The Mechanism of Ethylene Loss from the Oxonium Ion $CH_3CH_2{}^+O{=}CHCH_2CH_3$

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Ethylene expulsion from $CH_3CH_2{}^+O{=}CHCH_2CH_3$ is shown by collision-induced dissociation and ^2H-labelling experiments to involve specifically the O-ethyl group.

It has recently become clear that many reactions of isolated organic ions involve ion–neutral complexes (INCs) in which a partly formed ion and an associated neutral species are held together by a combination of ion-dipole and related long range forces.[1–3] Dissociations *via* INCs often compete with or even pre-empt alternative fragmentations that may be formulated in terms of 'conventional' intermediates or transition states linked by familiar steps (*e.g.*, 1,2-hydride shifts).

The slow dissociations of the oxonium ion $CH_3CH_2{}^+O{=}CHCH_2CH_3$, **1**, which have not previously been subjected to detailed scrutiny, provide an illustration of this possibility. Elimination of ethylene is the dominant reaction of **1**, Table 1, accounting for *ca.* 98% of the total metastable ion current. Two distinct mechanisms may be advanced to explain this process, Scheme 1. First, consecutive 1,2-hydride shifts could lead from **1** to **3** *via* **2**; σ-cleavage of **3** would then afford $CH_3CH_2{}^+O{=}CH_2$, **4**, and C_2H_4. This 'conventional' route for ethylene loss has been proposed to operate for $CH_3CH_2CH{=}OH^+$, **5**,[4,5] and $CH_3CH_2CH{=}O^+CH_3$, **6**.[4] The behaviour of ^2H-labelled analogues of **5** and **6** reveals that the four hydrogen or deuterium atoms in the eliminated ethylene are selected almost statistically from the six of the original $C_3H_{6-n}D_n$ moiety, with minor[5] and negligible[6] participation, respectively, from the OH and OCH_3 hydrogens. This is consistent with extensive hydrogen exchange, *via* 1,2-H-shifts, prior to decomposition of **5** and **6**. The second route for C_2H_4 loss from **1** involves stretching of the C–O σ-bond to form the INC **1a**; hydrogen transfer between the developing products ($CH_3CH_2{}^+$ and $CH_3CH_2CH{=}O$) then yields $CH_2{=}CH_2$ and $CH_3CH_2CH{=}OH^+$. Many onium ions containing the $={Z}^+{-}CH_2CH_3$ moiety (Z = O, NH, NCH_3) apparently expel C_2H_4 in this way.[1]

The isomeric daughter ions **4** and **5** produced by the two alternative routes for C_2H_4 loss from **1** may be distinguished by investigating their collision-induced dissociation (CID) spectra. It is evident from the relevant partial CID spectra, Table 2, that C_2H_4 elimination from **1** yields **5**, rather than **4**.

Table 1 Reactions of metastable $CH_3CH_2{}^+O{=}CHCH_2CH_3$ ions

Neutral species lost	Relative abundance[a]	Kinetic energy release $T_{\frac{1}{2}}$[b]
H_2O	<1	2.1
C_2H_4	>98	1.9
C_3H_6	1	1.6

[a] Values measured by ion counts, corresponding to metastable peak areas, and normalised to a total metastable ion current of 100 units for ions dissociating in the second field-free region of a research mass spectrometer ('MMM') of very large dimensions equipped with a post acceleration detector (P. G. Cullis, G. M. Neumann, D. E. Rogers and P. J. Derrick, *Adv. Mass Spectrom.*, 1980, **8**, 1729). [b] Values (in kJ mol^{-1}) measured from the width-at-half-height of the appropriate metastable peak after applying the usual correction for the width of the main beam.

Table 2 Partial collision induced dissociation spectra of $C_3H_7O^+$ ions[a]

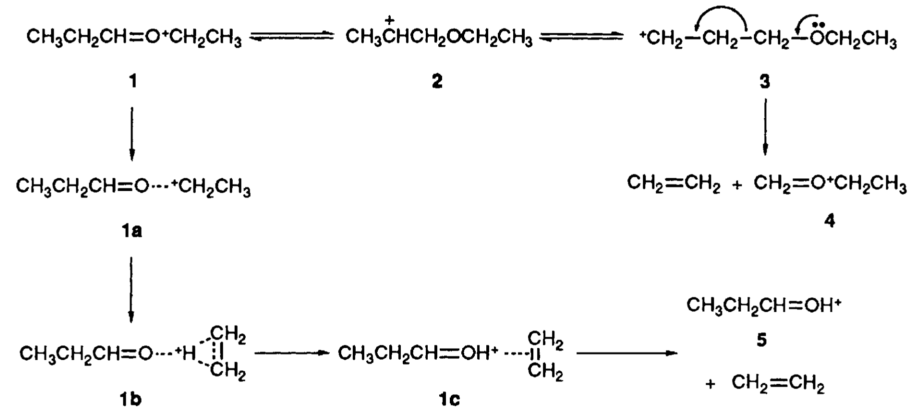
	Ion structure and origin		
	$CH_3CH_2{}^+O{=}CH_2$[b]	C_2H_4 loss from $CH_3CH_2{}^+O{=}CHCH_2CH_3$	$CH_3CH_2CH{=}OH^+$[c]
m/z	RI[d]	RI[d]	RI[d]
57	14.1	52.5	63.3
55	1.0	6.5	7.6
43	8.7	29.9	31.0
39	10.5	41.5	45.9
38	3.7	13.4	14.6
37	2.6	11.4	10.8
29	100	100	100
27	48.5	68.5	68.4
26	16.8	33.3	30.2
15	7.0	16.8	18.4

[a] Helium collision gas; 60% attenuation of initial $C_3H_7O^+$ ion signal. [b] Generated by ionisation and CH_3 loss from $(C_2H_5)_2O$. [c] Generated by ionisation and $C_2H_5{}^{\cdot}$ loss from $(C_2H_5)_2CHOH$. [d] Normalised to a value of 100 units for the most intense peak containing no unimolecular component.

Table 3 Reactions of metastable $C_3H_4D_3O^+$ ions

Ion structure and origin	H_2O		HOD		D_2O		C_2H_4		C_2H_3D		$C_2H_2D_2$		C_2HD_3	
	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]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]
$CH_3CD_2CD{=}OH^+$ from $(CH_3CD_2)_2CDOH$	53.1	2.1	34.3	2.1	3.3	2.2	0.3	1.0	3.1	1.1	4.8	1.3	1.2	1.6
$C_3H_4D_3O^+$ from $CH_3CD_2CD{=}O^+C_2H_5$	52.0	2.1	33.0	2.1	2.9	2.1	0.3	1.1	3.7	1.3	6.4	1.7	1.7	2.1

[a,b] See footnotes *a* and *b* to Table 1.



Scheme 1

This deduction is confirmed by ^2H-labelling experiments. Thus, metastable $CH_3CH_2{}^+O{=}CDCD_2CH_3$ undergoes C_2H_4 loss ($T_{\frac{1}{2}}$ = 1.8 kJ mol^{-1}) with very high specificity (>99%). This is consistent with expulsion of ethylene from the O-ethyl group of **1**. In contrast, ethylene loss from the $C_3H_3D_3$ entity of $CH_3CH_2{}^+O{=}CDCD_2CH_3$ would result in elimination of C_2H_3D, $C_2H_2D_2$ and C_2HD_3, but not the observed C_2H_4. Even at higher internal energies (source reactions), $CH_3CH_2{}^+O{=}CDCD_2CH_3$ eliminates C_2H_4 with at least 80% specificity. Moreover, the fragmentation of metastable $C_3H_4D_3O^+$ ions formed by C_2H_4 loss from $CH_3CH_2{}^+O{=}CDCD_2CH_3$ is almost identical to that of $CH_3CD_2CD{=}OH^+$ ions generated directly from $(CH_3CD_2)_2CDOH$, Table 3. This close similarity is further evidence that C_2H_4 elimination from $CH_3CH_2{}^+O{=}CDCD_2CH_3$ yields $CH_3CD_2CD{=}OH^+$, as opposed to a trideuteriated analogue of $CH_3CH_2{}^+O{=}CH_2$. The somewhat increased overall abundance of the higher energy reaction, ethylene loss, in the dissociation of $C_3H_4D_3O^+$ ions produced by fragmentation of $CH_3CH_2{}^+O{=}CDCD_2CH_3$ may indicate that these ions have a slightly higher average internal energy than the $CH_3CD_2CD{=}OH^+$ ions generated directly from $(CH_3CD_2)_2CDOH$.[7] This hypothesis would also account for the larger $T_{\frac{1}{2}}$ values associated with expulsion of deuteriated ethylenes from $C_3H_4D_3O^+$ ions formed from

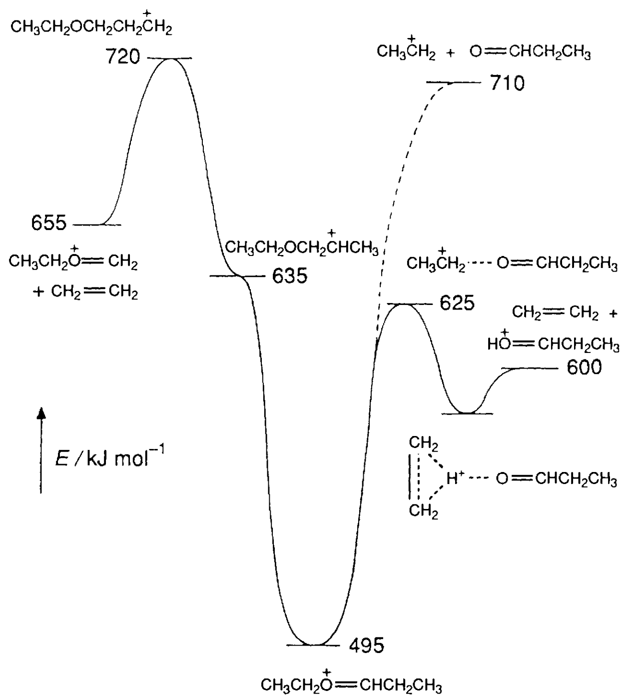


Fig. 1 Potential energy profile for isomerisation and dissociation of **1**

$CH_3CH_2{}^+O{=}CDCD_2CH_3$.[8] The same trend (greater $T_{\frac{1}{2}}$ values for loss of more heavily deuteriated ethylenes) is found for both classes of $C_3H_4D_3O^+$ ions.

The chemistry of **1** is conveniently summarised by the potential energy profile[9] (PEP) of Fig. 1. This PEP is constructed using known[10–14] or estimated[1,15–18] enthalpies of formation. The final hydrogen transfer step, **1a** → products, may involve the proton-bound complex (PBC) **1b**. However, the lowest-energy geometry of **1b** is possibly better represented by the INC **1c** in which the common proton is more closely associated with the oxygen atom of the propionaldehyde.

Notwithstanding the uncertainty concerning the precise geometry of the species **1a**, **1b**, and/or **1c** involved in C_2H_4 loss from **1**, it is evident that this route is energetically much more favourable than the alternative 'conventional' mechanism (**1** → **2** → **3** → products). The contrast between the behaviour of **1** and that of the lower homologue, **6**, which contains only an O-methyl group is striking. This reflects the ease of dissociation of **1** *via* the new channel for C_2H_4 loss involving INCs; no such route is open to **6**.

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References

1 For early work on INCs in oxonium ion systems, see: R. D. Bowen, B. J. Stapleton and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 24; R. D. Bowen and D. H. Williams, *Int. J. Mass Spectrom. Ion Phys.*, 1979, **29**, 47; *J. Am. Chem. Soc.*, 1978, **100**, 7454; 1980, **102**, 2752.

2 For reviews, see: T. H. Morton, *Tetrahedron*, 1982, **38**, 3195; D. J. McAdoo, *Mass Spectrom. Rev.*, 1988, **7**, 363.

3 S. Hammerum, *J. Chem. Soc., Chem. Commun.*, 1988, 858; S. Hammerum and H. E. Audier, 1988, 860.

4 D. H. Williams and R. D. Bowen, *J. Am. Chem. Soc.*, 1977, **99**, 3192; R. D. Bowen and D. H. Williams, 1977, **99**, 6822.

5 R. D. Bowen, D. H. Williams, G. Hvistendahl and J. R. Kalman, *Org. Mass Spectrom.*, 1978, **13**, 721.

6 T. J. Mead and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1972, 876.

7 H. M. Rosenstock, V. H. Dibeler and F. N. Harllee, *J. Chem. Phys.*, 1964, **40**, 591.

8 R. G. Cooks, J. H. Beynon, R. M. Caprioli and G. R. Lester, *Metastable Ions*, Elsevier, Amsterdam, 1973.

9 For reviews on PEPs, see: D. H. Williams, *Acc. Chem. Res.*, 1977, **10**, 280; *Philos. Trans. R. Soc. London, Ser. A*, 1979, **293**, 117; R. D. Bowen, D. H. Williams and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 451; R. D. Bowen and D. H. Williams, in *Rearrangements in Ground and Excited States*, ed. P. DeMayo, Academic Press, New York, 1980, vol. 1, ch. 2.

10 F. P. Lossing and A. Maccoll, *Can. J. Chem.*, 1976, **54**, 990; F. P. Lossing, *J. Am. Chem. Soc.*, 1977, **99**, 7526.

11 H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem., Ref. Data, Suppl. 1*, 1977, 6.

12 J. C. Traeger and R. G. McLoughlin, *J. Am. Chem. Soc.*, 1981, **103**, 3647.

13 S. G. Lias, J. F. Liebman and R. D. Levin, *J. Phys. Chem., Ref. Data*, 1984, **13**, 695.

14 J. B. Pedley, R. D. Nayler and S. P. Kirby, *Thermochemical Data of Organic Compounds*, 2nd edn., Chapman and Hall, London, 1986.

15 J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; *J. Chem. Phys.*, 1953, **21**, 2029.

16 S. W. Benson, *Thermochemical Kinetics*, 2nd edn., Wiley, New York, 1976.

17 L. Radom, J. A. Pople and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 5935.

18 J. L. Holmes, M. Fingas and F. P. Lossing, *Can. J. Chem.*, 1981, **59**, 80; F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 6917.