

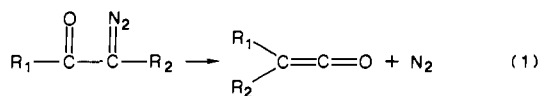
The Oxirene Radical Cation and Its Neutralization in the Gas Phase†

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Abstract: It has been concluded that oxirene radical cations, $[\overline{\text{CH}=\text{CHO}}]^{+\bullet}$, were produced as stable species in the gas phase in the dissociative ionization of vinylene carbonate, oxazole, and isoxazole. Vertical neutralization of $[\overline{\text{CH}=\text{CHO}}]^{+\bullet}$ with xenon, however, did not yield stable oxirene molecules, a species calculated by theory to reside in a shallow well ($32 \text{ kJ}\cdot\text{mol}^{-1}$) on its potential energy surface.

The possibility that oxirene, $\overline{\text{CH}=\text{CHO}}$, is stable has recently attracted considerable attention from theoreticians,¹ because it has been proposed² that oxirenes³ participate as short-lived intermediates in the Wolff rearrangement.



The new experimental technique called neutralization-reionization mass spectrometry⁴ (NRMS) holds considerable promise for the investigation of neutral molecules (like oxirene) and free radicals of unusual structure, which, although they may have been predicted by high-level ab initio molecular orbital theory calculations to be stable, have not yet successfully been generated in the laboratory. Potential fulfillment of the promise arises from the power of the current mass spectrometric methodology for assigning structures to ions in the gas phase.⁵ NR mass spectra are obtained by the partial neutralization of a beam of mass (and structure) selected ions by electron transfer from a target gas. Remaining ions are deflected away and the neutral species are reionized by collision with a second target gas. Thus, for example, the generation and unequivocal identification of the ylide ions $[\text{CH}_2\text{FH}]^{+\bullet}$,⁶ $[\text{CH}_2\text{ClH}]^{+\bullet}$,⁷ $[\text{CH}_2\text{OH}_2]^{+\bullet}$,⁷ and $[\text{CH}_2\text{NH}_3]^{+\bullet}$ ⁷ has given rise to several NRMS studies to investigate the stability of the neutral counterparts.^{8,9} Similar experiments with $[\text{HOC}(\text{O})\text{OH}]^{+\bullet}$ ^{10a} and $[\text{HOC}(\text{O})\text{NH}_2]^{+\bullet}$ ^{10b} yielded the first experimental evidence for the stability of their neutral counterparts, carbonic and carbamic acid.

The $[\text{H}_2, \text{C}_2, \text{O}]$ system has only one well-known neutral and radical-cation structure, namely ketene, $\text{CH}_2=\text{C}=\text{O}$. Recently, however, $[\text{HC}\equiv\text{COH}]^{+\bullet}$ was obtained via CO loss from $[\text{HC}\equiv\text{CC}(\text{O})\text{OH}]^{+\bullet}$, and neutralization-reionization of this species identified ethynol as a stable species in the gas phase.¹¹ In addition, collision-induced charge reversal of the ion $[\text{CHCH}=\text{O}]^+$ from vinylene carbonate was shown to generate stable $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ ions, which may well have the oxirene structure; their identity could, however, not be established from the charge-reversal spectrum.¹²

In addition to the ketene and ethynol radical cations, ab initio molecular orbital theory calculations¹³ predicted $[\overline{\text{CH}=\text{CHO}}]^{+\bullet}$, $[\text{C}=\text{OCH}_2]^{+\bullet}$, and $[\text{C}=\text{CHOH}]^{+\bullet}$ to be stable. The oxirene radical cation, $[\overline{\text{CH}=\text{CHO}}]^{+\bullet}$, was calculated to have a heat of formation, ΔH_f° , $257 \text{ kJ}\cdot\text{mol}^{-1}$ above ionized ketene, but ring-opening required no less than $161 \text{ kJ}\cdot\text{mol}^{-1}$. (The ring-opened form was predicted to rearrange to $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ and spontaneously fragment into $[\text{CH}_2]^{+\bullet} + \text{CO}$.) An ion residing in such a deep well should certainly be experimentally accessible. Since

neutral oxirene was also predicted to be stable,¹ vertical neutralization of the radical cation may suffice to produce the former, provided that geometry differences between them are not too great.^{4a} According to the most advanced ab initio molecular orbital theory calculations,^{1c} oxirene lies in a well, albeit shallow, $32 \text{ kJ}\cdot\text{mol}^{-1}$ being required for ring opening. The latter transition state (as with the ion) is predicted to decompose spontaneously to $\text{CH}_2 + \text{CO}$.

In this paper, we describe experiments performed on the m/z 42, $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ ions derived from the $\text{C}_3\text{H}_3\text{NO}$ isomers oxazole and isoxazole and from vinylene carbonate, $\text{C}_3\text{H}_2\text{O}_3$.

Experimental Section

Metastable ion (MI) and collisional activation (CA) mass spectra were recorded as described previously¹⁴ with a VG Analytical ZAB-2F mass spectrometer. A $100\text{-}\mu\text{A}$ electron beam of 70-eV energy was used. The accelerating voltage was 8 kV , and oxygen was the collisional activation gas. In the collision-induced dissociative ionization (CIDI) experiments¹⁵ only the metastably generated neutral species were allowed to enter the (second) collision cell, where they were ionized upon collision with helium. To record NR mass spectra the ZAB-2F was modified as described

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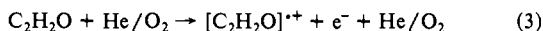
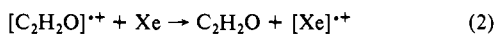
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† Dedicated to Professor F. W. McLafferty on the occasion of his 65th birthday.

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in ref 16. In the present NR experiments xenon was used as the neutralization agent (first collision cell) for the mass-selected ions (eq 2).



Helium and oxygen were present in the second collision cell for reionization of the neutrals (eq 3). The gas pressures were adjusted to give a main beam transmission (T) of 90%. All ion kinetic energy spectra as well as the neutralization-reionization efficiencies were corrected for isotopic contributions from adjacent ions of lower mass. (For oxazole and isoxazole, 4.0 and 5.6%, respectively, of the m/z 42 ion flux were isotopic contributions from m/z 41.) Unless otherwise stated, interference was negligible.

Additional experiments were performed with a hybrid mass spectrometer¹⁷ of BEQQ geometry, a VG Analytical ZAB-2FQ instrument. The $[H_2, C_2, O]^{++}$ ions were neutralized with Xe (70% T) and reionized with O_2 (70% T) in the second field-free region. The recovery signal, m/z 42 ions, was selectively transmitted through the electric sector, and the ions were analyzed via their N_2 (60% T) collision-induced dissociation in the quadrupole system,¹⁷ before which the ion translational energy had been reduced from 8 kV to 80 eV. Signal averaging (25 scans) was necessary to record these spectra. For comparison with the above spectra, CA mass spectra of $[H_2, C_2, O]^{++}$ ions, not neutralized-reionized in the second field-free region, were recorded with the quadrupole system under similar conditions.

In the above experiments all beam-defining slits were fully open to obtain maximum signal strength and to minimize energy-resolving effects. Metastable peak shapes were recorded under higher energy resolution conditions: the main ion beam width at half-height was 3 V at an accelerating voltage of 8 kV. Kinetic energy releases, $T_{0.5}$, were measured from the peak widths at half-height and evaluated using established methods.¹⁸

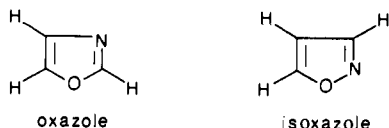
Daughter-ion appearance energy (AE) values were obtained with an apparatus comprising an electrostatic electron monochromator with a quadrupole mass analyzer and minicomputer data system.¹⁹

All samples were commercially available and showed no detectable impurities.

Results and Discussion

Energetics and Metastable Decompositions. C_3H_3NO Isomers.

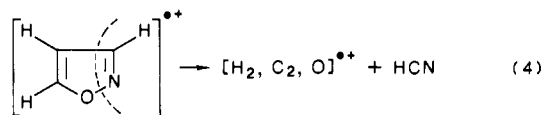
The normal mass spectra of oxazole and its isomer isoxazole contained a peak at m/z 42, $[H_2, C_2, O]^{++}$, being 19 and 10%, respectively, of the molecular ion, base peak. A low ion-source



pressure was of crucial importance, because under chemical ionization conditions part of the m/z 42 flux was $[H_4, C_2, N]^+$, generated by CO loss from the protonated molecules. In the present experiments $[H_4, C_2, N]^+$ interference was negligible.

The MI mass spectra of the molecular ions were dominated by m/z 41, $[H_3, C_2, N]^{++}$. (The structure of the latter ions will be discussed elsewhere.) However, for $[isoxazole]^{++}$ generation of m/z 42 was also metastable (4.8% of m/z 41).²⁰ The kinetic $[isoxazole]^{++}$ release, $T_{0.5}$, which accompanied generation of m/z 42, was 34 meV, from which it is proposed that (most of) the $[H_2, C_2, O]^{++}$ ions are produced not far from the thermochemical threshold. However, the metastable peak was very broad based, $T_{0.1} = 171$ meV, and is therefore probably composite, containing a second (minor) component with a large kinetic energy release.

The structure of the neutral $[H, C, N]$ lost upon metastable generation of $[H_2, C_2, O]^{++}$ from $[isoxazole]^{++}$ can be identified by means of its CIDI mass spectrum.¹⁵ Although the spectrum also contained peaks corresponding to $[CO]^{++}$, $[O]^{++}$, and $[C]^{++}$, it was evident from the m/z 26:27 ratio, ca. 0.3,²¹ the presence of m/z 13, $[CH]^+$, and the absence of m/z 15, $[NH]^{++}$, that the $[H, C, N]$ neutrals have the HCN structure, present as a unit in $[isoxazole]^{++}$.



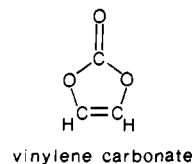
The AE of m/z 41, $[H_3, C_2, N]^{++}$, from $[isoxazole]^{++}$ was measured to be 11.34 ± 0.05 eV, reported earlier as 11.8 eV.^{22a} A direct measurement of the AE of the $[H_2, C_2, O]^{++}$ ions was not possible; at very low ionizing electron energy, m/z 42 was completely due to the ^{13}C and ^{15}N contributions from m/z 41. Thus, the AE of m/z 42, $[H_2, C_2, O]^{++}$, must significantly be greater than 11.34 eV. Now it was concluded (see above) that the majority of the $[H_2, C_2, O]^{++}$ ions were metastably generated at an energy near the thermochemical threshold. Thus, ΔH_f° for these ions must be greater than 1038 kJ·mol⁻¹ (from AE > 11.34 eV, ΔH_f° (isoxazole) = 78.6 ± 0.5 kJ·mol⁻¹²³ and ΔH_f° (HCN) = 135.1 kJ·mol⁻¹²⁴). For comparison, ΔH_f° ($[H_2C=C=O]^{++}$) = 880 kJ·mol⁻¹.²⁴

For $[oxazole]^{++}$ the loss of $[H, C, N]$ is not a metastable process, and therefore the AE of m/z 41, 11.34 ± 0.05 eV (0.3 eV higher than earlier reported^{22b}), cannot provide information about the heat of formation of the $[C_2, H_2, O]^{++}$ ions, whose AE is also greater than that of m/z 41.

The $[H_2, C_2, O]^{++}$ ions from the above two precursors underwent only one metastable decomposition, namely to m/z 14, $[CH_2]^{++}$. The kinetic energy releases and shapes of the metastable peaks were closely similar to those reported earlier for ketene radical cations²⁵ ($T_{0.5} = 2.8$ meV). It should be noted that the apparent, weak H^+ loss peak in the MI mass spectra of the $[H_2, C_2, O]^{++}$ ions from the $[C_3H_3NO]^{++}$ precursors was due to isotopic interference from m/z 41 ions.

Ethynol radical cations, $[HC\equiv COH]^{++}$, whose ΔH_f° has been calculated and measured to be 1070 – 1072 kJ·mol⁻¹,^{13,26} also lose CO metastably, but the kinetic energy release for that process is much larger, $T_{0.5} = 26$ meV.¹¹ Clearly, therefore, the $[H_2, C_2, O]^{++}$ ions derived from the two C_3H_3NO isomers cannot have the $[ethynol]^{++}$ structure.

Vinylene Carbonate. The AE of m/z 42, $[H_2, C_2, O]^{++}$, from vinylene carbonate was measured to be 11.86 ± 0.05 eV. (The process does not yield a metastable peak; CO loss is the sole metastable reaction.) ΔH_f° ($[H_2, C_2, O]^{++}$) = 1119 ± 10 kJ·mol⁻¹, using ΔH_f° (vinylene carbonate) = -419 ± 3 kJ·mol⁻¹²³ and ΔH_f° (CO₂) = -393.5 kJ·mol⁻¹.²⁴ The $[H_2, C_2, O]^{++}$ daughter



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(20) The signal at m/z 40 in the MI mass spectrum was completely due to isotopic interference from m/z 68 and not to metastable $[isoxazole]^{++}$ as reported earlier.^{22a}

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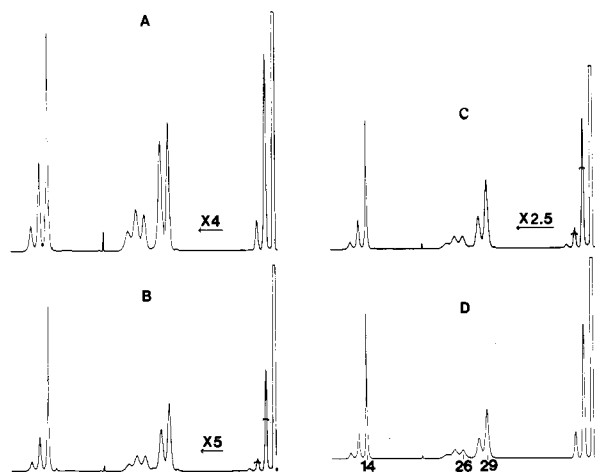


Figure 1. Oxygen (90% *T*) collisional activation mass spectra of [CH₂=C=O]^{•+} (A) and the source-generated *m/z* 42 daughter ions from [isoxazole]^{•+} (B), [oxazole]^{•+} (C), and [vinylene carbonate]^{•+} (D). Isotopic contributions from *m/z* 41 are indicated with bars; the peaks at *m/z* 15, 27, and 39 are completely due to isotopic interference from *m/z* 41 (see text for details).

ion also has a ketene-like MI mass spectrum (*m/z* 42 → *m/z* 14, *T*_{0.5} = 2.6 meV); moreover, the peak has the unusual shape, which has aroused earlier attention in studies of ionized ketene.^{25,27} Thus, generation of [HC≡COH]^{•+} can again be ruled out.

Before describing the collision characteristics of these [H₂, C₂, O]^{•+} ions, it is useful to consider the predictions of the theoretical calculations of Bouma et al.¹³ in comparison with our results from AE measurements. The former show Δ*H*_f[°]([oxirene]^{•+}) = 1137 kJ·mol⁻¹ and a barrier of 161 kJ·mol⁻¹ for rearrangement to [CH₂=C=O]^{•+}. On the basis of the AE measurement and the resulting Δ*H*_f[°] value, we propose *at this stage*, that [oxirene]^{•+} ions are generated upon dissociative ionization of vinylene carbonate (and possibly oxazole and isoxazole), although some co-generation of [CH₂=C=O]^{•+} cannot be ruled out.

The similar kinetic energy releases for CO loss from [CH₂=C=O]^{•+} and the [H₂, C₂, O]^{•+} daughter ions from [vinylene carbonate]^{•+} can be explained as follows. Upon metastable fragmentation the [CH₂=C=O]^{•+} ions have to cross the ridge on their potential energy surface, which separates the ²B₁ (ground) and ²A₁ (excited) states so as to yield the most stable [CH₂]^{•+} conformation, ²A₁.²⁷ Therefore, the transition state for rearrangement of [CH=CHO]^{•+} into [CH₂=C=O]^{•+}, calculated to have an energy of 1298 kJ·mol⁻¹,¹³ and the latter's dissociation limit (Δ*H*_f[°]([CH₂]^{•+}) + Δ*H*_f[°](CO) = 1275 kJ·mol⁻¹²⁴) are thus of similar energy. Consequently, CO loss from both isomers involves the same transition state, and so their MI mass spectra will be indistinguishable. This argument is however disputed; Bouma et al.¹³ stated that distortion of the ²B₁ to the ²A₁ structure can lead directly to ground state [CH₂]^{•+} (²A₁). An alternative explanation for the MI results is that the calculated energy of the

transition state for rearrangement of [CH=CHO]^{•+} into [CH₂=C=O]^{•+}, i.e. [CH=CHO]^{•+}, is too high by at least 23 kJ·mol⁻¹. This would also explain the presence of a signal at *m/z* 42 in the charge-reversal mass spectrum of [CH=CHO]^{•+}.

It now remains to describe and consider the CA and NR mass spectra of these ions in light of the above proposal.

Collision Experiments. The O₂ (90% *T*) CA mass spectra of the *m/z* 42 daughter ions from [isoxazole]^{•+}, [oxazole]^{•+}, and [vinylene carbonate]^{•+}, shown in Figure 1, can easily be distinguished from that of [HC≡COH]^{•+}. In the latter's spectrum¹¹ *m/z* 29 is ca. 3 times as intense as *m/z* 14, *m/z* 26 is only a minor peak, and a small but distinct peak at *m/z* 17, [OH]⁺, is present. The above CA mass spectra do contain the same peaks as the CA mass spectrum of [CH₂=C=O]^{•+} (shown in Figure 1A) but in

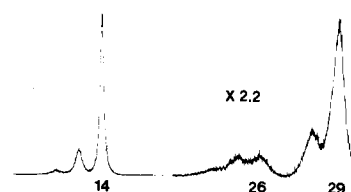


Figure 2. Oxygen (90% *T*) collisional activation mass spectrum of the [H₂, C₂, O]^{•+} ions generated upon N₂ collision-induced dissociation of [vinylene carbonate]^{•+} in the first field-free region. The *m/z* 24–29 region was recorded with a charge of –1800 V on the collision cell in order to increase the resolution and to free the region from interference.

different ratios: the *m/z* 29:28, 29:41, and 26:25 ratios are larger in the former, and *m/z* 21, the dication, is less intense. These differences are emphasized in the CA mass spectrum of the *m/z* 42 ions generated by collision-induced dissociation of ionized vinylene carbonate in the first field-free region of the mass spectrometer (see Figure 2); the *m/z* 29:28 and 26:25 ratios are 3.2 and 1.1, respectively. The [H₂, C₂, O]^{•+} ions generated in the first field-free region have a lower translational energy, 3900 eV. Comparison with the CA mass spectra of (faster) source-generated *m/z* 42 ions is nevertheless allowed because the latter spectra were not significantly affected by lowering the accelerating voltage. The above observations are in keeping with the proposal that [isoxazole]^{•+}, [oxazole]^{•+}, and [vinylene carbonate]^{•+} are

producing [CH=CHO]^{•+} ions. The presence of this isomer can explain the more prominent *m/z* 29, [HCO]⁺, and 26, [HC≡CH]^{•+}, peaks in the *m/z* 24–29 region, both of which are present as a unit in [CH=CHO]^{•+} (and indeed, not in the other two isomers, which are calculated¹³ to be stable, [C=OCH₂]^{•+} and [C=CHOH]^{•+}). The increasing *m/z* 29:28 ratio in going from Figure 1A to 1D and to the spectrum of the *m/z* 42 ions, generated from [vinylene carbonate]^{•+} in the first field-free region (Figure 2), can be explained by each successive spectrum having a higher [oxirene]^{•+} content (see also below). That some of the [H₂, C₂, O]^{•+} ions from [isoxazole]^{•+} have the ketene structure is in keeping with the presence of a broad component in the *m/z* 42 peak in the MI mass spectrum of [isoxazole]^{•+}. Thus, it is proposed that [isoxazole]^{•+}, [oxazole]^{•+}, and [vinylene carbonate]^{•+} lose HCN/CO₂ with ring closure to yield oxirene radical cations, [CH=CHO]^{•+}.

At this point it should be noted that Bouma et al.¹³ showed that rearrangement of [CH₂=C=O]^{•+} to other stable [H₂, C₂, O]^{•+} isomers is not possible, the calculated dissociation limit to [CH₂]^{•+} + CO being lower than the barriers for rearrangement. Therefore, the peaks at *m/z* 29 and 26 in the CA mass spectrum of [CH₂=C=O]^{•+} (see Figure 1A) are somewhat unexpected. To gain more insight into the generation of these fragment ions, CA mass spectra of [CH₂=C=O]^{•+} were recorded with the quadrupole system of the Toronto ZAB-2FQ.¹⁷ At an ion translational energy of 100 eV the signal at *m/z* 26 dominated the *m/z* 24–29 region of the spectrum, but it slowly decreased upon reducing the ion energy; *m/z* 29 was the sole peak in the *m/z* 24–29 region at an ion energy of 15 eV. Independent of the ion energy, *m/z* 14 was base peak of the spectrum, but its relative intensity increased upon reducing the ion energy. Thus, upon reduction of the ion collision energy, the thermochemically favorable dissociations become increasingly important (see below).²⁴



In addition, it can be concluded that in order to yield *m/z* 29 and 26, [ketene]^{•+} ions must be able to communicate with isomer(s) at energies below the dissociation limit to [CH₂]^{•+} + CO. Although this is in contradiction with the theoretical predictions¹³ (see above), excited states of [ketene]^{•+} may be involved, which

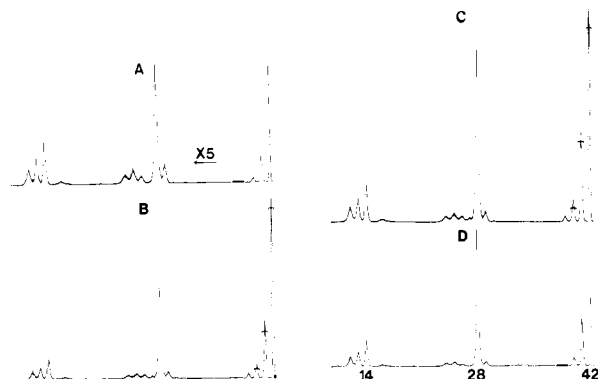
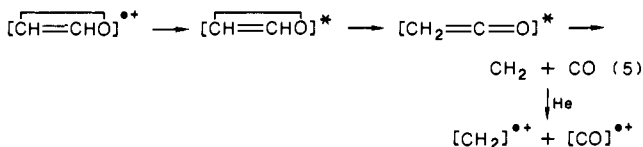


Figure 3. Xenon (90% *T*)-oxygen (90% *T*) neutralization-reionization mass spectra of $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ (A) and the source-generated m/z 42 daughter ions from $[\text{isoxazole}]^{+\bullet}$ (B), $[\text{oxazole}]^{+\bullet}$ (C), and $[\text{vinylene carbonate}]^{+\bullet}$ (D). Isotopic contributions from m/z 41 are indicated with bars; the peaks at m/z 27 and 39 are completely due to isotopic interference from m/z 41 (see text for details).

were not considered by Bouma et al.

Figure 3 presents the Xe (90% *T*)-O₂ (90% *T*) NR mass spectra of the m/z 42 daughter ions from $[\text{isoxazole}]^{+\bullet}$, $[\text{oxazole}]^{+\bullet}$, and $[\text{vinylene carbonate}]^{+\bullet}$. The spectra differ significantly from the corresponding CA mass spectra (see Figure 1), and the recovery signals at m/z 42 are not as intense as those in the NR mass spectra of $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ (see Figure 3A) and $[\text{HC}\equiv\text{COH}]^{+\bullet}$ (see ref 8). Instead, the spectra are dominated by m/z 28, $[\text{CO}]^{+\bullet}$, and 14, $[\text{CH}_2]^{+\bullet}$ (and their fragments), which are proposed largely to be generated via reaction 5.



According to the ab initio molecular orbital theory calculations,^{1c} oxirene molecules require 32 kJ·mol⁻¹ of internal energy before they can rearrange into ketene (an earlier study^{1b} reported 8 kJ·mol⁻¹ for the barrier), at which energy the latter will spontaneously fragment into CH₂ + CO. Thus, a considerable fraction of the $[\text{CH}=\text{CHO}]$ molecules, generated via vertical charge exchange neutralization of the corresponding radical cation, must have more than 32 kJ·mol⁻¹ internal energy (see also ref 16).

Compared with the CA mass spectrum, the NR mass spectrum of $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ contains more intense signals at m/z 28, $[\text{CO}]^{+\bullet}$, and 14, $[\text{CH}_2]^{+\bullet}$, especially when helium is the reionization agent (see ref 8). We therefore propose that here too, some of the neutralized ions fragment into CH₂ + CO, which are then ionized in the second cell. Analogous behavior was found for $[\text{CH}_3\text{CO}]^{+\bullet}$; although the acetyl radical is stable, the neutralized ions fragmented to a large extent into CO + $\cdot\text{CH}_3$.¹⁶

That generation of CH₂ + CO from neutralized $[\text{ketene}]^{+\bullet}$ and the neutralized m/z 42 ions from $[\text{vinylene carbonate}]^{+\bullet}$ takes place via different channels was evident from NR mass spectra recorded under high-energy resolution conditions; the width at half-height of the signal at m/z 28 was 67 and 42 V, respectively. Note that reionization does not lead to a major change in the spread of kinetic energies in the incident beam; the major cause of peak broadening in these processes is kinetic energy release on fragmentation.¹⁶

The presence of a recovery signal at m/z 42 in the NR mass spectrum of the (source-generated) $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ daughter ions from $[\text{isoxazole}]^{+\bullet}$ and $[\text{vinylene carbonate}]^{+\bullet}$ could be evidence for the stability of oxirene molecules on the time ($\sim 0.5 \mu\text{s}$) and energy scale of these experiments. This conclusion is only justifiable if these m/z 42 fluxes represent pure $[\text{CH}=\text{CHO}]^{+\bullet}$. However, from a comparison of the corresponding CA mass spectra (Figure 1C and D) with the CA mass spectrum of the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ ions from $[\text{vinylene carbonate}]^{+\bullet}$ generated in the

Table I. Relative Neutralization-Reionization (NR) Efficiencies, *R*, of $[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ Ions of Different Origin Using Xenon as Neutralization Agent (90% *T*) and Helium or Oxygen as Reionization Agent (90% *T*) (See Text for Details)

precursor	relative NR efficiency, <i>R</i>	
	Xe-He	Xe-O ₂
$[\text{H}_2\text{C}=\text{C}=\text{O}]^{+\bullet}$	1.00	1.00
$[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ (isoxazole)	0.51	0.47
$[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ (oxazole)	0.37	0.32
$[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ (vinylene carbonate)	0.17	0.17
$[\text{HC}\equiv\text{COH}]^{+\bullet}$	1.01	1.16

Table II. Collisional Activation (CA) Mass Spectra of Ion Source Generated (S) and Neutralized-Reionized (NR) $[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ Ions of Low Translational Energy (80 eV)^a (See Text for Details)

<i>m/z</i>	relative abundances			
	$[\text{H}_2\text{C}=\text{C}=\text{O}]^{+\bullet}$		$[\text{C}_2, \text{H}_2, \text{O}]^{+\bullet}$ from $[\text{oxazole}]^{+\bullet}$	
	S	NR	S	NR
29	55	54	100	66
28	30	30	13	47
26	100	100	34	100
25	37	38	14	30
14	79	90	43	74
13	13	24	6	20

^a The accuracy of the peak intensities in the S-CA and NR-CA mass spectra is ± 5 and $\pm 20\%$, respectively.

first field-free region (Figure 2), it was concluded that some $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ is cogenerated with $[\text{CH}=\text{CHO}]^{+\bullet}$ upon dissociative ionization in the source (see above). Additional information can be obtained from the neutralization-reionization efficiencies, *R*,⁹ in the Xe-O₂ and Xe-He NR mass spectra; *R* = [m/z 42 yield in the NR mass spectrum: m/z 42 flux entering the neutralization cell]. The results are presented in Table I. That changing the reionization agent did not significantly affect the relative NR efficiencies can be explained in two ways:

(1) $[\text{CH}=\text{CHO}]$ is indeed stable, as predicted by theory,¹ and the NR efficiencies of $[\text{CH}=\text{CHO}]^{+\bullet}$ and $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ are similarly affected by substituting O₂ for He.

(2) $[\text{CH}=\text{CHO}]$ is *not* stable, and the recovery signals in the NR mass spectra of the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ daughter ions from $[\text{isoxazole}]^{+\bullet}$, $[\text{oxazole}]^{+\bullet}$, and $[\text{vinylene carbonate}]^{+\bullet}$ arise solely from cogenerated $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$.

Note that the relative NR efficiencies of $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ and $[\text{HC}\equiv\text{COH}]^{+\bullet}$ did change upon substituting O₂ for He.

In order to identify the structure of the surviving $[\text{H}_2, \text{C}_2, \text{O}]$ neutral species, the CA mass spectra of the m/z 42 recovery signals, resulting from neutralization-reionization in the second field-free region, were measured in the quadrupole system of the Toronto ZAB-2FQ (see the Experimental Section). The results for $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ and the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ ions from $[\text{oxazole}]^{+\bullet}$ are shown in Table II. The CA mass spectra of the neutralized-reionized $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ ions and the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ ions from $[\text{oxazole}]^{+\bullet}$ are very closely similar. The reference spectra, i.e. CA mass spectra of ions *not* neutralized-reionized in the second field-free region, are, however, distinctly different. That from $[\text{CH}_2=\text{C}=\text{O}]^{+\bullet}$ matches its NR-CA mass spectrum, but the S-CA and NR-CA mass spectra of the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ daughter ions from $[\text{oxazole}]^{+\bullet}$ do not resemble each other. The neutralization-reionization conditions used in these latter experiments, although no longer single-collision conditions (double and triple encounters made up ca 20% of the collision events⁵), were highly unlikely to have caused complete collision-induced isomerization or decomposition of any neutral oxirene. We therefore conclude that *if neutral oxirene has any stability its detection lies outside the scope of the present experiments* and that the recovered m/z 42 ions in the NR mass spectra of the $[\text{H}_2, \text{C}_2, \text{O}]^{+\bullet}$ daughter

ions from [isoxazole]^{•+}, [oxazole]^{•+}, and [vinylene carbonate]^{•+} have the ketene structure. Thus, ca. 50, 35, and 17%, respectively, of the [H₂, C₂, O]^{•+} ions generated upon dissociative ionization of the three precursors must have the ketene structure. The observed instability of oxirene is in keeping with the absence of *direct* experimental evidence for the role of oxirenes in the Wolff rearrangement; although sought,³ no oxirenes have been isolated or spectroscopically observed.

The significant [CH₂=C=O]^{•+} content of the source-generated *m/z* 42 ions from [oxazole]^{•+} is compatible with the presence of only a weak broad component in the metastable peak for their generation in the second field-free region (see above). As found for [vinylene carbonate]^{•+}, for *source-generated* [H₂, C₂, O]^{•+} ions the more energy-demanding process, i.e. generation of [CH₂=C=O]^{•+}, becomes relatively more important. This behavior has been observed before. For example,⁹ (short-lived) [ClCH₂COOH]^{•+} ions fragmenting in the ion source produce mainly the less stable [H₃, C, Cl]^{•+} isomer, [H₂CClH]^{•+}, whereas the metastably fragmenting ions largely yield [CH₃Cl]^{•+}.

Conclusions

It has been shown that [vinylene carbonate]^{•+}, [oxazole]^{•+}, and [isoxazole]^{•+} generate the oxirene radical cation, [CH=CHO]^{•+}. The small differences in the collisional activation mass spectra of the source-generated *m/z* 42 ions from these precursors were explained by the cogeneration of [ketene]^{•+}. On the basis of neutralization-reionization experiments, it was established that vinylene carbonate, oxazole, and isoxazole generate ca. 17, 35, and 50%, respectively, of [CH₂=C=O]^{•+} in addition to

[CH=CHO]^{•+} upon dissociative ionization in the ion source of the mass spectrometer. A more pure flux of [CH=CHO]^{•+} was obtained upon collision-induced fragmentation of [vinylene carbonate]^{•+} in the first field-free region. From a comparison of the latter CA mass spectrum with that of the corresponding source-generated [H₂, C₂, O]^{•+} ions, which contain only 17% [CH₂=C=O]^{•+}, it can be concluded that the former spectrum will be close to that for pure [oxirene]^{•+}.

The neutralization-reionization mass spectra of the source-generated *m/z* 42 ions from the three precursors are dominated by *m/z* 28, [CO]^{•+}, and *m/z* 14, [CH₂]^{•+}, which arise from oxirene molecules, [CH=CHO], being unstable on the time and energy scale of these experiments. The presence of a recovery signal at *m/z* 42 in the neutralization-reorientation mass spectra is ascribed to cogeneration of [CH₂=C=O]^{•+}.

Experiments are in progress to identify the analogous species [CH=CHNH]^{•+}, [CH=CHS]^{•+}, and their neutral counterparts.

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Registry No. Oxirene radical cation, 94664-69-4; vinylene carbonate, 872-36-6; oxazole, 288-42-6; isoxazole, 288-14-2; oxirene, 157-18-6; xenon, 740-63-6.

Structure and Energetics of C₄H₄^{•+} in the Gas Phase. Photoelectron Spectrum of Methylene-cyclopropene

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Abstract: The adiabatic and vertical ionization energies of methylenecyclopropene (**1**) have been determined by photoelectron spectroscopy to be 8.15 ± 0.03 and 8.41 ± 0.05 eV, respectively. An analysis of the A₁ vibrational frequency difference (Δν) on going from the ground state to the ²B₂ (π) state of the radical cation of **1** (**1**^{•+}) has led to an explanation for the relatively small value of Δν obtained on comparing cyclopropenone (**3**) and **3**^{•+}. The heats of formation (Δ*H*_f^o) of **1**^{•+} and cyclobutadiene radical cation are calculated to be 281.5 ± 3 and 293 ± 4 kcal/mol, respectively. Both these values and the *m/z* 26/27 ratios obtained from collisionally activated decomposition spectra of *m/z* 52 ions generated from **1**, benzene, and pyridine support the assignment of **1**^{•+} as the lowest energy structure of C₄H₄^{•+} in the gas phase.

The energetics and structures of C₄H₄ radical cations (C₄H₄^{•+}) obtained as fragmentation products of larger molecules in the gas phase have attracted considerable interest in recent years. The consensus is that *at least* two different ions are formed, a cyclic species and one or more linear species, which occur in various proportions depending on the conditions and origin. Both the cyclobutadiene radical cation¹ and the methylenecyclopropene radical cation (**1**^{•+})^{1d,2} have been suggested as structures for the

lowest energy form of C₄H₄^{•+}, but firm evidence in support of either structure has not been reported. Since the values of the heats of formation (Δ*H*_f^o) of these cations are central to the analysis of this problem, the direct determination of the adiabatic ionization energy (IE_a) of methylenecyclopropene (**1**) is of considerable interest.

From a spectroscopic standpoint, **1** is an interesting molecule for several reasons. Because of its high ring strain, the manifolds of σ and σ* orbitals are expected to be shifted significantly relative to those of unstrained hydrocarbons. In addition, **1** is an ex-

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