

The Mechanism of Formaldehyde Loss from the Oxonium Ions $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$

Richard D. Bowen,* Alex W. Colburn, and Peter J. Derrick

Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.

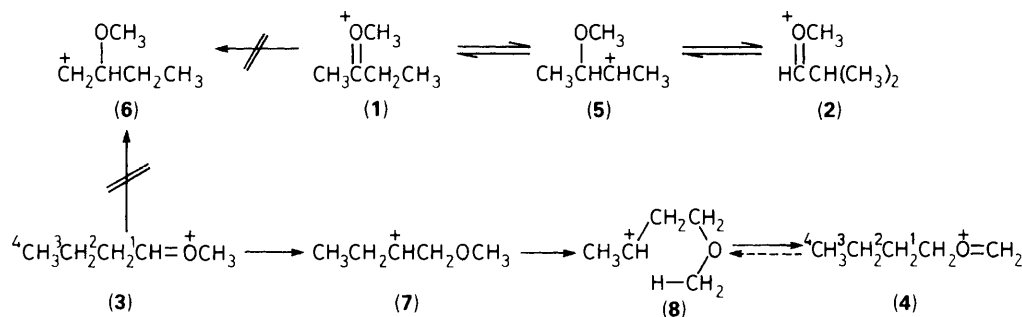
In contrast to $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{C}=\text{O}^+\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCH}=\text{O}^+\text{CH}_3$, which in slow dissociations lose mainly CH_3OH , metastable $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$ expels predominantly CH_2O by isomerising to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$, probably *via* two 1,2-H shifts and a subsequent 1,5-H shift; $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$ undergoes limited interconversion with $\text{CH}_3^+\text{CHCH}_2\text{CH}_2\text{OCH}_3$, prior to CH_2O elimination, *via* a 1,5-H shift.

Considerable progress has been made recently in understanding the unimolecular reactions of isolated organic ions.^{1,2} In closed-shell, even-electron cations, rearrangement steps involving 1,2-H or 1,2-alkyl migrations between adjacent carbon atoms occur readily at energies close to the thermochemical threshold.^{1,3} Similarly, 1,5-H and, to a lesser degree, 1,4-H shifts are apparently facile.¹ Little evidence is available, however, concerning the feasibility of 1,3-H migrations between carbon atoms separated by an intervening sp^2 carbon atom.

The reactions of four isomeric $\text{C}_5\text{H}_{11}\text{O}^+$ ions generated by ionisation and fragmentation of ethers are given in Table 1. The closely similar behaviour of $\text{CH}_3\text{CH}_2(\text{CH}_3)\text{C}=\text{O}^+\text{CH}_3$ (1), and $(\text{CH}_3)_2\text{CHCH}=\text{O}^+\text{CH}_3$ (2), is taken to reflect the ease of their conversion to the relatively stable secondary carbonium ion $\text{CH}_3^+\text{CH}(\text{CH}_3)\text{CHOCH}_3$ (5), by a 1,2-H and 1,2- CH_3 shift, respectively. In contrast $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$ (3), could presumably isomerise to (1) only by undergoing a 1,2- C_2H_5 shift to form the energetically inaccessible primary carbonium ion $\text{CH}_3\text{CH}_2^+(\text{CH}_2)\text{CHOCH}_3$ (6), Scheme 1. The reactions of

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$ (3) actually show some resemblance to those of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$ (4). Isomerisation of (3) to (4) can be envisaged to occur by two 1,2-H shifts [(3) \rightarrow (7) \rightarrow (8)], followed by a 1,5-H-migration [(8) \rightarrow (4)]. Alternatively, (3) \rightarrow (8) might conceivably take place *via* a direct 1,3-H shift. The chemistry of (1–4) is summarised by the potential energy profile¹ of Figure 1; this is constructed using known^{4–6} or estimated^{7–10} enthalpies of formation of reactants, intermediates and products.

Three pieces of experimental evidence show that interconversion of ions formed initially as (3) and (4) cannot be rapid and reversible compared to the rate of dissociation. Firstly, the relative abundances of the fragmentation processes of (3) and (4), although similar, are appreciably different: (4) expels significantly more H_2O than does (3). Secondly, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CD}_3$ expels CD_2O and C_3H_6 with high specificities (97 and 96%, respectively, in formaldehyde and propene losses). This is consistent with the step (8) \rightarrow (4) being essentially irreversible with σ -cleavage of (8) to $\text{CH}_3\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{O}^+\text{CH}_3$ occurring faster than equilibration of (8), formed from (3), with (4). Thirdly,



Scheme 1

Table 1. Reactions of metastable $\text{C}_5\text{H}_{11}\text{O}^+$ ions.

Ion	Neutral species lost							
	H_2O		CH_2O		CH_3OH		C_3H_6	
	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b
$\text{CH}_3\text{CH}_2(\text{CH}_3)\text{C}=\text{O}^+\text{CH}_3$ (1)	<1	c	6	1.9	86	1.7	7	1.9
$(\text{CH}_3)_2\text{CHCH}=\text{O}^+\text{CH}_3$ (2)	<1	c	9	1.8	83	1.7	7	1.9
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{O}^+\text{CH}_3$ (3)	<0.5	c	91	1.4	4	1.4	4.5	1.6
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CH}_2$ (4)	3	1.7	87	1.3	5	c	5	1.6

^a Relative abundances measured by metastable peak areas and normalised to a total metastable ion current of 100 units for ions decomposing in the second field-free region of a research mass spectrometer 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 Kinetic energy releases in kJ mol^{-1} measured from the width-at-half-height of the appropriate metastable peak. ^c Peak too weak to permit accurate measurement.

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CD}_2$ eliminates CD_2O , CHDO and CH_2O in the ratios 37:57:6, respectively. If formaldehyde loss from (4) occurred without any rearrangement of (4) to (8), then only CD_2O loss from $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CD}_2$ would be expected. Conversely, if (4) and (8) were in fast equilibrium prior to formaldehyde expulsion, then $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{OD}_2$ ought to eliminate CD_2O , CHDO and CH_2O in the ratios 17:67:17, respectively. It is clear, therefore, that limited interconversion of (4) and (8) precedes expulsion of formaldehyde from (4). A similar conclusion concerning propene loss from (4) follows from the observation that $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CD}_2$ expels C_3H_6 , $\text{C}_3\text{H}_5\text{D}$ and $\text{C}_3\text{H}_4\text{D}_2$ in the ratios 40:38:22 respectively.

The finding that (4) undergoes more extensive equilibration with (8) than is found starting from (3) has three important consequences. Firstly, there is evidently a significant barrier towards a direct 1,3-H shift in (3). If such a process could occur at or near the thermochemical threshold (dotted line in Figure

1), then there is no reason why (3) should not interconvert with (8) [and, therefore, (4)] prior to decomposition. However, if conversion of (3) to (8) takes place in two stages, via consecutive 1,2-H shifts involving (7), the energy barrier towards production of (8) from (3) is significantly raised. This reflects the higher estimated enthalpy of formation of (7), which is destabilised by interaction of the positive charge notionally localised on carbon with the nearby β -methoxy group. The destabilisation of (8), by interaction of the positive charge with the more distant γ -methoxy group, is significantly smaller than that in (7).¹¹ A logical interpretation is that the mechanism of CH_2O loss from (3) involves consecutive 1,2-H shifts, the former of which [(3) \rightarrow (7)] is probably the rate-determining step. An alternative possibility is that (3) \rightarrow (8) occurs directly, with a significant additional critical energy, thus circumventing or competing with the two-step route, (3) \rightarrow (7) \rightarrow (8). Secondly, the 1,5-H shift, (4) \rightarrow (8), evidently occurs relatively easily. Thus, the behaviour of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CD}_2$ can be explained on the basis of limited interconversion with $\text{CH}_3^+\text{CHCH}_2\text{CH}_2\text{OCHD}_2$ (and, subsequently, $\text{CH}_3\text{CHDCH}_2\text{CH}_2^+\text{O}=\text{CHD}$) without extensive involvement of $\text{CH}_3\text{CH}_2^+\text{CHCH}_2\text{OCHD}_2$ and related species. Only a few ions are able to rearrange to $\text{CH}_3^+\text{CDCHDCH}_2\text{OCH}_3$ (via $\text{CH}_3\text{CHD}^+\text{CHCH}_2\text{OCH}_2\text{D}$, $\text{CH}_3^+\text{CHCHDCH}_2\text{OCH}_2\text{D}$ and $\text{CH}_3\text{CHDCHDCH}_2^+\text{O}=\text{CH}_2$) and so expel $\text{C}_3\text{H}_4\text{D}_2$. If all six hydrogen atoms in the three CH_2 groups of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2^+\text{O}=\text{CD}_2$ were able to exchange with the two deuteriums, a much greater proportion (54%) of CH_2O loss would be expected than is actually observed (6%) in the formaldehyde elimination. Conse-

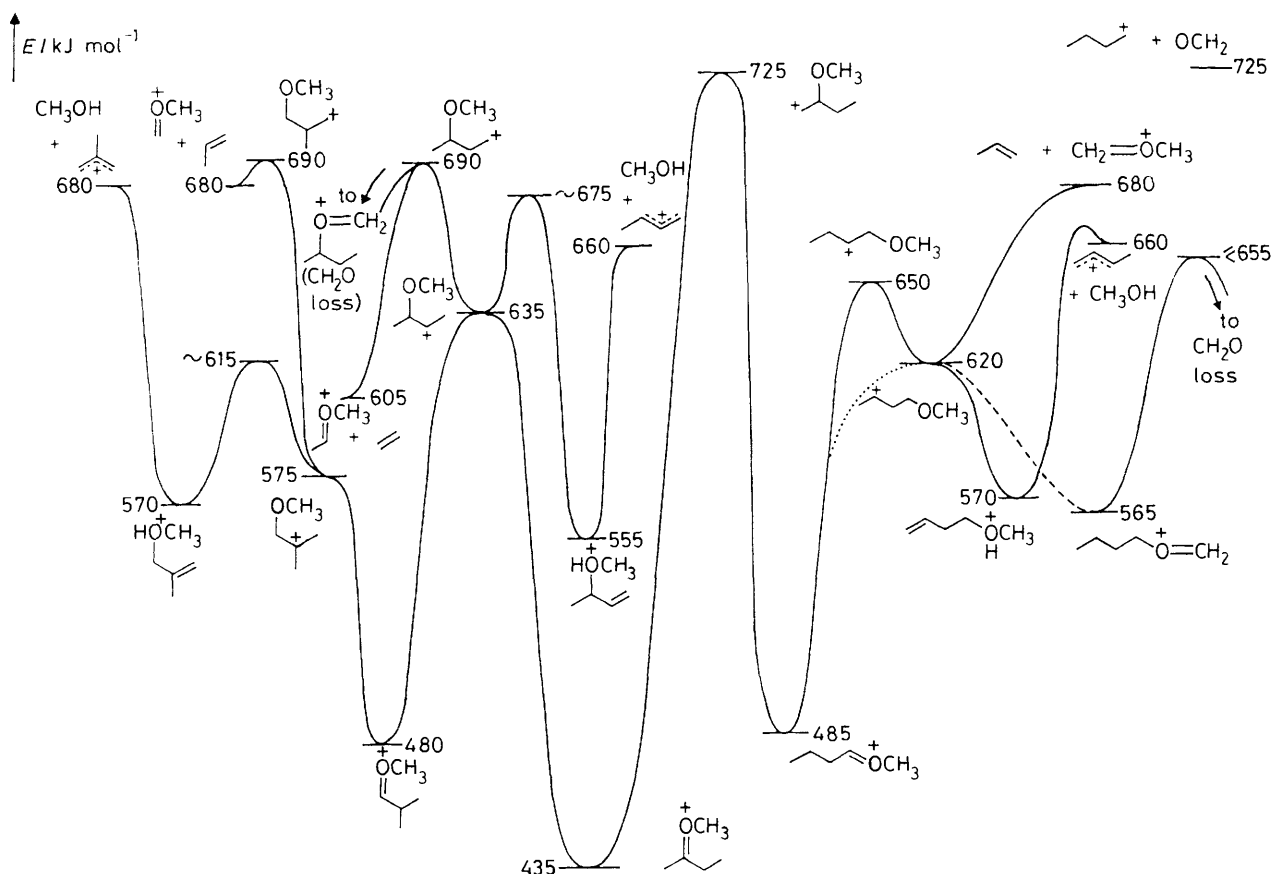
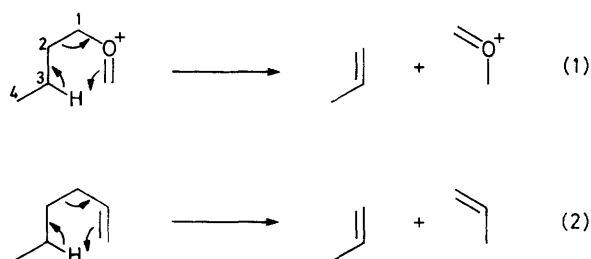


Figure 1. Potential energy profile for isomerisation and dissociation of (1)–(4).

quently, (4) → (8) evidently occurs at or near the thermochemical threshold (broken line in Figure 1), but further rearrangement to (7) [and thence (3)] requires more energy and takes place less readily. This supports the view that (7) suffers a greater destabilisation than (8), owing to the closer proximity of the electron withdrawing β-methoxy group to the cationic centre.¹¹ Elimination of formaldehyde from (4) has previously been interpreted¹² as involving ion-dipole complexes comprising a C₄H₉⁺ cation co-ordinated to O=CH₂. Rearrangement of the incipient cation in these complexes can occur, at energies below those needed to induce dissociation, thus permitting the eventual production of the thermodynamically most favourable products [(CH₃)₃C⁺ + O=CH₂]. The highest energy transition state *en route* to these products probably corresponds to CH₃CH₂CH₂CH₂⁺...O=CH₂.¹² The enthalpy of formation of this species is estimated to be at least 70 kJ mol⁻¹ lower than the combined enthalpies of formation (725 kJ mol⁻¹) of the corresponding separated products (CH₃CH₂CH₂CH₂⁺ + O=CH₂), Figure 1. Thirdly, loss of propene from (4) is best interpreted as a two-step process, involving a 1,5-H shift followed by subsequent σ-cleavage of (8). If propene loss occurred from (4) via a synchronously concerted pericyclic mechanism, equation (1), only C₃H₆ elimination from CH₃CH₂CH₂CH₂⁺O=CD₂ would be expected. Propene loss from (4) is formally isoelectronic with elimination of propene from hex-1-ene via a 'retro-ene' reaction, equation (2). The behaviour of CH₃CH₂CH₂CH₂⁺O=CD₂, therefore, indicates that when such oxonium ions expel alkenes by routes which may be formulated as pericyclic processes, these reactions do not necessarily occur *via* synchronously concerted mechanisms. Similar conclusions have been reached for other classes of organic ions: dissociation *via* pericyclic reactions usually appears to involve stepwise mechanisms, particularly at low internal energies,¹³⁻¹⁵ though exceptions to this generalisation have been reported.¹⁶

Financial support from the S.E.R.C., including the award of an Advanced Fellowship to R. D. B., is gratefully acknowledged.

Received, 8th May 1989; Com. 9/019211

References

- 1 D. H. Williams, *Acc. Chem. Res.*, 1977, **10**, 280; D. H. Williams, *Philos. Trans. Roy. Soc. London*, 1979, **A293**, 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. Mayo, Academic Press, New York, 1980, vol. 1, ch. 2.
- 2 J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.*, 1980, **12**, 383; J. L. Holmes, *Org. Mass Spectrom.*, 1985, **20**, 169.
- 3 J. V. Headley and A. G. Harrison, *Can. J. Chem.*, 1985, **63**, 609; M. Weiss, R. A. Crombie, and A. G. Harrison, *Org. Mass Spectrom.*, 1987, **22**, 216.
- 4 J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington DC, 1969; H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data Suppl. 1*, 1977, 6.
- 5 F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 1970, **48**, 955; F. P. Lossing, *Can. J. Chem.*, 1972, **50**, 3973; F. P. Lossing, *J. Am. Chem. Soc.*, 1977, **99**, 7526.
- 6 S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
- 7 J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; J. L. Franklin, *J. Chem. Phys.*, 1953, **21**, 2029.
- 8 S. W. Benson, 'Thermochemical Kinetics,' 2nd edn., Wiley, New York, 1976.
- 9 R. D. Bowen and D. H. Williams, *Org. Mass Spectrom.*, 1977, **12**, 475; see also ref. 10.
- 10 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.
- 11 L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 5935.
- 12 R. D. Bowen, B. J. Stapleton, and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 24.
- 13 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1219; 1982, 409.
- 14 F. P. Boer, T. W. Shannon, and F. W. McLafferty, *J. Am. Chem. Soc.*, 1968, **90**, 7239; J. S. Smith and F. W. McLafferty, *Org. Mass Spectrom.*, 1971, **5**, 483; D. J. McAdoo, D. N. Witiak, F. W. McLafferty, and J. D. Dill, *J. Am. Chem. Soc.*, 1978, **100**, 6639.
- 15 D. J. McAdoo and C. E. Hudson, *Int. J. Mass Spectrom. Ion Proc.*, 1984, **62**, 269.
- 16 C. E. Allison, M. B. Stringer, J. H. Bowie, and P. J. Derrick, *J. Am. Chem. Soc.*, 1988, **110**, 6291.