relative to the production of *tert*-butyl cation (m/e 57). Since the total rate constant was observed to be independent of electron energy, it is necessary to monitor only one of the products relative to m/e 59 as the pressure of the additive is increased. A particularly convenient collision gas is sulfur hexafluoride.[26] The ionization potential of SF_6 is ~15.3 eV.[27] Below 15.3 eV the marked changes with electron energy in the product distribution for reactions 4–6 can be examined without complications which would result from ionizing the buffer gas.

With an electron energy of 12 eV, *tert*-butyl alcohol was admitted to the icr cell at a fixed pressure of 2 × 10⁻⁶ Torr. Under these conditions the products due to reactions 3–6 appear, but collisional stabilization or

(24) E. P. Grimsrud and P. Kebarle, *J. Amer. Chem. Soc.*, **95**, 7939 (1973).

(25) For a general discussion of ion-solvation phenomena, see P. Kebarle in "Ions and Ion Pairs in Organic Reactions," Vol. I, M. Szarc, Ed., Wiley, New York, N. Y., 1972, Chapter 2; P. Kebarle in "Ion Molecule Reactions," Vol. 2, J. L. Franklin, Ed., Plenum Press, New York, N. Y., 1972, Chapter 7.

(26) S. P. Pavlou and B. S. Rabinovitch, *J. Phys. Chem.*, **75**, 3037 (1971); D. W. Setzer and E. E. Siefert, *J. Chem. Phys.*, **57**, 3623 (1972).

(27) D. W. Turner, C. Baker, A. D. Baker, and C. R. Bundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970, p 379.

higher order processes do not result in the formation of an appreciable amount of the proton bound dimer of acetone and tert-butyl alcohol. Single resonance spectra were then recorded as a function of the additive pressure. The variation of the abundance of the m/e 115 condensation product with SF_6 pressure is shown in Figure 8, along with the identical experiment performed at 15 eV. Above 10^{-4} Torr of SF_6 appreciable line broadening precluded measurement of the product ion intensities. At the higher electron energy the decreased abundance of m/e 115 is both expected and observed. However, in neither case is the abundance of m/e 115 observed to depend on SF_6 pressure, even with a 20-fold excess. Collisional relaxation of internal excitation should cause m/e 115 at 15 eV to approach the abundance observed at 12 eV. Identical behavior is observed for the m/e 77 dehydration product. The m/e 57 product could not be monitored at higher SF_6 pressures since there is a significant contribution from direct electron impact ionization, and ion ejection experiments are required to sort out the product distribution.

These results are somewhat unexpected. Studies with vibrationally excited neutrals formed in chemical activation processes have shown that SF_6 removes from 4 to 12 kcal/mol of internal excitation on each collision.[26] The results suggest that either the excitation is in a form which cannot be readily collisionally relaxed or that a structural reorganization has occurred which cannot be reversed by collision. The latter is unlikely since protonated acetone is the most stable of the various $C_3H_7O^+$ geometrical isomers.[28] If the former possibility is correct, then the internal excitation may be present as electronic rather than vibrational excitation. The lowest triplet state of protonated acetone may be sufficiently long-lived to persist in the experiments performed. Although little is known about the collisional quenching of electronically and vibrationally excited ions, it is likely that in the absence of resonant electronic energy transfer processes that vibrational excitation is more readily subject to collisional relaxation.

Collisional stabilization of the adduct of m/e 59 with tert-butyl alcohol was not observed with SF_6 pressures up to 2×10^{-4} Torr. Line broadening problems are reduced by using a lighter collision partner for stabilization experiments. With a lighter collision partner, momentum relaxation is reduced without causing an appreciable reduction in the number of stabilizing collisions. Using CH_4 for these reasons as a collision gas, the spectrum of tert-butyl alcohol was examined at 12.0 eV up to a pressure of 2×10^{-3} Torr of the additive. Even at this pressure it was not possible to collisionally stabilize the adduct of m/e 59 with tert-butyl alcohol. If it is assumed that one collision would stabilize a measurable fraction of the m/e 133 intermediate, then these results indicate that the intermediate lifetime is less than $\sim 10^{-5}$ sec.

Relation to Previous Studies

Comparison to Lower Aliphatic Alcohols. The systematic ion chemistry of aliphatic alcohols has been previously discussed.[7] The ion chemistry of tert-butyl alcohol parallels that of 2-propanol and 2-butanol, being
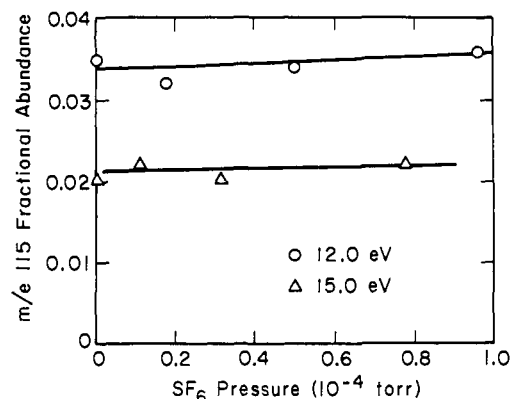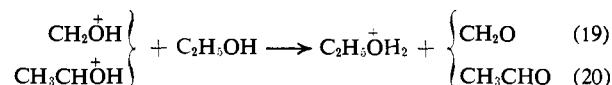

Figure 8. Variation of the fractional abundance (of total ionization) of the m/e 115 condensation product with SF_6 additive pressure. The pressure of tert-butyl alcohol was held fixed at 2×10^{-6} Torr. No ions were observed from SF_6 below 15 eV and no products implicating SF_6 as the neutral reactant were observed.
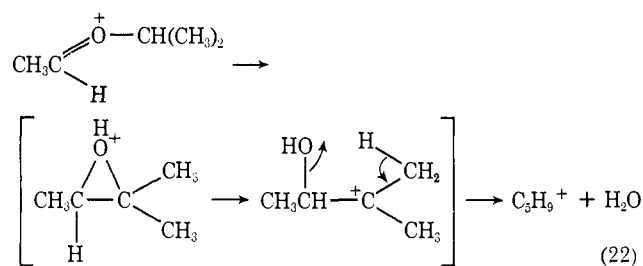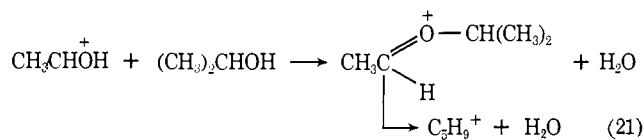
more complicated than that of methanol and ethanol. The main differences are due to reactions of α-cleavage fragment ions with the parent alcohol. In the case of ethanol, for example, the α-cleavage fragments react only to generate the protonated parent ion (reactions 19 and 20) in addition to certain decomposition products of

$$\left.\begin{array}{c} CH_2\overset{+}{O}H \\ CH_3CH\overset{+}{O}H \end{array}\right\} + C_2H_5OH \longrightarrow C_2H_5\overset{+}{O}H_2 + \left\{\begin{array}{cc} CH_2O & (19) \\ CH_3CHO & (20) \end{array}\right.$$

the protonated parent. This is in marked contrast to the sequence of condensation reactions illustrated for tert-butyl alcohol in Figure 2. The thermochemistry offers no clue to the difference in behavior, since many of the condensation reactions analogous to those shown in Figure 2 are exothermic in the case of ethanol.[7] The behavior of the longer chain primary alcohols 1-propanol and 1-butanol is similar to ethanol, and in particular condensation reactions related to that of tert-butyl alcohol with m/e 59 (reaction 5) and proceeding by way of mechanism II are not observed.[29] This is so even when the proton transfer step is exothermic. The structure of the reacting alcohol is clearly an important factor in promoting condensation over proton transfer, and since tertiary alcohols condense more readily than primary alcohols,[29] the reaction intermediate or transition state probably develops appreciable positive charge at the carbon undergoing displacement. In certain instances the difference in reactivity may be related to the lifetimes and relative stabilities of the reaction intermediates. Longer lifetimes are expected to allow the more complex condensation process to compete favorably with simple bond cleavage (i.e., proton transfer). Lifetimes are likely to be short for example, if proton transfer from the carbonyl group to the alcohol is very exothermic, as it is with CH_2OH^+, and this ion does not undergo condensation reactions with any of the C1–C4 alcohols.

The differences between the ion chemistry of 2-propanol and tert-butyl alcohol are twofold. First, the product of the process analogous to reaction 5 undergoes further unimolecular decomposition to lose H_2O in the case of 2-propanol (reaction 21). Since this is

(28) Relative stabilities of several of the $C_3H_7O^+$ structural isomers are discussed in ref 14. More recent studies in our own laboratory have considered all of the reasonable $C_3H_7O^+$ structural isomers, and protonated acetone is found to be the most stable.

(29) J. K. Pau, J. K. Kim, and M. C. Caserio, Chem. Commun., 120 (1974).

$$CH_3CH\overset{+}{O}H + (CH_3)_2CHOH \longrightarrow CH_3C\overset{\overset{+}{O}-CH(CH_3)_2}{\underset{H}{\diagdown}} + H_2O$$

$$\longrightarrow C_5H_9^+ + H_2O \qquad (21)$$

$$CH_3C\overset{\overset{+}{O}-CH(CH_3)_2}{\underset{H}{\diagdown}} \longrightarrow$$

$$\left[CH_3C\overset{H}{\underset{H}{\diagup}}\overset{\overset{+}{O}}{\underset{}{\diagdown}}C\overset{CH_3}{\underset{CH_3}{<}} \longrightarrow CH_3CH-\overset{+}{C}\overset{CH_2}{\underset{CH_3}{<}} \right] \longrightarrow C_5H_9^+ + H_2O$$

$$(22)$$

not observed for *tert*-butyl alcohol, the presence of hydrogen atoms on the carbon atoms adjacent to the oxygen in the product of reactions 5 and 21 may be an important consideration in the decomposition pathway. In a study of the electron impact induced fragmentation of aliphatic ethers, process 22 has been suggested as a mechanism for H_2O loss from α-cleavage products structurally similar to the product of reaction 21.[6] This mechanism is accommodated by the presence of H atoms on the carbon atoms adjacent to oxygen.

The second difference is with regard to the reactivity of the alkyl cations $C_3H_7^+$ and $C_4H_9^+$ generated in 2-propanol and *tert*-butyl alcohol, respectively. $C_3H_7^+$ reacts solely by proton transfer to 2-propanol, while $C_4H_9^+$ initiates the condensation sequence indicated by reactions 12 and 13. *tert*-Butyl alcohol is known to polymerize under acidic conditions in solution to produce high-molecular weight aliphatic species. A typical step for this process in the gas phase might be as indicated in reaction 23. The depicted process may be

$$(CH_3)_3C^+ + (CH_3)_3COH \longrightarrow$$

$$\left[\overset{CH_3}{\underset{CH_3}{>}}C=CH_2 \quad C(CH_3)_3 \right]^* \longrightarrow C_8H_{17}^+ + H_2O \qquad (23)$$
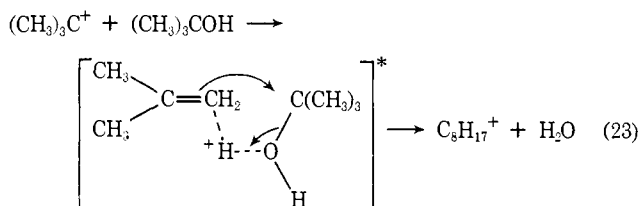
regarded as a nucleophilic displacement reaction where isobutylene serves as a π-donor base in contrast to the more unusual n-donor base for which such processes have been previously characterized.[20]
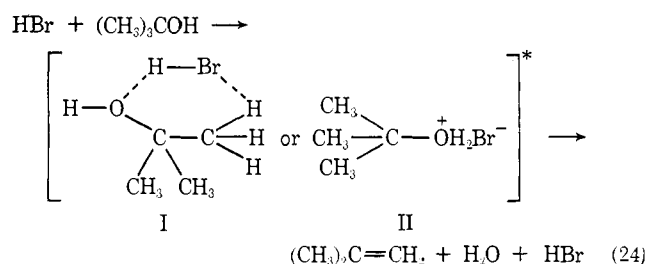
A similar variation in reactivity of α-cleavage ions from 2-propanol,[5] 2-butanol,[7] and *tert*-butyl alcohol is observed as the electron energy is varied. In all cases, internal excitation of the reactant ion is efficiently utilized in reactions which are endothermic for the reactants in their ground states. Although the evidence obtained in the present study suggests that the internal excitation takes the form of long-lived electronically excited states, the evidence is not definitive and the nature of the excitation in the reactant ion remains somewhat obscure.

Comparison of Present Results to Other Studies of *tert*-Butyl Alcohol Dehydration. The catalytic dehydration of alcohols on alumina and silica–alumina surfaces has been extensively studied.[30,31] The dehydra-

tion of *tert*-butyl alcohol on silica–alumina catalysts has been recently investigated in detail.[31] The mechanism of dehydration is generally thought to involve carbonium ions formed when tertiary alcohols bind to strongly acidic sites. Desorption of the alkene involves proton transfer from the carbonium ion to an adjacent basic site of the catalyst.

Of greater relevance to the present study are investigations of homogeneous catalysis of alcohol dehydration in the gas phase.[32] Pyrolysis of *tert*-butyl alcohol leads to formation of isobutylene with an observed activation energy of 55–60 kcal/mol.[33] Addition of hydrogen bromide results in dehydration at lower temperatures, with an activation energy of 30 kcal/mol.[34] The observed rate law indicates a bimolecular reaction between the alcohol and the hydrogen halide. Maccoll and Stimson[35] suggest several transition states for this process, favoring the intermediates indicated in reaction 24.

$$HBr + (CH_3)_3COH \longrightarrow$$

$$\left[\begin{array}{c} H-O\overset{\overset{H-Br}{\diagup}\diagdown}{\underset{}{}}H \\ C-C-H \\ CH_3\ CH_3 \end{array} \quad or \quad CH_3-\overset{CH_3}{\underset{CH_3}{>}}C-\overset{+}{O}H_2Br^- \right]^*$$

$$\overset{I}{} \qquad \overset{II}{} \longrightarrow$$

$$(CH_3)_2C=CH_2 + H_2O + HBr \qquad (24)$$

In the products of reaction 24, association of H_2O with HBr would somewhat lower the level of excitation required in the intermediate to promote the dehydration reaction but not to the extent afforded by the strong hydrogen bond in the product of the ionic dehydration reactions 1 and 2. It is difficult to estimate the internal excitation in the intermediates proposed for reaction 24, but it is likely to be less than the chemical activation provided by the strong hydrogen bond in the ionic intermediates for reactions 1 and 2. These combined factors, greater internal excitation in the intermediate and lower critical energy for decomposition, serve to rationalize the ease of the facile ionic dehydration process compared to the neutral acid-catalyzed process.

While the proposed six-membered ring in intermediate I for reaction 24 is particularly attractive for dehydration catalyzed by hydrogen halides, it does not appear reasonable to formulate such a transition state in the case of dehydration effected by ionic species possessing a labile proton. This may in fact suggest that a somewhat looser intermediate is more appropriate for reaction 24.

Implications for Further Study

The knowledge gained in the present study of the simplest tertiary alcohol combined with earlier studies of primary and secondary alcohols provides a fairly complete picture of the gas phase positive ion chemistry of aliphatic alcohols. Thus, an examination of the gas

(30) For recent reviews, see H. Knözinger, *Angew. Chem., Int. Ed. Engl.*, **7**, 791 (1968); B. Notari, *Chim. Ind. (Milan)*, **51**, 1200 (1969); and H. Pines and J. Manassen, *Advan. Catal. Relat. Subj.*, **16**, 49 (1966).

(31) F. Figueras, A. Nohl, L. De Mourgues, and Y. Trambruze, *Trans. Faraday Soc.*, **67**, 1155 (1971).
(32) For a general review of elimination reactions pertinent to the discussion here, see A. Maccoll, *Chem. Rev.*, **69**, 33 (1969).
(33) W. Tsang, *J. Chem. Phys.*, **40**, 1498 (1964).
(34) V. R. Stimson and J. R. Watson, *Aust. J. Chem.*, **19**, 401 (1966).
(35) A. Maccoll and V. R. Stimson, *J. Chem. Soc., London*, 2836 (1966).

phase ion chemistry of 2-methyl-2-butanol provides no new surprises,[36] the observed reaction sequences being analogous to those observed with *tert*-butyl alcohol, the only complication being that the sequences are initiated by two α-cleavage products (corresponding to protonated acetone and protonated 2-butanone).

While these studies focus attention on bimolecular processes occurring at low pressures, it is evident that the most abundant ionic species present at long times are clusters of the type $(ROH)_nH^+$. These dominate to an even greater extent at elevated pressures where they have been specifically studied to obtain information relating to ion solvation processes[24,25,37,38] and have been invoked by several investigators to explain neutral products observed in radiolysis studies.[39,40] Of particular interest in this regard are the chain reactions proposed by Freeman and coworkers[40] to account for the high yields of diethyl and diisopropyl ethers in the gas phase radiolysis of ethanol and isopropyl alcohol. Further work is warranted to interpret the mechanism of these processes.[24]

There are several investigations being actively pursued in our laboratories which were suggested by this and related studies of the gas phase ion chemistry of different functional groups. These include studies of functional group interactions in species such as substituted alcohols,[41] further investigations of reaction mechanisms where nucleophilic attack on substituted carbonium ions is possible,[22,29] studies of the negative ion chemistry of alcohols (with a particular emphasis on alkoxide ions), studies of the stability of ion clusters using the methodology described above in conjunction with the data of Figure 7, and further studies of the observed variation in reactivity with electron energy. The latter investigations involve the use of high resolution photoionization mass spectrometry to obtain better thermochemical data for protonated aldehydes and ketones and accurately determined thresholds for modified reactivity.[42]

(36) J. L. Beauchamp, unpublished results.

(37) P. Kebarle, R. N. Haynes, and J. G. Collins, *J. Amer. Chem. Soc.*, **89**, 5753 (1967).

(38) M. E. Russell and W. A. Chupka, *J. Phys. Chem.*, **75**, 3797 (1971).

(39) A. R. Anderson and J. A. Winter in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 197.

(40) K. M. Bansal and G. R. Freeman, *Radiat. Res. Rev.*, **3**, 209 (1971).

(41) J. K. Kim, M. C. Findlay, W. G. Henderson, and M. C. Caserio, *J. Amer. Chem. Soc.*, **95**, 2184 (1973).

(42) J. L. Beauchamp, S. E. Buttrill, and A. D. Williamson, unpublished results.