The Mechanism of Methyl Radical Loss from $CH_3CH{=}CHCH(CH_3)OCH_3^{+\cdot}$ and $CH_2{=}C(CH_3)CH(CH_3)OCH_3^{+\cdot}$: a Not-so-simple Cleavage

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Loss of a methyl radical from $CH_3CH{=}CHCH(CH_3)OCH_3^{+\cdot}$ and $CH_2{=}C(CH_3)CH(CH_3)OCH_3^{+\cdot}$ is shown by ^2H-labelling and collision-induced dissociation experiments to involve elimination of the methyl group originally attached to the double bond, with formation of $CH_2{=}CHC(CH_3){=}O^+CH_3$ as the fragment ion.

Expulsion of an alkyl radical from $M^{+\cdot}$ is perhaps the most common of all the fragmentations encountered in the electron ionisation mass spectra of aliphatic compounds.[1,2] For example, loss of an α-substituent *via* σ-cleavage is usually the principal primary dissociation pathway of radical-cations formed from amines, secondary and tertiary alcohols and the corresponding ethers, especially at relatively high internal energies.

The behaviour of $C_nH_{2n}O^{+\cdot}$ species is one of the continuing themes of mass spectrometry.[3] A very recent systematic survey of the mass spectra of alkenyl methyl ethers revealed that alkyl radical expulsion from $M^{+\cdot}$ is often the dominant reaction shown by this series of radical-cations.[4] However, this fragmentation is not always a simple σ-cleavage, even in cases for which such a process appears to be both kinetically and thermodynamically favourable. Thus, both $CH_3CH{=}CHCH(CD_3)OCH_3$, **1**, and $CH_2{=}C(CH_3)CH(CD_3)OCH_3$, **2**, show prominent $[M - CD_3]^+$ and $[M - CH_3]^+$ peaks of approximately equal intensity in their 70 eV spectra. Only $[M - CD_3]^+$ peaks would be anticipated on the basis of σ-cleavage with formation of a conjugated secondary oxonium ion. Moreover, as the internal energy of the decomposing ions is reduced, $CH_3^\cdot$ elimination from $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ is increasingly favoured over $CD_3^\cdot$ loss, until, for metastable ions, essentially exclusive $CH_3^\cdot$ expulsion is observed. The unexpected elimination of $CH_3^\cdot$ from $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ does not involve the *O*-methyl group, as is shown by the loss of specifically $CH_3^\cdot$ from the analogous $C_5H_9OCD_3^{+\cdot}$ species. Consequently, fragmentation of these ionised pentenyl methyl ethers proceeds *via* two mechanisms. The first route involves simple σ-cleavage, whereas the second, which is preferred at low internal energies, leads to loss of the methyl group attached to the double bond, *via* formal γ- and β-cleavages, respectively.

Direct dissociation of $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ *via* fission of the bond connecting the CH_3 group to the γ- and β-carbon atoms is energetically and mechanistically implausible because both these processes produce unstable vinyl cations. However, $CH_3^\cdot$ loss from $\mathbf{1}^{+\cdot}$ and $\mathbf{2}^{+\cdot}$ is logically explained in terms of rearrangements involving distonic[5,6] ions (**1δ** and **2δ**) and ionised dimethylmethoxycyclopropane, Scheme 1. This second route (σ′-cleavage, Scheme 1) leads eventually to

Table 1 CID Mass spectra of $C_5H_6D_3O^+$ ions[a]

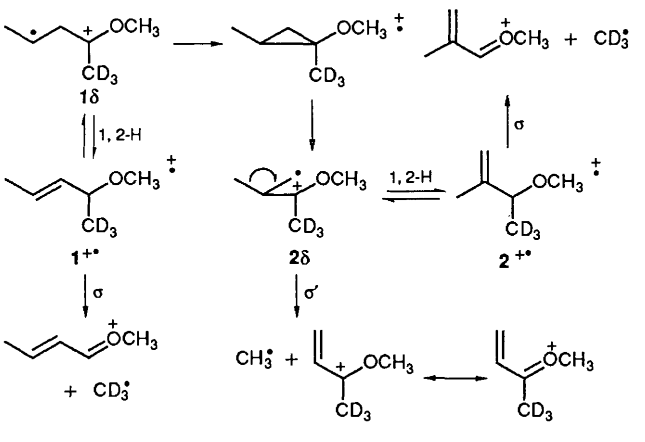
	Origin of ion		
m/z	$[M - CH_3]^+$ from **1**	$[M - CH_3]^+$ from **2**	$[M - CD_3]^+$ from **3**
86	4	4	6
73	3	3	4
69	2	2	2
59	<1	<1	2
58	76	76	71
57	14	14	15
56	11	11	13
55	47	48	47
54	2	2	3
53	3	3	5
52	2	1	3
51	<1	<1	2
46	100	100	100
45	16	18	18
44	11	11	12
43	7	7	8
42	3	4	5
41	22	22	21
40	18	19	19
39	9	8	9
38	<1	<1	2
32	1	1	3
31	10	10	12
30	10	10	12
29	19	20	21
28	12	12	14
27	31	32	35
26	4	3	6
18	8	8	11

[a] Spectra 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 initial parent ion signal was attenuated by 30%. The quoted data are averaged spectra, compiled from at least ten individual scans, normalised to a value of 100 units for the most abundant fragment ion. These spectra are almost entirely free from unimolecular contributions.

Table 2 CID Mass spectra of $C_5H_9O^+$ ions[a]

	Origin of ion							
m/z	$[M-CD_3]^+$ from **1**	$[M-C_2H_5]^+$ from **4**[b]	$[M-CD_3]^+$ from **2**	$[M-C_2H_5]^+$ from **5**[b]	$[M-CH_3]^+$ from **6**	$[M-CH_3]^+$ from **7**	$[M-CH_3]^+$ from **8**	$[M-C_2H_5]^+$ from **9**
70	4	2	3	4	5	2	4	3
69	43	48	23	22	26	14	3	4
68	1			1		2	1	
59				1	2	1		1
57	1	2	2	2	3	2	2	2
56			2	4	2	2	4	2
55	93	71	100	100	100	100	100	100
54	7	3	3	5	11	6	16	12
53	60	57	31	27	38	29	19	18
52	2		2	3	6	5	4	4
51	8	4	5	6	10	9	6	7
50	5	1	3	4	5	5	8	6
49					1		1	
45	42	39	20	15	29	16	15	10
44					1			
43	8		10	11	42	45	80	78
42	12	8	8	9	13	11	11	9
41	50	49	52	56	35	32	13	14
40	7	2	5	6	8	4	3	2
39	100	100	88	88	75	65	31	34
38	10	5	8	9	2	6	5	3
37	3		3	4	1	2	1	1
33	3				2	2		
31	1			1	1		4	1
30							1	
29	43	39	43	44	27	26	17	12
28	10	6	9	9	13	8	12	8
27	45	40	32	31	53	43	58	40
26	9	4	6	6	12	8	8	7

[a] See footnote to Table 1. [b] Apart from complications caused by unimolecular contributions, these spectra are in excellent qualitative agreement with those (ref. 10) reported previously for these ions.



Scheme 1

formation of a product ion $[CH_2{=}CHC(CD_3){=}O^+CH_3]$ that is more heavily substituted and therefore more stable than either of those $[CH_3CH{=}CHCH{=}O^+CH_3$ and $CH_2{=}C(CH_3)CH{=}O^+CH_3$, respectively] accessible by simple fission (σ-cleavage, Scheme 1) of $1^{+\cdot}$ and $2^{+\cdot}$. Accurate thermochemical data on these oxonium ions are not yet known. Fortunately, however, reliable enthalpies of formation are available for the homologous species containing the $=OH^+$ entity. Whereas $CH_3CH{=}CHCH{=}OH^+$ and $CH_2{=}C(CH_3)CH{=}OH^+$ have similar enthalpies of formation (603 and 607 kJ mol^{-1}, respectively), the value (567 kJ mol^{-1}) for $CH_2{=}CHC(CH_3){=}OH^+$ is substantially lower.[7] A parallel trend should be found in the enthalpies of formation of the oxonium ions containing the $=O^+CH_3$ function. The superior stability of the ion $[CH_2{=}CHC(CD_3){=}O^+CH_3]$ formed *via* rearrangement and eventual σ′-cleavage of $1^{+\cdot}$ and $2^{+\cdot}$ is such a favourable energetic factor that it more than offsets any disadvantageous energetic or entropic features of the additional isomerisation steps.

Support for this interpretation is furnished by the almost identical collision-induced dissociation (CID) spectra of the $C_5H_6D_3O^+$ ions generated either by $CH_3^\cdot$ loss from $1^{+\cdot}$ and $2^{+\cdot}$ or by $CD_3^\cdot$ elimination from $CH_2{=}CHC(CD_3)_2OCH_3^{+\cdot}$, 3^+, Table 1. Similarly, the CID spectra of the $[M-CD_3]^+$ ions in the spectra of **1** and **2** closely resemble those of the $[M-C_2H_5]^+$ ions in the spectra of $CH_3CH{=}CHCH(C_2H_5)OCH_3$, **4**, and $CH_2{=}C(CH_3)CH(C_2H_5)OCH_3$, **5**, respectively, Table 2. In the case of the ionised hexenyl methyl ethers, loss of the methyl group attached to the double bond does not compete effectively with elimination of the α-ethyl group *via* σ-cleavage. The contrasting behaviour of $1^{+\cdot}$ and $2^{+\cdot}$, compared to that of $4^{+\cdot}$ and $5^{+\cdot}$, may reflect the greater ease of elimination of the larger and more polarisable ethyl group from the second pair of ions.

The CID spectrum of the $[M-CH_3]^+$ ions in the spectra of $CH_3CH{=}CHCH(CH_3)OCH_3$, **6**, corresponds to a combination of the CID spectrum of $CH_2{=}CHC(CH_3){=}O^+CH_3$ $\{[M-CH_3]^+$ and $[M-C_2H_5]^+$, respectively, in the spectra of $CH_2{=}CHC(CH_3)_2OCH_3$, **8**, and $CH_2CHC(CH_3)(C_2H_5)OCH_3$, **9**$\}$ with an approximately equal proportion of the CID spectrum of $CH_3CH{=}CHCH{=}O^+CH_3$. Similarly, the

CID spectrum of $[M - CH_3]^+$ formed from $CH_2{=}C(CH_3)CH(CH_3)OCH_3$, **7**, corresponds to an analogous combination of the CID spectra of $CH_2{=}CHC(CH_3){=}O^+CH_3$ and $CH_2{=}C(CH_3)CH{=}O^+CH_3$, Table 2. These data confirm that rapid elimination of $CH_3^{\cdot}$ from $\mathbf{6}^{+\cdot}$ and $\mathbf{7}^{+\cdot}$ occurs *via* σ- and σ′-cleavages in comparable abundances.

The corresponding pentenols, from which **1** and **2** are derived by *O*-methylation, also show both $[M - CH_3]^+$ and $[M - CD_3]^+$ peaks in their mass spectra. Unfortunately, analysis in these systems is complicated by the possibility of ketonisation of the ionised alkenols prior to methyl radical expulsion.[3,8,9] Nevertheless, the CID spectrum of the $[M - CH_3]^+$ ion derived from $CH_2{=}C(CH_3)CH(CD_3)OH^{+\cdot}$ is very similar to that of the $[M - CD_3]^+$ ion formed from $CH_2{=}CHC(CD_3)_2OH^{+\cdot}$. This similarity points to a common structure $[CH_2{=}CHC(CD_3){=}OH^+]$ in both cases.

In all these systems, direct loss of an α-methyl substituent, *via* σ-cleavage, affords a secondary oxonium ion in which the charge is further stabilised by conjugation with the neighbouring C–C π-bond. Despite this, the alternative route involving rearrangement and subsequent expulsion of a different methyl group competes effectively with σ-cleavage, even for relatively fast dissociations. This phenomenon serves to emphasise both the ease of formation of distonic ions *via* 1,2-H shifts in ionised methyl ethers derived from secondary allylic alcohols and also the facility for rearrangement of these distonic ions *via* ionised methoxycyclopropanes or related species.

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References

1 H. Budzikiewicz, C. Djerassi and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holden-Day, San Francisco, 1967.

2 F. W. McLafferty, *Interpretation of Mass Spectra*, University Science Books, Mill Valley, California, 3rd edn., 1980, see especially ch. 4.

3 For an overview, see: G. Bouchoux, *Mass Spectrom. Rev.*, 1988, **7**, 1; 1988, **7**, 203.

4 R. D. Bowen, A. D. Wright, S. R. Thomas, K. R. Jennings and A. Maccoll, *Org. Mass Spectrom.*, 1991, **26**, 421.

5 B. F. Yates, W. J. Bouma and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5808.

6 S. Hammerum, *Mass Spectrom. Rev.*, 1988, **7**, 123.

7 S. G. Lias, J. F. Liebman and R. D. Levin, *J. Phys. Chem., Ref. Data*, 1984, **13**, 693.

8 J. J. Zwinselman, N. M. M. Nibbering, N. E. Middlemiss, J. Hegedus-Vajda and A. G. Harrison, *Int. J. Mass Spectrom. Ion. Phys.*, 1981, **38**, 163; K. R. Laderoute, J. J. Zwinselman and A. G. Harrison, *Org. Mass Spectrom.*, 1985, **20**, 25.

9 D. J. McAdoo, C. E. Hudson, F. W. McLafferty and T. E. Parks, *Org. Mass Spectrom.*, 1984, **19**, 353.

10 G. Bouchoux, Y. Hoppilliard and P. Jaudon, *Org. Mass Spectrom.*, 1987, **22**, 98.