mitted daughter ions. The resulting CA mass spectra were satisfactorily free from artifacts. IE and daughter ion AE values were obtained with an apparatus comprising an electrostatic electron monochromator with a quadrupole mass analyzer and minicomputer data system.[41] All other AE values were obtained by a comparative method[33] using a Kratos MS 902 mass spectrometer.

In the above experiments all slits were fully open to obtain maximum signal strength and to minimize energy resolving effects. Metastable peak shapes, however, were obtained using a main beam width of 0.2 V at an electric sector potential of 422 V, corresponding to an accelerating voltage of 8 kV. Kinetic energy releases were evaluated by established methods.[46]

Methyl glycolate was obtained by esterification of glycolic acid, $CH_2OHCOOH$, using methanol in the usual manner. All other compounds were commercially available and their purity was checked by gas chromatography. A methanol sample containing $^{13}CH_3OH$ (80%), $^{13}CH_3{}^{18}OH$ (10%), was purchased from Amersham, U.K.

Acknowledgment. The authors thank Dr. F.P. Lossing for ionization and appearance energy measurements and Dr. M. F. Guest and Dr. J. H. van Lente for making available the GAMESS and DIRECT-CI programs. R.P. and J.K.T. thank the Netherlands Organization for the Advancement of Pure Research (ZWO) and J.L.H. and P.C.B. the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. J.L.H. and J.K.T. are grateful to the NATO Scientific Affairs Division for a collaborative research award.

Registry No. 1, 83957-60-2; CH_2OH^+, 17691-31-5; $CH_2OH^{\cdot}$, 2597-43-5; $CH_3O^{\cdot}$, 2143-68-2; $CH_3OH_2{}^+$, 17836-08-7; $HCO^{\cdot}$, 2597-44-6; $CH_2OH^{\cdot+}$, 69784-92-5; CH_2O, 50-00-0; $HO(CH_2)_2OH$, 107-21-1; H_3CCH_2OOH, 3031-74-1; H_3COOCH_3, 690-02-8; $DOCH_2COOCH_3$, 53778-47-5; $D_3CO_2CCH_2OH$, 53778-49-7; $HOCH_2CO_2{}^{13}CH_3$, 110661-98-8; methyl glycolate, 96-35-5.

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$CH_3OCH^{\cdot+}$, a New Stable $C_2H_4O^{\cdot+}$ Isomer, and a Reassessment of the Oxirane$^{\cdot+}$ Potential Surface

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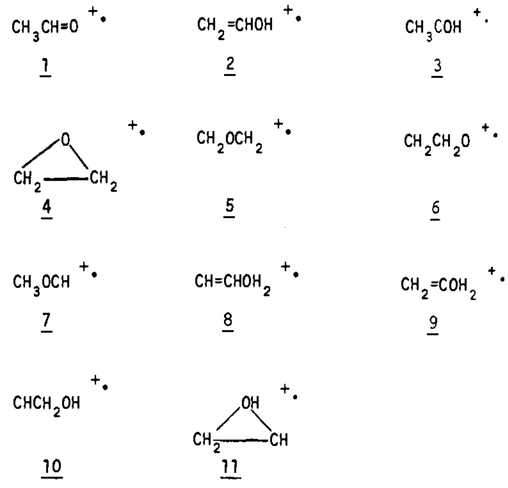
Abstract: The $[C_2H_4O]^{\cdot+}$ isomer of structure $[CH_3OCH]^{\cdot+}$ has been shown to be unambiguously generated by CO_2 loss from ionized methyl glyoxylate. $\Delta H_f°$ for this new ion was measured to be 224 ± 1 kcal mol^{-1}. The $[C_2H_4O]^{\cdot+}$ ion produced by the loss of CH_2O from ionized 1,3-dioxolane and by the loss of HCOOH from ionized methoxymethyl formate was proposed to have the structure $[CH_2OCH_2]^{\cdot+}$, $\Delta H_f° = 206 \pm 2$ kcal mol^{-1}. Ionized oxirane in either its $^2B_1$ or $^2A_1$ state was proposed to be generated by loss of CO_2 from ionized ethylene carbonate at a threshold energy corresponding to a $\Delta H_f° = 235 \pm 1$ kcal mol^{-1}. The structure assignments were aided by observations of collisional activation and metastable ion mass spectra. The common fragmentations of $[CH_2OCH_2]^{\cdot+}$ and [oxirane]$^{\cdot+}$ ions, loss of $CH_3^{\cdot}$ and $H^{\cdot}$, take place at similar high internal energies, leading to large kinetic energy releases in the metastable ion decompositions. Interpretations of the observations were in keeping with recent high-level ab initio molecular orbital theory calculations, but detailed mechanisms could not be established.

In recent years, advances in ab initio molecular orbital theory calculations and developments in experimental techniques for assigning structures to gas-phase ions have resulted in the successful, close collaboration of these methods. The role of experiment has been reviewed,[1] and theory[2] is well represented by the many contributions of Radom and his co-workers.

In an early ab initio paper,[3] the $[C_2H_4O]^{\cdot+}$ system was described, and it was calculated that no fewer than 11 isomers exist in potential wells; these are shown in Scheme I. At that time (1975), only **1**, **2**, and **4** had been studied by experiment, but the calculations showed that isomers **3** and **5–9** lay in sizable potential wells and so were reasonable prospects for experimental identification.

The present situation can be summarized as follows. The keto–enol pair **1** and **2** have been thoroughly investigated; their enthalpy of formation,[4a] $\Delta H_f°$, and dissociation characteristics (metastable ion (MI) fragmentations[4b] and collision-induced decompositions[4c]) are well established. The ionized hydroxycarbene **3** not only plays an important role in the major dissociation of the enol **2**, but has also been independently generated and characterized. For this isomer too, theory[3,5a] and experiment[5b] are in excellent agreement.

Scheme I



For ionized oxirane **4**, $\Delta H_f°$ (231 kcal mol^{-1} [6]) and its MI[4b] and collisional activation (CA) mass spectra[4c] have been reported. Its

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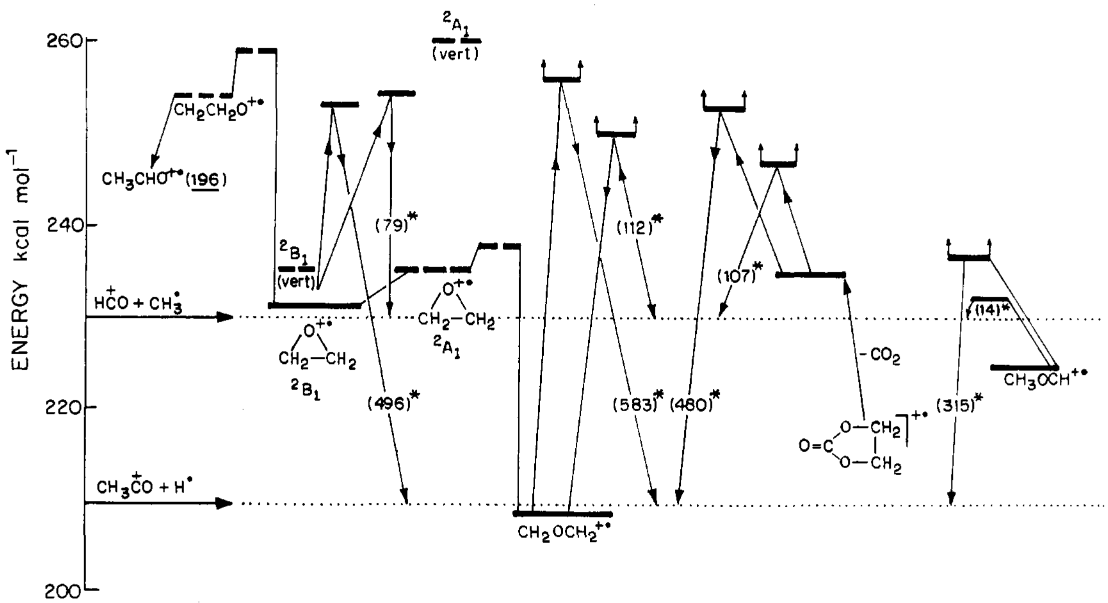
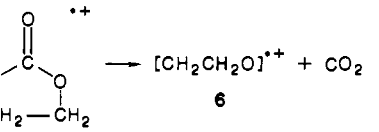


Figure 1. Energy diagram for $[C_2H_4O]^{\bullet+}$ isomers **4**, **5**, **6**, and **7**. The heavy broken lines are energies established by ab initio calculations.[7] Heavy horizontal lines represent experimentally determined energies; those with two upward arrows are lower limits (see Discussion). Kinetic energy releases ($T_{0.5}$) in meV are shown in starred parentheses.

relationship with the ring-opened isomers **5** and **6** has received considerable attention. The first calculations by Radom et al.[3] showed **5** to be 14 kcal mol^{-1} lower in energy than **4**, but the isomers were separated by a barrier of about 27 ± 2 kcal mol^{-1}, above **4**. Isomer **6** was calculated to lie 13 kcal mol^{-1} above **4** but with only a small barrier (<7 kcal mol^{-1}) between them.

However, very recently, higher level calculations also by Radom et al.[7] have changed the picture greatly. Isomer **6** is now much higher in energy, 23 kcal mol^{-1} above **4** and separated from the latter by a barrier of 28 kcal mol^{-1}. Moreover, **6** was shown to rearrange without an energy requirement to $[CH_3CHO]^{\bullet+}$ (**1**); at this energy level **1** can fragment to both $[CH_3CO^+] + H^\circ$ and $[HCO^+] + CH_3^\bullet$. Isomer **6** has, however, been sought by experiment. For example, in a carefully designed ion cyclotron resonance experiment using labeled ethylene carbonate, Baumann and MacLeod[8] concluded that the reactive $[C_2H_4O]^{\bullet+}$ ions generated from the carbonate by electron impact induced loss of CO_2, and which formally would have the structure $[CH_2CH_2O]^{\bullet+}$, must have rearranged into a species having equivalent methylene groups. This they chose to be ion **5**.

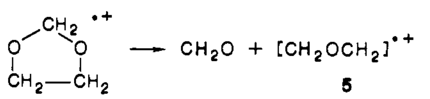


6

The consensus, from a variety of *experimental* techniques,[8,9] was that ion **6**, if ever formed, rapidly isomerizes to **4** and, moreover, that the energy barrier for ring opening, **4** → **5**, is low.

This latter is in direct conflict with the theoretical calculations[7] and rested upon the observation[9d] that oxirane ions and the $[C_2H_2D_2O]^{\bullet+}$ ion from $[4,4,5,5\text{-}^2H_4]$-1,3-dioxolane, which was proposed to have the structure $[\dot{C}H_2OC^+D_2]$, displayed the same methylene transfer reactions.

Ion **5**, $[CH_2OCH_2]^{\bullet+}$, is believed to be produced from 1,3-dioxolane as shown below:



5

The appearance energy has been accurately measured,[4a] and the resulting ΔH_f° $[C_2H_4O]^{\bullet+}$ of 206 kcal mol^{-1} compared favorably with that predicted for ion **5** by the high-level ab initio calculations,[7,10] 211 kcal mol^{-1}. However, the MI[4b] and CA[4c] mass spectra for this ion from 1,3-dioxolane have been interpreted as a mixture of structures **4** and the enol ion **2** (ΔH_f° = 181 kcal mol^{-1} [4a]).

Theoretical calculations[3] have predicted that the remaining isomers, **7**–**11**, also lie in potential wells but with **8**–**11** all having heats of formation above that of **4**. The carbene ion **7**, however, is relatively stable, ΔH_f° = 214 kcal mol^{-1}. The heights of barriers to the isomerizations and dissociations of these remaining ions have not been calculated and so the experimental generation of some of these isomers may not be feasible. The new calculations[7] introduce the $^2A_1$ (first-excited) state of ionized oxirane, **4A**. This species lies 4.1 kcal mol^{-1} above the $^2B_1$ ground state of the ion, **4B**. The potential energy curves for these states are such that vertical ionization of oxirane leads to the ground ($^2B_1$) state with ca. 4 kcal mol^{-1} excess energy, whereas for the $^2A_1$ state vertical ionization produces an ion having 29 kcal mol^{-1} of excess energy, leading directly to fragmentation (see Figure 1).

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Table I. CA Mass Spectra of $[C_2H_4O]^{\bullet+}$ Ions[a]

precursor molecule	12	13	14	15	16	24	25	26	27	28	29	30	31	40	41	42	43	assigned structure	rel X-section[b]
oxirane	10	33	158	227	64	4	11	24	18	84	(1740)	52	23	14	40	235	(720)	$\overline{CH_2-CH_2-O}^{\bullet+}$	1.0
acetaldehyde	5	17	43	85	11	6.5	23	50	26	48	472	1		12	53	150	(1650)	$CH_3CHO^{\bullet+}$	
cyclobutanol	8.5	26	51	127		8.5	38	126	141	16	(219)	22	1.5	17	62	354	(2710)	$CH_2CHOH^{\bullet+}$	1.8
1,3-dioxolane	13	36	186	185	54	2	5	13	14	94	(1860)	73	29	10	32	253	(950)	$CH_2OCH_2^{\bullet+}$	1.3
ethylene carbonate	12	35	175	190	64	1	4.5	14	16	112	(1740)	61	24	10	35	246	(750)	$CH_2CH_2O^{\bullet+}$	0.86
methyl glyoxylate	5	34	62	270	60			2	4	250	(3785)	75	4	8	50	170	(510)	$CH_3OCH^{\bullet+}$	

[a] Abundances normalized to $\Sigma = 1000$. Peaks in parentheses omitted because they are partially metastable. Peaks at m/z 28, 16, and 12 are not corrected for a possible small contribution from CO_2. [b] Relative ratio of Σ to m/z 44 ion abundance.

We describe here the properties of ion **7**, [methoxycarbene]$^{\bullet+}$, which was unambiguously formed by the loss of CO_2 from ionized methyl glyoxylate, $[HCOCOOCH_3]^{\bullet+}$, a fragmentation preceded by a formal [1,4]-methyl shift. Loss of formic acid from ionized methoxymethyl formate, $[HCOOCH_2OCH_3]^{\bullet+}$, was found to generate ion **5** at threshold. These ions and their relationship with the states of ion **4** are discussed in the light of new experimental observations on $[C_2H_4O]^{\bullet+}$ ions produced from ethylene carbonate and 1,3-dioxolane.

Results and Discussion

Generation of Methoxycarbene, 7, $[CH_3OCH]^{\bullet+}$. The mass spectrum of methyl glyoxylate, $HCOCOOCH_3$ (m/z 88), contains a significant peak at m/z 44, $[C_2H_4O]^{\bullet+}$, of abundance 32% relative to the base peak $[CH_3OCO]^+$, m/z 59. In the trideuterio ester, m/z 44 is cleanly shifted to m/z 47, $[C_2HD_3O]^{\bullet+}$. The MI mass spectra of the molecular ions each contain only one peak at m/z 44 and 47, respectively, showing that there is no loss of positional identity of the label atoms in the reaction m/z 88 $\rightarrow$ m/z 44. The kinetic energy release, $T_{0.5}$, evaluated from the half-height width of these Gaussian-type metastable peaks, was 0.015 ± 0.002 eV. This small kinetic energy release indicates that the fragmentation has neither a reverse energy barrier nor a significant kinetic shift, so the appearance energy (AE) of the daughter ion, 10.32 ± 0.05 eV (measured using energy selected electrons[11]), is expected to yield a reliable $\Delta H_f°$ for the $[C_2H_4O]^{\bullet+}$ ion.[12] $\Delta H_f°[HCOCOOCH_3] = -107.9$ kcal mol^{-1}, by additivity;[13] $\Delta H_f°[CO_2] = -94.1$ kcal mol^{-1},[6] whence $\Delta H_f°[C_2H_4O]^{\bullet+} = 224 \pm 1$ kcal mol^{-1}. The AE of the metastable peak, measured by a comparative method,[14] was 10.45 ± 0.1 eV, in satisfactory agreement with the energy selected electron measurement and shows moreover that the metastable peak corresponds to the threshold process.

The fragmentation characteristics of this $[C_2H_4O]^{\bullet+}$ ion, described below, were compatible only with the structure $[CH_3OCH]^{\bullet+}$; the $\Delta H_f°$ derived from experiment is therefore in only modest agreement with theory. The MI mass spectrum contained two peaks, m/z 43 $[C_2H_3O]^+$, and m/z 29, $[CHO]^+$. For the ion $[C_2HD_3O]^{\bullet+}$ generated from the CD_3 ester, only m/z 46 and 29 were observed in the MI mass spectrum, showing that no H/D positional mixing precedes either fragmentation. This conclusion was emphasized by the observation that the m/z 45 ion $[^{13}CCH_4O]^{\bullet+}$, cleanly produced from $[HCOCOO^{13}CH_3]^{\bullet+}$, shows only ($m/z$ 44 and) m/z 29 in its MI mass spectrum. These observations are compatible only with an ion containing the group HCO and a methyl group; the ion cannot be ionized acetaldehyde ($\Delta H_f° = 196$ kcal mol^{-1};[6] MI mass spectrum only contains m/z 43[4b]) and so the carbene structure, $[CH_3OCH]^{\bullet+}$, can confidently be assigned. The collisional activation (CA) mass spectrum is also in keeping with this structure and is dominated by m/z 43 and 29 (see Table I). Note that it contains virtually *no* peaks at m/z 24 to 28, $[CO]^{\bullet+}$, showing that the ion does not communicate prior to fragmentation with any species containing a C–C bond. This is the only $[C_2H_4O]^{\bullet+}$ ion so far examined to have this feature. The AE values for the two metastable peaks m/z 44 $\rightarrow$ m/z 43 and m/z 44 $\rightarrow$ m/z 29 were measured. For the latter a good onset was observed at 10.75 ± 0.1 eV. This is close to the calculated threshold energy for $HCO^+ + CH_3^{\bullet}$, 10.6 eV ($\Delta H_f°[HCO^+] = 195$ kcal mol^{-1},[6] $\Delta H_f°[CH_3^{\bullet}] = 35$ kcal mol^{-1} [15]),and the $T_{0.5}$ value for this peak, 0.014 eV, is in keeping with the AE. For the m/z 44 $\rightarrow$ m/z 43 peak, $T_{0.5} = 0.315$ eV, a satisfactory onset could not be observed, the ion abundance curves tailing badly to give an uncertain threshold. The relative abundance of the m/z 43 and 29 peaks, 7:1, indicates that the difference in appearance energies for the two reactions cannot be large.

Ionized Oxirane, 4, and Its Ring-Opened Isomers, 5 and 6. In order to try to understand the relationship between these three ions, the thermochemistry and fragmentation characteristics of ionized oxirane and the $[C_2H_4O]^{+\bullet}$ ions from 1,3-dioxolane and ethylene carbonate were carefully reevaluated.

The oxirane molecular ion fragments in the metastable (μs) time frame to yield m/z 43 and 29. The energy requirements for these decompositions are well established from photoionization (PI) mass spectrometry[16] and by energy selected electron impact as 11.62 eV (PI), 11.55 eV and 11.54 eV (PI), 11.53 eV, respectively. The metastable peak AE values of 11.56 ± 0.1 and 11.77 ± 0.2 eV are in satisfactory agreement with the high-precision results and show that they correspond to the ion source threshold energies. As can be seen from the energy diagram, Figure 1, these AE values lie far above the calculated thresholds for the fragmentations. The kinetic energy releases, $T_{0.5}$, are 0.496 ± 0.005 eV for the H loss (compares with 0.430 eV,[4b] a value which was *overcorrected* for the energy spread of the main ion beam), and 0.079 ± 0.003 eV.

The daughter ions formed in these two fragmentations cannot be in question; m/z 29 has to be $[HCO]^+$, because its isomer $[COH]^+$ has $\Delta H_f° = 37$ kcal mol^{-1} above $[HCO]^+$.[17,18] The large kinetic energy release for the $H^{\bullet}$ loss reaction is only compatible with the formation of $[CH_3CO]^+$. Note that only one isomer, $[CH_2COH]^+$, $\Delta H_f° \simeq 200$ kcal mol^{-1},[19] can be an alternative daughter ion (see Figure 1), but its AE would be within 0.1 eV of the observed threshold.

The $\Delta H_f°$ for m/z 44 for 1,3-dioxolane was reported[4a] to be 205.5 kcal mol^{-1}, a value fairly close to that calculated for $[CH_2OCH_2]^{\bullet+}$, 211 kcal mol^{-1}.[3] The MI mass spectrum of the ion contains m/z 43 and 29, as does that of [oxirane]$^{\bullet+}$. Unlike [oxirane]$^{\bullet+}$ (see below), the metastable peaks are of equal intensity, and are each 0.058% of the m/z 44 ion flux, but the $T_{0.5}$ values for the two metastable peaks m/z 44 $\rightarrow$ 43, 0.583 ± 0.02 eV, and m/z 44 $\rightarrow$ 29, 0.112 ± 0.005 eV, are significantly greater than those for ionized oxirane. This result is not easily reconciled with a facile isomerization **4** (A,B) $\leftrightarrow$ **5** which would be expected to

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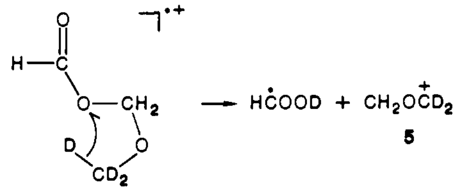
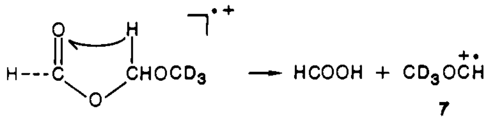
produce identical metastable peak shapes for the two ions.

Attempts to measure the AE values of the m/z 44 → 43 and m/z 44 → 29 metastable peaks were unsatisfactory in that the ion abundance curves tailed badly near threshold. This problem notwithstanding, approximate AE values of ca. 12.8 and ca. 13.1 eV were obtained. These are shown in Figure 1.

In the course of a search for another precursor molecule for $[C_2H_4O]^{\bullet+}$ ions, the behavior of ionized methoxymethyl formate was examined. It was observed that its MI mass spectrum contained only an $[M - H]^+$ ion, m/z 89 and 44 $[C_2H_4O]^{\bullet+}$, loss of formic acid, HCOOH. The labeled ester $[HCOOCH_2OCD_3]^{\bullet+}$ specifically lost HCOOD in the metastable time frame, but source-generated ions lost HCOOH as well. The AE (EM) values for m/z 44 from the unlabeled and m/z 46 from the $-CD_3$ ester were 10.49 ± 0.05 and 10.51 ± 0.05 eV, respectively, and 10.54 ± 0.1 and 10.56 ± 0.1 eV for the metastable peak ($T_{0.5} = 0.003$ eV) AE results. The ΔH_f° for the daughter ion, 208 ± 1 kcal mol^{-1} ($\Delta H_f^\circ[HCOOCH_2OCH_3] = -124.6$ kcal mol^{-1},[13] $\Delta H_f^\circ[HCOOH] = -90.5$ kcal mol^{-1} [6]), and the mechanism for its production (cf. the labeling experiments) indicate a structure $[CH_2OCH_2]^{\bullet+}$ (**5**). The metastable peaks for loss of $H^\bullet$ and $CH_3^\bullet$ from the m/z 44 ion from $[HCOOCH_2OCH_3]^{\bullet+}$ were, however, composite and were interpreted as arising from a mixture of $[CH_2OCH_2]^{\bullet+}$ and $[CH_3OCH]^{\bullet+}$.





Finally, the AE m/z 44 from ethylene carbonate was measured (EM), 11.34 ± 0.05 eV, in good agreement with that for the metastable peak, m/z 88 → 44 ($T_{0.5} = 0.021$ eV), 11.35 ± 0.1 eV. ΔH_f°[ethylene carbonate] = −121.2 kcal mol^{-1},[20] $\Delta H_f^\circ[CO_2] = -94.1$ kcal mol^{-1},[6] and so $\Delta H_f^\circ[C_2H_4O]^{\bullet+} = 235 \pm 1$ kcal mol^{-1}, slightly but significantly above ΔH_f°[oxirane]$^{\bullet+}$ = 231 kcal mol^{-1}. The small kinetic energy release associated with this reaction is compatible with the formation of an ion at or close to its thermochemical threshold. Baumann and MacLeod[8] believed that $CH_2OCH_2^{\bullet+}$ was the ion's structure but this is incompatible with the measured ΔH_f°. The fragmentation characteristics of the $[C_2H_4O]^{\bullet+}$ ion from ethylene carbonate are, as described below, significantly different from those of [oxirane]$^{\bullet+}$ and the $[C_2H_4O]^{\bullet+}$ from 1,3-dioxolane, $[CH_2OCH_2]^{\bullet+}$. The MI mass spectrum of this $[C_2H_4O]^{\bullet+}$ ion again only contains m/z 43 and 29, $T_{0.5}$ values 0.480 ± 0.017 and 0.107 ± 0.007 eV, respectively. The former is within experimental error the *same* as that for [oxirane]$^{\bullet+}$, but the latter is significantly higher. The relative abundances of the metastable peaks were also measured; m/z 44 → 43 for [oxirane]$^{\bullet+}$ and the ethylene carbonate $[C_2H_4O]^{\bullet+}$ ion were 0.031 and 0.028% of the main m/z 44 beam, respectively, but m/z 44 → 29 for oxirane was *twice* as intense as m/z 44 → 43, while for the other $[C_2H_4O]^{\bullet+}$ ion the two metastable peaks had similar abundances. These results are in keeping with a common fragmentation for $H^\bullet$ loss but different behavior for $CH_3^\bullet$ loss. We conclude that the $[C_2H_4O]^{\bullet+}$ ion from ethylene carbonate is at threshold, an oxirane ion, **4A** or **4B**; the low barrier recently calculated for rearrangement to **5** now makes our conclusion compatible with the observations of Baumann and MacLeod.[8]

Metastable peak AE measurements were made for the two fragmentations, again with difficulty. AE m/z 44 → 43 was ca. 11.8 eV and for m/z 44 → 29, 12.2 eV. These energies, which should probably be regarded as lower limits, are included in Figure 1; note that all these dissociations have large energy barriers.

Finally, the CA mass spectra of the $[C_2H_4O]^{\bullet+}$ ions from oxirane, 1,3-dioxolane and ethylene carbonate were measured under identical instrument conditions (see Experimental Section). These are shown in Table I. The main conclusion from the CA mass spectra is that C–C bonded ions are not significantly involved as nonfragmenting species. A problem that should be addressed first concerns the earlier work in which it was concluded from the kinetic energy release ($T_{0.5}$) for the metastable decomposition m/z 44 → 43[4b] and from the CA mass spectra[4c] that 1,3-dioxolane generated a mixture of [oxirane]$^{\bullet+}$ and $[CH_2CHOH]^{\bullet+}$. The kinetic energy release certainly allows for $[CH_2CHOH]^{\bullet+}$ ions (with their characteristic large $T_{0.5}$ value, 0.620 eV[4b]) to be present with [oxirane]$^{\bullet+}$ (a) to make up for the larger proportion of m/z 44 → 43 (relative to [oxirane]$^{\bullet+}$) in the MI mass spectrum of the $[C_2H_4O]^{\bullet+}$ species from 1,3-dioxolane, and (b) to account for the large $T_{0.5}$ value (see above). However, the present CA results show the 1,3-dioxolane $[C_2H_4O]^{\bullet+}$ ion as having a *less* intense m/z 24–27 cluster (the structure characteristic region of the CA mass spectrum of $[CH_2CHOH]^{\bullet+}$) than [oxirane]$^{\bullet+}$. Thus, except for its possible participation as a high-energy reacting configuration in the collision-induced fragmentation of ionized oxirane and **5**, there can be little or no $[CH_2CHOH]^{\bullet+}$ among the $[C_2H_4O]^{\bullet+}$ ions from 1,3-dioxolane. This is contrary to the earlier CA results.[4c] It is difficult to identify a reason for this discrepancy; the present experiments were performed with research grade 1,3-dioxolane and under single-collision CA conditions (see Experimental Section) and were reproducible (to within 5% even for the weak m/z 24–27 peaks) on four separate occasions. Differences between the CA mass spectra of m/z 44 ions from ionized oxirane, 1,3-dioxolane, and ethylene carbonate are small but sufficient for the three ions to be distinct, e.g., the m/z 14:m/z 15 ratios and the m/z 24–27 regions. It remains to discuss the relationship between isomers **4**(**AB**) and **5**.

The results incorporated in the energy diagram (Figure 1) will now be considered. The dissociation energies for [oxirane]$^{\bullet+}$ have been accurately measured, but the remaining four threshold energies shown have relatively large experimental uncertainties and should be taken as reasonable *lower limits*. However, the kinetic energy releases are precise and the ensuing proposals rest more heavily upon these observations.

All six reactions have a large energy barrier; theory has shown that at such internal energies decomposition via $[CH_2CH_2O]^{\bullet+}$ and $[CH_3CHO]^{\bullet+}$ is possible. If this were the only available reaction channel, then all the differences in kinetic energy release and relative metastable peak abundances would have to arise from kinetic shift effects. We propose that this may be the case for all the $H^\bullet$ loss fragmentations; e.g., the $[C_2H_4O]^{\bullet+}$ ions from ethylene carbonate and 1,3-dioxolane rearrange to **6** via the $^2B_1$ [oxirane]$^{\bullet+}$ surface. For oxirane itself, the excited $^2A_1$ state is reached by vertical ionization; this can cross to the excited ground-state ion.[7] We propose, however, that the excited $^2A_1$ state can alternatively rearrange with a concomitant 1,3-H shift to energy-rich $[CH_3OCH]^{\bullet+}$. This, the only other C–O–C bonded ion, will immediately fragment by $CH_3^\bullet$ loss and this route then accounts for the significant differences in metastable ion behavior.

At present, the involvement of the $[CH_3OCH]^{\bullet+}$ ion with the $[CH_2OCH_2]^{\bullet+}$ potential energy hypersurface has not been investigated by high-level calculations, but such work should certainly shed further light on this complex problem.

Experimental Section

Collisonal activation (CA) mass spectra and metastable peaks were measured[21] using a V.G. Analytical ZAB-2F mass spectrometer, as described elsewhere. Metastable peak appearance energy (AE) values were obtained by a comparative method[14] using a Kratos MS902S mass spectrometer, and fragment ion AE values were obtained using energy selected electrons.[11]

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Methoxymethyl formate was prepared by the reaction of chloromethyl methyl ether[22] (doubly distilled) with sodium formate and 0.05 mol% tetra-*n*-butylammonium hydrogen sulfate. The reactants were refluxed at 100 °C for 2 h.[23] The product, bp 100–103 °C (103 °C[24]) had the following ^{1}H NMR (10% $CDCl_3$): δ 8.05 (8.15[24]) (s, 1), 5.22 (5.34[9]) (s, 2), 3.42 (3.50[9]) (s, 3).

The trideuterio analog was prepared similarly, using CD_3OCH_2Cl. ^{1}H NMR (10% $CDCl_3$) showed δ 8.1 (s, 1) and 5.2 (s, 2). Methyl glyoxylate was prepared by heating glyoxylic acid (Aldrich) with the appropriate labeled or unlabeled methanol in sealed tubes and also by the $Pb(OAC)_4$ oxidation of trimethyl L-tartrate using the procedure of Wolf and Weijland.[25] Oxirane was purchased from Matheson Gas Products (Canada).

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Registry No. 1, 36505-03-0; **4**, 57062-76-7; **5**, 72192-21-3; **6**, 72192-22-4; **8**, 57239-63-1; CD_3OCH_2Cl, 54716-95-9; ionized methyl glyoxylate, 110661-93-3; ionized 1,3-dioxolane, 81027-69-2; ionized methoxymethyl formate, 110661-94-4; ionized ethylene carbonate, 110661-95-5; ionized methoxymethyl formate-d_3, 110661-96-6; oxirane, 75-21-8; methoxymethyl formate-d_3, 110661-97-7; acetaldehyde, 75-07-0; cyclobutanol, 2919-23-5; 1,3-dioxolane, 646-06-0; ethylene carbonate, 96-49-1; methyl glyoxylate, 922-68-9; methoxy methyl formate, 4382-75-6; chloromethyl methyl ether, 107-30-2; sodium formate, 141-53-7.

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Propellanes. 91.[1] Fragmentation Mechanism of Alcohols under Isobutane Chemical Ionization. Highly Stereospecific Formation of [M – OH]$^+$ Ions from [4.3.3]Propellane-8,11-diols

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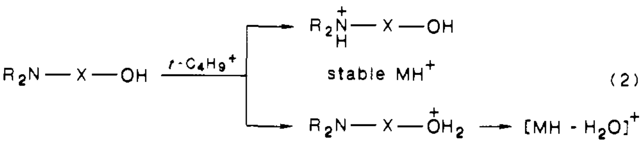
Abstract: The stereoisomeric title diols afford different isobutane chemical ionization mass spectra: the anti,anti diol affords an abundant MH$^+$ ion while the syn,syn and syn,anti isomers give very abundant [M – OH]$^+$ ions. A stereospecific ^{18}O-labeling study shows that the *syn*-hydroxyl group is preferentially lost in the syn,anti diol. This high syn specificity indicates that the mechanism of formation of the [M – OH]$^+$ ions involves a reversible interaction of the diol molecules with the *t*-$C_4H_9^+$ ions followed by loss of *tert*-butyl alcohol rather than elimination of H_2O from the MH$^+$ ions. This conclusion is supported by the low stereospecificity of this process under propane CI conditions.

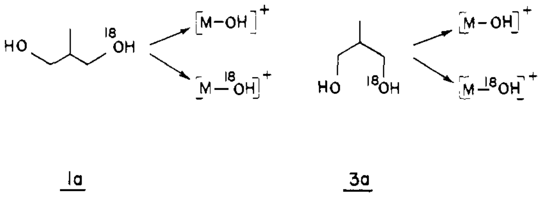
Two general features of isobutane CI mass spectra of alcohols containing more than four carbon atoms are the instability of MH$^+$ and the very high abundance of [M – OH]$^+$ ions.[2] The formation of the [M – OH]$^+$ ions has been often described in terms of H_2O elimination from MH$^+$ (eq 1). If a *second* functional group is present in a configuration which allows formation of *intramolecular* hydrogen bridging, the MH$^+$ ion is greatly stabilized.[3,4] In several β-amino alcohols where such bridging was possible, no elimination of H_2O was observed.[5] In other amino alcohols in which the interfunctional distance was increased, the elimination of H_2O appeared, and its extent was correlated to the distance between the OH and amino groups. The loss of H_2O in the latter was assumed to occur from those ions which had been protonated at the hydroxyl (eq 2); moreover, it has been suggested that the abundance ratio be used as a quantitative measure of the oxygen–nitrogen protonation ratio.[5] We report herein isobutane CI results of stereoisomeric propellane diols which cast new light on the formation of [M – OH]$^+$ ions.

$$ROH \xrightarrow{t\text{-}C_4H_9^+} \underset{\text{unstable}}{R\overset{+}{O}H_2} \rightarrow R^+ + H_2O \qquad (1)$$



$$R_2N{-}X{-}OH \xrightarrow{t\text{-}C_4H_9^+} \begin{cases} R_2\overset{+}{\underset{H}{N}}{-}X{-}OH \quad \text{stable MH}^+ \\ R_2N{-}X{-}\overset{+}{O}H_2 \rightarrow [MH - H_2O]^+ \end{cases} \qquad (2)$$

Scheme I



1a

3a

Results and Discussion

The stereoisomeric propellane diols **1–3** exhibit pronounced stereospecificity under isobutane CI (Figure 1). Only the anti,anti isomer **3**, which is capable of internal hydrogen bridging, gives

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