

Unimolecular Reactions of Isolated Organic Ions: Loss of Carbon Monoxide from the Oxonium Ion $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ via Double Hydrogen Transfer

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The reactions of the metastable oxonium ion $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ have been investigated. This $\text{C}_4\text{H}_7\text{O}^+$ species was generated by ionisation and alkyl radical loss from allyl ethyl or allyl propyl ether. $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ is apparently ideally suited to fragmentation via simple cleavage to form the favourable products $\text{CH}_2=\text{CHCH}_2^+$ and CH_2O . However, at low internal energies, expulsion of a neutral species having a mass of 28 amu takes place essentially to the exclusion of CH_2O loss. ^2H - and ^{13}C -labelling experiments reveal that it is carbon monoxide which is eliminated, via double hydrogen transfer between the developing products accessible to C–O bond fission. The role of ion–neutral complexes in these hydrogen transfer steps is discussed.

The chemistry of $\text{C}_n\text{H}_{2n+1}\text{O}^+$ oxonium ions has attracted considerable attention from organic mass spectroscopists for at least thirty years.¹ The behaviour of the lower members of this homologous series of ions has been well documented and is intelligible in some detail. Several ions derived from ionised ethers fragment via formal simple cleavage [e.g. $\text{CH}_3\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$ and $(\text{CH}_3)_2\text{CH}^+\text{O}=\text{CH}_2$ expel CH_2O^2] or by C–O bond fission with an associated single hydrogen transfer (SHT) [e.g. $\text{CH}_3\text{CH}_2^+\text{O}=\text{CH}_2$ eliminates C_2H_4^3].

In contrast, the reactions of the corresponding $\text{C}_n\text{H}_{2n-1}\text{O}^+$ oxonium ions have not been studied in such a systematic fashion. Aside from the acylium ions, $\text{C}_{n-1}\text{H}_{2n-1}\text{CO}^+$, which tend to dissociate exclusively by CO loss,⁴ only a few $\text{C}_n\text{H}_{2n-1}\text{O}^+$ ions have been investigated.^{5–10} The limited amount of experimental information suggests that elimination of CO often occurs from metastable $\text{C}_4\text{H}_7\text{O}^+$ ions, even when there is no intact carbonyl group in the initial structure. Thus, a preliminary account of the chemistry of $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$, **1**, reported that this ion expels a neutral of mass 28 amu, rather than CH_2O , at low internal energies.⁸ Similarly, $\text{CH}_2=\text{CHCH}=\text{O}^+\text{CH}_3$, **2**, loses $\text{CO}/\text{C}_2\text{H}_4$, CH_2O or H_2O .^{9,10} In the latter case, ^2H and ^{13}C -labelling data revealed that the neutral species of mass 28 amu which was lost was mainly or wholly carbon monoxide.¹⁰ Elimination of CO from **1** and **2** corresponds to double and triple hydrogen transfer (DHT and THT, respectively).

Results and Discussion

The reactions of metastable $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ ions are shown in Table 1. Corresponding data for the dissociation of ^2H - and ^{13}C -labelled analogues of **1** are given in Tables 2 and 3, respectively.

The oxonium ions were generated by dissociative electron ionisation of the appropriate allyl ethyl or allyl propyl ethers. It is assumed that fragmentation of the ionised ethers via α -cleavage takes place more rapidly than rearrangement of the original radical cation. This assumption is in accord with the well known propensity of ionised ethers to undergo α -cleavage in fast dissociations occurring in the ion source.¹¹

Structure of the Neutral Species Lost from 1.—The data of Table 1 confirm the earlier finding⁸ that **1** fragments at low internal energy by loss of CO and/or C_2H_4 , rather than by expelling CH_2O via σ -cleavage. The relative abundance (RA) of CH_2O and H_2O loss from metastable **1** is at most 0.5% of that of the dominant channel for $\text{CO}/\text{C}_2\text{H}_4$ elimination. This

Table 1 Reactions of metastable $\text{C}_4\text{H}_7\text{O}^+$ ions generated as $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$

	Neutral species lost			
	H_2O	$\text{CO}/\text{C}_2\text{H}_4$	CH_2O	C_3H_6
RA ^a	<0.5	99	<0.5	<0.5
$T_{\frac{1}{2}}^b$	c	10.7	c	c

^a RA = relative abundance, measured by product ion counts (corresponding to metastable peak areas) for ions dissociating in the second field-free region of the 'MMM' instrument, and normalised to a total product ion count of 100 units. ^b $T_{\frac{1}{2}}$ = Kinetic energy release, quoted in kJ mol^{-1} , as estimated from the width at half height of the relevant metastable peak. ^c Peak too weak to permit a meaningful measurement.

behaviour is remarkable. Loss of CH_2O from **1** appears to be favoured by both kinetic and thermodynamic parameters: it can occur by simple fission of the C–O σ -bond in **1**; moreover, it affords the delocalised allyl cation, which is the most stable isomer of C_3H_5^+ ,^{12–14} as the ionic product.

However, consideration of the relevant energetics,^{15–20} Table 4, reveals that rearrangement to give $(\text{CH}_3)_2\text{CH}^+$ and CO leads to products of lower total enthalpy of formation than those accessible by CH_2O loss. Furthermore, elimination of C_2H_4 from **1** also affords products which are lower in energy than $\text{CH}_2=\text{CHCH}_2^+$ and CH_2O .

The ^2H - and ^{13}C -labelling data establish that the neutral species lost from **1** is CO rather than C_2H_4 . Thus, $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$ expels a neutral of mass 28 amu, which can only be CO; the corresponding signals for loss of heavier neutral species of mass 29 ($\text{C}_2\text{H}_3\text{D}$), 30 ($\text{C}_2\text{H}_2\text{D}_2$), 31 (C_2HD_3) and 32 ($\text{CD}_2\text{O}/\text{C}_2\text{D}_4$) amu are of negligible importance ($\leq 1\%$ of that for CO loss), Fig. 1. Similarly, $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{C}^{13}\text{CH}_2$ eliminates ^{13}CO with high selectivity ($> 99\%$). This result shows that the carbon atom in the eliminated carbon monoxide originates exclusively from the formaldehyde entity of **1**.

Structure of the Product Ion.—Attempts to determine the structure of the product ion at m/z 43 by accurate mass measurements or collision-induced dissociation (CID) experiments did not lead to such unambiguous conclusions as those which follow from the ^2H - and ^{13}C -labelling results. This ambiguity reflects the rather low relative intensity of the m/z 43 signal in the conventional mass spectra of some of the precursors from which **1** is generated. An additional complication is that at least part of the signal at m/z 43 may arise by routes other than $\text{CO}/\text{C}_2\text{H}_4$ loss from **1**.

Table 2 Reactions of metastable $C_4H_{7-n}D_nO^+$ ions

Initial ion structure	Neutral species lost									
	CO/C_2H_4		C_2H_3D		$C_2H_2D_2/CH_2O$		$C_2HD_3/CHDO$		C_2D_4/CD_2O	
	RA ^a	$T_{\frac{1}{2}}$ ^b	RA ^a	$T_{\frac{1}{2}}$ ^b	RA ^a	$T_{\frac{1}{2}}$ ^b	RA ^a	$T_{\frac{1}{2}}$ ^b	RA ^a	$T_{\frac{1}{2}}$ ^b
$CH_2=CHCH_2^+O=CD_2$	>98	10.8	<0.5	<i>c</i>	<0.5	<i>c</i>	<0.5	<i>c</i>	<1	<i>c</i>
$CH_2=CHCD_2^+O=CH_2$	>98	11.0	<0.5	<i>c</i>	<0.5	<i>c</i>	<1	<i>c</i>	<0.5	<i>c</i>
$CH_2=CHCD_2^+O=CD_2$	>98 ^d	10.9	<0.5	<i>c</i>	<0.5	~2	<0.5	~2	1	0.3

^a RAs normalised to a total of 100 units for signals attributable to loss of carbon monoxide and/or ethylene and formaldehyde. Some of these ions also expel a minor amount of water, but these peaks are probably artefacts. ^{b,c} See footnotes to Table 1. ^d This signal must arise by CO loss, since C_2H_4 loss from $C_4H_3D_4O^+$ is impossible.

Table 3 Reactions of metastable ions generated as $CH_2=CHCH_2^+O=^{13}CH_2$

	Neutral species lost			
	CO/C_2H_4	$^{13}CO/^{13}CCH_4$	CH_2O	$^{13}CH_2O$
RA ^a	<0.5	>99	~0	<0.5
$T_{\frac{1}{2}}$ ^b	<i>c</i>	10.8	<i>c</i>	<i>c</i>

^a See footnotes to Table 2. ^{b,c} See footnotes to Table 1.

Table 4 Energy data relevant to the dissociation of $CH_2=CHCH_2^+O=CH_2$

Products and ΔH_f^a	$\Sigma\Delta H_f^a$
$CH_2=C=CH_2$ (190 ¹⁵) + $CH_2=OH^+$ (705 ¹⁶)	895
$CH_2=CHCH_2^+$ (945 ^{12,14}) + $CH_2=O$ (-115 ¹⁵)	830
$CH_3CH=CH_2$ (20 ¹⁵) + HCO^+ (820 ¹⁷)	840
$(CH_3)_2CH^+$ (805 ^{14,18}) + CO (-110 ¹⁵)	695
$C_4H_5^+$ (990-1050 ¹⁹) ^b + H_2O (-240 ¹⁵)	750-810
CH_3CO^+ (650 ²⁰) + $CH_2=CH_2$ (50 ¹⁵)	700

^a Values quoted in $kJ\ mol^{-1}$ and rounded to $\pm 5\ kJ\ mol^{-1}$. ^b The range of values reflects the possibility of several isomeric structures for this ion. These data are possibly subject to a greater degree of uncertainty than the rest of the data in this Table.

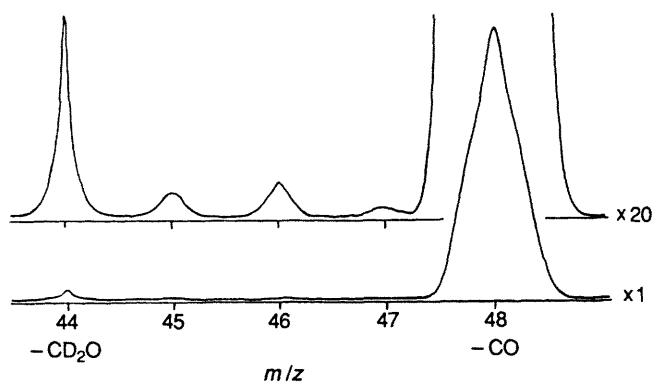
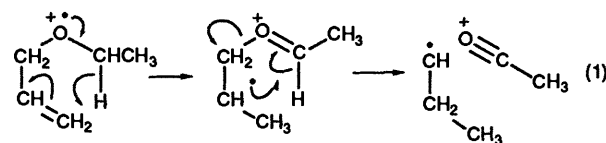


Fig. 1 Metastable peaks for loss of formaldehyde, ethylene and carbon monoxide from $CH_2=CHCD_2^+O=CD_2$. The abscissa gives the m/z of the product ions. The ordinate corresponds to the signal intensity (in arbitrary units): the upper trace is amplified by a factor of 20 compared to the lower trace.

In the case of $CH_2=CHCH_2OCH_2CH_3$, from which **1** is formed in relatively low yield by ionisation and CH_3^+ expulsion, the peak at m/z 43 appears from high resolution measurements to be mainly CH_3CO^+ . This deduction is confirmed by CID experiments. The isobaric product ions have distinctive CID spectra: CH_3CO^+ shows an intense signal at m/z 42 (H^+ loss), but only small peaks at 41 and 27; in contrast, the spectrum of $(CH_3)_2CH^+$ contains a weak or negligible peak at m/z 42, but

intense signals at 41 and 27. Similarly, an appreciable signal at m/z 39 is found in the spectrum of $(CH_3)_2CH^+$ (overall loss of $2H_2$), but this peak is of negligible significance in the CID spectrum of CH_3CO^+ . Relevant ratios of the intensities of these important peaks are given in Table 5. The most likely explanation for the presence of CH_3CO^+ is that this ion is not formed by C_2H_4 loss from **1**, at least at energies appropriate to the fragmentation of metastable ions. One possibility is that CH_3CO^+ is produced by $C_3H_7^+$ elimination from $CH_2=CHCH_2OCH_2CH_3^{*+}$, perhaps by the route suggested in eqn. (1).



In the case of $CH_2=CHCH_2OCH_2CH_2CH_3$, from which **1** is formed in much higher yield after ionisation and $C_2H_5^+$ elimination, the peak at m/z 43 is a doublet, consisting of predominantly $C_3H_7^+$ at slightly higher m/z than the smaller component corresponding to $C_2H_3O^+$. Analysis of the CID spectra of these components confirms their structure as $(CH_3)_2CH^+$ and CH_3CO^+ , respectively, Table 5. However, the presence of an enhanced signal for $C_3H_7^+$ could be wholly or partly attributed to direct fragmentation of $CH_2=CHCH_2OCH_2CH_2CH_3^{*+}$ to give $CH_2=CHCH_2O^+$ and $C_3H_7^+$.

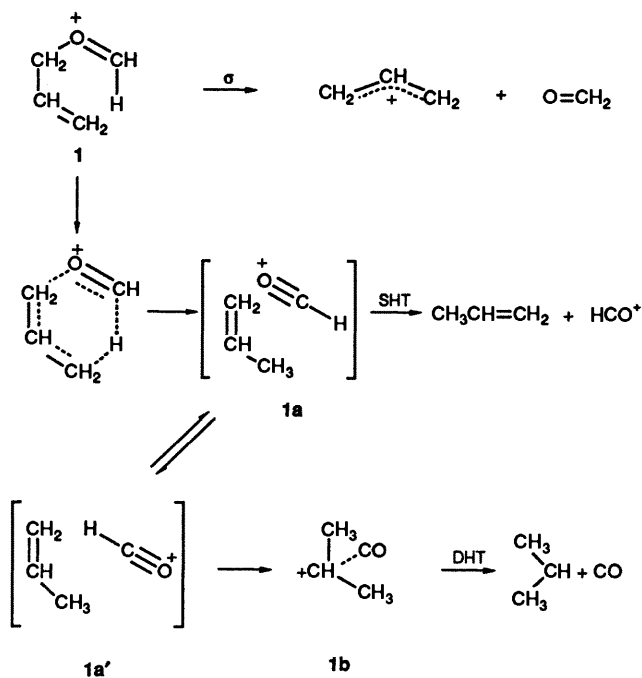
It is known that $(CH_3)_2CH^+$ is much the more stable classical isomer of $C_3H_7^+$.²¹ Indeed, $(CH_3)_2CH^+$ is probably either the global minimum on the $C_3H_7^+$ hypersurface or else very close in energy to that minimum. However, attempts to probe the structure of the $C_3H_7^+$ product ion formed by CO loss from **1** by CID experiments are unlikely to succeed because of the ease of interconversion of the various $C_3H_7^+$ isomers. Thus, attempts to generate and characterise $CH_3CH_2CH_2^+$ will probably always be circumvented by the facility of such a primary cation to rearrange to the thermodynamically more favourable isomer, $(CH_3)_2CH^+$, at the threshold for $C_3H_7^+$ formation.^{22,23} In the present case, the possibility that two different $C_3H_7^+$ structures are generated when CO is expelled from **1** complicates the picture still further (see below).

Mechanism of CO Loss from 1.—A plausible route for DHT in **1** is depicted in Scheme 1. An initial hydrogen transfer from the methylene group of the $O=CH_2$ entity to the terminal carbon atom of the allyl substituent, accompanied by stretching of the C–O σ -bond, would yield HCO^+ and $CH_3CH=CH_2$. This process should be facile because it occurs through a relatively strain-free six-membered ring transition state. If the developing ionic and neutral species separated completely, the result would be SHT, which would yield products of comparable total

Table 5 Ratios of the relative intensities of important peaks in the CID spectra of ions at m/z 43 formed from various precursors^a

Ratios	Origin and/or structure of ion				
	CH_3CO^+ {[M - CH ₃] ⁺ from (CH ₃) ₂ CO}	(CH ₃) ₂ CH ⁺ {[M - Br] ⁺ from (CH ₃) ₂ CHBr}	$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ Lower m/z^b	$\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_3$ Lower m/z^b	Higher m/z^b
42/41	2.5	0.16	2.7	1.1	>0.01
39/41	~0	0.80	~0	~0	0.85
27/28	0.09	9.5	0.03	0.30	7.8

^a Spectra were determined on a Kratos Analytical Concept II HH four-sector mass spectrometer, with helium collision gas, and with 30% attenuation of the initial precursor ion signal. These spectra are almost entirely free from contributions arising from dissociation of ions that have not been energised by collision. ^b This ion consisted of two isobaric components which were sufficiently clearly resolved to permit their individual spectra to be recorded.



enthalpy of formation to those accessible by simple cleavage of **1**. However, assuming that the HCO^+ and $\text{CH}_3\text{CH}=\text{CH}_2$ formed by the original hydrogen transfer remain bound together by ionic forces within an ion-neutral complex (INC),²⁴⁻²⁷ a second hydrogen transfer to form $(\text{CH}_3)_2\text{CH}^+$ and CO may take place. This second hydrogen transfer, which is energetically very favourable, requires that the INC, **1a**, comprising $\text{CH}_3\text{CH}=\text{CH}_2$ and HCO^+ , is sufficiently long-lived to permit the formyl cation to rotate with respect to the molecule of propene. Such a facility for the partners to undergo 'mutual rotation' is now recognised as an important (perhaps definitive) property of a true INC (*i.e.* a genuine intermediate that exists within an appreciable potential energy well).

If Scheme 1 is an accurate description of CO elimination from **1**, it is clear that **1a** does satisfy the 'Longevialle'²⁶ criterion of mutual rotation of the components. However, it is not possible to decide whether the species **1b**, containing C_3H_7^+ attached to CO, is an INC in the same sense. It is most unlikely that **1b** reverts to **1a'** since the proton affinity of CO is much lower than that of C_3H_6 (594 as opposed to 751 kJ mol^{-1} ,²⁸ respectively). On the other hand, the initial hydrogen transfer, **1** \rightarrow **1a**, is approximately thermoneutral; consequently, this step may be wholly or partially reversible. Unfortunately, the reversibility of this step cannot be probed by direct ²H-labelling experiments because all the protium and deuterium atoms become part of the ionic fragment when CO is lost.

Collision-induced Dissociation of 1.—When low-energy ions generated as **1** are energised by collision, the resultant CID spectrum (Table 5) is dominated by the base peak at m/z 41 arising by direct σ -cleavage (CH_2O loss). Although DHT still occurs, it is greatly reduced in importance (RI ~ 20%). There is also a minor signal (RI ~ 10%) corresponding to SHT (C_3H_6 elimination). The presence of signals attributable to σ -cleavage and SHT in the CID spectrum of **1** offers some circumstantial support for the mechanistic interpretation of Scheme 1.

These CID spectra are in accord with the assumption that ionisation and R^* loss from $\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{R}$ yields $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$. The intensity of the signal at m/z 41 corresponding to σ -cleavage of **1** suggests strongly that this ion does indeed contain an intact CH_2O unit. Similarly, the presence of base peaks which can be attributed to σ -cleavage of labelled analogues of **1** in the CID spectra of these species also supports the assignment of structures given in this paper. Moreover, the high selectivity found in σ -cleavage indicates that the positional integrity of the initial formaldehyde entity is very largely conserved. Thus, $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$ and $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$ show base peaks arising by loss of CD_2O ; the peaks attributable to CHDO or CH_2O elimination from these ions are only 1–2% of the intensity of those arising by σ -cleavage without rearrangement. These data are what would be expected if both α -cleavage if the precursor ionised allyl propyl ethers and σ -cleavage of **1** and its ²H-labelled analogues occurred with high selectivity.

The CID spectra of $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CH}_2$, $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$ and $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$ all contain appreciable peaks at both m/z 29 and 30. If these signals arise by SHT, then they correspond to the formation of HCO^+ and DCO^+ , respectively, thus indicating that some exchange of the protium and deuterium atoms precedes this fragmentation. In turn, this finding suggests that the initial hydrogen transfer step analogous to **1** \rightarrow **1a** in Scheme 1 is not always unidirectional. However, the ions at m/z 29 and 30 need not necessarily originate in one step from **1** or its ²H-labelled analogues. Consequently, any deductions concerning the reversibility of the hydrogen transfer step based on the signals corresponding to SHT in the CID spectra must be regarded as tentative at best.

Kinetic Energy Release for CO Loss from 1.—The metastable peak for CO loss from **1** has a rather unusual shape: it is neither Gaussian nor flat-topped, but instead presents an approximately triangular profile with a crest and basal edges that are rounded. Moreover, the peak is composite, consisting of two components of different shapes, though these components are not resolved very clearly, even at narrow slit-settings. Fig. 2 shows the peak for CO elimination from $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$; in this case, complications caused by the possibility of overlapping signals for CO and C_2H_4 expulsion do not arise because C_2H_4 loss from $\text{C}_4\text{H}_3\text{D}_4\text{O}^+$ is impossible. The

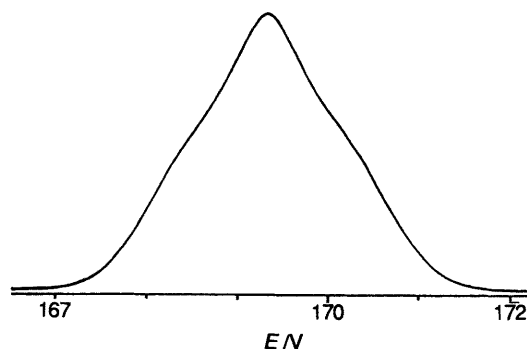


Fig. 2 Expanded plot of the metastable peak for CO loss from $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$. The abscissa scale corresponds to the voltage difference between the plates of the electric sector; the voltage difference required to transmit the parent ion is 270 volts. The ordinate corresponds to the signal intensity (in arbitrary units).

composite nature of the peak suggests that there are two channels for CO elimination from **1**, to give the same products *via* different mechanisms or else to yield different products. The latter alternative would require that two structures for the C_3H_7^+ fragment ion are involved, since the neutral species must be CO.

The metastable peak is also very broad: the corresponding $T_{\frac{1}{2}}$ value [kinetic energy (KE) release estimated from the width at half-height of the peak] is 10.7 kJ mol^{-1} . Consequently, when CO is eventually expelled after rearrangement of **1**, there is an appreciable excess energy in the transition state(s) for the final step(s).^{29,30}

Both the overall shape of the metastable peak and the $T_{\frac{1}{2}}$ value for the loss of carbon monoxide from ²H- and ¹³C-labelled analogues of **1** are essentially the same as those found for fragmentation of the unlabelled parent ion. All the $T_{\frac{1}{2}}$ values lie in the range $10.7\text{--}11.0 \text{ kJ mol}^{-1}$, with an estimated uncertainty of $\pm 0.3 \text{ kJ mol}^{-1}$. The magnitude of the $T_{\frac{1}{2}}$ value and its invariance with deuteration suggest that the rate-limiting step in CO expulsion is one of the two hydrogen transfers, which are eventually followed by rapid dissociation of an ion containing a propyl group attached to a CO entity. If a C–H/D bond were broken during the final step, it is at least possible that this would result in a change in the $T_{\frac{1}{2}}$ value and/or the overall shape of the metastable peak for CO elimination. However, no such isotope effect is discernible for CO loss from $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$ or $\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$, in which CO expulsion requires the fission of two C–D bonds instead of the two C–H bonds which must be broken before CO may be lost from **1**.

The mechanism depicted in Scheme 1 is consistent with these facts, provided it is assumed that a step (probably **1a'** \rightarrow **1b**) prior to elimination of CO is rate-limiting. A necessary (but not sufficient) condition attached to this explanation is that CO loss from **1** should have a greater KE release than the same reaction starting from $(\text{CH}_3)_2\text{CHCO}^+$. It is known that CO elimination from $(\text{CH}_3)_2\text{CHCO}^+$ is characterised by an extremely small KE release ($T_{\frac{1}{2}} < 0.5 \text{ kJ mol}^{-1}$);⁴ consequently, this requirement is satisfied. Indeed, the $T_{\frac{1}{2}}$ value (3.5 kJ mol^{-1}) for CO loss from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ is also much smaller than that for fragmentation of **1**.⁴ Expulsion of CO from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$ has been interpreted in terms of rate-limiting rearrangement of the developing $\text{CH}_3\text{CH}_2\text{CH}_2^+$ cation within the species in which C_3H_7^+ and CO are loosely co-ordinated together.⁴ Thus, if **1** does expel CO *via* isomerisation and dissociation over the same energy surface as that involved in fragmentation of $(\text{CH}_3)_2\text{CHCO}^+$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$, it must do so with a still greater amount of excess energy in the transition state for the final step than that pertaining to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}^+$.

An attractive explanation for the composite peak for CO loss from **1** is that the energy released by the rate-limiting hydrogen transfer is so large that two structures for the C_3H_7^+ product

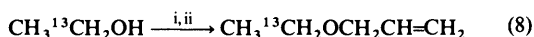
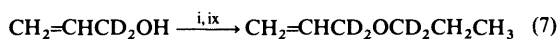
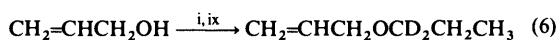
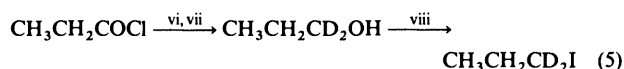
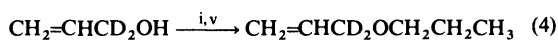
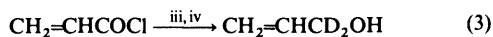
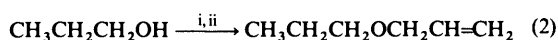
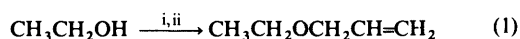
ion are energetically accessible. The broader component, corresponding to the greater KE release, is associated with the formation of the more stable product ion. The narrower component arises from the production of the less stable fragment ion, because the excess energy in the transition state for the final step is reduced. Analogous interpretations have been put forward for other fragmentations which yield composite peaks. Thus, H_2 elimination from C_3H_5^+ gives a peak consisting of two flat-topped components; the broader component was ascribed to production of the cyclopropenium ion, while the narrower component was attributed to formation of the less stable propargyl isomer.³¹

However, in the present system, this explanation remains only tentative. The structure of the alternative isomer of C_3H_7^+ [assuming that the broader component corresponds to formation of $(\text{CH}_3)_2\text{CH}^+$] which results from CO loss from **1** cannot be established from the present data. Consequently, a more detailed examination of the energetics of CO elimination from **1** cannot yet be attempted without undue speculation.

Comparison of the Reactions of 1 and 2.—The related ion, **2**, in which the C=O entity has the notional double bond conjugated with the terminal $\text{CH}_2=\text{CH}$ - group, also expels CO with the production of a composite metastable peak.^{9,10} In contrast to **1**, the isolated carbon atom attached to oxygen in **2**, is not always lost in the eliminated molecule of carbon monoxide. Thus, $\text{CH}_2=\text{CHCH}=\text{O}^+{}^{13}\text{CH}_3$ expels CO in greater abundance than ¹³CO. Nevertheless, the metastable peak for ¹³CO loss from $\text{CH}_2=\text{CHCH}=\text{O}^+{}^{13}\text{CH}_3$ is composite; it resembles that for ¹³CO elimination from $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$, but the $T_{\frac{1}{2}}$ value ($14\text{--}16 \text{ kJ mol}^{-1}$) is somewhat larger.¹⁰ Therefore, this portion of carbon monoxide loss, which is a formal THT, can be interpreted in terms of rearrangement of $\text{CH}_2=\text{CHCH}=\text{O}^+{}^{13}\text{CH}_3$ on to the same energy surface as that over which $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$ fragments. The excess energy in the final transition state(s) must be even greater starting from $\text{CH}_2=\text{CHCH}=\text{O}^+{}^{13}\text{CH}_3$ than from $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$.

Elimination of CH_2O and H_2O compete with CO loss from **2**.^{9,10} The occurrence of these fragmentations, which have higher critical³² energies than CO expulsion from **1**,¹⁰ supports the supposition that ions generated as **2** are able to reach transition states that are energetically inaccessible to **1**. The loss of CH_2O from **2**, which does not contain an intact formaldehyde entity, but not from **1**, which does contain such a group, is interesting. This behaviour is the reverse of that which would have been anticipated on a naive basis (preferential expulsion of CH_2O from the ion containing a formaldehyde entity). However, CH_2O elimination from **1** takes place only at relatively high internal energies (faster reactions occurring in the ion source or after low-energy ions have been energised by collision). Starting from **2**, rearrangement to $\text{CH}_3\text{CH}=\text{CH}^+\text{O}=\text{CH}_2$ is followed by rate-limiting isomerisation of the incipient $\text{CH}_3\text{CH}=\text{CH}^+$ ion to $\text{CH}_2=\text{CHCH}_2^+$; this isomerisation releases energy, thus permitting CH_2O loss to occur from the energetically excited $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ species.¹⁰

A parallel trend is found for CH_2O loss from metastable $\text{CH}_3\text{CH}_2^+\text{O}=\text{CH}_2$ and $\text{CH}_3\text{CH}=\text{O}^+\text{CH}_3$: the former, which contains an intact formaldehyde entity, eliminates H_2O and C_2H_4 ; the latter, which possesses no complete formaldehyde unit, expels CH_2O , C_2H_4 and a little H_2O . This peculiarity led to the proposal that $\text{CH}_3\text{CH}_2^+\text{O}=\text{CH}_2$ dissociates *via* the pathways (loss of C_2H_4 and, especially, H_2O) having the lowest critical energies, whereas $\text{CH}_3\text{CH}=\text{O}^+\text{CH}_3$ fragments only after undergoing a rate-limiting isomerisation to $\text{CH}_3\text{CH}_2^+\text{O}=\text{CH}_2$ (or related structures).³⁰ This rearrangement over a high energy barrier again results in an energetically excited form of $\text{C}_3\text{H}_7\text{O}^+$, such as $\text{CH}_3\text{CH}_2^+\text{O}=\text{CH}_2$, which undergoes



Scheme 2 Reagents and conditions: i, NaH (1.3 equiv. of 60% dispersion in mineral oil) in triglyme; ii, $\text{CH}_2=\text{CHCH}_2\text{Br}$ (0.9 equiv.), stir 24 h; iii, Addition to LiAlD_4 (2.3 equiv.) in diethyl ether at -30°C ; iv, H_2O /aqueous NaOH solution; v, $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ (0.9 equiv.), stir 24 h; vi, Addition to LiAlD_4 (2.2 equiv.) in triglyme, stir 2–6 h; vii, Tetragol {tetraethylene glycol [$\text{HO}(\text{CH}_2\text{CH}_2\text{O})_4\text{H}$]}; viii, I_2 , red P; ix, $\text{CH}_3\text{CH}_2\text{CD}_2\text{I}$ (0.9 equiv.); stir 24 h.

relatively rapid simple cleavage with expulsion of CH_2O . Many other examples of this behaviour have since been documented.

Conclusions

At high internal energies, the oxonium ion $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ expels CH_2O , as would be expected on the basis of σ -cleavage of the C–O bond. However, metastable $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ eliminates almost exclusively CO, *via* double hydrogen transfer between the products accessible to σ -cleavage. This process yields a broad composite metastable peak, thus indicating that two separate pathways are involved, possibly leading to isomeric C_3H_7^+ product ions. Loss of CO from $\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ is logically interpreted in terms of an ion–neutral complex comprising HCO^+ and $\text{CH}_3\text{CH}=\text{CH}_2$.

Experimental

The oxonium ions studied in this research were generated by dissociative ionisation of the appropriate ethyl or propyl allyl ethers. The ethers were prepared by condensation of the requisite alkoxides and alkyl iodides or bromides in suspension/solution in triglyme {triethylene glycol dimethyl ether [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$]}. The estimated isotopic purity of the [$^2\text{H}_2$] and [$^2\text{H}_4$] labelled ethers was 98% and 95%, respectively. That of the ^{13}C -labelled ether, which was prepared from a commercial sample (Aldrich) of $\text{CH}_3^{13}\text{CH}_2\text{OH}$, was 99%.

Scheme 2 summarises the synthetic routes by which the ethers were made. Details of the experimental procedures are illustrated by the following descriptions of the preparation of $\text{CH}_2=\text{CHCD}_2\text{OCD}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{O}^{13}\text{CH}_2\text{CH}_3$.

$\text{CH}_2=\text{CHCD}_2\text{OCD}_2\text{CH}_2\text{CH}_3$.— $\text{CH}_3\text{CH}_2\text{CD}_2\text{OH}$. A suspension of lithium aluminium deuteride (4.2 g, 0.1 mol) in triglyme (100 cm^3) was stirred magnetically under a nitrogen atmosphere as a solution of propionyl chloride (16.7 g, 0.18 mol) in triglyme (75 cm^3) was added dropwise over 3 h. The temperature in the reaction flask was maintained below 60°C during this addition. After stirring overnight, tetragol (50 cm^3) was added cautiously. When the initial frothing and gas evolution had ceased, the mixture was carefully distilled to give [1,1- $^2\text{H}_2$]propanol (10.1 g, 90%) having b.p. 98 – 102°C .

$\text{CH}_3\text{CH}_2\text{CD}_2\text{I}$. A mixture of [1,1- $^2\text{H}_2$]propanol (6.2 g, 0.10 mol) and purified red phosphorus (0.4 g, 0.013 mol) in a 25 cm^3

pear flask was heated gently until refluxing began. Resublimed iodine (13.0 g, 0.105 mol) was added in small portions (0.2–0.5 g) through the condenser at such a rate as to maintain gentle refluxing without causing an excessive development of iodine colouration in the vapour. After all the iodine had been added (45 min), the mixture was refluxed for a further 15 min by application of external heating (oil bath). Distillation gave 16 g of crude 1-iodo[1,1- $^2\text{H}_2$]propane (b.p. 70 – 105°C). This material was washed with aqueous potassium metabisulfite solution ($2 \times 10 \text{ cm}^3$) and water (10 cm^3), dried (magnesium sulfate) and distilled to give colourless 1-iodo[1,1- $^2\text{H}_2$]propane (14.0 g, 81%) having b.p. 101 – 103°C .

$\text{CH}_2=\text{CHCD}_2\text{OH}$. A suspension of lithium aluminium deuteride (5.0 g, 0.12 mol) in 300 cm^3 dry diethyl ether was stirred magnetically under a nitrogen atmosphere and cooled to -35°C . A solution of acryloyl chloride (19.0 g, 0.21 mol) in 60 cm^3 dry diethyl ether was added dropwise over 2.75 h; the reaction temperature was maintained between -45 and -25°C . After addition had been completed, the stirred reaction mixture was allowed to warm to -5°C ; the reaction flask was then immersed in a large bowl filled with ice and stirring was continued overnight. Hydrolysis was effected by cautious dropwise addition of water (5 cm^3), 10% aqueous sodium hydroxide solution (15 cm^3) and water (5 cm^3). The ethereal phase was separated by filtration at the pump and the inorganic salts were washed with diethyl ether ($3 \times 50 \text{ cm}^3$). The combined ethereal phases were dried (magnesium sulfate), filtered and distilled through a 4 in helix-packed fractionating column. The bulk (approximately 450 cm^3) of the diethyl ether was removed (b.p. 33.5 – 35°C), and the residual material was redried (magnesium sulfate), filtered into a smaller distillation flask (100 cm^3 capacity), and triglyme (40 cm^3) was added. Careful distillation through the fractionating column gave an ethereal fore run (b.p. 33.5 – 35°C), followed by [1,1- $^2\text{H}_2$]allyl alcohol as a pale yellow liquid (5.55 g, b.p. 87 – 96°C). Redistillation from a small quantity (0.2 g) of sodium hydride (60% dispersion in mineral oil) gave colourless [1,1- $^2\text{H}_2$]allyl alcohol (5.05 g, 41%) having b.p. 93 – 96°C . This procedure is a modification of that previously published.³³

$\text{CH}_2=\text{CHCD}_2\text{OCD}_2\text{CH}_2\text{CH}_3$. A solution of [1,1- $^2\text{H}_2$]allyl alcohol (0.72 g, 0.012 mol) in triglyme (12 cm^3) was stirred magnetically under a nitrogen atmosphere. Sodium hydride (0.65 g, 0.016 mol of 60% dispersion in mineral oil) was added in three portions. After gas evolution had ceased (20 min), a solution of 1-iodo[1,1- $^2\text{H}_2$]propane (1.8 g, 0.0105 mol) in triglyme (4 cm^3) was added during 15 min. The mixture was stirred overnight. Distillation gave [1,1- $^2\text{H}_2$]allyl [1,1- $^2\text{H}_2$]-1-propyl ether (0.635 g, b.p. 88 – 90°C). This material was washed with water ($3 \times 1.5 \text{ cm}^3$), dried (magnesium sulfate), filtered and distilled to give [1,1- $^2\text{H}_2$]allyl [1,1- $^2\text{H}_2$]-1-propyl ether (0.244 g, 22%) having b.p. 88 – 90°C .

$\text{CH}_2=\text{CHCH}_2\text{O}^{13}\text{CH}_2\text{CH}_3$.—A solution of [1 - ^{13}C]ethyl alcohol (0.25 g, 0.0053 mol) in triglyme (6 cm^3) was stirred magnetically under a nitrogen atmosphere. Sodium hydride (0.30 g, 0.0075 mol, of 60% dispersion in mineral oil) was added in one portion. After gas evolution had ceased (15 min), a solution of allyl bromide (0.60 g, 0.00495 mol) in triglyme (2 cm^3) was added during 10 min. The mixture was stirred overnight. Distillation gave allyl [1 - ^{13}C]ethyl ether (0.15 g, 35%) having b.p. 66 – 68°C .

The data of Tables 1–3 were determined from mass-analysed ion kinetic energy (MIKE)²⁹ spectra obtained on a research mass spectrometer (MMM) of unusually large dimensions in which ions were transmitted through the magnetic sector before entering the electric sector.³⁴ The MIKE spectra were measured by repetitive microcomputer-controlled scanning of the electric sector voltage over the range of voltages required to transmit

Table 6 CID mass spectra of **1** and ^2H -labelled analogues of **1**^{a,b}

<i>m/z</i>	Initial precursor ion structure			
	$\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CH}_2$ (71)	$\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CH}_2$ (73)	$\text{CH}_2=\text{CHCH}_2^+\text{O}=\text{CD}_2$ (73)	$\text{CH}_2=\text{CHCD}_2^+\text{O}=\text{CD}_2$ (75)
48				1
47				12(DDT)
46				1
45	5	17(DPT)	16(DDT)	1
44	3		2	1
43	23(DPT)	100(σ)		100(σ)
42	4	5	2	3
41	100(σ)	11	100(σ)	11
40	4	17	6	16
39	25	7	36	5
38	3	2	8	2
37	3	2	8	2
33			4	1
32			2	<1
31	2			
30	1	10(SDT?)	9(SDT)	7(SDT)
29	11(SPT)	14(SPT)	5(SPT?)	5(SPT?)
28	1	3	1	2
27	12	6	14	4
26	4	2	6	2

^a See footnote to Table 5. ^b Relative intensities measured from peak heights and normalised to a value of 100 units for the most intense fragment ion peak. The annotations ' σ ', 'SPT' and 'DPT' given in parentheses denote peaks attributable to σ -cleavage, single and double protium transfer, respectively; similarly 'SDT' and 'DDT' denote peaks corresponding to overall single and double deuterium transfer, respectively.

fragment ions formed by dissociation of metastable ions in the second field-free region between the magnetic and electric sectors. The quoted data are integrated spectra derived from 200–500 individual scans. Typical source conditions were: ionising electron energy, 70 eV; pressure 2×10^{-6} Torr; accelerating voltage 8065–8075 V. Kinetic energy release data were estimated from the widths at half-height of the corresponding metastable peaks, after applying the usual correction for the width of the main beam,³⁵ by means of the standard one-line equation.^{29,36}

The data of Tables 5 and 6 were measured on a Kratos Analytical Concept II HH four-sector mass spectrometer. The collision cell was floated at 4 kV above ground potential; the collision gas was helium and the precursor ion signal was attenuated to 70% of its initial intensity. The quoted data are integrated spectra, compiled from 10–15 individual scans. These CID spectra are essentially free from contributions arising from the fragmentation of ions that have not been energised by collision.

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