the simplicity of the model. The energies involved in the interaction of the molecule and ion were elucidated, and the degree of delocalization of the excess electron was calculated. The PKS analysis indicates the ion is strongly localized and would be best described as a "solvated" ion. An alternative description of the excitation which includes a distance dispersion would describe the dimer ion as being delocalized.

Acknowledgement is made to the National Science Foundation for support of this research and to the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor Noel Hush for many useful suggestions regarding the interpretation of the charge resonance spectrum.

Registry No. $(TQ)_2^{\bullet-}$, 110850-67-4; quinhydrone, 106-34-3.

Ion/Surface Interactions as a Tool for Characterizing Isomers: $[C_2H_4O]^{\bullet+}$ Ions

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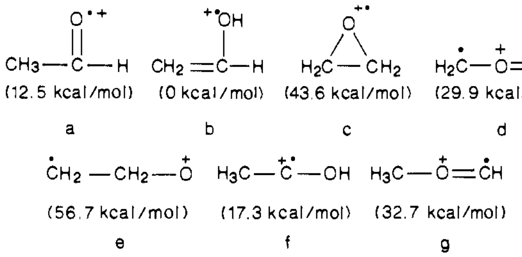
Abstract: Mass-selected $[C_2H_4O]^{\bullet+}$ ions, subjected to low-energy (25–60 eV) collisions at a solid surface, undergo inelastic scattering leading to surface-induced dissociation (SID) in competition with hydrogen atom abstraction. The spectra of isomeric ions show more pronounced differences than observed in gas-phase collision-activated dissociation (CAD). Control of the energy transferred to the selected ion is achieved by control of the collision energy in low-energy gas-phase and surface collisions and by selection of the scattering angle (0–5° lab) in high-energy gas-phase collisions. The SID and CAD data agree well and confirm the structures of the $[C_2H_4O]^{\bullet+}$ ions generated from acetaldehyde and butyraldehyde as the ketonic and enolic species a and b, that from ethylene carbonate as d, and that from pyruvic acid as the ionized carbene f. The ions derived from both ethylene oxide and ethylene carbonate behave indistinguishably to those derived from ethylene oxide in CAD and SID, indicating that they have the same structure or mixture of structures. While the cyclic ion c is not excluded, ring opening of ethylene oxide is argued to occur and to take place by C–C rather than by C–O bond cleavage, giving structure d rather than e as the major $[C_2H_4O]^+$ ion derived from ethylene oxide, ethylene carbonate, and 1,3-dioxolane. Either prior to or, more probably, upon activation, rearrangement occurs to give the ionized carbene f and the ylide g. Both of these ions have free methyl groups which are readily recognized upon collisional activation. The new methods used here clarify ion structural questions regarding the $[C_2H_4O]^+$ ion and provide the first experimental evidence for the participation of the isomer g.

The problem of characterizing the structures of gaseous organic ions has drawn upon a range of techniques,[1] including ion/molecule reactions,[2] collisional activation,[3] metastable ion dissociations,[4] and charge stripping.[5] Neutralization-reionization sequences[6] are a recent addition to this list.

Polyatomic ion/surface collisions provide a means of characterizing ions through their dissociation products.[7] Daughter spectra of selected ions can be obtained after inelastic collisions, the internally excited ions fragmenting in the gas phase by a process referred to as surface-induced dissociation (SID). The amount of internal energy deposited in the activated ion can be controlled by selection of the collision energy.[7,8] This method allows higher average energy deposition than does gas-phase collisional activation in either the low (eV) or high (keV) range of collision energies,[7] a result that may prove significant in the mass spectrometry of large molecules which are difficult to dissociate.[9] Parent, neutral loss, charge exchange, and reflection spectra, additional ways of accessing the data domain of tandem mass spectrometry, are also available through ion/surface interactions.[10,11]

In the course of studies of ion/surface collision phenomena, we have observed that certain ions pick up a hydrogen atom(s) or a methyl group upon colliding with the (gas-covered) surface. Reactive collisions of organic ions at solid surfaces have not previously been reported. The nature of this and related reactive collisions is currently being systematically studied, and the results will be reported elsewhere. In the present investigation we employ daughter spectra that include ions resulting from both ion/surface reactive collisions as well as surface-induced dissociation, to distinguish between isomeric ions.

Chart I



Both as a test of the capabilities of the SID method and for its intrinsic importance, we have chosen a classic problem in ion structure, that of the isomeric $[C_2H_4O]^{\bullet+}$ ions. Calculations have

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predicted the existence of eleven stable isomers, and experimental evidence for six (a–f) has been reported[12–24] (the relative energies[24] of these isomers are shown in parentheses). A significant early study,[17] applying collision-activated dissociation (CAD), reported the existence of three distinct stable structures that were assigned as the molecular ions of acetaldehyde (a), vinyl alcohol (b), and ethylene oxide (c). Holmes et al.[18] identified these same three structures by the characteristic metastable peaks accompanying their fragmentation by H atom loss. Heat of formation data for a, b, and c (196, 181, and 231 kcal/mol, respectively) also allow them to be distinguished. The $[C_2H_4O]^{\bullet+}$ ion derived from 1,3-dioxolane has been suggested to be a mixture of b and c, the composition of the mixture varying with the ionizing electron energy.[17,20] Metastable ion studies[18] again supported these findings but other authors,[26] perhaps examining ions of different internal energy, suggest that only the ring-opened ion d is generated.

While studying ion–molecule reactions of ethylene oxide, Blair and Harrison[13] and Beauchamp et al.[14] independently found evidence for a reactive form of $[C_2H_4O]^{\bullet+}$ that undergoes $[CH_2]^{\bullet+}$ transfer. The latter workers found that a bimolecular collision of energetic ethylene oxide is essential for the generation of the reactive structure. They suggested structure d to be the reactive species, viz. the product of C–C bond cleavage in ethylene oxide. Kumakura et al.[15] have instead invoked structure e, formed by C–O bond cleavage in ethylene oxide, also based on results of ion–molecule reactions. It has been argued that less energy is required to break the C–O bond compared to the C–C bond.[25] Nevertheless, dissociation of labeled 1,3-dioxolane in an ICR cell shows that formation of $[C_2H_4O]^{\bullet+}$ from this precursor involves cleavage of one C–O bond and one C–C bond and not two C–O bonds, suggesting that structure d is indeed involved in this case.[26] Van Velzen and Van der Hart[27] concluded from photodissociation studies in an ICR spectrometer that d is formed directly following electron impact on ethylene oxide. They also observed identical photodissociation spectra for the ions derived from 1,3-dioxolane and ethylene oxide in the 300–700-nm range.[27] This result suggests that these $[C_2H_4O]^{\bullet+}$ ions have common or interconverting structures. Theoretical studies of Bouma et al.[24,28] predict the C-C ring-opened structure, d, to be lower in energy than the ring-closed ethylene oxide structure, c.

Although it is one of the structures predicted by ab initio calculations to lie at a minimum in the potential energy surface, structure e may not be experimentally observable because of its high heat of formation and the low barrier to isomerization to the cyclic structure c.[24] Attempts have been made to support these conclusions by employing labeled ethylene carbonate.[16] Ethylene carbonate was judged a suitable precursor for the structure e since it readily loses carbon dioxide. ICR experiments on $[C_2H_4O]^{\bullet+}$ ions generated from ethylene carbonate, however, showed $[CH_2]^{\bullet+}$ transfer to neutral pyridine and nitriles as is typical of isomer d.[16] This observation raises the possibility that isomer e, if formed initially, rearranges to d (perhaps via c) before reacting with a neutral substrate. The ICR spectrum of a labeled analogue was recorded and it was found that the two CH_2 groups become equivalent prior to CH_2 transfer,[16] a result that is consistent with reaction via the cyclic intermediate. Structure f was postulated in an early study by McLafferty and co-workers[29] as an unstable intermediate in the formation of $[C_2H_4O]^{\bullet+}$ ions from pyruvic acid before isomerization to the acetaldehyde structure, a.[29] Later, based on kinetic energy release data, Holmes and co-workers[18] suggested $[C_2H_4O]^{\bullet+}$ from pyruvic acid to correspond to the vinyl alcohol structure b rather than to a. However, theoretical studies[23,24,30,31] predicted the hydroxymethylcarbene structure (f) to be a stable ion in the gas phase. Recent experiments, also by Holmes and co-workers, show that dissociation of pyruvic acid does indeed produce f via loss of CO_2.[22] The hydroxymethylcarbene (f) has also been found, experimentally, to be the reacting configuration for $H^\bullet$ loss from the cation radical of vinyl alcohol (b),[21,22] a result supported by theory.[23,30,31] Summarizing these findings, it appears that there is good evidence for structures a, b, c, d, and f. Evidence for e is less complete,[16,19] and there was no experimental evidence, prior to the present study, for structure g.

Experimental Section

The SID experiments employed a BQ mass spectrometer that was modified by replacing the collision quadrupole of a BQQ mass spectrometer with a solid surface and repositioning the mass analyzing quadrupole at 90° with respect to the incident beam.[32] The method used to acquire SID daughter spectra has been described earlier.[7] Ions were generated by 70 eV electron impact in a source held at a potential in the range 20–100 V with respect to ground. The ion beam was accelerated to 6 keV prior to mass analysis by the magnetic sector and decelerated to ground potential prior to collision at a stainless steel surface. A picoammeter was connected to the surface and the current due to the primary ion beam was recorded continuously during experiments. Lenses used for extraction of the emerging beam and its subsequent transfer into the quadrupole were adjusted to maximize the total ion current reaching the final detector, without significantly reducing the surface current. Mass analysis of the emerging beam was achieved with a quadrupole mass filter. All data were taken at a nominal incident angle at 25° (estimated uncertainty 3°) with respect to the surface normal. The angle of deviation was 121° from the original beam direction. The pressure in the chamber containing the target surface was maintained at 5.0×10^{-7} Torr by means of diffusion pumps. At this pressure the stainless steel target is assumed to carry adsorbed gases. No attempt has been made to clean the surface. Data obtained under these conditions were highly reproducible over a period of months. Samples were obtained commercially and used without purification. Data acquisition was carried out with a custom built acquisition system. All isomeric ions were run one after another without adjustment of any instrumental parameters.

The low-energy gas-phase collisions were studied with use of a Finnigan triple quadrupole instrument. Ions were again generated by 70 eV electron impact. The collisionally activated dissociation (CAD) spectra were obtained at collision energies ranging from 5 to 30 eV with argon as collision target. Argon pressure was monitored by a Bayard-Alpert ionization gauge situated outside the collision chamber. The indicated pressure was less than 3×10^{-6} Torr, corresponding to single-collision conditions.

The high-energy gas-phase data were obtained with use of a Finnigan-MAT 212 instrument. A collision needle constructed from $^1/_{16}$ in.

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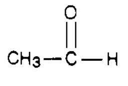
stainless steel, narrow bore LC tubing was placed just after the source slit. The upper z-deflection plate of the EI/CI ion source was connected to an auxiliary power supply to allow its potential to be varied by several hundred volts from the normal value of 1330 V, thereby causing the ion beam to approach the source slit at an angle up to 6° from the ion-optical axis of the instrument.[34] All experiments employed 3 keV ion beams generated by 70 eV electron impact. Argon collision gas was introduced until the main beam was attenuated by 50%. Products of collision-induced dissociation were analyzed by using a linked scan (B/E = constant) to record all daughters arising from a selected parent ion.

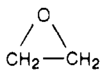
Results and Discussion

Ion/Surface Collisions. $[C_2H_4O]^{\bullet+}$ ions were generated from six precursors: acetaldehyde (**1**), ethylene oxide (**2**), butyraldehyde (**3**), 1,3-dioxolane (**4**), pyruvic acid (**5**), and ethylene carbonate (**6**). Figure 1 compares the daughter spectra of the ions derived from **1**–**5** arising as a consequence of collisions at 25 eV, with a stainless steel surface held under vacuum in the 10^{-7} Torr range. These conditions result in efficient dissociation of the selected ion with strong ion currents due to the fragments. Two significant features should be noted: (i) in some of the spectra the presence of an abundant product ion at m/z 45 which is due to hydrogen atom abstraction from the surface by the incident ion of m/z 44 is seen, and (ii) four of the six ions give distinctly different daughter spectra.



$CH_3-\overset{\overset{O}{\|}}{C}-H$

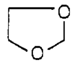
1



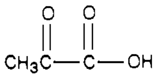
2

$CH_3(CH_2)_2CHO$

3

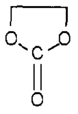


4



$CH_3\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH$

5



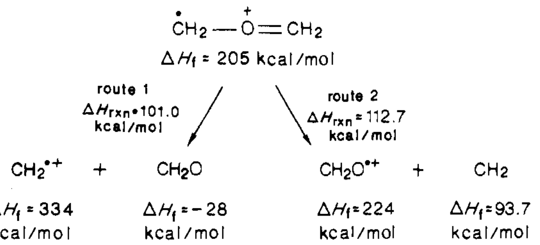
6

The reactive collision (probably involving residual hydrocarbon molecules on the metal target surface) is a particularly useful feature in distinguishing the $[C_2H_4O]^{\bullet+}$ ions. While spectra of the ions generated from **1** and **3** show a considerable amount of $[M + H]^+$ ion, the ions derived from **2**, **4**, **5**, and **6** show very little hydrogen atom pickup. Differences are also seen in the types and relative abundances of the fragment ions in the daughter spectra, except in the cases of the $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide, 1,3-dioxolane, and ethylene carbonate.

The SID daughter spectrum of the molecular ion of acetaldehyde exhibits characteristic peaks at m/z 43 $[CH_3CO]^+$, m/z 29 $[HCO]^+$, and m/z 15 $[CH_3]^+$, which are the expected fragmentation products from the proposed[17] structure a. A number of additional features are also observed in this SID spectrum. The base peak appears at m/z 45 and it represents the product of hydrogen atom abstraction in an ion/surface reaction. The probable product is O-protonated acetaldehyde, thermodynamically one of the most stable of the $[C_2H_5O]^{\bullet+}$ isomers.[35] Subsequent fragmentation of this ion can account for $[C_2H_3]^+$ (m/z 27) via loss of water and for $[H_3O]^+$ (m/z 19) by loss of acetylene (Figure 1a). The ion m/z 16, attributed to $[CH_4]^{\bullet+}$, is probably due to CO loss from the molecular ion, $[M]^{\bullet+}$. All this information conforms with structure a, which is therefore assigned to the $[C_2H_4O]^{\bullet+}$ ion from acetaldehyde, in agreement with the literature already cited.

The $[C_2H_4O]^{\bullet+}$ ion derived from butyraldehyde is generally accepted[17] to have the enol structure, b. In comparison to the keto form a, its SID spectrum exhibits lower abundances of $[CH_3]^+$ and $[CH_4]^{\bullet+}$, and increased abundances of $[C_2H_3]^+$ (m/z 27), all consistent with the structural units present in the enol ion. The daughter spectrum recorded under SID conditions shows again the presence of an $[M + H]^+$ peak, the result of an ion/surface reaction. The structure of this ion was not the subject of enquiry but it can be noted that the O-protonated enol structure accounts for m/z 19 (acetylene loss) and for the low abundance of C_1 fragment ions observed in Figure 1b.

Scheme I



The base peak in the butyraldehyde SID spectrum is the $[M - H]^+$ ion, thus the abundance ratio of m/z 45/43 is reversed compared to that of structure a. The same is true of the m/z 29/27 ratio; $[C_2H_3]^+$ is more important in the spectrum of b, since it can be formed from both $[M]^{\bullet+}$ by simple cleavage with loss of $OH^\bullet$ and from $[M + H]^+$ ions via loss of H_2O also in a simple cleavage process. A further notable feature of the spectrum of the butyraldehyde-derived ion is the appearance of the m/z 31 ion for which loss of CH_2 from m/z 45 is the only reasonable source. This again speaks to the presence of a methylene group in both the molecular ion and the protonated molecule. The loss of CH_2 from $(M - H)^+$ is probably responsible for the fragment at m/z 29. The possibility that an incipient methyl group is involved cannot be ruled out; some of the $[C_2H_4O]^{\bullet+}$ ions may rearrange via 1,2-hydrogen atom shift to structure f during dissociation. In summary, the SID data support the existing evidence for the enol structure, b.

The $[C_2H_4O]^{\bullet+}$ ion derived from pyruvic acid has been reported to possess the hydroxymethylcarbene structure, f.[22] The 25 eV SID daughter spectrum of this $[C_2H_4O]^{\bullet+}$ ion (Figure 1e) is distinctly different than those of the acetaldehyde, butyraldehyde, ethylene oxide, and 1,3-dioxalane derived $[C_2H_4O]^{\bullet+}$ ions. Unlike the other cases studied, the molecular ion $[M]^{\bullet+}$ constitutes the base peak in the 25 eV SID daughter spectrum. The spectrum also shows only a small $[M + H]^+$ ion. No ion of m/z 26 is observed in the 25 eV SID daughter spectrum, although this is a characteristic peak in the corresponding high-energy CAD daughter spectrum.[22]

The spectrum is readily rationalized on the basis of the ionized carbene structure f. The principal fragment ions are of m/z 43, 29, and 15 and are proposed to arise by loss of $H^\bullet$, $CH_3^\bullet$, and $CHO^\bullet$ to yield $[CH_3C{=}O]^+$, $[COH]^+$, and $[CH_3]^+$, respectively. The loss of $OH^\bullet$, by contrast, is not expected to give rise to a particularly stable ion and its product, m/z 27, is of low abundance. The fragment ion of m/z 16, probably $[CH_4]^{\bullet+}$, arises formally by CO expulsion from ion f. The SID daughter spectrum therefore provides convincing additional evidence that the structure f assigned in the literature is indeed correct. Correspondingly, these data together with that for ions a and b provide assurance that ion/surface collisions are a valuable new method of characterizing gas-phase ion structures. With this base of information, the structures of the $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide and 1,3-dioxolane can be considered by examining their ion/surface collisions.

The 25 eV SID daughter spectrum of the $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide is identical with that of the 1,3-dioxolane derived species (Figure 1b,d). *Direct* fragmentation from the cyclic structure c is precluded by the fact that the major ions in the daughter spectrum are even-electron species. Ion c cannot be excluded as being present in the stable $[C_2H_4O]^{\bullet+}$ beam, but it shows no fragmentation to betray its presence in spite of the facile fragmentation evident in Figure 1b.

An alternative possibility, based on the literature cited in the introduction, is that the stable ions derived from ethylene oxide have the structure d. If this is so, there is little direct fragmentation from structure d that should form $[CH_2]^+$ and $[CH_2{=}O]^{\bullet+}$ by low-energy cleavage processes. The energetics of these two reactions based on simple thermochemical calculations[36] are shown

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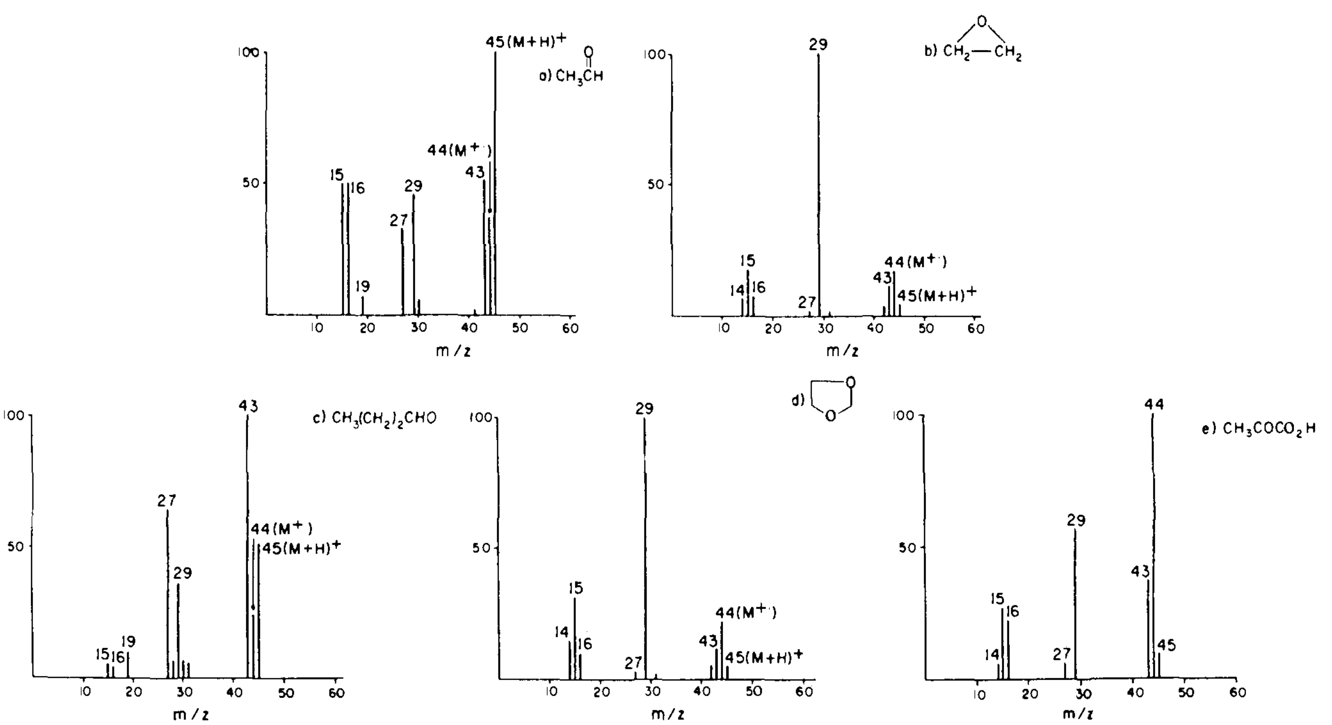

Figure 1. Surface-induced dissociation daughter spectra of $[C_2H_4O]^{\bullet+}$ ions, generated by collision with a stainless steel surface at 25 eV, from precursors (a) acetaldehyde, (b) ethylene oxide, (c) butyraldehyde, (d) 1,3-dioxolane, and (e) pyruvic acid.

in Scheme I. The formation of $[CH_2O]^{\bullet+}$, which is not observed experimentally, is estimated to be 12 kcal mol^{-1} more endothermic than the formation of $[CH_2]^+$. As an alternative to direct dissociation, ion d might isomerize to give f, an exothermic reaction, or g, which is almost thermoneutral. Such isomerization occurring after excitation can be distinguished from the occurrence of f or g, rather than d (or e), as stable ion structure by comparison with the spectra of authentic ions having these structures. As indicated above, the spectra of ion f derived from pyruvic acid and d derived from ethylene carbonate were obtained. The former was very different to the SID daughter spectrum of the ethylene oxide (and 1,3-dioxolane) derived ions, and the latter was indistinguishable.

On this basis, the stable $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide and from 1,3-dioxolane must be ascribed the structure d, although as emphasized already, the presence of the ring-closed ion c could well escape detection. Although relative ion abundances in the spectra of the ions generated from pyruvic acid and ethylene oxide are different, the ratios of *m/z* 44/43, 29/27, and 15/14 are similar in **2**, **4**, and **5**. This strengthens the possibility that d fragments via rearrangement to f.

The remaining unexplained feature of the ethylene oxide spectrum is the abundant ion at *m/z* 29. This behavior is unique among the systems studied but can be explained as the result of fragmentation of ion g, $CH_3O^+{=}CH^\bullet$. This ion has not previously been observed and a suitable model is not available. However, considering the structure–spectrum correlations developed in this paper the only significant reaction expected for this ion is the loss of $CH_3^\bullet$, to yield the formyl cation. We therefore propose that both f and g are significant contributing structures to the population of *fragmenting* ions generated from ethylene oxide and 1,3-dioxolane.

Note the suggestion[17,18,20] that $[C_2H_4O]^{\bullet+}$ derived from 1,3-dioxolane consists of a mixture of structure b and c in proportions that vary with the ionizing electron energy is clearly not the case for the ions examined in our experiment; in particular, some of the key peaks found in the SID spectrum of b, i.e., *m/z* 45, 27, and 19, are either very weak or absent altogether from the dioxolane spectrum.

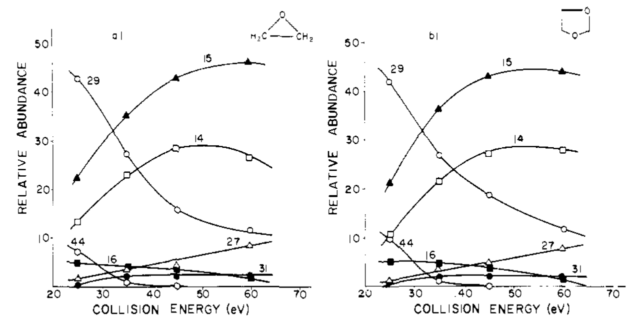

Figure 2. Energy-resolved mass spectra (ERMS) of $[C_2H_4O]^{\bullet+}$ ions from (a) ethylene oxide and (b) 1,3-dioxolane, plotted from SID daughter spectra.

More information on the $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide and 1,3-dioxolane was obtained by recording SID daughter spectra over a range of collision energies. The energy resolved mass spectra (ERMS) are plotted in the form of breakdown curves in Figure 2. These curves are identical, a strong indication that the two precursors indeed give identical ion structures or mixtures of structures. The daughter spectra of $[C_2H_4O]^{\bullet+}$ ions derived from ethylene oxide and 1,3-dioxolane were also recorded at various ionizing electron energies (down to 23 eV). No change in the SID behavior could be observed. Together these observations suggest that a single stable structure is probably present in both the ethylene oxide and dioxolane cases. It seems likely that this is the ring-opened isomer d given its formation from dioxolane and its low enthalpy compared with that of c. Further isomerization of d to give f and/or g occurs primarily on activation rather than prior to collision.

The ERMS data show a rapid fall in the abundance of *m/z* 29 with collision energy, suggesting that at higher energy the contribution of the rearrangement fragmentation of d to f or g is reduced. The increase in abundance of *m/z* 14 further supports this argument. However, the sharp rise of *m/z* 15 seems at first sight to contradict this conclusion. An explanation of the observed behavior is the fact that the ion $[CH_3]^+$ does not actually arise from $[C_2H_4O]^{\bullet+}$, but rather from the $[M + H]^+$ ion formed in the ion/surface reaction. To examine this possibility, we obtained ERMS data from deuteriated ethylene oxide $[C_2D_4O]^{\bullet+}$, using SID at various collision energies. The breakdown curve is shown

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[36] Heat of formation (ΔH_f) of $^\bullet CH_2{-}O^+{=}CH_2$ is 205 kcal/mol.[12] ΔH_f data for other ions and neutrals were obtained from the following: Rosenstock, H. M.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1.

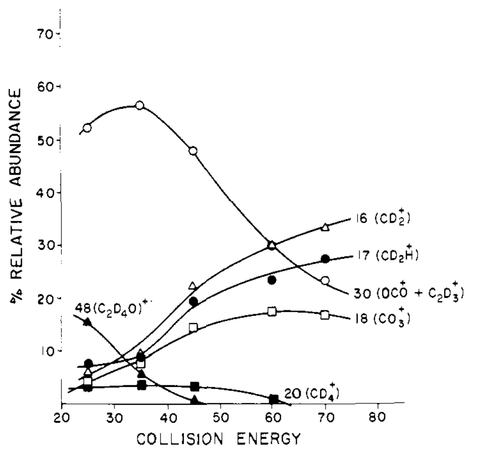

Figure 3. Energy-resolved mass spectrum of $[C_2D_4O]^{\bullet+}$ ion from ethylene-d_4 oxide plotted from SID daughter spectra.

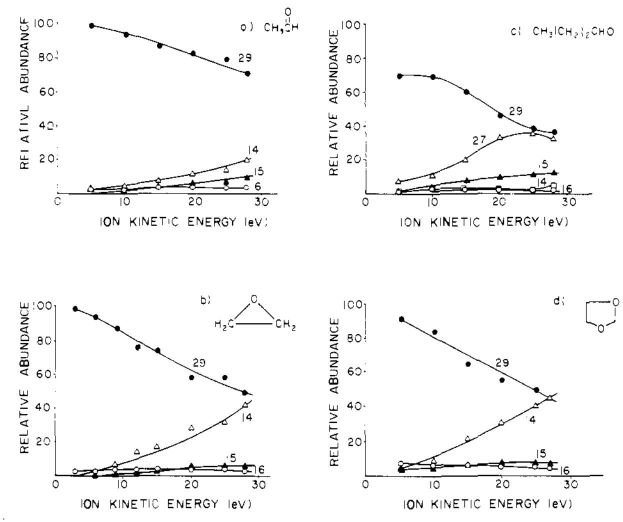

Figure 4. Energy-resolved mass spectra of $[C_2H_4O]^{\bullet+}$ ions from (a) acetaldehyde, (b) ethylene oxide, (c) butyraldehyde, and (d) 1,3-dioxolane, plotted from CID daughter spectra.

in Figure 3. At high collision energies, $[CD_2]^+$ (m/z 16) is the major fragment, in agreement with structure d. Of the two isotopic methyl ions CD_2H^+ (m/z 17), which must be formed exclusively from the $[M + H]^+$ ion, is the more abundant. While the ion $[CD_3]^+$ (m/z 18) could, in principle, arise from the molecular ion $[M]^{\bullet+}$, it can also be formed from the molecular ion $[M + H]^+$ depending on the extent of H/D scrambling prior to fragmentation. Thus, the labeling data provide the proof that at higher collision energies the $[CH_3]^+$ ion in the ERMS SID spectra of $[C_2H_4O]^{\bullet+}$ from ethylene oxide is mainly due to $[M + H]^+$ ion fragmentation; the breakdown curves obtained are therefore entirely consistent with the conclusion that direct fragmentation from structure d becomes dominant at high collision energies.

Gas-Phase Data. In an effort to obtain supporting evidence for the structural conclusions reached from the ion/surface experimental data, gas-phase collisions were studied as a function of collision energy and scattering angle for the same systems. These two methods were used to achieve control over the internal energy of the ions in the low-energy and high-energy gas-phase studies of $[C_2H_4O]^{\bullet+}$ ions derived from acetaldehyde, butyraldehyde, pyruvic acid, ethylene oxide, and 1,3-dioxolane. These results show trends that agree in detail with the SID results.

Figure 4 and 5 show gas-phase energy-resolved mass spectra (ERMS) and angle-resolved mass spectra (ARMS) of some of these ions. The ERMS data of acetaldehyde are dominated by the 29^+ ion and are consistent with its generation by direct cleavage from structure a. In the same vein, the presence of an ion at m/z 15 also suggests structure a. The presence of small amounts of $[CH_2]^{\bullet+}$ (m/z 14), which was completely absent in the SID daughter spectrum of acetaldehyde, may be due to isomerization of acetaldehyde in gas-phase collisions, because simple hydrogen transfers interconnect structure a and other isomers. The angle-resolved mass spectrum (ARMS) data of acetaldehyde, shown in Figure 5, show reasonable agreement with the results of varying the collision energy in spite of the very different energy regimes in which the experiments are done. The dominance of 29^+ and 15^+ ions as the major fragments in the ARMS data again suggests structure a for the ions derived from acetaldehyde.

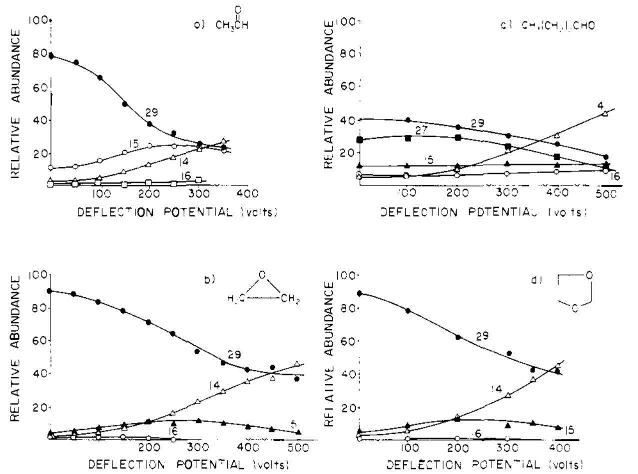

Figure 5. Angle-resolved mass spectra of $[C_2H_4O]^{\bullet+}$ ions from (a) acetaldehyde, (b) ethylene oxide, (c) butyraldehyde, and (d) 1,3-dioxolane, employing 3-keV collisions with argon.

Structure b, suggested by SID data for the butyraldehyde-derived ion, is readily characterized by the abundant m/z 27 ion previously seen in the SID spectrum (Figure 1) and now observed in both the ERMS and ARMS spectra (Figures 4 and 5, respectively). The fragment ion at m/z 27 can arise by simple cleavage with loss of $OH^{\bullet}$ from ionized vinyl alcohol b. The formation of a 14^+ ion in the ARMS spectrum is suggestive of the methylene group although the reaction is not important in the ERMS experiment. Differences in the internal energy resolved spectra obtained by the two techniques (ERMS and ARMS) are probably due in part to differences in the shapes of the internal energy distributions associated with low- and high-energy collisions, the latter showing a long tail to high internal energies.[37]

The $[C_2H_4O]^{\bullet+}$ ion derived from ethylene oxide showed fragmentation behavior in the ERMS and ARMS experiments (Figures 4 and 5, respectively), which is similar to that of the 1,3-dioxolane derived ion. The agreement is remarkable and confirms the conclusions drawn from the SID results that ethylene oxide and 1,3-dioxolane yield the same ion or mixture of ions in both these experiments.

The $[C_2H_4O]^{\bullet+}$ ion derived from ethylene oxide and 1,3-dioxolane shows fragmentation behavior in the ERMS and ARMS experiments (Figures 4 and 5, respectively), which is substantially different from that of acetaldehyde and butyraldehyde. Observation of $[CH_2]^{\bullet+}$ (14^+) as the most abundant ion at ion energies above 25 eV is consistent with the structure d proposed from consideration of the SID data. The fact that 14^+ is one of the abundant ions above 25 eV and 29^+ is the most abundant ion below 25 eV points to the possibility of isomerization of structure d occurring as a function of its internal energy. At higher internal energies there is more chance of direct fragmentation of d without intervening isomerization to g. These trends parallel those observed in the SID breakdown curves.

In the ARMS data, 15^+ is also the second most abundant ion at lower scattering angles, which correspond to smaller degrees of excitation. It is clear that three ions 14^+, 15^+, and 29^+ have to be considered in proposing a structure for the 1,3-dioxolane derived $[C_2H_4O]^{\bullet+}$ ion. The same set of ions were also found to

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(37) Wysocki, V. H.; Kenttämaa, H. I.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *75*, 181.

be crucial in interpreting the SID studies of 1,3-dioxolane. The conclusion that was reached based on the SID data applies here too, i.e., the formation of ring-opened structure d from 1,3-dioxolane and subsequent isomerization of d to g (and/or f) accounts for the fragmentation behavior. It is important to note that, in agreement with SID data, CAD data do not support the suggestion that the vinyl alcohol structure b makes a significant contribution to the dioxolane-derived ion. The agreement between the surface and gas-phase data also confirms the earlier conclusion that the contributions of $[M + H]^+$ to the SID spectra are not predominant.

Further confirmation that the peak at m/z 29 in the gas-phase ERMS spectra is due to a structure of the type f or g was obtained by recording the ERMS spectrum (5-25 eV collision energy) of the $[C_2H_4O]^{\bullet+}$ ion derived from pyruvic acid. The spectrum was dominated by m/z 29 (at 10 eV, $29^+ = 63\%$, $27^+ = 5\%$, $16^+ = 4\%$, and $15^+ = 4\%$). Even more significantly, the spectrum changed little with collision energy. This is in marked contrast with the behavior of the ions derived from ethylene oxide and dioxolane. These results therefore provide further evidence for isomerization of d to f and g.

Conclusions

The results of the SID and the gas-phase collision experiments (ERMS and ARMS) for $[C_2H_4O]^+$ ions generated from six different precursors agree very well and can be summarized as follows

1. The majority of acetaldehyde, butyraldehyde, and pyruvic acid derived $[C_2H_4O]^{\bullet+}$ ions have the structures a, b, and f, respectively, assigned earlier.
2. The $[C_2H_4O]^{\bullet+}$ ions formed from ethylene oxide have stable structure d, although a fraction isomerize to structure f and g, during collisions with the gaseous or metal target. It is not possible to exclude the presence of some ions with structure c in the stable ion beam.
3. $[C_2H_4O]^{\bullet+}$ ions derived from 1,3-dioxolane and ethylene oxide are identical with those from ethylene carbonate. There is no evidence for a contribution from structure b in the 1,3-dioxolane derived $[C_2H_4O]^{\bullet+}$ ions studied.

This study shows that the ion/surface interaction method can be successfully applied to ion structural problems especially in cases where a mixture of structures is represented. Features of this technique of ion characterization are the following: (i) considerable excitation occurs yielding high-energy ions that fragment by readily interpreted bond cleavage reactions; (ii) it provides results that in many respects are comparable to other methods that are used for structure characterization; however, (iii) reactive collisions occur simultaneously and add a new dimension of information to the daughter spectra recorded. It is also evident that the ability to preclude reactive collisions so as to separate out their contributions to the daughter spectra is desirable. This capability will require the use of surface conditions (e.g., ultra high vacuum conditions) that are not presently available.

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On the Mechanism of Base-Induced Gas-Phase Elimination Reactions of Thioethers

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Abstract: The base-induced gas-phase elimination reactions of diethyl sulfide have been studied by using the method of Fourier transform ion cyclotron resonance mass spectrometry. Reaction with the nitrogen bases NH_2^-, $EtNH^-$, and Me_2N^- preferentially proceeds via an α',β-elimination mechanism, where α' proton abstraction of the sulfide results in the formation of an α-thio carbanion, which undergoes an intramolecular syn elimination to generate the ethyl thiolate anion. Reaction with OH^-, MeO^-, and F^- exclusively proceeds via an E2 mechanism. However, for the reaction with OH^-, rapid exchange is observed within the reaction complex between the α-hydrogens of the sulfide and the hydroxide hydrogen prior to E2 elimination. For the E2 eliminations the α- and β-deuterium isotope and leaving group effects have been determined as a function of the base strength. As in our previous study of the mechanism of base-induced gas-phase elimination reactions of ethers, the isotope and leaving group effect data are interpreted in terms of a variable E2 transition-state structure. Combining the results of our previous study with those of the present study has led to the conclusion that the perturbation of the transition-state character effected by changing the leaving group or the base follows the rules established for condensed phase β-elimination reactions. For the nearly thermoneutral elimination reaction of diethyl sulfide induced by F^- it is concluded that two reaction mechanisms are operative, both characterized by a bent proton transfer: an E2C mechanism involving a two-side attack of F^- on the β-hydrogen and α-carbon of the sulfide, yielding free ethyl thiolate anions and a syn elimination involving a two-side attack of F^- on the β-hydrogen and the leaving group, generating HF solvated ethyl thiolate anions.

Over the years, the scope of concerted base-induced elimination reactions (E2) has proven to be an inexhaustible source for mechanistic studies. The interest in this class of reactions derives from the widely held view that these one-stage processes involve a mechanism in which at the transition state the C_β-H and C_α-X bond breaking are electronically coupled, although these bond cleavages need not to be synchronous.

$$H_3{}^{\beta}C\text{-}{}^{\alpha}CH_2X + B^- \rightarrow HB + C_2H_4 + X^- \qquad (1)$$

Various workers have pointed out that the C_α-X bond breaking may lag behind hydrogen transfer, or vice versa, a concept which has become known as the "variable transition state theory".[1] Within this concept refinements are introduced with respect to the geometry of the transition state involving linear proton transfer

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(1) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; pp 197-210.

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