Identification of $C_2H_5O^+$ Structural Isomers by Ion Cyclotron Resonance Spectroscopy

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Abstract: The ion–molecule reactions of $C_2H_5O^+$ fragment ions with parent neutrals from which they were generated have been investigated using ion cyclotron resonance spectroscopy. Specific reactions that can distinguish the $C_2H_5O^+$ structural isomers corresponding to the methoxy methyl cation (I), protonated acetaldehyde (II), and protonated ethylene oxide (III) are considered in detail. Structure I can be distinguished on the basis of methyl cation and hydride abstraction reactions, which II and III do not undergo. The marked similarities in reactivity observed do not allow II and III to be distinguished. The heat of formation of III, determined indirectly by measuring the proton affinity of ethylene oxide, is 27 kcal/mole greater than the heat of formation of II. The relative stabilities and similarities in reactivity of both suggest that III rearranges to II during or after generation. In the generation of II from 2-alkanols an interesting variation of reactivity with electron energy is observed. It is shown that this probably results from the generation of II in a high state of internal excitation, rather than rearrangement to III. In all twelve cases examined, the $C_2H_5O^+$ isomeric structure identified is in agreement with previously postulated pathways of ion decomposition.

$\mathbf{I}$ on cyclotron resonance spectroscopy is uniquely useful for establishing relationships between reactant ions and product ions in complex ion–molecule reaction sequences.[2-5] Ion cyclotron double resonance experiments have in fact been used to identify[2-4] ion–molecule reactions and determine product ion distributions[5] even when the reactant and product ions are involved in several concurrent processes.

Ion–molecule reactions which occur at low energies are sensitive to the nature of the functional groups and the details of the molecular structure of both the ionic and neutral reactants.[6-8] It is of interest to explore whether ion–molecule reactions, detected by ion cyclotron resonance techniques, can be used to characterize unknown ion structural features once the specific reactivity of a particular functional group has been ascertained. The implied methodology is directly analogous to classical chemical methods for structure determination and has been successfully applied to distinguish the parent ion of acetone from its enol modification.[9]

A variety of techniques have been employed in an attempt to identify the structural isomers of $C_2H_5O^+$, including thermochemical studies,[10-15] a detailed analysis

of metastable ion characteristics,[16-18] and collision induced decompositions.[18] Of the five isomers of $C_2H_5O^+$ represented by structures I–V
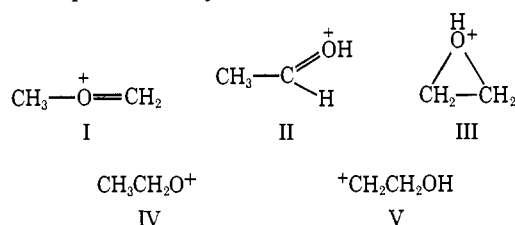
previous investigators[10-18] have concluded that only the first three commonly occur to a significant extent. The reason for this is partially evident in the thermochemical data summarized in Table I. Structure II is the most

Table I. Heats of Formation of $C_2H_5O^+$ Structural Isomers

Structural isomer	ΔH_f, kcal/mole	Ref
(I) $CH_3{-}\overset{+}{O}{=}CH_2$	170 ± 5	10, 13
(II) $CH_3CH{=}\overset{+}{O}H$	143 ± 2	10, 13, 15
(III) $\overset{\overset{\textstyle O^+}{\diagup\;\diagdown}}{CH_2{-\!\!\!-\!\!\!-}CH_2}$	170 ± 4	a
(IV) $CH_3CH_2O^+$	211 ± 2	14
(V) $^+CH_2CH_2OH$	b	

^{a} Derived in the present study by measuring the proton affinity of ethylene oxide. ^{b} No reliable value available. The production of this isomer from 1-propanol is discussed in ref 15, but the results are inconclusive.

(1) (a) Alfred P. Sloan Foundation Fellow, 1968-1970, California Institute of Technology; (b) Allied Chemical Predoctoral Fellow, Stanford University.

(2) (a) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. D. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966); (b) J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967).

(3) J. L. Beauchamp and S. E. Buttrill, *J. Chem. Phys.*, **48**, 1783 (1968).

(4) M. T. Bowers, D. D. Elleman, and J. L. Beauchamp, *J. Phys. Chem.*, **72**, 3599 (1968).

(5) J. L. Beauchamp and J. T. Armstrong, *Rev. Sci. Instrum.*, **40**, 123 (1969).

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

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(9) J. Diekman, J. K. MacLeod, C. Djerassi, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **91**, 2069 (1969).

(10) M. S. B. Munson and J. L. Franklin, *J. Phys. Chem.*, **68**, 3193 (1964).

(11) D. Van Raalte and A. G. Harrison, *Can. J. Chem.*, **41**, 3118 (1963).

(12) A. G. Harrison and B. G. Keyes, *J. Amer. Chem. Soc.*, **90**, 5046 (1968).

(13) A. G. Harrison, A. Ivko, and D. Van Raalte, *Can. J. Chem.*, **44**, 1625 (1966).

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(15) K. M. A. Refaey and W. A. Chupka, *ibid.*, **48**, 5205 (1968).

(16) T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5021 (1966).

(17) F. W. McLafferty and W. T. Pike, *ibid.*, **89**, 5951 (1967).

(18) F. W. McLafferty and H. D. R. Schuddemage, *ibid.*, **91**, 1866 (1969).

stable, with I and III being comparable and somewhat higher in energy. Structure V, for which reliable data are not available, probably possesses a heat of formation comparable to structure IV, which is ~27 kcal/mole less stable than I and III. On the basis of metastable ion characteristics[16,17] and isotopic labeling studies,[11,12] the protonated oxirane structure III, rather than the expected structure II, has been postulated as the favored structure produced by isomerization of the initial $C_2H_5O^+$ ions from $HOCH_2CH_2R$, $HOCH(CH_3)R$, and CH_3CH_2OR compounds. Recently, Harrison and Keyes have reported studies of 2-propanol-2-^{13}C, which indicate that the fraction of the higher energy structure III relative to II varies with electron energy, decreasing from 64% at 20 eV to 52% at 70 eV.[12] Using evidence derived from collision-induced metastables, McLafferty and Schuddemage report an analogous trend, namely that with higher internal energy the degree of isomerization prior to unimolecular decomposition is reduced.[18] In view of the possibility that the structure of ions undergoing unimolecular decomposition and appearing as metastable peaks in the mass spectrum may not be representative of the structural species comprising the majority of the observed m/e 45 ion peak, it must be considered that the relative extent of production of II and III from the above cited neutral species has not yet been settled. The occurrence of structural isomer I is less controversial, it being generally acknowledged that this species is generated from neutrals which possess the structural moiety CH_3OCH_2R.

In the present studies ion cyclotron resonance techniques have been used to investigate reactions which can distinguish the $C_2H_5O^+$ structural isomers represented by I–III. In addition, the proton affinity of ethylene oxide has been measured, yielding the heat of formation quoted in Table I for structure III. In several instances the variation of reactivity with electron energy has been examined, particularly in the generation of m/e 45 ions from 2-alkanols.

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. Pulsed double resonance experiments were performed as previously described,[2-4] employing irradiating field strengths in the range 10–100 mV/cm. In the usual pulsed double resonance experiment, the magnetic field and observing oscillator are fixed, and a pulsed irradiating frequency field swept through the cyclotron frequencies of the possible reactant ions.[2-4] An alternative procedure, as previously described,[4] involves fixing the magnetic and pulsed irradiating fields and sweeping the observing oscillator through the cyclotron frequencies of possible product ions. By employing strong irradiating fields ($\geq$100 mV/cm) in the source region it is possible to effectively remove the reactant ion from the cell when it is neutralized upon striking the cell electrodes in the source region. This is verified by noting a concomitant decrease in the total ion current in proportion to the single resonance intensity of the ion ejected. The spectrum observed in this fashion represents the product ion distribution, rather than reflecting the change in reaction rate with ion energy.[3,4] Although it can presently be employed only over a narrow mass range,[4] this ion ejection technique has a higher resolution than the methods developed to eject ions by exciting their oscillatory motion in the trapping field.[5]

For the determination of product ion distributions the variation in the sensitivity of the spectrometer with magnetic field strength was determined[19] and all single resonance intensity measurements

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(19) The straightforward but tedious procedure for doing this is the subject of a forthcoming publication (P. G. Miasek and J. L. Beauchamp, to be published). These corrections are necessary when product ion m/e values differ appreciably.

were corrected accordingly. Reported product distributions are also corrected for the variation of the extent of reaction with magnetic field strength.[4,19] Except where calibration procedures are indicated, all electron energies reported are measured as the difference between the filament potential and the space potential at the center of the cyclotron resonance cell. Experience dictates that these values may be in error by as much as ±1 eV. Also, except as as noted, all pressure measurements reported are those read from the ion pump control, and may be in absolute error by as much as an order of magnitude. The linearity of the ion pump for making relative pressure measurements was checked against an ionization gauge with good agreement. Above 10^{-4} Torr the pressure was increased by throttling the ion pump. The relative pressure under the circumstances was monitored by noting the increase in the total ion current as the pump was throttled.

Except as noted, all chemicals employed were spectroquality or reagent grade and were checked for purity by gas chromatography. The mass spectrum of dimethyl carbonate was examined at low pressures for impurities and found to be in good agreement with the previously published spectrum.[20] $CH_3OCH_2CH_3$ and CD_3-OCH_2CH_3 were kindly prepared, using the standard Williamson synthesis, and purified by Professor L. J. Altman. Acetaldehyde-d_4, ethylene oxide-d_4, and 2-propanol-1,1,1,3,3,3-d_6 were obtained from Merck Sharp and Dohme of Canada and used as supplied. All samples were prepared and degassed under vacuum utilizing freeze–pump–thaw cycles.

Identification of Specific Reactions for $C_2H_5O^+$ Isomeric Ions

A. **Reactions of $CH_3O{=}CH_2^+$ (I).** The $C_2H_5O^+$ isomeric ion corresponding to structure I can be readily generated by electron impact from species containing the structural moiety CH_3OCH_2R. Methyl ethyl ether was chosen for this purpose. The partial mass spectrum recorded for $CH_3OC_2H_5$ and $CD_3OC_2H_5$ at 70 eV in Table II indicates that in the latter case the m/e 45
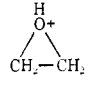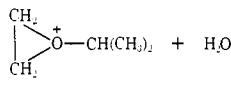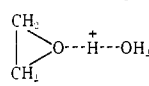
Table II. Mass Spectra of Methyl Ethyl Ether

m/e	$CH_3OCH_2CH_3$ 70 eV[a]	$CD_3OCH_2CH_3$ 70 eV[a] 10^{-7} Torr	$CD_3OCH_2CH_3$ 15.0 eV[b] 2×10^{-6} Torr	$CD_3OCH_2CH_3$ 15.0 eV[b] 8×10^{-5} Torr[c]
45	100.0	0.0	0.0	0.0
48		100.0	52.0	40.0
59	18.0			
60	50.0			
61		0.0		
62		17.0	11.0	25.0
63		50.0	29.0	4.0
64			5.0	14.0
65			3.0	13.0
81			0.0	4.0

[a] Only species above m/e 45 at 70 eV are given; peak intensities are reported as single resonance intensities relative to the base peak as 100.0. [b] All ion species reported; peak intensities are per cent of summed single resonance intensities. [c] The sum of m/e 48, 62, and 81 = 63% at low pressure and 69% at high pressure. This results from the change in extent of reaction with magnetic field, which enhances the high mass product peaks in the single resonance spectrum. See ref 3 and 4.
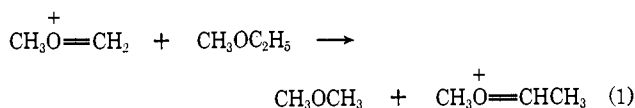
ion intensity shifts 100% to m/e 48 for the labeled species. Generation of the ethoxy cation (IV) does not occur, α-cleavage yielding the isomeric ion of interest. At low electron energy (15 eV) the reaction products indicated in Table II appear in the spectrum as the pressure is increased and double resonance experiments confirm the reactions listed in Table III. The two reactions corresponding to hydride abstraction

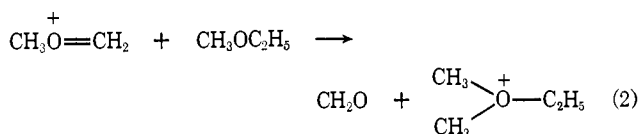(20) P. Brown and C. Djerassi, J. Amer. Chem. Soc., **88**, 2469 (1966).

Table III. Characteristic Reactions of $C_2H_5O^+$ Structural Isomers

| Isomer	Process	Product distribution[a]	Reaction type
I $CH_3—\overset{+}{O}=CH_2$ + $CH_3OC_2H_5$ —	$CH_3—\overset{+}{O}=CHCH_3$ + CH_3OCH_3	0.94	Hydride abstraction
	$CH_3 \overset{+}{O} \diagdown_{C_2H_5}^{CH_3}$ + CH_2O	0.06	Methyl cation transfer
$II^{b,d}$ $CH_3—C\diagup_H^{\nearrow OH}$ + $(CH_3)_2CHOH$ —	$(CH_3)_2\overset{+}{CHOH}$ + CH_3CHO	0.44	Proton transfer
	$C_3H_7^+$ + H_2O + CH_3CHO	0.0^c	Proton transfer followed by decomposition
	$CH_3C\diagdown_H^{\nearrow \overset{+}{O}—CH(CH_3)_2}$ + H_2O	0.20	Proton transfer followed by displacement
	$C_3H_5^+$ + $2H_2O$	0.19	Proton transfer followed by displacement and decomposition
	$CH_3C\diagdown_H^{\nearrow \overset{+}{O}--\overset{..}{H}---OH_2}$ + C_3H_6	0.16	Dehydration
$III^{d,e}$ $\overset{\overset{H}{O^+}}{CH_2—CH_2}$ + $(CH_3)_2CHOH$ —	$(CH_3)_2\overset{+}{CHOH}$ + C_2H_4O	0.38	Proton transfer
	$C_3H_7^+$ + H_2O + CH_3CHO	~0.0	Proton transfer followed by decomposition
	$\overset{CH_2}{\underset{CH_2}{\diagup}}\overset{+}{O}—CH(CH_3)_2$ + H_2O	0.20	Proton transfer followed by displacement
	$C_3H_5^+$ + $2H_2O$	0.24	Proton transfer followed by displacement and decomposition
	$\overset{CH_2}{\underset{CH_2}{\diagup}}\overset{+}{O}--\overset{..}{H}---OH_2$	0.18	Dehydration

[a] Product distributions are corrected for variation of detection system sensitivity and extent of reaction with magnetic field. [b] Product distribution measured at 12.8 eV (corrected) electron energy. [c] Process observed at electron energy above 12.8 eV (see text). [d] Clustering of the reactants is observed at higher pressures ($\sim10^{-5}$ Torr). [e] Product distribution measured in mixtures of ethylene oxide-d_4 with $(CH_3)_2$CHOH and ethylene oxide with $(CD_3)_2$CHOH. Essentially identical product distributions were obtained from each mixture.

$$\overset{+}{CH_3O}=CH_2 + CH_3OC_2H_5 \longrightarrow$$

$$CH_3OCH_3 + \overset{+}{CH_3O}=CHCH_3 \quad (1)$$

and methyl cation transfer

$$\overset{+}{CH_3O}=CH_2 + CH_3OC_2H_5 \longrightarrow$$

$$CH_2O + \overset{CH_3}{\underset{CH_3}{\diagup}}\overset{+}{O}—C_2H_5 \quad (2)$$

are found to be characteristic of the $C_2H_5O^+$ isomeric ion with structure I. The former process is favored, the relative rates of reactions 1 and 2 being 16:1. An examination of reaction 1 with $CD_3OC_2H_5$ (Table II) indicates that hydride abstraction occurs only from the ethyl group as can be seen from eq 3a and 3b

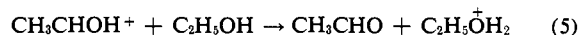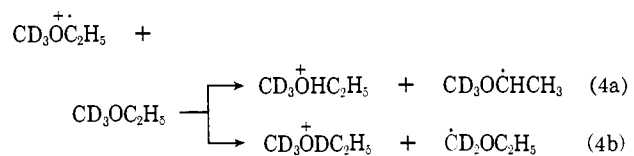$$\overset{+}{CH_3O}=CH_2 + CD_3OC_2H_5 \longrightarrow$$
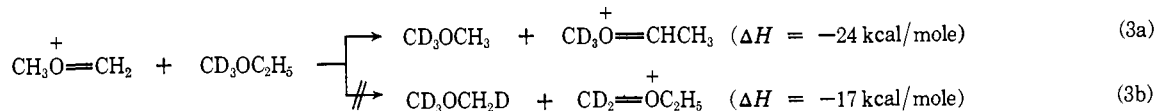
even though both indicated processes are exothermic.[21] At 13 eV the protonated parent is generated only from the parent ion either by a proton transfer or hydrogen abstraction process. An examination of this process with $CD_3OC_2H_5$ reveals no specificity in that both the methyl and ethyl groups are involved in the reaction, the relative rates of the two processes (eq 4a and 4b) being 1.1:1. Under no condition was proton transfer from the m/e 45 ion generated from $CH_3OC_2H_5$ to the parent neutral found to be an important process. At 15.0 eV the reaction could not be detected. At 70 eV

(21) Enthalpy changes calculated employing $\Delta H_f(CH_3O^+CHCH_3) = 135$ kcal/mole and $\Delta H_f(CH_2O^+C_2H_5) = 144$ kcal/mole (ref 13).

a small contribution from m/e 45 to the protonated parent was detected in the pulsed double resonance spectrum of the latter ion, the sign of the double resonance indicating that the reaction rate increased with increasing ion energy.[3,4]

B. Reactions of Protonated Acetaldehyde. Protonated acetaldehyde can be generated either indirectly by ion–molecule reactions of acetaldehyde[22] or directly by α cleavage of 2-alkanols. Although in the latter case the ion structure is presumed, which may be hazardous in view of the controversy discussed above, it is of interest to examine the reactions of $C_2H_5O^+$ ions generated from this source.

The m/e 45 ion comprises 16% of the total ionization in the mass spectrum of ethanol at 70 eV. Only one reaction (5) of this species has previously been identified[23]

$$\overset{+}{CD_3O}=CHCH_3 \quad (\Delta H = -24 \text{ kcal/mole}) \quad (3a)$$

$$CD_3OCH_2D + CD_2=\overset{+}{O}C_2H_5 \quad (\Delta H = -17 \text{ kcal/mole}) \quad (3b)$$

$$CD_3\overset{+\cdot}{O}C_2H_5 +$$

$$CD_3OC_2H_5 \begin{cases} \overset{+}{CD_3OHC_2H_5} + CD_3O\dot{C}HCH_3 & (4a) \\ \overset{+}{CD_3ODC_2H_5} + \dot{C}D_2OC_2H_5 & (4b) \end{cases}$$

$$CH_3CHOH^+ + C_2H_5OH \rightarrow CH_3CHO + C_2H_5\overset{+}{O}H_2 \quad (5)$$

involving rapid proton transfer to the parent neutral. This result was confirmed by an examination of the ion

(22) H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, **48**, 5623 (1968).
(23) L. W. Sieck, J. H. Futrell, and F. P. Abramson, *ibid.*, **45**, 2859 (1966).
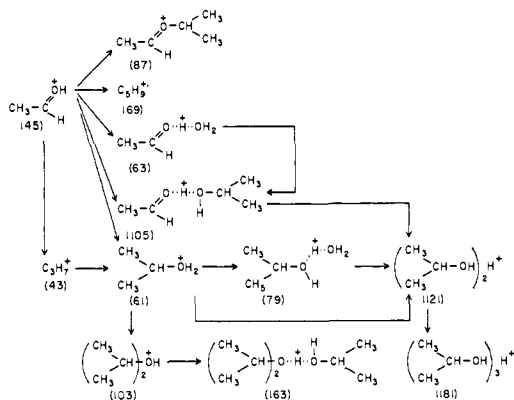
Figure 1. Reaction sequence observed in 2-propanol starting with CH_3CHOH^+ as the principal fragment ion. Each step involves 2-propanol as the neutral reactant. All reactions indicated were identified by ion cyclotron double resonance techniques. The importance of the various reaction pathways is indicated in Figures 2 and 3.
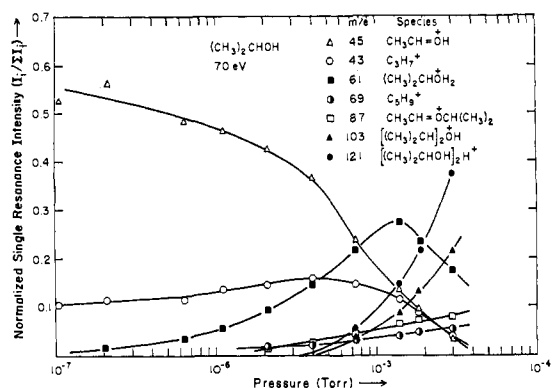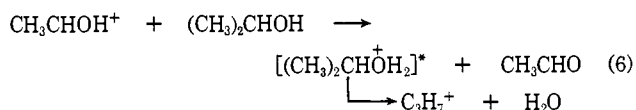

Figure 2. Variation of normalized single resonance intensities with pressure for the major ionic species in 2-propanol at an electron energy of 70 eV.
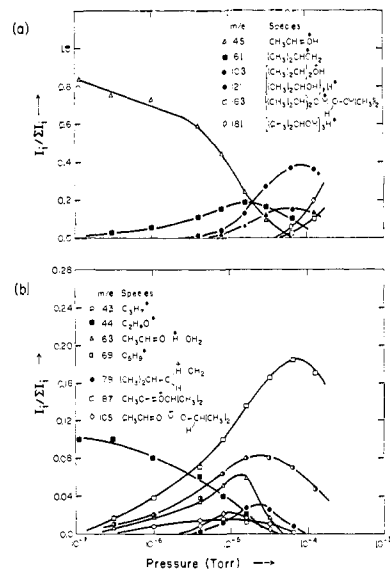

Figure 3. Variation of normalized single resonance intensities with pressure for the ionic species in 2-propanol at an electron energy of 13.5 eV: (a) major ionic species; (b) minor ionic species.

chemistry of ethanol by ion cyclotron single and double resonance techniques.[24]

While investigations on the ion–molecule reactions of methanol and ethanol have been reported in detail in the literature,[6,23,25–27] no study of the ion chemistry of 2-propanol has yet appeared. The electron impact ionization of 2-propanol leads to α cleavage and the production of protonated acetaldehyde (II) as the principal fragment ion at all electron energies. At higher electron energies the only other fragment of importance appears at m/e 43, comprising $C_2H_3O^+$ (63%) and $C_3H_7^+$ (37%) at 70 eV.[28] The reaction sequence delineated by double resonance analysis is exhibited in Figure 1. At high electron energies (70 eV) $C_3H_7^+$ is generated both by direct electron impact and decomposition following exothermic proton transfer from CH_3CHOH^+

$$CH_3CHOH^+ \quad + \quad (CH_3)_2CHOH \quad \longrightarrow$$

$$[(CH_3)_2C\overset{+}{O}H_2]^* \quad + \quad CH_3CHO \quad (6)$$
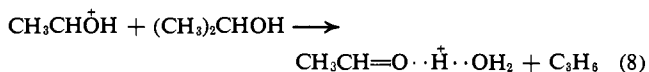$$\longrightarrow C_3H_7^+ \quad + \quad H_2O$$

This is evident in the variation of single resonance intensities with pressure presented in Figure 2. The m/e 43 ion intensity increases with pressure, goes through a maximum, and then decreases. The reactivity of the CH_3CHOH^+ ion in reaction 6 depends on the electron energy employed in its generation. For example, at 13.5 eV where $C_3H_7^+$ is not generated as a primary ion, it appears only as a minor secondary ion (Figure 3). Clearly, internal excitation of CH_3CHOH^+ plays an important role in reaction 6. The proton affinities of acetaldehyde[29] and 2-propanol[30] are 183 ± 2 and $\sim 193 \pm 5$ kcal/mole, respectively, making proton transfer from acetaldehyde to 2-propanol exothermic by ~ 10 kcal/mole. The decomposition process

$$[(CH_3)_2C\overset{+}{O}H_2]^* \longrightarrow C_3H_7^+ + H_2O \quad (7)$$
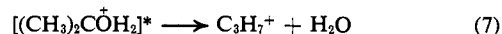
requires an excitation energy of 25 kcal/mole, explaining the requirement of excess internal energy in the ionic reactant to observe process 6.

The reactions of protonated acetaldehyde with 2-propanol can be classified according to general reaction types characteristic of the reaction of protonated carbonyl compounds with alcohols.[30] The product distribution for the different processes measured with 12.8 eV electron energy[31] is reported in Table III. The variation of the product distribution with electron energy is illustrated in Figure 4a.[31] The overall reaction rate did not vary outside the range $1.5 \pm 0.3 \times 10^{-9}$ cm³ molecule⁻¹ sec⁻¹ from 12.8 to 70 eV electron energy.[31]

The ionic dehydration reaction (Table III)

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

$$CH_3CH=O\cdots\overset{+}{H}\cdots OH_2 + C_3H_6 \quad (8)$$

(24) J. L. Beauchamp, unpublished results, described in part in ref 7.
(25) P. Wilmenius and E. Lindholm, Arkiv Fysik, 21, 97 (1962).
(26) E. Lindholm and P. Wilmenius Arkiv Kemi, 20, 255 (1963).
(27) J. M. S. Henis, J. Amer. Chem. Soc., 90, 844 (1968).
(28) R. A. Saunders and A. E. Williams in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press, New York, N. Y., 1963, p 364.
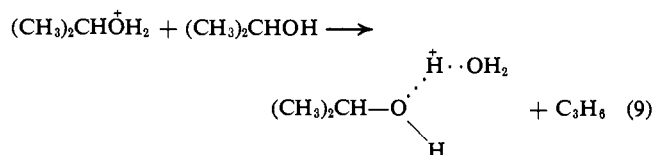
(29) Calculated from thermochemical data in Table I; the proton affinity of a species M is defined as the negative of the enthalpy change incurred in attaching a proton to form MH^+.
(30) J. L. Beauchamp, unpublished results.
(31) The electron energy scale in Figure 4a was calibrated against the known appearance potential (10.4 eV, ref 15) of CH_3CHOH^+ from 2-propanol. The total reaction rate was measured using the technique outlined in ref 4 by assuming a total ionization cross section of 12 Å² for 2-propanol to determine the pressure.

according to which a water molecule is removed from isopropyl alcohol and loosely bound to the reactant ion by the labile proton is of considerable interest since this process is not observed in the reactions of the lower aliphatic alcohols.[23,25-27] While other structures for the ionic product of reaction 8 can be postulated, the observation that the protonated parent undergoes a similar reaction (Figure 1)

$$(CH_3)_2CH\overset{+}{O}H_2 + (CH_3)_2CHOH \longrightarrow$$

$$(CH_3)_2CH-O\overset{\overset{\displaystyle \overset{+}{H}\cdot\cdot OH_2}{\vdots}}{\underset{\displaystyle H}{\big\backslash}} + C_3H_6 \quad (9)$$

suggests that the dehydration process is associated only with the presence of a labile proton. In a subsequent collision the water molecule in the ionic products of reactions 8 and 9 is displaced by 2-propanol, attesting to a loosely bound complex. The energetics of the dehydration reaction, which has also been observed in the case of cyclopentanol, 2-butanol, and t-butyl alcohol, have been previously discussed.[32] The enthalpy change for the dehydration process

$$(CH_3)_2CHOH \longrightarrow H_2O + C_3H_6 \quad (10)$$
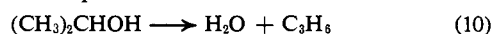
is only 12 kcal/mole. Since the strength of the proton bond in the above complexes is $\sim$36 kcal/mole,[32] reactions 8 and 9 are exothermic by as much as 20-30 kcal/mole.
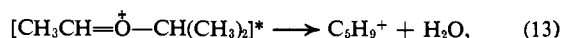
The reaction

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

$$CH_3CH=\overset{+}{O}-CH(CH_3)_2 + H_2O \quad (11)$$
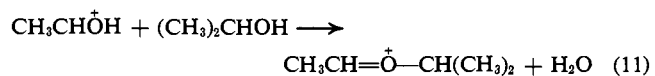
involving proton transfer followed by displacement of H_2O is similar to the condensation reaction of the protonated parent ion which generates protonated isopropyl ether (Figure 1)

$$(CH_3)_2CH\overset{+}{O}H_2 + (CH_3)_2CHOH \longrightarrow$$

$$[(CH_3)_2CH]_2\overset{+}{O}H + H_2O \quad (12)$$
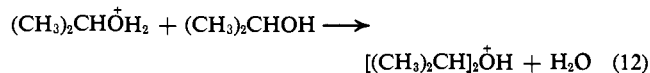
The condensation reaction analogous to (12) also is observed in the case of CH_3OH, as discussed in detail by Henis.[27] The product of reaction 11 is apparently formed with sufficient internal excitation to undergo further decomposition

$$[CH_3CH=\overset{+}{O}-CH(CH_3)_2]^* \longrightarrow C_5H_9^+ + H_2O, \quad (13)$$

yielding one of the major products in the reaction of protonated acetaldehyde with 2-propanol (Table III). Evidence for this conjecture is obtained from the observation that the decomposition can be collisionally induced by irradiating the precursor ion at m/e 87.[33] Further evidence for the postulated sequence of events is the analogous unimolecular decomposition of the α-cleavage products of electron impact ionization of aliphatic ethers.[34] Isopropyl ether, for instance, has a rearrangement peak at m/e 69 which results from the sequential decomposition[34,35]

$$[(CH_3)_2CH]_2O^+ \longrightarrow CH_3CH=\overset{+}{O}-CH(CH_3)_2 + \overset{\cdot}{C}H_3$$
$$\longrightarrow C_5H_9^+ + H_2O \quad (14)$$
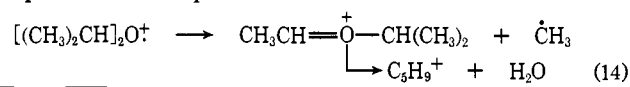
(32) J. L. Beauchamp, *J. Amer. Chem. Soc.*, **91**, 5925 (1969). The energy of the proton bond is defined as the negative of the enthalpy change for the process MH$^+$ + M $\longrightarrow$ (M)$_2$H$^+$.

(33) F. Kaplan, *J. Amer. Chem. Soc.*, **90**, 4483 (1968).

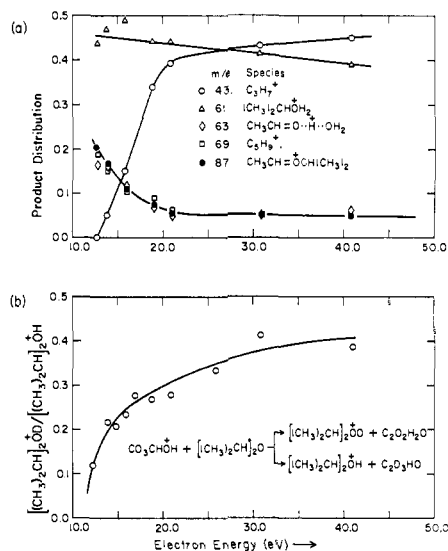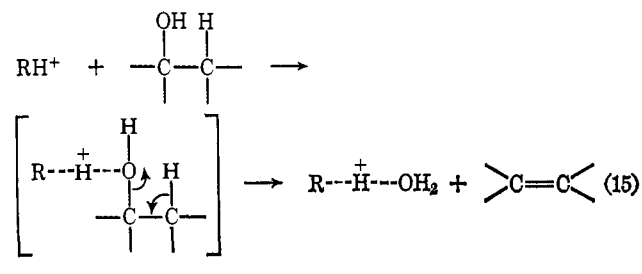(34) W. Carpenter, A. M. Duffield, and C. Djerassi, *ibid.*, **89**, 6165 (1967).

Figure 4. (a) Variation with electron energy of the product distribution from the reaction of CH_3CHOH^+ with 2-propanol. For clarity a line is drawn only through the points for the condensation product appearing at m/e 87. The behavior of the condensation products at m/e 63 and m/e 69 is similar. The total product distribution is normalized to unity at each electron energy. (b) Variation with electron energy of the ratio of deuteron to proton transfer from CD_3CHOH^+ [generated from $(CD_3)_2CHOH$] to diisopropyl ether. Below 12 eV the ratio could not be accurately determined. The electron energy scale is calibrated against the known appearance potential of CH_3CHOH^+ from 2-propanol.

From the variation in the product distribution with electron energy (Figure 4a) it is apparent that the importance of process 6 involving proton transfer and decomposition increases at the expense of the major condensation and rearrangement processes 8, 11, and 13. Process 6 occurs only above 12.8 ± 0.5 eV, approximately 2.4 eV above threshold for production of CH_3-$CHOH^+$ from 2-propanol. The internal energy of the reactant ion is thus as high as 55 kcal/mole, which is more than sufficient to observe process 6.

The reactions of CH_3CHOH^+ listed in Table III initiate the sequence (Figure 1) which leads at high pressure (10^{-3} Torr) predominately to the production of the proton-bound trimer of 2-propanol and the proton-bound dimer of isopropyl ether and 2-propanol.

The above postulated reaction sequences and mechanisms have been confirmed by an examination of the ion chemistry of 2-propanol-1,1,1,3,3,3-d_6. In particular, the product of reaction 6 shifts to m/e 48, confirming generation of the propyl cation rather than $C_2H_3O^+$. With $(CD_3)_2CHOH$ as the neutral reactant, reaction 9 involves transfer of HDO, suggesting a simple 1,2 elimination induced by the labile proton on the reactant ion

$$RH^+ + \underset{\displaystyle \underset{H}{\overset{\displaystyle \overset{OH}{|}}{-}C}\overset{\displaystyle \overset{H}{|}}{\underset{\displaystyle \underset{|}{}}{-}C}- \longrightarrow$$

$$\left[\begin{array}{c} R\text{---}\overset{+}{H}\text{---}O \overset{\displaystyle H}{\diagdown} H \\ \underset{\displaystyle \underset{|}{}}{-}C\overset{\displaystyle \curvearrowleft}{-}C\underset{\displaystyle \underset{|}{}}{-} \end{array} \right] \longrightarrow R\text{---}\overset{+}{H}\text{---}OH_2 + \overset{\displaystyle }{\diagup}C=C\overset{\displaystyle }{\diagdown} \quad (15)$$
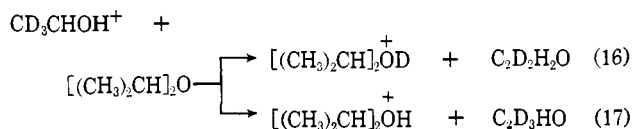
(35) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957).

Table IV. Ion-Molecule Reactions of Ethylene Oxide

| Mixture or species	Reaction	$(dk/dE)^0$ a	Thermochemical inferences
$CH_2{-}CH_2$ (O)	$RH^+ + C_2H_4O \longrightarrow C_2H_4\overset{+}{O}H + R$	—	
	$RH^+ = H_3O^+, C_2H_5^+, CHO^+, CH_2OH^+, C_2H_4O^+$		
	$CH_3^+ + C_2H_4O \longrightarrow C_2H_5O^+ + CH_4$	—	
	$C_2H_4O^+ + C_2H_4O \longrightarrow C_3H_6O^+ + (CH_2O)$?	—	
	$C_2H_4\overset{+}{O}H + C_2H_4O \longrightarrow (C_2H_4O)_2H^+$	—	
$CH_2{-}CH_2$ (O) + CD_3CDO	$CH_3\overset{+}{O}H_2 + \overset{O}{CH_2{-}CH_2} \longrightarrow \overset{O}{CH_2{-}CH_2} + CH_3OH$	—	$\left.\begin{array}{c} \end{array}\right\}$ $PA(\overset{O}{CH_2{-}CH_2})$
	$\overset{H}{\overset{+O}{CH-CH_2}} + CH_3OH \longrightarrow CH_3\overset{+}{O}H_2 + \overset{O}{CH_2{-}CH_2}$	+	$\geq PA(CH_3OH)$
$CH_2{-}CH_2$ (O) + CD_3CDO	$CD_3CD{=}\overset{+}{O}D + \overset{O}{CH_2{-}CH_2} \longrightarrow \overset{D}{\overset{O+}{CH_2{-}CH_2}} + CD_3CDO$	—	$\left.\begin{array}{c} \end{array}\right\}$ $PA(\overset{O}{CH_2{-}CH_2})$
	$\overset{D}{\overset{O+}{CH_2{-}CH_2}} + CD_3CDO \longrightarrow CD_3CD{=}\overset{+}{O}D + \overset{O}{CH_2{-}CH_2}$	—	$\cong PA(CD_3CDO)$
$CD_2{-}CD_2$ (O) + CH_3OCH_3	$\overset{H}{\overset{O+}{CD_2{-}CD_2}} + (CH_3)_2O \longrightarrow (CH_3)_2\overset{+}{O}H + \overset{O}{CD_2{-}CD_2}$	—	$\left.\begin{array}{c} \end{array}\right\}$ $PA(\overset{O}{CD_2{-}CD_2})$
	$(CH_3)_2\overset{+}{O}H + \overset{O}{CD_2{-}CD_2} \longrightarrow \overset{H}{\overset{+O}{CD_2{-}CD_2}} + (CH_3)_2O$	+	$\leq PA(CH_3OCH_3)$

a $(dk/dE)^0$ refers to the change in reaction rate with ion energy above thermal ion energies as observed in pulsed double resonance experiments (see ref 3). An endothermic reaction must have $(dk/dE)^0$ positive (+), while exothermic processes normally have $(dk/dE)^0$ negative (−).

In a mixture of acetaldehyde with $(CD_3)_2CHOH$ the reactions of CH_3CHOH^+ were compared to the reactions of CD_3CHOH^+. Both the reactions and product distributions were found to be similar, suggesting that both ions possess identical structures. The labeled alcohol can also be employed to examine the origin of the proton transferred to the parent neutral, since this presumably involves the proton bound to the carbonyl group. The determination of the site specificity of proton transfer from CD_3CHOH^+ to $(CD_3)CHOH$ is complicated by the product of the ionic dehydration reaction (8) appearing at the same mass (m/e 67) as the protonated parent. In a mixture of diisopropyl ether and $(CD_3)_2$-CHOH, the ratio of deuteron to proton transfer in the process

$CD_3CHOH^+ +$

$[(CH_3)_2CH]_2O \left\{ \begin{array}{l} \longrightarrow [(CH_3)_2CH]_2\overset{+}{O}D + C_2D_2H_2O \quad (16) \\ \longrightarrow [(CH_3)_2CH]_2\overset{+}{O}H + C_2D_3HO \quad (17) \end{array} \right.$

was determined (Figure 4b) as a function of electron energy. The ion ejection technique discussed in the previous section facilitated these measurements. Beginning at 11.0 eV[31] appreciable deuteron transfer occurs, indicating either scrambling in the reactant or a loss of specificity in the transfer of the proton initially bound to oxygen. It has previously been shown[11] that the origin of H_3O^+ in the mass spectrum of 2-alkanols

is most likely in the decomposition process

$$C_2H_5O^+ \longrightarrow H_3O^+ + C_2H_2 \qquad (18)$$
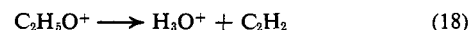
In experiments with labeled alcohols, it is found for process 18 that the proton initially on oxygen is retained in the H_3O^+ product, and the remaining sites are scrambled.[11] If this is the case then our experiments indicate a loss of specificity in the transfer of the proton initially bound to oxygen. The neutral product of reaction 16 is thus likely to be the enol form of acetaldehyde and not ethylene oxide or acetaldehyde.

The reactions of CH_3CHOH^+ (II) derived from electron impact of 2-butanol with the parent were analogous to those listed in Table III for 2-propanol as the neutral reactant, with a similar product distribution and variation of reactivity with electron energy. With polar species other than 2-alkanols, proton transfer from the m/e 45 ion with structure II is the predominant mode of reaction.
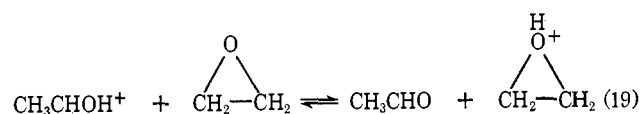
The observed variation of reactivity with electron energy of the m/e 45 ion from 2-propanol, as noted above and illustrated in Figure 4a and 4b, is of considerable interest. Photoelectron spectroscopy reveals two low-lying excited states of the parent ion of 2-propanol, at 11.30 and 12.32 eV.[36] Fragmentation from these states could account for the breaks observed in the photoionization efficiency curves for the generation of CH_3-$CHOH^+$ from 2-propanol at 11.3 and 12.4 eV, respec-

(36) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

tively.[15] Fragmentation from either state could leave the m/e 45 ion with sufficient internal excitation to influence its reactivity, enhancing those channels which are endothermic for the ion in its ground state, and in particular process 6. If, as previous investigations have suggested,[11,12,16,17] the m/e 45 ion from 2-propanol experiences a structural reorganization to III, then endothermic channels of reaction such as process 6, involving III as the reactant ion and ethylene oxide as the neutral product, will be less favored. The structural reorganization will absorb excess energy, owing to the higher energy content of the neutral product in process 6 if it is to be ethylene oxide ($\Delta H_f = -12.2$ kcal/mole) rather than acetaldehyde ($\Delta H_f = -39.7$ kcal/mole).

C. Reactions of Protonated Ethylene Oxide (III).

Protonated ethylene oxide can be generated only *indirectly* by ion–molecule reactions in ethylene oxide. Ion–molecule reactions occurring in ethylene oxide have previously been considered by Pritchard and Harrison.[22] The reactions postulated[22] to occur have been confirmed and several additional processes have been identified (Table IV). The major reaction product at all electron energies is the protonated parent ion. Other than the clustering process which forms the proton bound dimer, no further reaction of this species with ethylene oxide is observed.

The heat of formation of protonated ethylene oxide cannot be directly measured since this species cannot with assurance be generated by direct electron impact processes as can the $C_2H_5O^+$ structural isomers represented by I and II. Cyclotron resonance techniques have been developed[3] which permit the proton affinity of ethylene oxide to be determined; from this the heat of formation of the protonated species can be calculated. Included in Table IV are the reactions which limit the affinity of ethylene oxide to a value very close to that of acetaldehyde, between methanol (180 kcal/mole[30]) and dimethyl ether (186 kcal/mole[30]). Double resonance results indicate that the reaction

$$CH_3CHOH^+ \; + \; \underset{\displaystyle CH_2}{\overset{\displaystyle O}{\diagup\!\!\!\diagdown}}\!\!\!\!CH_2 \; \rightleftharpoons \; CH_3CHO \; + \; \underset{\displaystyle CH_2}{\overset{\displaystyle \overset{+}{O}H}{\diagup\!\!\!\diagdown}}\!\!\!\!CH_2 \quad (19)$$

proceeds in both directions at thermal ion energies, implying that the reaction is very nearly thermoneutral. The variation of single resonance intensities with pressure in a 1:1 mixture of ethylene oxide and acetaldehyde-d_4 with an electron energy of 12 eV is indicated in Figure 5. With increasing pressure between 10^{-4} and 10^{-3} Torr there is little tendency for reaction 19 to proceed in either direction, confirming the double resonance results. Cluster formation occurred only above 8×10^{-4} Torr. A proton affinity of 183 kcal/mole corresponds to a heat of formation of 170 kcal/mole for protonated ethylene oxide. While the heat of formation of protonated ethylene oxide (III) is comparable to the $C_2H_5O^+$ isomeric ion with structure I, it is significantly less stable than the protonated acetaldehyde (II). The same conclusion on a less quantitative basis was reached by Harrison and Keyes.[12] On energetic grounds, the possibility of protonated ethylene oxide rearranging during or after generation to protonated acetaldehyde cannot be excluded. Furthermore, $C_2H_5O^+$ ions generated from 1-alkanols have structure II at the threshold for production, and fragmentation
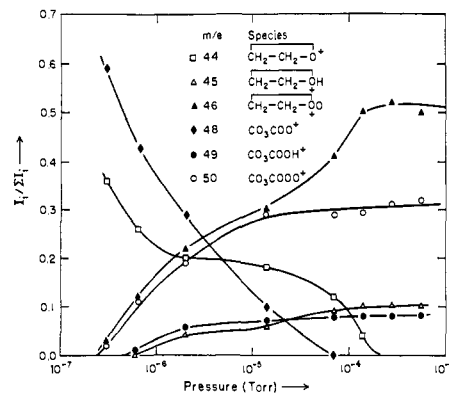

Figure 5. Variation of normalized single-resonance intensities with pressure for ionic species appearing in a mixture of ethylene oxide and acetaldehyde-d_4 at an electron energy of 12.0 eV. Only above 8×10^{-4} Torr is clustering of the protonated species observed.

of this ion which proceeds through the symmetrical protonated ethylene oxide intermediate can do so only for ions with appreciable internal excitation.

In mixtures of ethylene oxide-d_4 with 2-alkanols a pattern of reactivity identical with that discussed above for protonated acetaldehyde is observed. The product distribution measured in a mixture of ethylene oxide-d_4 with 2-propanol and confirmed by examining a mixture of ethylene oxide with 2-propanol-1,1,1,3,3,3-d_6 is reported in Table III. This similarity of reactivity for isomers II and III again suggests the possibility of protonated ethylene oxide rearranging to the more stable isomer II. With polar species other than 2-alkanols, proton transfer is the predominant mode of reaction.

It is interesting to note (Table III) that $C_3H_7^+$ is not produced in the reaction of protonated ethylene oxide (III) with 2-propanol. If, as suggested, this species undergoes unimolecular rearrangement to protonated acetaldehyde it should possess an excitation energy of $\sim$27 kcal/mole (Table I). As noted above, the decomposition process (7) requires an excitation energy of 25 kcal/mole; this is probably greater than the excess energy available to the ionic product in proton transfer from protonated ethylene oxide to 2-propanol and accounts for the fact that $C_3H_7^+$ is not observed as a product ion.

Discussion and Applications

The characteristic reactions of $C_2H_5O^+$ isomeric ions corresponding to structures I–III are detailed in Table III. It is apparent that I can be discerned from II and III, but II and III cannot be distinguished. This may result from rearrangement of III to II, which as shown above is feasible on an energetic basis and provides a reasonable explanation of the observed similarities in reactivity for II and III. While methyl cation transfer and hydride abstraction reactions identify I, it is possible to identify II and III on the basis of proton transfer reactions. The reactions of I (generated from dimethyl ether), II (generated in acetaldehyde), and III (generated in ethylene oxide) were examined with acetone as a common neutral reactant. The expected reactions were observed, with methyl cation transfer from I and proton transfer from II and III to acetone being the only processes detected. These characteristic reactions do not appear to be dependent on the structure of the neu-

Table V. Identification of $C_2H_5O^+$ Structural Isomers

	$\overset{+}{CH_3}-O=CH_2$		$CH_3-C\overset{\overset{+}{O}H}{\underset{H}{<}}$ or $\underset{CH_2-CH_2}{\overset{\overset{H}{\overset{+}{O}}}{\bigwedge}}$		
Parent species	Hydride abstraction[b]	Methyl cation transfer[b]	Proton transfer[b]	$\Delta H_f(C_2H_5O^+)$,[a] kcal/mole	Ref
CH_3CH_2OH			X	143, 141	
$(CH_3)_2CHOH$			X	144, 141	13, 15
$CH_3C(OH)HCH_2CH_3$			X	144	13
CH_3OCH_3	c	X		170	13
$CH_3OCH_2CH_3$	X	X		168	13
$(CH_3CH_2)_2O$			X	147	13
$(CH_3)_2CHOCH_2CH_2$			X		
$[(CH_3)_2CH]_2O$			X		
$C_5H_{10}O$ (tetrahydropyran)	X	X		176	39b
$C_4H_7OCH_3$ (1-methyltetrahydrofuran)	X				
$CH_3OCH_2CH_2OCH_3$	X	X			
$(CH_3O)_2C=O$		X			

[a] Reported for $C_2H_5O^+$ generated from the parent species. [b] Reactions examined with parent species as neutral reactant. [c] Product and reactant have same mass, preventing observation of reaction.

tral reactant. In general the examination of these processes with the parent species (M) as the neutral reactant should suffice as a means of distinguishing I from II and III.

The m/e 45 ion generated by electron impact from dimethyl carbonate serves as an example of the identification of $C_2H_5O^+$ isomeric ion structures employing the developed methodology. The single resonance spectrum of dimethyl carbonate at 3×10^{-5} Torr with 70 eV electron energy is displayed in Figure 6.[37] The
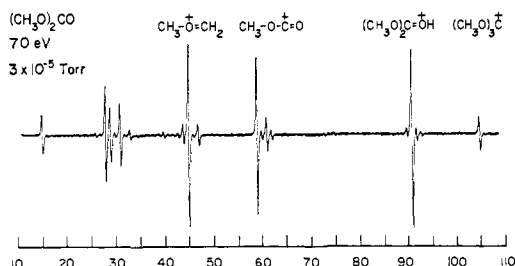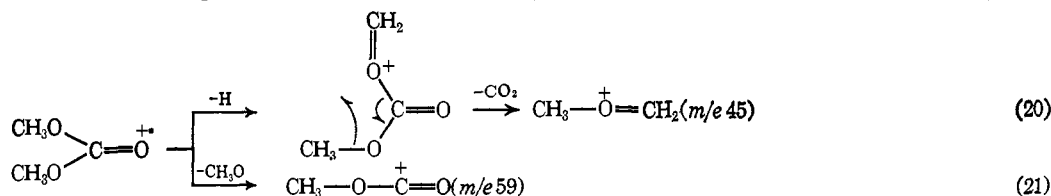
Figure 6. Single resonance spectrum of dimethyl carbonate at 70 eV and 3×10^{-5} Torr. Ionic species pertinent to the discussion in the text are identified.

rearrangement peak in the spectrum at m/e 45 has been resolved by high resolution mass spectrometry into a doublet, comprising 85% $C_2H_5O^+$ and 15% CO_2H^+.[20] It has been suggested[20] that $C_2H_5O^+$ is generated in the decomposition sequence shown in eq 20 and 21

bonium ion $(m/e$ 105). The double resonance spectrum of the m/e 105 product (Figure 7b) exhibits contributions from m/e 45 and m/e 59, indicating the two methyl cation transfer reactions shown in eq 22 and
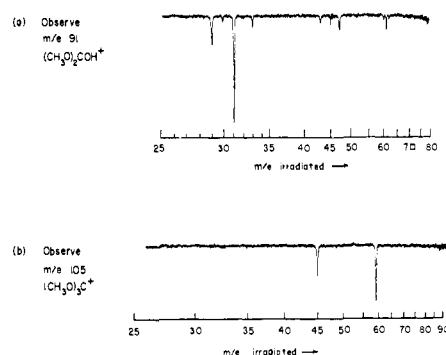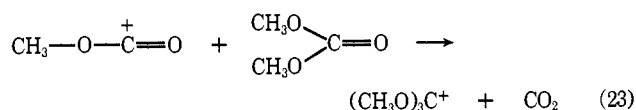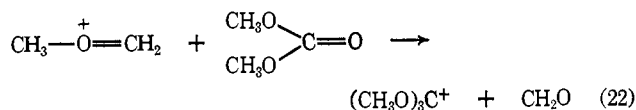
Figure 7. (a) Pulsed double resonance spectrum of protonated dimethyl carbonate $(m/e$ 91). (b) Pulsed double resonance spectrum of the trimethoxycarbonium ion $(m/e$ 105). The conditions for obtaining these spectra are as illustrated in Figure 6.

23. These reactions are consistent with the postulated structures of the ionic reactants. The m/e 45 ion does not react by hydride abstraction with dimethyl carbonate, the generation of the stable trimethoxycarbonium ion being favored. The pulsed double resonance spectrum (Figure 7a) of protonated dimethyl carbonate $(m/e$ 91) exhibits no contribution from m/e 59.

which proceeds by loss of H· followed by methyl migration with elimination of CO_2. The major reaction products evident in Figure 6 correspond to protonated dimethyl carbonate $(m/e$ 91) and the trimethoxycar-

(37) The m/e 47 ion apparent in Figure 6 is not due to an impurity but rather is produced by the decarboxylation reaction $CHO^+ + (CH_3O)_2CO \rightarrow (CH_3)_2OH^+ + CO_2 + CO$, as confirmed by double resonance.

The small contribution from m/e 45 can be attributed to CO_2H^+. CH_3O^+ $(m/e$ 31) is the major precursor to the protonated parent.[37]

As additional examples of the developed methodology a summary of the reactions of $C_2H_5O^+$ ions with the neutrals from which they were generated by electron impact at 70 eV is presented in Table V. Included is the

$$CH_3\!-\!\overset{+}{O}\!=\!\!CH_2 \ + \ \overset{CH_3O}{\underset{CH_3O}{\diagup}}C\!=\!O \ \longrightarrow$$

$$(CH_3O)_3C^+ \ + \ CH_2O \quad (22)$$

$$CH_3\!-\!O\!-\!\overset{+}{C}\!=\!O \ + \ \overset{CH_3O}{\underset{CH_3O}{\diagup}}C\!=\!O \ \longrightarrow$$

$$(CH_3O)_3C^+ \ + \ CO_2 \quad (23)$$

heat of formation of $C_2H_5O^+$ derived from the same source, where such data are available. *In each case where previously considered the structures identified are in agreement with postulated pathways of ion decomposition.*[38,39]

Conclusion

Distinguishing between ionic species having the same chemical constitution and mass but differing structures

(38) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.
(39) Of particular interest are the results obtained for cyclic ethers whose fragmentation pathways have only recently been considered in detail by (a) R. Smakman and T. J. de Boer, *Org. Mass. Spectrosc.*, 1, 403 (1968); (b) J. E. Collin and G. Conde-Caprace, *Intern. J. Mass*

is both a difficult and interesting problem in mass spectrometry. It is apparent that specific reactivity of functional groups can be employed, in conjunction with the facility of ion cyclotron resonance spectroscopy for identifying ion–molecule reactions, to provide ion structural information. This constitutes a powerful addition to the methods involving thermochemical considerations,[10–15] metastable ion characteristics,[16,17] and collision-induced decompositions.[18] It is of interest to note that the present method can be employed to determine the structures of *products* of ion–molecule reactions. This application is currently under active scrutiny.

Spectrom. Ion Phys., 1, 213 (1968); (c) M. Vandewalle, N. Schamp, and K. Van Cauwenberghe, *Bull. Soc. Chim. Belges*, 77, 33 (1968).

The Microwave Spectrum, Structure, and Dipole Moment of Methylenecyclopropane[1]

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey. Received October 30, 1969

Abstract: The microwave spectrum of the normal isotopic species and the three monosubstituted ^{13}C species of methylenecyclopropane has been studied in the ground state and effective rotational constants have been obtained. Moments of inertia calculated from the rotational constants lead to the following substitution values for the carbon structural parameters: $r(C_1C_2) = 1.3317 \pm 0.0014$, $r(C_2C_3) = 1.4570 \pm 0.0014$, $r(C_3C_3') = 1.5415 \pm 0.0003$ Å, $\angle C_3C_2C_3' = 63° 52' \pm 3'$. With assumption of the ethylenic CH bond length to be 1.088 Å, the other H parameters are calculated to be: $r(CH) = 1.09 \pm 0.01$ Å, $\angle HCH$ (ethylenic) $= 114.3 \pm 1°$, $\angle HCH$ (ring) $= 113.5 \pm 1°$ with the HCH plane bisecting $\angle C_2C_3C_3'$. From the Stark effect the dipole moment is determined to be 0.402 ± 0.004 D.

The structures and dipole moments of small ring compounds are interesting because of the unusual geometrical constraints which are imposed. Determination of accurate values for these parameters gives insight into the nature of the bonding and is useful in understanding effects such as angle strain.

A particularly interesting molecule is methylenecyclopropane. Here additional angle strain should be introduced by the presence of a nominally sp^2-hybridized carbon in a three-membered ring. It is of interest, therefore, to ascertain in what way the structural parameters differ from those of cyclopropane and related molecules in which only nominally sp^3-hybridized carbons are present in the ring. Methylenecyclopropane

also provides an opportunity to study the interaction between a three-membered ring and a double bond.

In this work we report the microwave spectrum of methylenecyclopropane, including the three monosubstituted ^{13}C isotopic species, and the determination of the molecular structural parameters and dipole moment.

Experimental Section

Methylenecyclopropane was synthesized from 3-chloro-2-chloromethyl-1-propene by the method of Gragson, *et al.*[3] The precursor was obtained from Aldrich Chemical Co. After synthesis the sample was purified by gas chromatography and was stored at $-78°$ to avoid polymerization. ^{13}C species were studied in their naturally occurring abundance.

All transitions except the $2 \rightarrow 3$ R-branch transitions of the main isotopic species were measured on a 100-KHz Stark modulation

(3) J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, 75, 3344 (1953).