Analysis of the Mechanism of Reaction of H_3^+ with Ethylene Oxide and Acetaldehyde[1]

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Abstract: The reaction of H_3^+ with ethylene oxide and acetaldehyde yields the following products: $H_3^+ + C_2H_4O \rightarrow C_2H_4O^+ + H_2 + H$ (charge exchange), $C_2H_3O^+ + 2H_2$ (hydride abstraction), or $[C_2H_5O^+]^* + H_2$ (proton transfer); $[C_2H_5^+]^* \rightarrow C_2H_4O^+ + H_2$, $HCO^+ + CH_4$, $C_2H_3^+ + H_2O$, or $H_3O^+ + C_2H_2$. The charge-exchange reaction and hydride-ion-abstraction reaction occur only for H_3^+ molecules with a large amount of internal energy. Variations in the product distribution with H_2 pressure allow investigation of the importance of vibrational energy in H_3^+ on the reaction dynamics. Comparison is made with variations of the product distribution as a function of H_3^+ translational energy. The qualitative effects are similar for both vibrationally and translationally excited H_3^+. The charge-transfer rate increases with energy, as does the hydride-ion-transfer rate. The proton-transfer rate decreases. These energy-dependent studies coupled with the isotopic distributions from D_3^+–C_2H_4O and H_3^+–C_2D_4O (and their energy dependence) allow a clear elucidation of the detailed mechanism of decomposition of excited $[C_2H_5O^+]^*$ ions to yield $C_2H_3O^+$, HCO^+, $C_2H_3^+$, and H_3O^+ ions. Comparison is made with data of other workers.

The H_3^+ ion is an easily accessible source of protons that can readily be transferred to all gaseous molecules. Such transfers are often highly exothermic due to the low proton affinity (PA) of the H_2 molecule.[2] The large amount of energy transferred often leads to considerable fragmentation of the protonated species.[3,4] Since the proton affinities of many simple molecules are known,[4–7] protonation with H_3^+ offers the opportunity to investigate fragmentations of molecular ions with a known amount of internal energy. Utilizing selectively deuterated acceptor molecules, considerable information can be obtained about the details of the reaction mechanism.[4] In addition, calculations based on the quasi equilibrium theory (QET) of unimolecular reactions[8] can be carried out in an attempt to predict the proton-transfer-induced fragmentation patterns.

H_3^+ proton-transfer reactions also offer an opportunity to study the effect of H_3^+ vibrational excitation on product distributions. H_3^+ is initially formed in a highly excited vibrational state[9,10] which is subsequently relaxed by collisions with neutral H_2 molecules. The nature of the vibrational relaxation mechanism has been discussed in detail[4,10,11] and evidence exists for the following qualitative mechanism.

$$\begin{array}{ccccccc} H_2^+ & \xrightarrow{H_2} & (H_3^+)^* & \xrightarrow[\text{fast}]{H_2} & (H_3^+)\dagger & \xrightarrow[\text{slow}]{} & H_3^+ \\ & & & \text{1–5 collisions} & & \text{10–100 collisions} & \end{array}$$

$(H_3^+)^*$ contains 45 ± 5 kcal/mol of internal energy,[4] while $(H_3^+)\dagger$ is a metastable configuration with 23 ± 4 kcal/mol of internal energy.[4,10,11] H_3^+ is presumably at the ground vibrational state. If product distributions are monitored as a function of H_2 pressure, then the effects of the internal energy in H_3^+ on these distributions can be studied. The effects of H_3^+ translational energy on product distributions of H_3^+-acceptor reactions can also be studied and compared to the internal energy studies.

In this paper we report the reactions of H_3^+ and D_3^+ with ethylene oxide, acetaldehyde, and their perdeuterio analogs. The prevalent reaction in these systems is protonation of C_2H_4O to form $(C_2H_5O^+)^*$. This highly excited ion can either decompose or subsequently be collisionally stabilized. The mechanism of the decomposition of $(C_2H_5O^+)^*$ is one of the major focal points of this paper. The $C_2H_5O^+$ ion has been the focus of several previous works,[12–20] with the most pertinent studies being those of Harrison,[12,17] McLafferty,[15] and Beauchamp.[20] Comparison will be made with the data of these workers.

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[1] Supported by Grant No. GP-15628 from the National Science Foundation.

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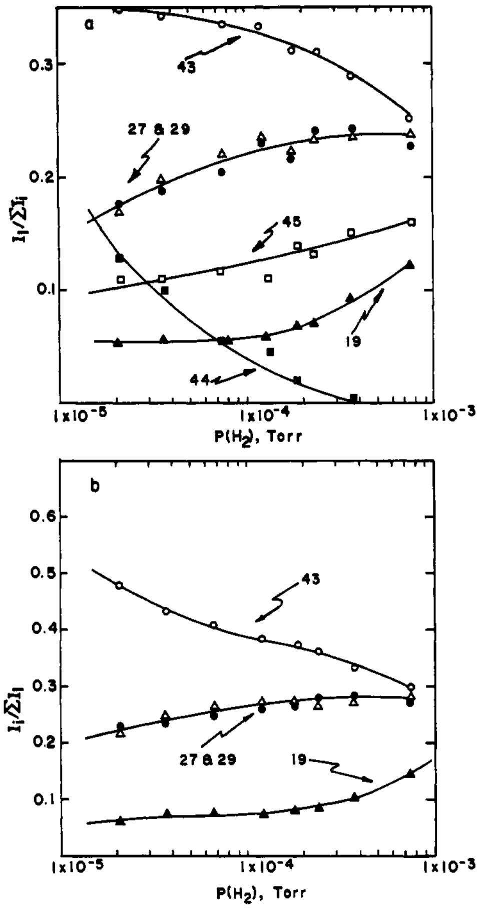

Figure 1. Product distribution resulting from the reaction of H_3^+ with ethylene oxide as a function of H_2 pressure. The ethylene oxide pressure was held constant at 2×10^{-7} Torr. The electron energy was 50 eV. Data were obtained by pulse ejecting H_3^+. In (b) the decomposition products only are displayed.

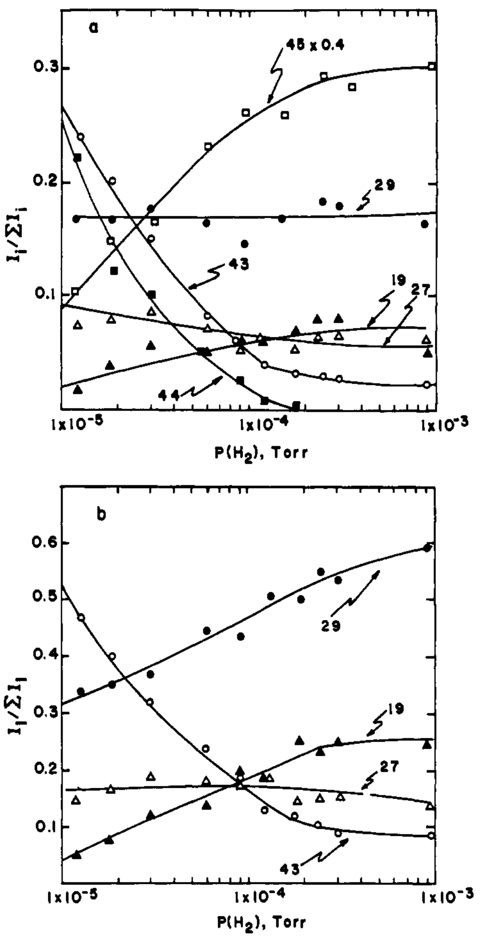

Figure 2. Product distribution resulting from the reaction of H_3^+ with acetaldehyde as a function of H_2 pressure. Conditions are the same as those of Figure 1. In (b) the decomposition products only are displayed.

Experimental Section

The experiments were carried out on a homemade ion cyclotron resonance (icr) spectrometer of conventional design.[21] The multiple resonance oscillators used are the Hewlett-Packard 675A sweeping signal generator with a calibrated output and a Wavetek Model III. Electron trap currents were measured on a Keithly 414A picoammeter which is part of a feedback current control loop. Currents can readily be regulated with essentially zero drift between 1×10^{-6} and 1×10^{-10} A.[22] During all experiments electron currents were maintained between 10^{-10} and 10^{-8} A with resulting ion currents of 10^{-12} A or less. It was found essential to maintain extremely low currents when performing ion-ejection experiments to avoid marginal oscillator pulling due to ion–ion interaction.[23] Pressure was measured on a calibrated Granville-Phillips ion gauge. Absolute pressures are probably not accurate to better than a factor of 2 but relative pressures should be much more reliable.[24]

The ethylene oxide was purchased from Matheson and purified by freeze–pump–thaw cycles. Acetaldehyde was Baker reagent grade and also purified by freeze–pump–thaw cycles. Low-pressure cyclotron resonance indicated no measurable impurities were present. The acetaldehyde-d_4 was purchased from ICN and the ethylene-d_4 oxide from Merck Sharpe and Dohme Ltd. Both samples were used as received. Isotopic purity was of the order of 95% in both cases. The hydrogen and deuterium used were Air Products research grade further purified by passing them through an Englehard Industries Inc. hydrogen purifier of the palladium diffusion type. The only detectable impurity was trace amounts of H_2O apparently leached from the walls of the gas inlet system. Appropriate corrections were made for this impurity.

A two section "square" cell of 1 in. × 1 in. cross section was used in all experiments. While something is lost in drift-field homogeneity using the square cell, considerable advantage is gained in the facile application of trapping field-ejection techniques.[23] Since absolute rate constants were not measured, it was felt the loss in electric field homogeneity did not significantly affect our results.

Results and Discussion

General Reaction Scheme. The product distributions from the reaction of H_3^+ with ethylene oxide and acetaldehyde as a function of H_2 pressure are given in Figures 1 and 2, respectively. These data were obtained by pulse ejecting the H_3^+ with the trapping field as described by Beauchamp and Armstrong.[23] It is clear reactions 1–6 are occurring in both systems, with

$$H_3^+ + C_2H_4O \left\{ \begin{array}{ll} \xrightarrow{45} C_2H_5O^+ + H_2 & (1) \\ \xrightarrow{44} C_2H_4O^{+\cdot} + H_2 + H\cdot & (2) \\ \xrightarrow{43} C_2H_3O^+ + 2H_2 & (3) \\ \xrightarrow{29} HCO^+ + CH_4 & (4) \\ \xrightarrow{27} C_2H_3^+ + H_2O & (5) \\ \xrightarrow{19} H_3O^+ + C_2H_2 & (6) \end{array} \right.$$

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[21] For recent reviews of the icr technique and instrumentation see J. D. Baldeschwieler, *Science*, **159**, 263 (1968), and G. Gray, *Advan. Chem. Phys.*, **19**, 141 (1971).

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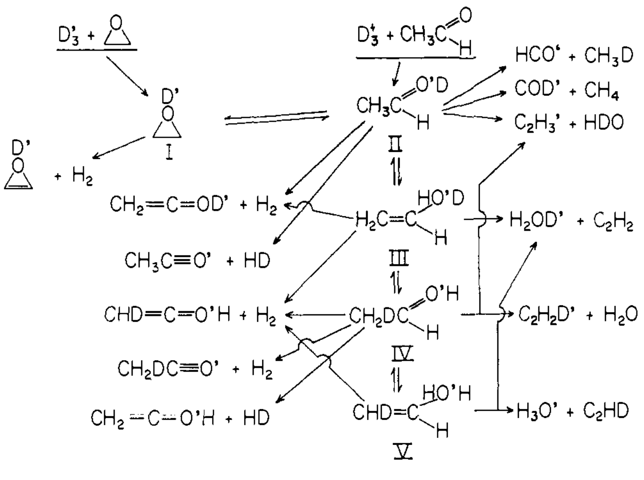

Figure 3. Detailed reaction mechanism for reaction of D_3^+ with ethylene oxide and acetaldehyde.

the thermochemical inferences and product distributions as listed in Table I. All of the reactions are strongly exothermic for ground-state H_3 ions except (2), the charge-transfer reactions. From Figures 1a and 2a it is apparent that charge transfer occurs only at the lowest H_2 pressures, indicating that vibrationally excited $(H_3^+)^*$ is responsible for this reaction in both systems. There are several major differences between the ethylene oxide and acetaldehyde systems. In ethylene oxide there is a much greater percentage of fragment ion relative to protonated parent than in acetaldehyde. This willingness to fragment of the oxirane probably reflects the contribution of the ring strain energy to the reaction kinetics. Secondly, the HCO^+ ion is the major fragment ion in acetaldehyde, while in the oxirane system $C_2H_3O^+$, HCO^+, and $C_2H_3^+$ all have roughly the same intensity. These data suggest that a pathway for formation of HCO^+ may be available in the aldehyde that is not available in the oxirane, possibly methide ion abstraction. There is evidence for the methide-ion abstraction process in ethanol. Beauchamp[25] has observed the reaction

$$D_3^+ + CH_3CH_2OH \longrightarrow CH_2OH^+ + CH_3D + D_2 \quad (7)$$

where no isotopic mixing occurs in the CH_2OH^+ product.

Table I. Thermochemistry and Product Distributions of Reactions of $H_3\cdot^+$ with Acetaldehyde and Ethylene Oxide

	CH_3CHO		$(CH_2)_2O$	
Product ion	ΔH^a	Product distribution[b]	ΔH^a	Product distribution[b]
$C_2H_5O\cdot^+$	−78		−77[c]	
$C_2H_4O\cdot^+$	+27		+36	
$C_2H_3O^+$	−68	9	−95	35
HCO^+	−21	57	−47	28
$C_2H_3^+$	−14	16	−46	28
H_3O^+	−13	25	−39	8

[a] Values are in kilocalories per mole. Calculated from the data in J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Heron, K. Draxl, and F. H. Field, NSRDS-NBS 26, 1969, except as otherwise noted. [b] Product distributions from unimolecular decomposition of excited $(C_2H_5O^+)^*$ ions formed by proton transfer at 3 × 10^{-4} Torr H_2 pressure. [c] ΔH_f of protonated ethylene oxide taken as 170 kcal/mol (ref 20).

We infer from these data that the protonated alcohol is not an intermediate in the formation of CH_2OH^+.

The overall pressure dependence of the product distributions in Figures 1 and 2 is the result of collisional deactivation of $(H_3^+)^*$ and collisional stabilization of $(C_2H_5O^+)^*$. The effects on the product distribution due to the variation of internal energy in H_3^+ will be dealt with at length in the following sections.

D_3^+–C_2H_4O Reactions. The reactions of D_3^+ with ethylene oxide and acetaldehyde yield qualitatively the same results as reactions of H_3^+. The isotopic product distributions are collected in Table II for the fragment ions. It is clear that the observed isotopic ratios bear little resemblance to those expected for random scrambling in a $(C_2H_4DO^+)^*$ complex intermediate. Certain of the isotopic ratios given in Table II are dependent on the D_2 pressure, indicating that the mechanism for their formation is a function of the internal energy in the D_3^+ ion. More will be said about these ratio changes in the following section.

Table II. Isotopic Ratios for Reactions of D_3^+ with Ethylene Oxide and Acetaldehyde[a,b]

Product ion	$(CH_2)_2O$	CH_3CHO	Random
$C_2H_2O^+D$	7.0	1.3	1.5
$C_2H_2O^+H$	1.0	1.0	1.0
DCO^+	0.16	0.16	0.25
HCO^+	1.0	1.0	1.0
$C_2H_2D^+$	0.25	0.3	1.5
$C_2H_3^+$	1.0	1.0	1.0
H_2DO^+	1.0	1.0	1.0
H_3O^+	0.1	0.1	0.66

[a] Data are for a $C_2H_4O^+$ pressure of 2 × 10^{-7} Torr and a D_2 pressure of 1 × 10^{-4} Torr. H_2DO^+ and H_3O^+ data are taken at 2 × 10^{-5} Torr to avoid interference from the exchange reaction $H_3O + D_2 \rightarrow H_2DO^+ + HD$. [b] All ratios are approximate due to their pressure dependence, as discussed in the text.

A detailed reaction mechanism appropriate to the reaction of D_3^+ with ethylene oxide and acetaldehyde is given in Figure 3. Direct reactions, such as hydride- and methide-ion abstraction reactions, are omitted. From the data of Table II it is apparent that virtually all of the protonated water is formed from intermediate III in both the aldehyde and oxirane. This result indicates that the excited protonated species undergo decomposition rapidly relative to the number of isomerizations it takes to make structure V (four isomerizations for ethylene oxide and three for acetaldehyde). Hence, structure V and, most likely, structure IV are not important in the decomposition process at low pressures. In fact, in the H_3^+–C_2H_4O systems (Figures 1 and 2), formation of H_3O^+ requires at least one isomerization to obtain a structure similar to III. At low H_2 pressure (1 × 10^{-5} Torr), H_3O^+ comprises only 5% of the ionization in the H_3^+–oxirane system, while at 1 × 10^{-3} Torr H_3O^+ accounts for 12.5% of the ionization (Figure 1). A similar trend is observed for H_3^+–acetaldehyde (Figure 2). Apparently, as the H_2 pressure is raised, both $(H_3^+)^*$ and $(C_2H_5O^+)^*$ are collisionally deactivated, allowing a greater number of isomerizations to occur before decomposition.

Additional support is given for the proposed scheme of Figure 3 by the D_2 pressure variation of $C_2H_3^+$: $C_2H_2D^+$ plotted in Figure 4. At low pressures, the

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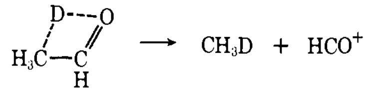
(25) J. L. Beauchamp, private communication.

mass 27:mass 28 ratio drops rapidly, while at higher pressures a more gradual decline exists. The reaction mechanism in Figure 3 indicates that $C_2H_3^+$ (mass 27) originates directly from structure II (requiring no isomerizations in the aldehyde case and only one in the oxirane), while $C_2H_2D^+$ originates from IV, requiring either two or three isomerizations. The completely randomized result predicts the intensity of mass 27: mass 28 = 0.66, a figure only slowly approached if at all. In addition, at the highest pressures the very slow exchange reaction

$$C_2H_3^+ + D_2 \longrightarrow C_2H_2D^+ + HD \qquad (8)$$

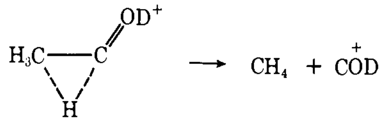
observed by Aquilanti and Volpi[3a] undoubtedly contributes to the decrease in the mass 27 : mass 28 ratio.

The strong dependence of the mass 27 : mass 28 ratio on D_2 pressure is in contrast to the very weak pressure dependence of mass 30 : mass 29. By previous arguments the bulk of the HCO^+ and DCO^+ ions must then come from structure II at low pressures. There are two distinct mechanisms possible



$\longrightarrow CH_3D + HCO^+$ (9)

and



$\longrightarrow CH_4 + \overset{+}{C}OD$ (10)

If both processes were equally likely then mass 30 : mass 29 = 1 would result. Since experimentally the intensity of mass 30 : mass 29 ≅ 0.17, process 9 is favored by a factor of 6. This result could be due to differences in the transition states [(9) is four centered and (10) is three centered] or to the fact that HCO^+ is a lower energy species (*i.e.*, more stable product) than COD^+. An H/D migration isotope effect would favor (10) over (9). In the aldehyde, methide-ion-abstraction would favor (9) over (10). However, since essentially the same mass 30 : mass 29 ratio is observed for both the oxirane and aldehyde at all pressures, either the methide ion-abstraction reaction is independent of H_3^+ internal energy or methide ion abstractions are unimportant.

By far the largest difference in product ion isotopic distribution between the aldehyde and oxirane systems is in $C_2H_3O^+$ and $C_2H_2DO^+$ (Table II). At low pressures charge exchange contributes to the mass 44 peak ($C_2H_4O\cdot^+$ and $C_2H_2DO^+$). Little interference is expected at medium-to-high pressures, however (see Figures 1a and 2a), and the data of Table II should be reasonably accurate. The large mass 44 : mass 43 ratio in the oxirane relative to the aldehyde indicates that a mechanism is available to the oxirane for forming $C_2H_2DO^+$ that is not available to the aldehyde. One reasonable possibility is that the protonated oxirane immediately loses H_2 from the ring (before undergoing isomerization), as shown in Figure 3, to form the corresponding oxirene. This contention is further supported by the fact that in H_3^+–C_2H_4O systems (Figures 1 and 2), $C_2H_3O^+$ is the major product ion in the oxirane and a relatively minor product ion in acetaldehyde. The nearly statistical mass 44 : mass 43 ratio in the aldehyde at high pressures is expected, since $C_2H_3O^+$ and $C_2H_2DO^+$ can be formed from any of the structures II–V in two stable isomeric forms.

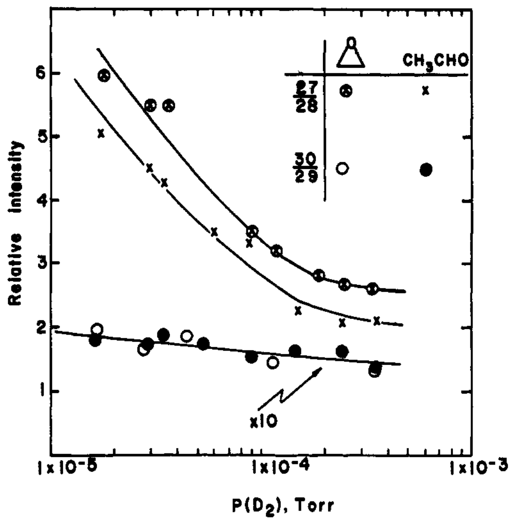
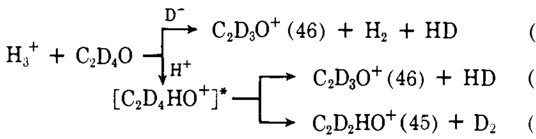


Figure 4. Relative intensities of the mass 27 : mass 28 and mass 30 : mass 29 ratios resulting from reaction of D_3^+ with ethylene oxide and acetaldehyde as a function of D_2 pressure. C_2H_4O pressure was held constant at 2 × 10^{-7} Torr.

There is a strong D_2 pressure dependence of the mass 44 : mass 43 ratio in both systems. It is not possible to accurately subtract out the contribution of the charge-exchange reaction to the mass 44 peak at low pressures, however. Such complications do not exist in the H_3^+–C_2D_4O systems, and these systems will be considered next.

H_3^+–C_2D_4O Reactions. The reactions of interest in these systems are



$$H_3^+ + C_2D_4O \xrightarrow{D^-} C_2D_3O^+(46) + H_2 + HD \qquad (11a)$$

$$H_3^+ + C_2D_4O \xrightarrow{H^+} [C_2D_4HO^+]^* \longrightarrow C_2D_3O^+(46) + HD \qquad (11b)$$

$$[C_2D_4HO^+]^* \longrightarrow C_2D_2HO^+(45) + D_2 \qquad (11c)$$

The upper reaction path represents a direct D^- abstraction reaction, while the lower path represents proton transfer followed by loss of HD or D_2 from the excited intermediate complex. The H_2 pressure dependence of the mass 46 : mass 45 ratio is given in Figure 5. In both cases the ratio decreases sharply with pressure, indicating that the mass 46 ion is losing a preferred pathway, as $(H_3^+)^*$ and/or $(C_2D_4HO)^*$ are deactivated collisionally. There is no apparent reason that deactivating $(C_2D_4HO^+)^*$ should appreciably change the mass 46 : mass 45 ratio since both 46 and 45 can come from each of the structures analogous to II, III, and IV in Figure 3. A plausible explanation is that the D^- abstraction reaction is strongly enhanced for vibrationally excited $(H_3^+)^*$ and plays little part in the reactions of deactivated $(H_3^+)\dagger$ or H_3^+. Similar results have been obtained in reactions of H_3^+ with substituted methanes.[4] Isotopic exchange reactions of $C_2D_3O^+$ with H_2 molecules do not account for the change, as $C_2DH_2O^+$ (44) and $C_2H_3O^+$(43) ions were not formed at very high H_2 pressures.[26] To our knowledge these

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(26) A referee has suggested that the observed variation in the mass 46 : mass 45 ratio may be due to dissociative charge exchange between excited $(H_3^+)^*$ and the C_2D_4O substrate molecules. Charge-transfer-induced dissociation would produce only the mass 46 ion, while dissociative proton transfer would form both the 46 and the 45 ions. As the H_2

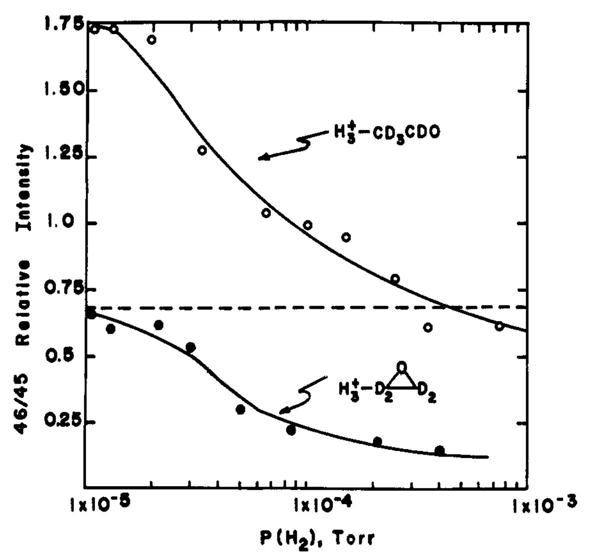


Figure 5. Relative intensities of the mass 46:mass 45 ratios resulting from the reaction of H_2^+ with ethylene-d_4 oxide and acetaldehyde-d_4 as a function of H_3^+ pressure. C_2D_4O pressure was held constant at 2×10^{-7} Torr. The dashed line gives the random scrambling result.

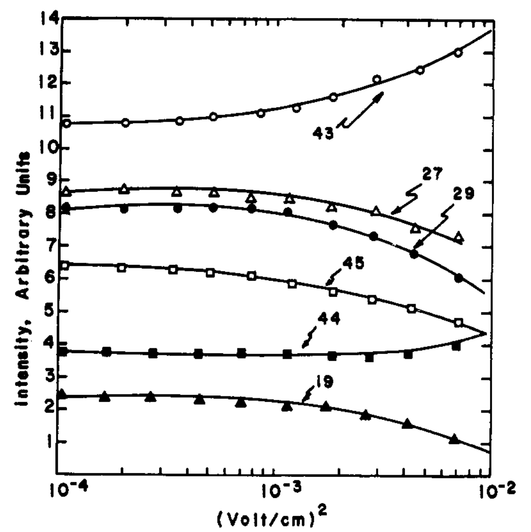


Figure 6. Dependence of the product distribution resulting from the reaction of H_3^+ with ethylene oxide as a function of H_3^+ kinetic energy. The C_2H_4O pressure was held constant at 2×10^{-7} Torr and the H_2 pressure at 1×10^{-4} Torr.

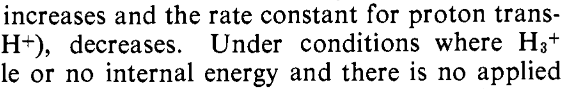
studies, along with those in ref 4, provide the only available experimental data on the importance of vibrational energy in the dynamics of hydride ion abstraction reactions.

At high pressures the acetaldehyde-d_4 mass 46:mass 45 ratio approaches statistical, while in ethylene-d_4 oxide the mass 46:mass 45 ratio is much smaller than statistical. These results correlate with the data on the D_3^+-C_2H_4O systems given in Table II and substantiate the mechanism outlined in Figure 3.

Translational Energy Dependence. The qualitative kinetic energy dependence of ion-molecule reactions can be conveniently studied using icr double-resonance techniques.[5,21] The translational energy dependence of the product distributions due solely to H_3^+ (or D_3^+) can be observed using pulsed-ion-ejection double-resonance experiments.[29,30] In these experiments H_3^+ is continually cyclotron heated by an applied rf field on the source drift plates while being pulse ejected from the cell by an applied rf field on the trapping plates. Since H_3^+ and D_3^+ are secondary ions, and since most experiments are carried out under conditions where multiple collisions occur in the irradiation zone, the actual average kinetic energy of H_3^+ (D_3^+) is not well known. What is important is that it increases with increasing rf field strength.

The translational energy dependence of the reaction of H_3^+ with ethylene oxide is given in Figure 6. Similar results are obtained for acetaldehyde. The $C_2H_5O^+$, HCO^+, $C_2H_3^+$, and H_3O^+ products all decrease with H_3^+ reactant ion energy, while the $C_2H_3O^+$ product increases with kinetic energy. This situation is exactly analogous to the H_2 pressure dependence of Figure 1. In that instance, as the H_2 presure is lowered, $C_2H_3O^+$ increases in relative intensity while $C_2H_5O^+$, HCO^+, $C_2H_3^+$, and H_2O^+ decrease. Lowering the H_2 pressure is equivalent to *increasing* the internal energy in H_3^+. Hence there is a strong correlation between the effects of internal and translational energy on the observed product distribution.

These results suggest the scheme shown by reactions 12. As kinetic or vibrational energy is pumped into



$$H_3^+ + C_2H_4O \xrightarrow{H^-} C_2H_3O^+ + 2H_2O \qquad (12a)$$

$$H_3^+ + C_2H_4O \xrightarrow{H^+} (C_2H_5O^+)^* + H_2$$

$$(C_2H_5O^+)^* \longrightarrow C_2H_3O^+ + H_2 \qquad (12b)$$

$$(C_2H_5O^+)^* \longrightarrow HCO^+ + CH_4 \qquad (12c)$$

$$(C_2H_5O^+)^* \longrightarrow C_2H_3^+ + H_2O \qquad (12d)$$

$$(C_2H_5O^+)^* \longrightarrow H_3O^+ + C_2H_2 \qquad (12e)$$

H_3^+, the rate constant for the hydride abstraction, $k(H^-)$, increases and the rate constant for proton transfer, $k(H^+)$, decreases. Under conditions where H_3^+ has little or no internal energy and there is no applied rf heating, $k(H^-)$ becomes less important and the majority of the reaction takes place *via* proton transfer. The decrease in $C_2H_3O^+$ at high pressures is balanced

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pressures increased $(H_3^+)^*$ would be deactivated and less mass 46 ion relative to mass 45 ion would be formed. The charge-transfer processes are approximately 27 and 36 kcal/mol endothermic from ground-state H_3^+ to acetaldehyde and ethylene oxide, respectively (assuming $\Delta H_f \cdot (H_3^+) \cong 260$ kcal/mol[2]). Appearance potential studies indicate that AP − IP ≅ 7 kcal/mol for acetaldehyde[27] and AP − IP ≅ 37 kcal/mol for ethylene oxide.[23] Thus, approximately 34 kcal/mol of excitation energy in $(H_3^+)^*$ is needed for the aldehyde to dissociate and 73 kcal/mol for the oxirane. The best estimate currently available indicates that $(H_3^+)^*$ contains about 45 kcal/mol of internal energy when first formed.[4] It is thus feasible that charge-exchange-induced decomposition is occurring to a certain extent in the aldehyde at low pressures. It appears to be energetically unfeasible in the oxirane system, however. The very similar H_2 pressure dependence of the mass 46:mass 45 ratio in the aldehyde and oxirane systems indicates that a similar process is occurring in both. Similar remarks pertain to the kinetic energy experiments of Figure 7. In addition, there is unequivocal evidence that in H_3^+-CH_3NH_2 and H_3^+-CH_3OH systems H^- transfer occurs and the ratio of H^- to H^+ transfer reactions is a strongly decreasing function of the H_2 pressure.[4] At low pressures H^- abstraction reactions dominate, while at high H_2 pressures all reactions proceed *via* H^+ transfer. We conclude that similar processes are occurring in the H_3^+-acetaldehyde and H_3^+-ethylene oxide systems.

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(28) E. J. Gallegos and R. W. Kiser, *J. Amer. Chem. Soc.*, **83**, 773 (1961).

(29) M. T. Bowers, D. D. Elleman, and J. King, Jr., *J. Chem. Phys.*, **50**, 4787 (1969).

(30) M. T. Bowers and D. D. Elleman, *J. Amer. Chem. Soc.*, **92**, 1847 (1970).

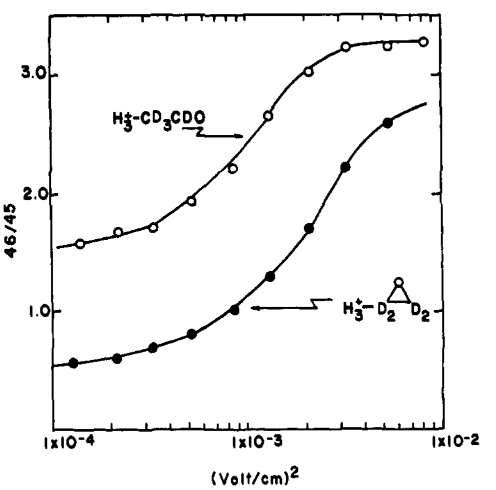


Figure 7. Dependence of the mass 46 : mass 45 ratio resulting from reaction of H_3^+ with ethylene-d_4 oxide and acetaldehyde-d_4 as a function of H_3^+ kinetic energy. The C_2D_4O pressure was held constant at 2×10^{-7} Torr and the H_3 pressure at 6×10^{-5} Torr.

quantitatively with an increase in H_3O^+ product (see Figure 1b). This fact reflects the collisional stabilization of the $(C_2H_5O^+)^*$ complex and the subsequent enhancement of $C_2H_5O^+$ intermediate isomeric structures analogous to III and V in Figure 3.

It is of interest to compare the dependence of various isotopic ratios on H_3^+ (or D_3^+) kinetic energy with the analogous pressure-dependence results. Of particular interest are the relative intensities of the various $C_2(H, D)_3O^+$ isotopic species. The results for the $C_2D_3O^+ : C_2D_2HO^+$ ratio originating from H_3^+ on C_2D_4O at 6×10^{-5} Torr of H_2 pressure are given in Figure 7. The mass 45 ion ($C_2D_2HO^+$) originates solely from proton transfer, while the 46 ion ($C_2D_3O^+$) comes both from proton transfer and D^- abstraction (see reactions 11a–c). As the irradiating field is increased, mass 46 : mass 45 dramatically increases, indicating that $k(D^-)/k(H^+)$ significantly increases with H_3^+ translational energy. An exactly analogous effect is found for the variation in $k(D^-)/k(H^+)$ with vibrational energy in H_3^+ (Figure 5), as previously discussed. Since the mass 45 ion *decreases* in absolute intensity with increasing kinetic energy and the mass 46 ion *increases* in intensity with kinetic energy, $dk(H^-)/dE$ is positive and $dk(H^+)/dE$ is negative in the H_3^+–C_2H_4O systems at low pressure.

A second interesting comparison can be made between the kinetic and vibrational energy dependence of the mass 27 : mass 28 ratios in the D_3^+–C_2H_4O system. The kinetic energy dependence is given in Figure 8 and qualitatively agrees with the vibrational energy dependence (Figure 4). That is, as the kinetic, or vibrational, energy increases, mass 27 : mass 28 increases. This is reasonable in light of the mechanism in Figure 3, since only the 27 ion ($C_2H_3^+$) can be formed from structure II, while both 27 and 28 are formed from structure IV. Evidently, some of the available kinetic energy of the D_3^+ ion is transferred to the $[C_2H_4O^+D]^*$ complex, which results in an increased rate of decomposition relative to isomerization followed by decomposition. This kind of behavior is typical of the situation where the amount of available internal energy in an excited ion is considerably greater than the barrier to either isomerization or decomposition and decomposition occurs rapidly relative to isomerization.[31]

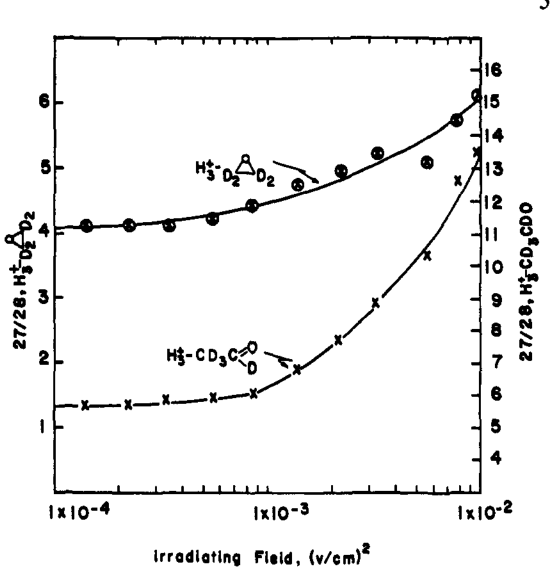


Figure 8. Dependence of the mass 27 : mass 28 ratio resulting from reaction of D_3^+ with ethylene oxide and acetaldehyde as a function of D_3^+ kinetic energy. The C_2H_4O pressure was held constant at 2×10^{-7} Torr and the D_2 pressure at 3×10^{-4} Torr.

Finally, the mass 29 : mass 30 ratio in D_3^+–C_2H_4O systems showed very little dependence on the D_3^+ kinetic energy. This observation is consistent with the vibrational results and the mechanism of Figure 3, as discussed earlier.

Comparison with Data of Other Workers. The initial study on the decomposition of the $C_2H_5O^+$ ion was performed by Van Raalte and Harrison[12] in a medium-pressure mass spectrometer. They observed the reactions

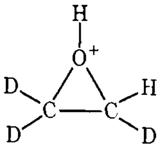
$$[(CD_3)_2CH\overset{+}{O}H]^* \longrightarrow [CD_3CH\overset{+}{O}H]^* + \cdot CD_3$$

$$\longrightarrow H_2DO^+ + C_2D_2 \quad 49\% \quad (13a)$$

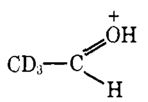
$$\longrightarrow HD_2O^+ + C_2DH \quad 47\% \quad (13b)$$

$$\longrightarrow D_3O^+ + C_2H_2 \quad 4\% \quad (13c)$$

In order to explain the observed product distribution, they assumed that the H atom on the oxygen remained on the oxygen and the remaining H atom and three D atoms were completely scrambled. The predicted result of 50% H_2DO^+ and 50% HD_2O^+ is very close to the experimental. This isotopic mixing led Van Raalte and Harrison to postulate the protonated oxirane structure VI as the structure of the $[C_2D_3H_2O^+]^*$ intermediate in reaction 13. From the structure of the *sec*-propyl



VI



VII

alcohol parent ion, it is reasonable that protonated acetaldehyde is the structure first formed, however (structure VII). The aldehyde could reversibly isomerize to the oxirane and subsequently decompose to

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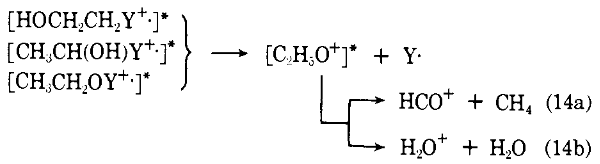
[31] See, for example, M. Vestal, "Fundamental Processes in Radiation Chemistry," P. Ausloos Ed., Interscience, New York, N. Y., 1968, Chapter 2.

products *via* a mechanism analogous to Figure 3. The fact that D_3O^+ accounts for 4% of the reaction is also strong support of a mixing scheme similar to Figure 3 and indicates that many of the excited $[C_2D_3H_2O^+]^*$ ions are sufficiently long-lived to undergo a large number of isomerizations before decomposition. Apparently virtually all of them reversibly isomerize from the protonated aldehyde to the oxirane and back. Similar results were observed by Van Raalte and Harrison in *sec*-butyl-*1,1,1,3,3*-d_5 alcohol.

Shannon and McLafferty[15] have measured metastable transitions for the reactions

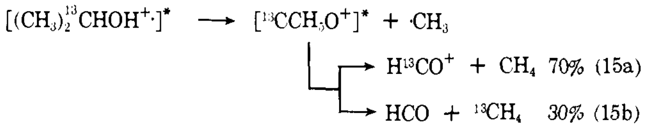


$$\left.\begin{matrix}[HOCH_2CH_2Y^{+}\cdot]^* \\ [CH_3CH(OH)Y^{+}\cdot]^* \\ [CH_3CH_2OY^{+}\cdot]^*\end{matrix}\right\} \longrightarrow [C_2H_5O^+]^* + Y\cdot$$

$$[C_2H_5O^+]^* \longrightarrow HCO^+ + CH_4 \quad (14a)$$

$$[C_2H_5O^+]^* \longrightarrow H_2O^+ + H_2O \quad (14b)$$

where the Y's are a wide variety of functional groups. The ratios of the metastable intensities of (14a) and (14b) are constant within experimental error. This result lead Shannon and McLafferty to conclude that both (14a) and (14b) proceeded from a $[C_2H_5O^+]^*$ ion of identical structure. Their preferred intermediate structure is the protonated oxirane, as suggested by Van Raalte and Harrison.[12] Harrison and Keyes[17] have also studied the formation of HCO^+ *via* reaction 15. If the $[^{13}CCH_5O^+]^*$ intermediate were the protonated oxirane, then (15a) and (15b) should be equally probable



$$[(CH_3)_2{}^{13}CHOH^{+}\cdot]^* \longrightarrow [^{13}CCH_5O^+]^* + \cdot CH_3$$

$$[^{13}CCH_5O^+]^* \longrightarrow H^{13}CO^+ + CH_4 \quad 70\% \quad (15a)$$

$$[^{13}CCH_5O^+]^* \longrightarrow HCO + {}^{13}CH_4 \quad 30\% \quad (15b)$$

instead of 70 and 30%. The metastable intensities that correspond to (15a) and (15b) are equal,[17] however, which confirms the conclusion of Shannon and McLafferty[15] that H_3O^+ and HCO^+ resulting from metastable transitions are both formed from a common precursor.

All of these data on HCO^+ can be understood in terms of our reaction scheme analogous to Figure 3. The $C_2H_5O^+$ ions yielding the metastable transitions are long-lived relative to those decomposing in the source of the mass spectrometer. These relatively long-lived ions have ample time to undergo some isomerization before decomposition and hence randomize the carbon atoms and partially randomize the five hydrogens. The HCO^+ ions formed in the source come from a $[C_2H_5O^+]^*$ intermediate of shorter lifetime and hence have less time to isomerize. In reaction 15, for example, the initial $C_2H_5O^+$ ionic structure most probably is $[CH_3{}^{13}CHO^+H]^*$ formed from direct loss of $\cdot CH_3$. The higher energy $C_2H_5O^+$ ions will tend to decompose to products before isomerization, thus enhancing the $H^{13}CO^+$ product. The lower energy ions (including the metastables) will isomerize to a greater extent before decomposing and hence the ^{12}C and ^{13}C carbons become equivalent. This effect is similar to the decrease in scrambling with internal energy discussed in the previous sections.

The H_3O^+ fragments are interesting in that even the short-lived $C_2H_5O^+$ ions appear to reversibly isomerize to the oxirane structure before decomposing. The reaction leading to H_3O^+ is about 8 kcal/mol less exothermic than that leading to HCO^+. Perhaps this difference in thermochemistry is sufficient to allow isomerization in the H_3O^+ case, where it does not occur for HCO^+. A kinetic effect could also contribute to the difference in mechanism between the two systems.

Finally, our conclusions are consistent with those of Beauchamp and Dunbar,[20] who found that there was no observable difference in reactivity between protonated acetaldehyde and protonated ethylene oxide. They concluded that there is rapid isomerization of the protonated ethylene oxide to the aldehyde structure, which is consistent with our results.

Summary

The conclusions on the reactions of H_3^+ with ethylene oxide and acetaldehyde are as follows. (1) Internally excited $(H_3^+)^*$ undergoes H^- abstraction reactions with a large rate constant relative to collisionally deactivated H_3^+. (2) The rate of H^- abstraction, $k(H^-)$, increases with kinetic (or vibrational) energy, while the rate of proton transfer, $k(H^+)$, decreases with kinetic energy. (3) Isotopic substitution studies coupled with the energy dependence of isotopic ratios established the detailed reaction mechanism of Figure 3. All experimental data can be explained in terms of this mechanism. (4) Translational and vibrational energy dependence of product distributions and isotopic ratios offers a powerful tool for probing the details of reaction mechanisms.

Acknowledgments. This work was supported by a grant from the National Science Foundation, No. GP-15628. In addition, we wish to sincerely thank Professor J. L. Beauchamp for giving us a sample of acetaldehyde-d_4 and Professor J. D. Baldeschwieler for the ethylene-d_4 oxide sample. Thanks are also due Professor A. G. Harrison for suggesting the palladium diffusion process for purifying hydrogen gas. Finally we would like to acknowledge Mrs. Ruth Hasman for preparing the figures in this manuscript, and Mr. Fred Skinner for building most of the electronic circuitry in the icr instrument.