we chose these compounds as substrates (eq 4). α-Chloro-

$$^{*}X^{-} + \overset{CN}{\overset{|}{CH_2}}—X \rightleftharpoons {}^{*}X—\overset{CN}{\overset{|}{CH_2}} + X^{-} \quad (4)$$

acetonitrile reacts with $^{37}Cl^-$ with an efficiency of 0.12, which is significantly below the collision limit. This corresponds to an increase in efficiency of a factor of 6000 compared to methyl chloride and a larger increase compared to n-propyl chloride. With reaction efficiencies of this magnitude trace impurities will not have a significant effect on rate measurements. We next studied α-bromoacetonitrile and found that it reacts, as expected, somewhat faster with Cl^- (efficiency 0.49). It also reacts quite readily with $^{81}Br^-$ (efficiency 0.20). Since α-chloro- and α-bromoacetonitrile undergo symmetrical, thermoneutral substitution reactions with nearly the same efficiency, it seems reasonable to predict that methyl chloride and bromide will also do so, and that for all the halogens the top of the barrier is quite similar in energy to that of the reactants.

The most unusual results of this study pertain not so much to the gas-phase S_N2 reaction but rather to the E2. It has often been assumed that E2 reactions are favored over S_N2 reactions in the gas phase when both processes are structurally and thermodynamically accessible, possibly because the E2 transition state is a looser one and so favored entropically. However, as the data in Tables IV and V show, this is only true for oxy anions; sulfur anions do not appear to induce gas-phase E2 reactions even if they are sufficiently basic to do so. This is not because of an increase in rate for the S_N2 process but rather because of a decrease in the E2 rate. Since the exothermicity of an E2 reaction is the same for any two anions of the same basicity, this result must have a kinetic rather than a thermodynamic explanation. RS^- attacks a β-proton to induce elimination much less readily than does RO^- even when the two anions have identical basicities. We will not propose an explanation for this phenomenon, but it is in line with our previous observations[20] that proton transfers to and from second-row elements (e.g. in SiH_4, PH_3, H_2S) are slow in the gas phase compared to proton transfers to and from the oxygen atom in H_2O or alcohols.

Acknowledgment. We thank Dr. Michele Krempp and Mr. Roger Simon for their assistance and we gratefully acknowledge support of this work by the National Science Foundation (Grants CHE-8815459 and CHE-8815446).

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The Isomerization of Oxirane. Stable $^{\cdot}CH_2OCH_2^{\cdot}$, $^{\cdot}CH_2CH_2O^{\cdot}$, and $:CHOCH_3$ and Their Counterpart Ions

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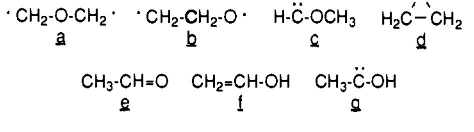
Abstract: Unimolecular C–C bond rupture in oxirane leading to $^{\cdot}CH_2OCH_2^{\cdot}$ is favored over C–O rupture to $^{\cdot}CH_2CH_2O^{\cdot}$, but the latter is the first-step in the lowest energy dissociation pathway through excited $CH_3CH{=}O$ to $CH_3^{\cdot}$ + $^{\cdot}CHO$. With collisional activation, $^{\cdot}CH_2OCH_2^{\cdot}$ isomerizes mainly to oxirane, not methoxycarbene, $:C(H)OCH_3$, while $^{\cdot}CH_2CH_2O^{\cdot}$ isomerizes mainly to CH_3CHO. All of these neutral isomers were prepared in the gas-phase via neutralization of the corresponding radical cations. Their structures, and those of their precursor cations, were established by collisionally activated dissociation (CAD), neutralization–anionization, and CAD of the mass-selected recovered molecular ions (MS/MS/MS) from neutralization–cationization. All of the neutrals and cationic isomers are found to represent stable bound structures, clarifying in particular previous contrary evidence concerning $^{\cdot}CH_2CH_2O^{\cdot}$, $^{+}CH_2CH_2O^{\cdot}$, and the oxirane cation. Anionization showed the isomers $^{\cdot}CH_2CH_2O^-$, $^{-\cdot}C(H)OCH_3$, and $^{-\cdot}C(OH)CH_3$ to be stable.

The unusual reactivity of diradicals (in polymerization, stereoisomerization, synthesis)[1] and of carbenes (insertion into C–H bonds, addition to multiple bonds, skeletal rearrangements)[2] also makes difficult their study by usual experimental methods. Recently, neutralization–reionization mass spectrometry (NRMS)[3,4] has provided new information on the stabilities and reactivities of hydroxycarbene, $:C(H)OH$,[4a] and hydroxymethylcarbene, $:C(OH)CH_3$ (**g**).[4b] In NRMS such species are formed in the gas phase by neutralization[5] of the corresponding molecular cations, and their unimolecular isomerization and dissociation products characterized by reionization. In this paper NRMS is used to provide the first experimental characterization of the diradicals $^{\cdot}CH_2OCH_2^{\cdot}$ (**a**) and $^{\cdot}CH_2CH_2O^{\cdot}$ (**b**), of methoxycarbene, $:C(H)OCH_3$ (**c**), and of their tendencies to isomerize to the stable C_2H_4O isomers oxirane (**d**) and acetaldehyde (**e**). Similar studies of the C_2H_4O isomers **e**–**g**[4b] and the ylide $^{-}CH_2{}^{+}OH_2$[4c] (**a** is a carbonyl ylide, $^{-}CH_2{}^{+}O{=}CH_2$) have been reported recently.



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The dissociation of oxirane has been extensively studied over many years.[6] Although initial loss of either $H^{\bullet}$ or O:[6f] is still considered,[6e] the initial unimolecular steps proposed by Benson[6b] of **d** → **b** → **e*** → $^{\bullet}CH_3$ + $^{\bullet}CHO$ are generally accepted[6] for both the thermal and photochemical[6c] decomposition of **d**. However, the energy requirements for producing the diradicals **a** and **b** from oxirane (**d**) via C–C or C–O bond rupture, respectively, should be similar. Isomer **a** and its substituted homologs are intermediates in the cis–trans isomerization of oxiranes,[7] while **b** is the postulated intermediate in the electrophilic addition of oxygen to ethylene.[8] Theoretical calculations predict singlet **a** to represent an energy minimum, 143–270 kJ mol^{-1} above **d**, from which it is separated by a barrier of 37–57 kJ mol^{-1},[9] with the triplet 70–85 kJ mol^{-1} higher in energy.[9b] The **a** homolog $^{\bullet}C(CH_3)_2OCH_2^{\bullet}$ has been characterized recently by photoacoustic calorimetry, with ΔH_f = 19 kJ mol^{-1}.[10] In contrast to lower level theory,[9a] recent calculations also find a minimum for singlet **b** lying 297–341 kJ mol^{-1} above **d**[11] and separated from **d** and **e** by barriers of approximately 40 and 30 kJ mol^{-1}, respectively[11a] (Benson proposed the opposite relative order for these barriers),[6b] while triplet **b** requires >25 kJ mol^{-1} for its lowest energy dissociation to $H^{\bullet}$ + $^{\bullet}CH_2CH{=}O$ and >150 kJ mol^{-1} for its isomerization to $^{3}CH_3CHO$.[11a,12] Theory predicts the carbene **c** to be located 308 kJ mol^{-1} (singlet; 397 for the triplet) above **e** and separated from it by 426 kJ mol^{-1}.[13] Figure 1 represents our estimates in light of such literature values and the data reported here.

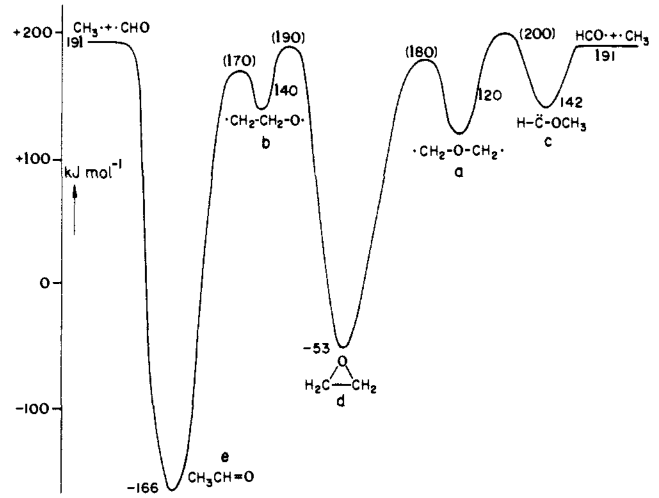

Figure 1. Postulated isomerization and dissociation pathways of the C_2H_4O isomers **a**–**e**. ΔH_f values are from refs 9c and 19 except that for **a** is a compromise of the theoretical values[9] and that estimated from the value for $^{\bullet}C(CH_3)_2OCH_2^{\bullet}$;[10] that for **b** is based on the predicted increase versus **a**[9g] and the predicted[11a] and our observed isomerization barriers for **b**; and that for **c** is based on that for **e** and their theoretically calculated energy difference.[13] Barrier values, in parentheses, are estimated as follows. (170): the stability of **b** indicates an appreciable activation energy for **b** → **e**, while our observed rearrangement of **b** mainly to **e** indicates this requires substantially less energy than dissociation. (180): based on the smaller isomerization extent of **a**, the barrier for **a** → **d** is larger than that for **b** → **e**. (190): the collisional activation of **a** and **d** produces **e** of sufficient internal energy to undergo nearly complete dissociation to $CH_3^{\bullet}$ + $^{\bullet}CHO$, and theory finds **b** → **d** 10 kJ mol^{-1} higher than **b** → **e**.[11a] (200): since **a** and **d** do not dissociate via **c**, nor **c** via **d** or **e**, this is set above the minimum dissociation energy. Note that some values of this figure in ref 3e have been adjusted.

Of the corresponding cations, $\mathbf{a}^{\bullet+}$, $\mathbf{c}^{\bullet+}$, and $\mathbf{e}^{\bullet+}$[9,14] as well as $\mathbf{f}^{\bullet+}$ and $\mathbf{g}^{\bullet+}$[4b,14] have been identified unequivocally by both experiment and theory. The molecular ion of oxirane, $\mathbf{d}^{\bullet+}$, has been characterized by its collisionally activated dissociation (CAD)[15] spectrum as a stable ion;[14a–d] in contrast, ab initio calculations suggest that electron ionization of **d** produces $\mathbf{d}^{\bullet+}$ close to its threshold for ring opening to $\mathbf{a}^{\bullet+}$.[14e] Extensive ESR studies of the radical cation are also contradictory; from the radiolytic oxidation of **d** in a $CFCl_3$ matrix at 77 K Williams et al.[16a] conclude that the ring-opened isomer $\mathbf{a}^{\bullet+}$ is generated, while Symons et al.[16b] state that the ring-closed structure $\mathbf{d}^{\bullet+}$ is formed. There has also been a substantial controversy[14c–e] concerning the stability of cation $\mathbf{b}^{\bullet+}$; it and the radical anions $\mathbf{a}^{\bullet-}$–$\mathbf{g}^{\bullet-}$ have not yet been experimentally documented.

Experimental Section

The measurements were performed on a tandem double focusing (EB-EB) mass spectrometer described in detail elsewhere.[17] Precursor ions are formed by 70-eV electron ionization (Figure 2), accelerated through 10 kV, mass selected by MS-I (EB), and undergo charge-exchange with a target gas in a differentially pumped collision cell (Cls-I), with remaining ions removed by a deflector electrode. The resulting fast neutrals undergo dissociating and/or reionizing collisions in a second collision cell (Cls-II, also differentially pumped). For the separate dissociation of neutrals in Cls-II, any newly formed ions are removed by Dfl-II, and the neutral products and remaining precursors are reionized in Cls-III. For charge-reversal experiments, a single target such as benzene is used for neutralization, dissociation, and reionization in the same cell (Cls-II).[4a] The reionized products are mass analyzed (MS-II) in the second electrostatic analyzer (ESA-II) with detection by a retractable channeltron. For MS/MS/MS structure elucidation of the reionized products, these are made to undergo CAD at Cls-IV located after the MS-II exit slit (Figure 2); the resulting fragments are mass analyzed (MS-III) with magnet-II,[17] and reference spectra of isomers are measured by transmitting the corresponding precursor ions from the ion source to Cls-IV. Neutral beam intensities for neutralization cross section values were measured by using a retractable channeltron at Cls-III.

Experimental conditions are described by abbreviations defined earlier,[3,17] e.g., a $^{+}NR^{+}$, Hg(90%T)/He(80%T), spectrum is one obtained by neutralization of cations at Cls-I with Hg at a pressure allowing 90% precursor transmittance, residual ion deflection (slash), and neutral reionization with He at pressure giving 80% transmittance of the original precursor ions at Cls-II; a $^{+}NCR^{-}$, benzene(25%T), spectrum combines

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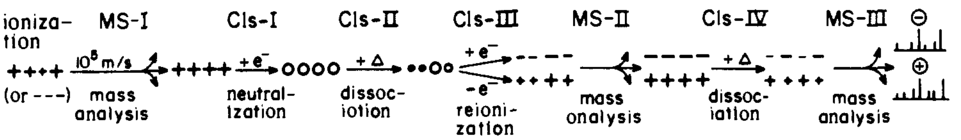

Figure 2. Formation of a neutral species (CIs-I) and the characterization of its structure (reionization in CIs-III, MS-II), its dissociation (CIs-II, CIs-III, MS-II), and its isomerizations (CIs-II, CIs-III, MS-II, CIs-IV, MS-III).

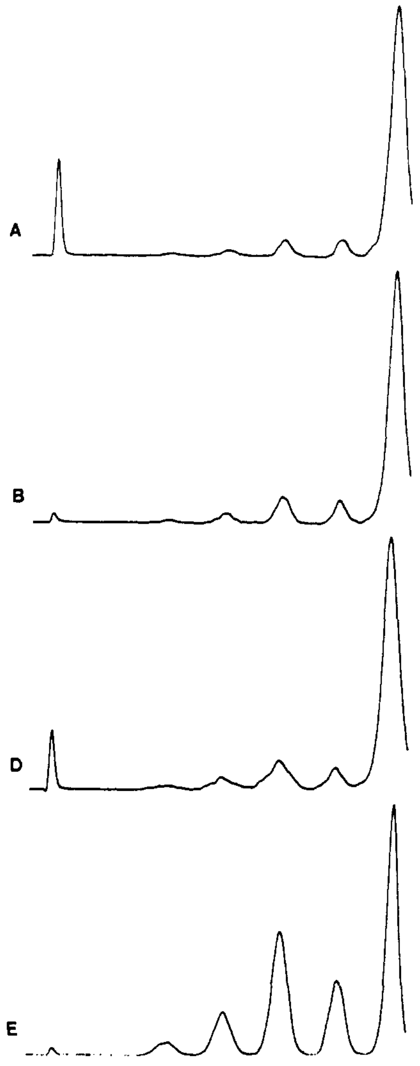

Figure 3. Partial CAD, O_2(30%T), spectra of $C_2H_4O^{\bullet+}$ ions from (A) 1,3-dioxolane, (B) ethylene carbonate, (D) oxirane, and (E) acetaldehyde. CAD efficiency, [m/z 28]:[precursor $C_2H_4O^{\bullet+}$]: (A) 6.2 × 10^{-4}; (B) 4.5 × 10^{-4}; (D) 6.8 × 10^{-4}; and (E) 5.1 × 10^{-4}.

neutralization, CAD, and anionization (and even CAD of the anions) by multiple collisions with benzene. MS/MS spectra shown represent 20–50 computer-averaged scans,[18] while the MS/MS/MS spectra combine 250–400 scans measured over several hours. The relative abundances of some structurally characteristic peaks, especially the doubly charged ion, changed substantially (even ±50%) in measurements over several months (compare Figure 3D vs 9B); isomeric compositions were derived from sequential same-day measurements (peak areas) of unknown and reference spectra to minimize errors (±<20%, relative).

All samples were commercially available and used without further purification.

Results and Discussion

Structural Characterization of the Precursor $C_2H_4O^{\bullet+}$ Isomers. Previous thermochemical data[19] and CAD spectra[14] have shown that the isomers $\mathbf{a}^{\bullet+}$, $\mathbf{c}^{\bullet+}$, $\mathbf{d}^{\bullet+}$, $\mathbf{e}^{\bullet+}$, $\mathbf{f}^{\bullet+}$, and $\mathbf{g}^{\bullet+}$ are the principal $C_2H_4O^{\bullet+}$ products from electron ionization of 1,3-dioxolane, methyl glyoxylate, oxirane, acetaldehyde, cyclobutanol, and pyruvic acid, respectively; our CAD spectra (Figure 3; those of **f** and **g** reported previously[4b]) are consistent

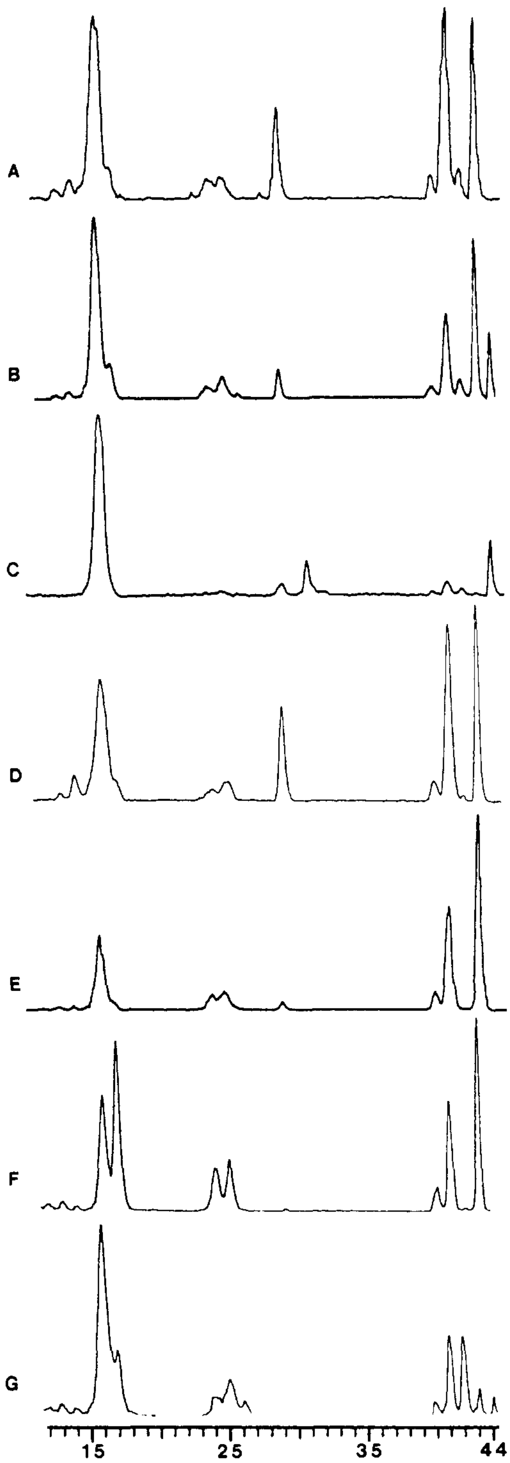

Figure 4. $^+$NR$^-$, benzene(30%T), spectra of $C_2H_4O^{\bullet+}$ ions from the following: (A,B,D,E) see Figure 2; (C) methyl glyoxylate, (F) cyclobutanol, and (G) pyruvic acid. NR efficiency, [base peak$^-$]:[precursor $C_2H_4O^{\bullet+}$]: (A) 3.9 × 10^{-7}; (B) 9.3 × 10^{-7}; (C) 1.1 × 10^{-6}; (D) 6.1 × 10^{-7}; (E) 3.6 × 10^{-6}; (F) 1.3 × 10^{-6}; and (G) 1.5 × 10^{-6}.

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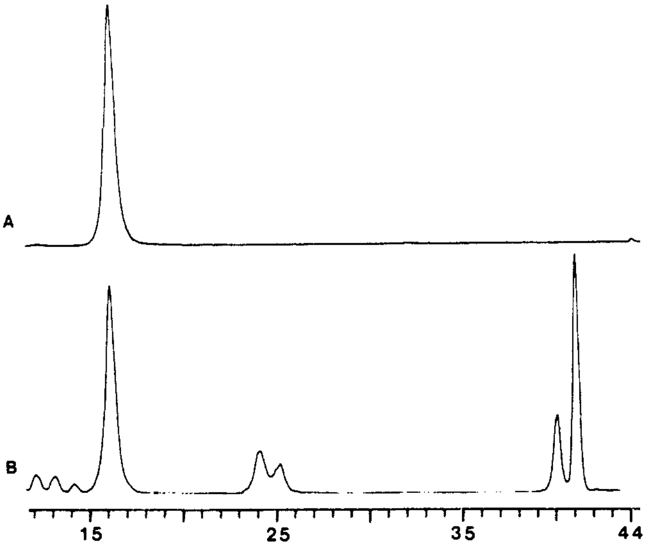
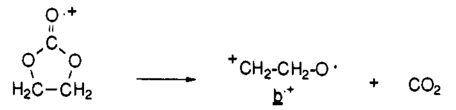


Figure 5. $^+$NR$^-$, benzene (30%T), spectra of (A) $CO_2^{\bullet+}$ and (B) CH_3CO^+. NR efficiency, [base peak$^-$]:[precursor $C_2H_4O^{\bullet+}$]: (A) 3.3 × 10^{-5} and (B) 9.3 × 10^{-6}.

with this. Additionally, our measurements used O_2 as a target gas to increase the abundance of charge-stripping peaks,[20] which were not reported in the previous CAD or surface-induced dissociation spectra.[14] In Figure 3 the $C_2H_4O^{2+}$ (*m*/*z* 22) peak is particularly characteristic, as its low abundance (and those of *m*/*z* 25–27) in the CAD spectrum of the $C_2H_4O^{\bullet+}$ ions from ethylene carbonate indicates that these contain <20% of **a**$^{\bullet+}$,[14c] **d**$^{\bullet+}$,[14d] or **e**$^{\bullet+}$ ions. Thus these ions must represent yet another stable isomer, presumably **b**$^{\bullet+}$ (eq 1). The low abundance of $C_2H_4O^{2+}$ in the spectra of **b**$^{\bullet+}$ and **e**$^{\bullet+}$ is consistent with the reduction in charge separation caused by the electronegativity of their terminal oxygen atoms.



(1)

Charge reversal of $C_2H_4O^{\bullet+}$ to the corresponding negative ions using multiple collisions[4a] with benzene also produces spectra (Figure 4) showing substantial differences for these isomers. The $C_2H_4O^{\bullet+}$ ions from ethylene carbonate (but not from **a**$^{\bullet+}$, **d**$^{\bullet+}$, **e**$^{\bullet+}$, or **f**$^{\bullet+}$) produce an undissociated *m*/*z* 44, consistent with the expected stability of the oxyanion $^\bullet CH_2CH_2O^-$ (**b**$^{\bullet-}$), while the *m*/*z* 43 corresponds to the expected facile dissociation $CH_2CH_2O^{\bullet-} \rightarrow CH_2{=}CHO^-$. Because the $^+$NR$^-$ spectra of $CO_2^{\bullet+}$ and CH_3CO^+ (Figure 5) show no undissociated parent ions, the *m*/*z* 44 anion in the $^+$NR$^-$ spectrum of **b**$^{\bullet+}$ cannot be due to isobaric $CO_2^{\bullet-}$[21] or $^{12}C^{13}CH_3O^-$. Finally, the stability of **b**$^{\bullet+}$ was also tested in an MS/MS/MS experiment by collisional activation (Cls-II) of mass-analyzed (MS-I) **b**$^{\bullet+}$ ions with He (30% transmittance), mass separation of the excited $C_2H_4O^{\bullet+}$ products in MS-II, followed by CAD and spectrum measurement using MS-III. The resulting spectrum is identical within experimental error (<±20%) with the Figure 3B spectrum of **b**$^{\bullet+}$. We conclude that $CH_2CH_2O^{\bullet+}$ (**b**$^{\bullet+}$) is a stable structure, in contrast to previous experimental results and theoretical predictions.[14]

The anions of carbenes **c** and **g**[4b] are also stable (Figure 4C,G), as expected.[4a] Their unique *m*/*z* 31 and 17 peaks are consistent with $HCOCH_3^{\bullet-} \rightarrow {}^-OCH_3$ and $CH_3COH^{\bullet-} \rightarrow {}^-OH$, respectively.

Theory[14e] also predicts that the ring-opening isomerization **d**$^{\bullet+}$ → **a**$^{\bullet+}$ proceeds with negligible (<10 kJ mol^{-1}) activation energy. Although the $^+$NR$^-$ spectra (Figure 4) of **a**$^{\bullet+}$ and **d**$^{\bullet+}$ are somewhat similar, the CAD (Figure 3) and especially the $^+$NR$^+$, Hg(90%T)/O_2(70%T), and $^+$NCR$^+$, Hg(90%t)/He(30%T)/O_2(70%T), spectra (Figure 6) display significant differences, showing <20% **a**$^{\bullet+}$ in **d**$^{\bullet+}$. The stability of **d**$^{\bullet+}$ was also tested in an MS/MS/MS experiment by collisional activation (He,30%T) of mass analyzed **d**$^{\bullet+}$; mass separation of the excited $C_2H_4O^{\bullet+}$ products yielded a CAD spectrum consistent with that of **d**$^{\bullet+}$ (Figure 3) and showing <20% **a**. These conditions can add up to several electronvolts of internal energy to the **b**$^{\bullet+}$ (above) or **d**$^{\bullet+}$ ions[22] but have not caused appreciable isomerization of the nondissociating ions, suggesting that the isomerization barriers are at least comparable to the respective fragmentation thresholds (~1 eV for **d**$^{\bullet+}$)[14d] and certainly higher than indicated by theory.[14e] Additionally, the $^+$NR$^-$ spectra (Figure 4B,D) show that **d**$^{\bullet+}$ contains <5% **b**$^{\bullet+}$.

Figure 6. $^+$NR$^+$, Hg(90%T)/O_2(70%T), spectra (left column) and $^+$NCR$^+$, Hg(90%T)/He(30%T)/O_2(70%T), spectra (right column) of **a**$^{\bullet+}$–**f**$^{\bullet+}$. Neutralization efficiencies, [total neutral flux]:[precursor $C_2H_4O^{\bullet+}$]: (A) 3.6 × 10^{-2}; (B) 4.3 × 10^{-2}; (C) 3.3 × 10^{-2}; (D) 4.2 × 10^{-2}; (E) 8.4 × 10^{-2}; (F) 5.0 × 10^{-2}. NR efficiencies, [*m*/*z* 44]:[precursor $C_2H_4O^{\bullet+}$]: (A) 8.8 × 10^{-6}; (B) 7.9 × 10^{-5}; (C) 6.7 × 10^{-6}; (D) 2.3 × 10^{-4}; (E) 7.6 × 10^{-3}; and (F) 4.0 × 10^{-4}.

Structural Characterization of the Neutral C_2H_4O Isomers a, b, and c. As a test of stability, the structures of these neutrals, 1 μs after their formation (Cls-I → Cls-II flight time), were probed by using their reionization spectra.[17b] The $^+$NR$^-$, Hg(70%T)/benzene(30%T), spectra of **b**$^{\bullet+}$ and **c**$^{\bullet+}$ show the uniquely stable $C_2H_4O^{\bullet-}$ molecular anions and are closely similar to the corresponding benzene 30%T spectra (Figure 7B vs 4B and 7C vs 4C). For isomer **a**, the recovered $C_2H_4O^{\bullet+}$ molecular cations in the $^+$NR$^+$ spectrum (Figure 6A) were mass analyzed (MS-II) and subjected to CAD in an MS/MS/MS experiment.[17] The resulting spectrum is closely similar to that of Figure 3A, indicating that little isomerization has taken place; even after collisional activation of the neutrals (discussed below) the majority of reionized $C_2H_4O^{\bullet+}$ species are of structure **a**$^{\bullet+}$ (Figure 8, obtained sequentially with Figure 3). Thus

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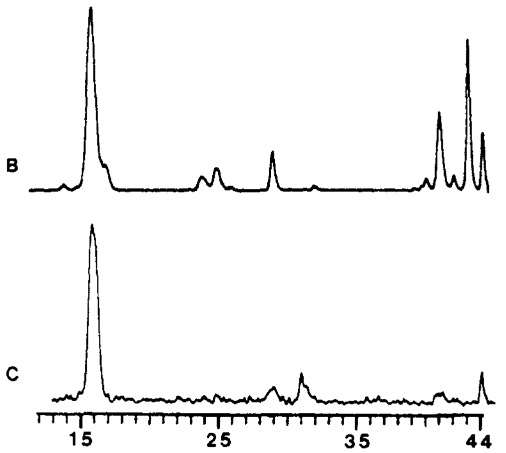

Figure 7. $^+NR^-$, Hg(70%T)/benzene (30%T), spectra of $b^{\bullet+}$ and $c^{\bullet+}$ ($C_2H_4O^{\bullet+}$ ions as in Figure 4B,C).

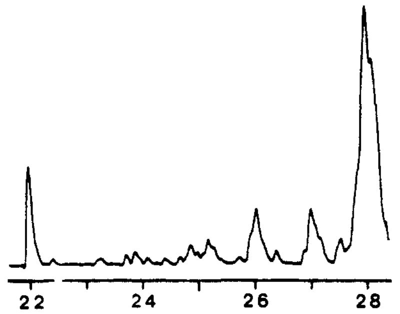

Figure 8. CAD, O_2 (30%T), spectrum of recovered $C_2H_4O^{\bullet+}$ from $^+NCR^+$, Hg(30%T)/O_2(30%T), of $a^{\bullet+}$.

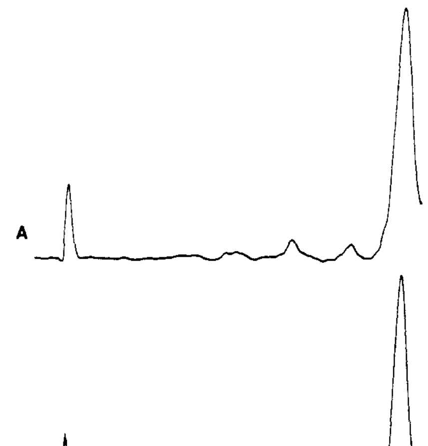

Figure 9. CAD, O_2(30%T), spectra of (A) recovered $C_2H_4O^{\bullet+}$ from $^+NCR^+$, Hg(30%T)/O_2(30%T), of $d^{\bullet+}$, (B) pure $d^{\bullet+}$ ions, and (C) pure $a^{\bullet+}$ ions.

the radicals **a**, **b**, and **c** all represent stable structures (Figure 1).

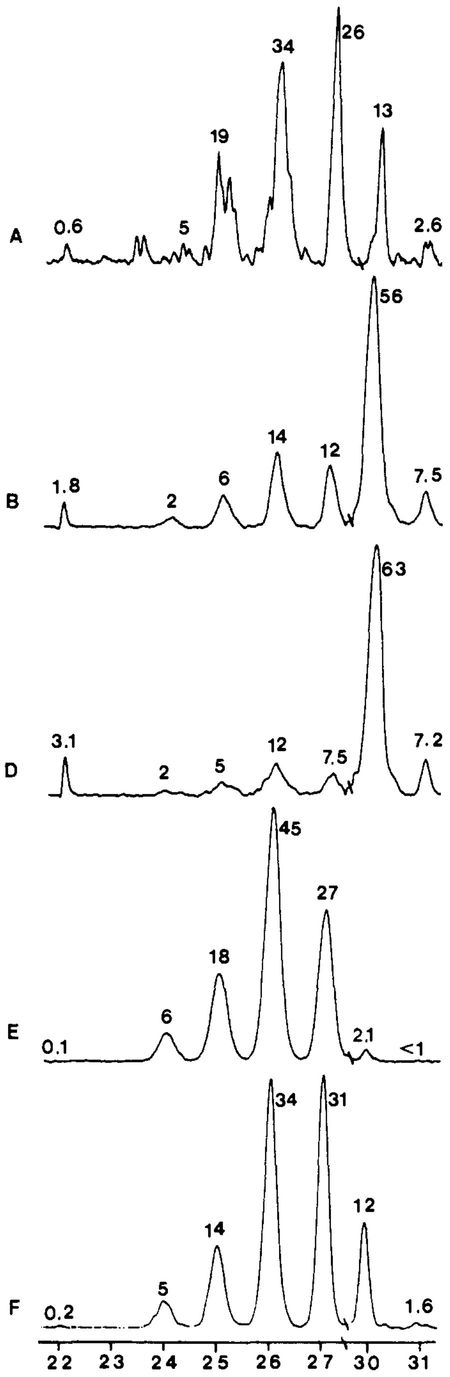

Figure 10. CAD, O_2(30%T), spectra of (A) recovered $C_2H_4O^{\bullet+}$ from $^+NCR^+$, Hg(30%T)/O_2(30%T), of $b^{\bullet+}$, and of pure (B) $b^{\bullet+}$, (D) $d^{\bullet+}$, (E) $e^{\bullet+}$, and (F) $f^{\bullet+}$ ions. Relative peak areas are given above peaks. The peak at *m/z* 28 is omitted, as this can arise from $CO_2^{\bullet+}$ cogenerated with $b^{\bullet+}$ (eq 1).

Gaseous Unimolecular Reactivities of a–e. To probe further the chemistry of neutrals **a–d**, their internal energies were increased by collisional activation. As illustrated by comparison of the $^+NR^+$ and $^+NCR^+$ (Figure 6) spectra of $a^{\bullet+}$–$f^{\bullet+}$, the major observable products from CAD of the neutral C_2H_4O isomers are $CH_3CO^\bullet$ (yielding *m/z* 43$^+$)[23] for **a**, **b**, **e**, and **f** (but not for **c** and **d**), some $HCO^\bullet$ (yielding *m/z* 29), and, in significant yield from all isomers, CO (which exhibits an unusually high cationization efficiency[4b] to yield *m/z* 28). Formation of the isobaric C_2H_4 (O: loss) would require 45 kJ mol^{-1} more energy[19] and is not observed to any appreciable extent, as evidenced by the absence

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(23) *m/z* 43 is the base peak in the reionization (He, 90%T or 30%T) spectrum of $CH_3CO^\bullet$ formed by He CAD (80%T) of $CH_3COCOCH_3^{\bullet+}$, with *m/z* 28 and 42 nearly as abundant, even though the $^+NR^+$ spectrum of CH_3CO^+ from either acetone or ethylene carbonate shows [*m/z* 43]/[*m/z* 28] = ~5%, presumably because the initially formed $CH_3CO^\bullet$ is excited.[4b,24] The neutrals from CAD of $CH_3CO{-}OCH{=}CH_2^{\bullet+}$, presumably $^\bullet OCH{=}CH_2$,[25] on reionization show [*m/z* 43]/[*m/z* 28] = ~5%, with *m/z* 29 comparable in abundance to *m/z* 28.

of the intense $C_2H_n^+$ (n = 0–3) fragments expected upon C_2H_4 reionization.[3,26] As observed[4b] for **e**, **f**, and **g**, the experimental data are consistent (Figure 1) with isomerization of **a**, **b**, and **d** to **e**, dissociation to $CH_3^•$ + $^•CHO$ ($\sum\Delta H_f$ = 191 kJ mol^{-1}) and $CH_3CO^•$ + $^•H$ ($\sum\Delta H_f$ = 194 kJ mol^{-1}), and further dissociation to CO. A similar sequence has been suggested by Benson[6b] for the thermal decomposition of oxirane, with **b** → **e** as the rate-determining step (experimental activation energy, 238 kJ mol^{-1}). Isomer **c** can form $HCO^•$ + $^•CH_3$ by direct O–C bond cleavage (Figure 1). These postulates are completely supported by MS/MS/MS experiments. After collisional activation of the neutrals from **d**$^{•+}$, the recovered $C_2H_4O^{•+}$ ions ($^+$NCR$^+$ spectrum, Figure 6) are subjected to CAD; the spectrum thus produced from **d**$^{•+}$ (Figure 9A) is identical within experimental error with the CAD spectrum of the original **d**$^{•+}$ precursors (Figure 9B) and different from the CAD spectrum of pure **a**$^{•+}$ ions (Figure 9C), consistent (Figure 1) with high isomerization barriers for **d** (as well as for its cation **d**$^{•+}$, vide supra).

Similarly for the isomerization of **b**, the corresponding CAD spectrum of recovered $C_2H_4O^{•+}$ from $^+$NCR$^+$ of **b**$^{•+}$, is compared in Figure 10 with reference spectra of pure **b**$^{•+}$, **d**$^{•+}$, **e**$^{•+}$, and **f**$^{•+}$ cations measured under the same conditions. The much lower abundances of 30$^+$, 31$^+$, and 44^{2+} in the CAD spectrum of the recovered cations, versus those from **b**$^{•+}$, indicates that neutral **b** has been extensively isomerized by collisional activation but not to **d**, which is also consistent with the large m/z 24–27 peaks. Similarly, [27$^+$]:[26$^+$] and [30$^+$]:[31$^+$] indicate that **f**$^{•+}$ is not a major component; the data of Figure 10 are best reconciled as representing a mixture of 20% **b**$^{•+}$ and 80% **e**$^{•+}$. Thus the barrier for **b** → **d** is considerably higher than that for **b** → **e** (Figure 1), the only significant disagreement with Benson's proposed mechanism,[6b] but supporting theoretical predictions.[11a]

Under multiple collision conditions that lead to CO formation from **a**, no $C_2H_4O^{•-}$ is observed in the $^+$NCR$^-$, Hg/benzene, spectrum of **a**$^{•+}$, showing a much higher activation energy for the H migration **a** → **c** than for the ring closure **a** → **d**. The MS/MS/MS data for the collisional activation of isomer **a** (Figure 8) show less isomerization for this diradical, with **d** favored over **e** (approximate values 60% **a**$^{•+}$, 30% **d**$^{•+}$, and 10% **e**$^{•+}$), consistent with the transition state for **a** → **d** lying well below that for **d** → **b**. Consequently, C–C ring opening in oxirane requires less energy than C–O bond rupture (Figure 1).

Conclusions

These neutralization–reionization experiments clearly show that the ring-opened oxirane isomers **a** and **b** and the carbene **c**, key intermediates on the C_2H_4O energy surface, represent stable structures. Product abundances from their fragmentation and isomerization reactions, monitored in NCR/CAD (MS/MS/MS) experiments, establish the relative order of activation energy values for the potential energy profile of Figure 1, clarifying predictions of molecular orbital theory[9] and oxirane pyrolysis studies.[6] $^+$NR$^{+,-}$ spectra have also provided the first direct evidence that cation **b**$^{•+}$ and the anions **b**$^{•-}$, **c**$^{•-}$, and **g**$^{•-}$ represent stable structures.

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Oscillatory Oxidation of Benzaldehyde by Air. 1. Experimental Observations[†]

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Abstract: In 90% aqueous acetic acid at 70 °C, the oxidation of benzaldehyde to benzoic acid by air is catalyzed by a mixture of cobalt(II) and bromide. Jensen has shown that the concentration of cobalt(III) undergoes major oscillations during this reaction. Consistent with these prior observations, we find that the rate of formation of cobalt(III) increases exponentially until at about 10^{-5} M s^{-1} it becomes comparable to the maximum rate at which O_2 can be transported from atmosphere to solution. A virtually discontinuous change of behavior then causes the concentration of cobalt(III) to decrease at about 10^{-4} M s^{-1}; the rate of this decrease is almost constant and independent of [Co^{III}] until most of this species has been consumed. We have examined most of the subsystems that we could prepare and study independently. Among other observations, we find that increasing acidity increases the rate at which bromide catalyzes the oxidation of benzaldehyde by cobalt(III). We also find that free Br_2 is formed and can be entrained by gas flow. We propose a detailed molecular mechanism for the oscillations that seems to be consistent with most of what we know about the behavior of the subsystems, and we have initiated modeling computations with encouraging results. We also suggest additional experiments and computations that could further test the validity of our proposed mechanism.

I. Introduction

In 1983, Jensen[2] reported oscillatory behavior during the air oxidation of benzaldehyde in aqueous acetic acid catalyzed by a combination of cobaltous and bromide ions. Both electrode potentials and visual observation indicated that the dominant oxidation state of cobalt underwent major repetitive changes with a period of a few minutes.

Roelofs, Wasserman, Jensen, and Nader[3] (RWJN) subsequently proposed a mechanism of 11 steps that did indeed generate oscillations during computer simulations.

Roelofs, Wasserman, and Jensen[4] (RWJ) have since published a more detailed study of the same system and have proposed an

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(1) Based in part on the Ph.D. thesis of Zhi Yuan, University Oregon, August 1987. Copies are available on microfilm/microfiche or on paper from UMI Dissertation Information Service, 300 North Zeeb Road, Ann Arbor, MI 48106, or call (800) 521-3042. Order No. DA8800562.

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