Classification of Isomeric $C_4H_9O^+$ Ions according to their Unimolecular Gas-phase Decompositions

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Isomeric $C_4H_9O^+$ (*m/e* 73) ions have been generated in the mass spectrometer from 12 different alcohols, ethers, acetals, and ketals. Using the criterion of competing metastable abundance ratios, these ions have been shown to decompose, with rate constants *ca.* 10^5 s^{-1}, from one of five distinct structures or mixtures of structures. Extensive ^2H-labelling has been used to investigate the structures of the decomposing ions, and the mechanisms of decomposition.

ONE of the major uses of mass spectrometry in recent years has been in the study of the unimolecular decompositions of gaseous organic ions, and especially in investigating the structures of the decomposing ions, and the extent of scrambling and isomerisation reactions that precede decomposition. For example, $C_4H_9^+$ ions generated from n-, iso-, sec-, and tert-butyl precursors have been shown to isomerise completely to the same structure or mixture of structures before decomposition in the metastable drift regions ($k \sim 10^5$ s^{-1}).[1] In addition, complete scrambling of carbon and hydrogen before fragmentation is observed.[1] Similar studies of organic ions containing heteroatoms have been made. Shannon and McLafferty have classified $C_2H_5O^+$ ions generated from a variety of precursors into two distinct groups, by a study of their metastable abundance ratios.[2] This criterion of competing metastable abundance ratios has been used to classify isomeric $C_3H_8N^+$ ions into three

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[1] B. Davis, D. H. Williams and A. N. H. Yeo, *J. Chem. Soc.* (*B*), 1970, 81.

[2] T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5021.

distinct groups.[3] It would therefore appear that in ions containing heteroatoms (O, N), isomerisation reactions are generally less prevalent than in hydrocarbon ions, because the activation energies for decomposition paths are more frequently lower than the corresponding energies for internal rearrangement (relative to the hydrocarbon cases).

In order to investigate the ability of oxygen atoms to direct fragmentation in an ion with numerous possible isomerisation and fragmentation reactions, we have generated $C_4H_9O^+$ ions from a variety of precursors. Throughout the discussion use will be made of the criterion of competing metastable abundance ratios: that when two or more ions of the same composition have isomerised completely to the same structure or mixture of structures before decomposition in the metastable regions of a mass spectrometer, they should undergo competing metastable transitions in the same or similar ratios.[2,4] All the results presented are for first drift region metastable transitions ($^1m^*$).

TABLE 1

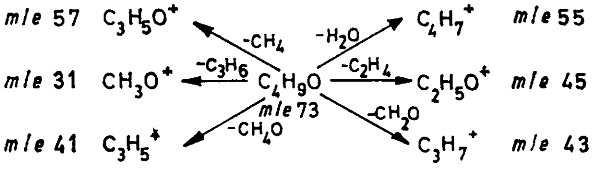
Origin of $C_4H_9O^+$ (*m/e* 73) ions, and the relative abundances of competing metastable transitions ($^1m^*$) from them [a]

Origin of *m/e* 73	Ion no.	Neutral lost in decomposition					
		$-CH_4$	$-H_2O$	$-C_2H_4$	$-CH_2O$	$-CH_4O$	$-C_3H_6$
$\mathrm{CH_3CH_2CH(OH)CH_2CH_2CH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{\underset{\underset{+OH}{\Vert}}{C}HCH_2CH_2CH_3}$	(*1*)		99	1			
$\mathrm{(CH_3)_2CHCH(OH)CH(CH_3)_2}\,]^{+\cdot} \xrightarrow{-\mathrm{Pr}} \mathrm{\underset{\underset{+OH}{\Vert}}{C}HCH{<}^{CH_3}_{CH_3}}$	(*2*)		90	3	7		
$\mathrm{(CH_3CH_2)_2C(OH)CH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{CH_3\underset{\underset{+OH}{\Vert}}{C}CH_2CH_3}$	(*3*)		89	3	8		
$\mathrm{(CH_3CH_2CH_2)_2O}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{CH_3CH_2CH_2\overset{+}{O}{=}CH_2}$	(*4*)		85		15		
$\mathrm{CH_3CH_2CH_2OCH_2CH_2CH_2CH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Pr}} \mathrm{CH_3CH_2CH_2\overset{+}{O}{=}CH_2}$	(*5*)		76		24		
$\mathrm{(CH_3)_2CHOCH_2CH_2CH_2CH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Pr}} \mathrm{{}^{CH_3}_{CH_3}{>}CH\overset{+}{O}{=}CH_2}$	(*6*)		88		12		
$\mathrm{CH_3CH_2CH(CH_3)OCH_2CH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{CH_3CH{=}\overset{+}{O}CH_2CH_3}$	(*7*)		4	96			
$\mathrm{CH_3CH(OCH_2CH_3)_2}\,]^{+\cdot} \xrightarrow{-\mathrm{OEt}} \mathrm{CH_3CH{=}\overset{+}{O}CH_2CH_3}$	(*8*)		1	99			
$\mathrm{CH_3CH_2CH(OCH_3)_2}\,]^{+\cdot} \xrightarrow{-\mathrm{OCH_3}} \mathrm{CH_3CH_2CH{=}\overset{+}{O}CH_3}$	(*9*)	2·5	1·5	53	8	34	1
$\mathrm{(CH_3CH_2)_2CHOCH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{CH_3CH_2CH{=}\overset{+}{O}CH_3}$	(*10*)	0·5	1	54·5	8	35	1
$\mathrm{CH_3CH_2C(CH_3)_2OCH_3}\,]^{+\cdot} \xrightarrow{-\mathrm{Et}} \mathrm{{}^{CH_3}_{CH_3}{>}C{=}\overset{+}{O}CH_3}$	(*11*)	3	18·5	14	41	16·5	7
$\mathrm{(CH_3)_2C(OCH_3)_2}\,]^{+\cdot} \xrightarrow{-\mathrm{OCH_3}} \mathrm{{}^{CH_3}_{CH_3}{>}C{=}\overset{+}{O}CH_3}$	(*12*)	3	11	14	45	19	8

[a] Abundances are expressed as a percentage of the total metastable intensity ($^1m^*$) from *m/e* 73.

RESULTS AND DISCUSSION

Twelve isomeric $C_4H_9O^+$ (*m/e* 73) ions (*1*)—(*12*) were generated by electron bombardment of various alcohols, ethers, acetals, and ketals. A total of six fragmentations from $C_4H_9O^+$ were observed (Scheme 1), and the $^1m^*$ abundances for these for (*1*)—(*12*) are summarised in Table 1, together with the generation of (*1*)—(*12*). The specific α-cleavages undergone by the molecular ions suggest that there has been no rearrangement prior to these low activation-energy processes and that structures (*1*)—(*12*) do represent the structures of the $C_4H_9O^+$ ions at the threshold. From the data summarised in Table 1 it is apparent that ions which were assumed to have been formed with the same structure [*e.g.* (*4*) and (*5*), (*7*) and (*8*)] do have similar relative abundances of the same competing metastable transitions. Using the criterion of competing metastable abundance ratios



SCHEME 1

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[3] N. A. Uccella, I. Howe, and D. H. Williams, *J. Chem. Soc.* (*B*), 1971, 1933.

[4] H. M. Rosenstock, V. H. Dibeler, and F. N. Harlee, *J. Chem. Phys.*, 1964, **40**, 591; R. G. Cooks, I. Howe, and D. H. Williams, *Org. Mass Spectroscopy*, 1969, **2**, 137.

ions (*1*)—(*12*) may be divided into five distinct groups, each reacting from a different structure or mixture of structures: (*1*); (*2*) and (*3*); (*4*)—(*6*); (*7*) and (*8*); and (*9*)—(*12*). Extensive ^2H labelling has been carried out in each of these groups, to provide more detailed information on the mechanisms of isomerisation and of decomposition. The reasons for placing ions (*9*), (*10*) and (*11*), (12) into one group may not be immediately obvious in the light of the relative abundance variations (although these four ions are the only ones to undergo all six metastable transitions—Table 1), but this point is discussed subsequently.

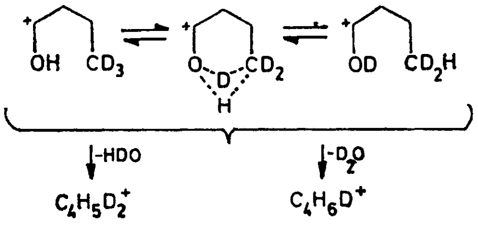
Ion (*1*).—The major transition from (*1*) is to *m*/*e* 55, loss of 18 mass units (m.u.) (H_2O). The results of ^2H labelling in (*1*) for water loss are summarised in Table 2. From these data, three conclusions are evident. First, although water loss involves a substantially intact O–H bond, there is appreciable scrambling among the hydroxy-hydrogen and the hydrogens of the alkyl chain (*13*). Secondly, water loss involves mainly the hydroxy-hydrogen and the hydrogens of the terminal methyl group. Thus, ions (*14*), (*16*), and (*18*) (labelled α, β, and γ to the hydroxy-group) lose almost exclusively H_2O, whereas (*19*) (labelled γ and δ) loses mainly a mixture of HDO and D_2O. Thirdly, scrambling occurs initially between the hydroxy-hydrogen and the hydrogens of terminal methyl group. Thus ions labelled in the α, β, and γ positions show little scrambling (*14*), (*16*), and (*18*), whereas those labelled in the hydroxy or terminal methyl groups show a much greater degree of scrambling. These conclusions may be represented in terms of Scheme 2. Together with scrambling of the hydroxy-hydrogen, there is a small amount of scrambling between the α, β, γ, and δ positions of the alkyl chain. The water loss, which may be seen as a 1,4-elimination from structure (*1*), probably has an activation energy comparable to that for the scrambling reactions. It is interesting to note that water loss from the molecular ions of primary alcohols [5] and cyclohexanol [6] occurs mainly by 1 : 4 elimination.

TABLE 2

Water loss from ^2H labelled ions of structure (*1*) ($^1m^*$)

Origin	Ion no.	Percentage loss of H_2O	HDO	D_2O
$CH_3CH_2CH(OD)CH_2CH_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OD}{\underset{\|}{C}}HCH_2CH_2CH_3$	(*13*)	28	72	
$CH_3CH_2CD(OH)CH_2CH_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OH}{\underset{\|}{C}}DCH_2CH_2CH_3$	(*14*)	98	2	
$CH_3CH_2CD(OD)CH_2CH_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OD}{\underset{\|}{C}}DCH_2CH_2CH_3$	(*15*)	25	73	2
$CH_3CD_2CH(OH)CD_2CH_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OH}{\underset{\|}{C}}HCD_2CH_2CH_3$	(*16*)	95	5	
$CH_3CD_2CH(OD)CD_2CH_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OD}{\underset{\|}{C}}HCD_2CH_2CH_3$	(*17*)	26·5	72·5	1
$CH_3CH_2CH(OH)CH_2CD_2CH_3\ ]^{+\cdot} \longrightarrow \underset{+OH}{\underset{\|}{C}}HCH_2CD_2CH_3$	(*18*)	92·5	7·0	0·5
$CH_3CH_2CH(OH)CH_2CD_2CD_3\ ]^{+\cdot} \longrightarrow \underset{+OH}{\underset{\|}{C}}HCH_2CD_2CD_3$	(*19*)	9	67	24

Ions (*2*) *and* (*3*).—The three reactions from these ions are loss of 18 m.u. (H_2O), 28 m.u. (CO, C_2H_4), and 30 m.u. (CH_2O). For (*2*) and (*3*) the ratio of these three reactions is very close to 30 : 1 : 2·5, and by the criterion of competing metastable abundance ratios it is concluded that (*2*) and (*3*) have isomerised to the same structure or mixture of structures before $^1m^*$ transitions. As in (*1*), the major reaction is loss of H_2O, and the results of ^2H labelling in (*2*) and (*3*) on water loss are summarised in Table 3. Several conclusions are evident from these data. First, as might be expected, the O–H bond remains substantially intact during water loss (*20*) and (*25*). Although there is some scrambling between the hydroxy-hydrogen and the alkyl chain in (*20*) and (*25*), it is considerably less than in ions of structure (*1*) [*e.g.* (*13*)]. Secondly, water loss appears to involve almost exclusively the hydroxy and methyl groups of ions



SCHEME 2

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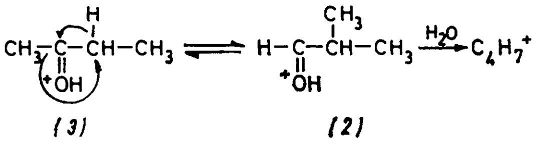
[5] W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, 1964, **86**, 2375.

[6] R. S. Ward and D. H. Williams, *J. Org. Chem.*, 1969, **34**, 3373.

(*20*)—(*27*). Thus ion (*21*) (labelled in the β-methylene group) loses almost exclusively H_2O. HDO loss is probably due to scrambling in the alkyl chain. Similarly, ion (*26*) loses mainly HDO, loss of H_2O and D_2O again probably being due to scrambling. These data may be interpreted as either (*a*) rearrangement of (*3*) to (*2*) followed by a 1 : 3 elimination of water (Scheme 3), or



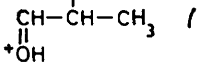
SCHEME 3

(*b*) rearrangement of (*2*) to (*3*) followed by competitive 1 : 2 and 1 : 3 eliminations. However, there is no rearrangement to structure (*1*). Thus, ion (*23*) may rearrange according to Scheme 3 to give (*28*), which then eliminates water by a 1 : 3 process, a small ^2H isotope effect accounting for the ratio of H_2O : HDO lost being 1·35 : 1. In the absence of isotope effects this ratio should be 1 : 1.

TABLE 3

Water loss from ^2H labelled ions of structures (*2*) and (*3*) (in $^1m^*$)

Origin	Ion no.	Percentage loss of H_2O	HDO	D_2O
$(CH_3CH_2)_2C(OD)CH_3]^{+\cdot} \longrightarrow CH_3\underset{\overset{\|}{+OD}}{C}CH_2CH_3$	(*20*)	5	95	
$(CH_3CD_2)_2C(OH)CH_3]^{+\cdot} \longrightarrow CH_3\underset{\overset{\|}{+OH}}{C}CD_2CH_3$	(*21*)	90	10	
$(CH_3CD_2)_2C(OD)CH_3]^{+\cdot} \longrightarrow CH_3\underset{\overset{\|}{+OD}}{C}CD_2CH_3$	(*22*)	3	91	6
$(CH_3CH_2)_2C(OH)CD_3]^{+\cdot} \longrightarrow CD_3\underset{\overset{\|}{+OH}}{C}CH_2CH_3$	(*23*)	57	42	1
$(CH_3CH_2)_2C(OD)CD_3]^{+\cdot} \longrightarrow CD_3\underset{\overset{\|}{+OD}}{C}CH_2CH_3$	(*24*)	1	62	37
$(CH_3)_2CHCH(OD)CH(CH_3)_2]^{+\cdot} \longrightarrow \begin{matrix}CH_3\\CH_3\end{matrix}\!>CH\underset{\overset{\|}{+OD}}{CH}$	(*25*)	6	94	
$(CD_3)_2CHCH(OH)CH(CH_3)_2]^{+\cdot} \longrightarrow \begin{matrix}CD_3\\CD_3\end{matrix}\!>CH\underset{\overset{\|}{+OH}}{CH}$	(*26*)	13	83	4
$(CD_3)_2CHCH(OD)CH(CH_3)_2]^{+\cdot} \longrightarrow \begin{matrix}CD_3\\CD_3\end{matrix}\!>CH\underset{\overset{\|}{+OD}}{CH}$	(*27*)		13	87



$$\overset{+}{O}H{=}CH{-}\overset{CD_3}{\overset{|}{C}H}{-}CH_3$$

(*28*)

Ions (*4*), (*5*), *and* (*6*).—Two reactions are observed from (*4*)—(*6*): loss of 18 m.u. (H_2O) and 30 m.u. (CH_2O), and the similarity of the ratios between these reactions suggests that (*4*)—(*6*) have isomerised to the same structure or mixture of structures before $^1m^*$ transitions. Table 4 summarises the ^1H labelling results for (*4*)—(*6*). Two conclusions are evident from these data. First, formaldehyde loss involves specifically the two hydrogens of the isolated methylene group. Thus ions (*30*) and (*31*) lose only CD_2O. It is therefore almost certain that formaldehyde loss occurs by a single bond cleavage of the oxygen and isolated methylene group from the C_3 chain. Secondly, the hydrogen involved in water loss comes in each case only from the intact C_3 chain (*30*)—(*32*). This is obviously a deep-seated rearrangement which cannot be simply represented, but it is interesting that the hydrogens lost originate exclusively from the chain which was not involved in the α-cleavage reaction occurring in the molecular ion. This specific involvement of hydrogens from the intact alkyl chain in water loss from ions derived from aliphatic ethers has also been observed by other workers.[7] A recent study of the $C_5H_{11}O^+$ ion (*33*) has been made by ion-cyclotron resonance spectroscopy,[8] and a mechanism proposed for its dehydration (Scheme 4). However, the present results do not support an analogous mechanism occurring from (*4*)—(*6*) in the mass spectrometer.

Ions (*7*) *and* (*8*).—As was noted earlier, these ions were expected to be formed at the threshold with the same

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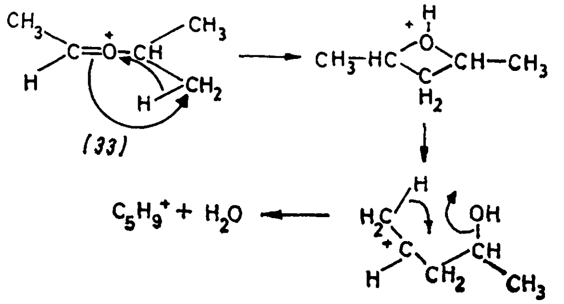
[7] (*a*) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 1965, **87**, 5747; (*b*) G. A. Smith and D. H. Williams, *J. Amer. Chem. Soc.*, 1969, **91**, 5254.

[8] T. A. Lehman, T. A. Elwood, J. T. Bursey, M. M. Bursey, and J. L. Beauchamp, *J. Amer. Chem. Soc.*, 1971, **93**, 2108.

structure, and the relative abundances of their competing metastable transitions (${}^1m^*$) supports this (Table 1).



SCHEME 4

The major reaction is loss of 28 m.u. (CO or C_2H_4), and the results of ${}^2H$ labelling on this fragmentation are summarised in Table 5. These data confirm that the loss of 28 m.u. from (*7*) and (*8*) is due solely to ethylene, and that ethylene loss occurs only from the intact ethyl group as had been noted by previous workers.[9] This may be interpreted as involving a four membered cyclic transition state and formation of the protonated acetaldehyde ion (*38*) (Scheme 5). Ethylene loss apparently proceeds in competition with hydrogen scrambling in the ethyl group [(*36*) and (*37*)], and so probably has an activation energy comparable with that for the scrambling reaction. Unlike ions (*4*)—(*6*), water loss from (*7*) and (*8*) is a very minor reaction, reflecting the considerably lower activation energy for ethylene loss. Also, the single bond cleavage from (*7*) and (*8*) to form acetaldehyde and $C_2H_5^+$, analogous to the loss of formaldehyde from (*4*)—(*6*), is not observed. This reflects the higher heat of formation of $C_2H_5^+$ compared with n- or iso-$C_3H_7^+$ (219, 209, and 190 kcal mol^{-1} respectively[10]).

TABLE 4

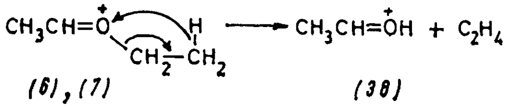
${}^2H$ Labelling results for ions of structures (*4*)—(*6*) (in ${}^1m^*$)

Origin	Ion no.	Percentage loss of H_2O	HDO	D_2O	CH_2O	CHDO	CD_2O
$CH_3CH_2CH_2OCD_2CH_2CH_3\,]^{+\cdot} \longrightarrow CH_3CH_2CH_2\overset{+}{O}{=}CD_2 + CH_3CH_2CD_2\overset{+}{O}{=}CH_2$	(*29*)	57	22	1	11		9
$CH_3CH_2CH_2CD_2OCH_2CH_2CH_3\,]^{+\cdot} \longrightarrow CH_3CH_2CH_2\overset{+}{O}{=}CD_2$	(*30*)	69					31
$(CH_3)_2CHOCD_2CH_2CH_2CH_3\,]^{+\cdot} \longrightarrow \begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!\!>CH{-}\overset{+}{O}{=}CD_2$	(*31*)	86					14
$(CD_3)_2CDOCH_2CH_2CH_2CH_3\,]^{+\cdot} \longrightarrow \begin{smallmatrix}CD_3\\ CD_3\end{smallmatrix}\!\!>CD\overset{+}{O}{=}CH_2$	(*32*)			80	20		

TABLE 5

${}^2H$ Labelling results for the observed loss of 28 m.u. (CO or C_2H_4) from ions (*7*) and (*8*) (${}^1m^*$)

Origin	Ion no.	Percentage loss of CO or C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3
$CH_3CH_2CD(CH_3)OCH_2CH_3\,]^{+\cdot} \longrightarrow CH_3CD{=}\overset{+}{O}CH_2CH_3$	(*34*)	100			
$CH_3CD_2CH(CD_3)OCH_2CH_3\,]^{+\cdot} \longrightarrow CD_3CH{=}\overset{+}{O}CH_2CH_3$	(*35*)	100			
$CH_3CH(OCD_2CH_3)_2\,]^{+\cdot} \longrightarrow CH_3CH{=}\overset{+}{O}CD_2CH_3$	(*36*)		17	83	
$CH_3CH(OCH_2CD_3)_2\,]^{+\cdot} \longrightarrow CH_3CH{=}\overset{+}{O}CH_2CD_3$	(*37*)			90	10



SCHEME 5

Ions (*9*)—(*12*).—These ions undergo six competing reactions in the first drift region of the mass spectrometer: loss of 16 m.u. (CH_4), 18 m.u. (H_2O), 28 m.u. (CO or C_2H_4), 30 m.u. (CH_2O), 32 m.u. (CH_4O), and 42 m.u. (C_3H_6 or CH_2CO). The pairs of ions which might be expected to have the same structure at the threshold [(*9*) and (*10*), and (*11*) and (*12*)] undergo the six reactions in very similar ratios (Table 1). However the ratios for ions (*9*) and (*10*) are in some cases much different from those for ions (*11*) and (*12*). This suggests that rearrangement of (*9*)—(*12*) to a common structure or mixture of structures is in competition with fragmentation. Further light is thrown on this problem by the ${}^2H$ labelling results summarised in Tables 6 and 7. The data summarised in Table 6 suggest three conclusions. First, the loss of 28 m.u. from (*9*) and (*10*) is due exclusively, or almost exclusively, to the expulsion

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[9] A. G. Harrison and C. W. Tsang, *Org. Mass Spectrometry*, 1970, **3**, 647.

[10] 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 (U.S.), 1969.

of ethylene from the C_3 chain. This is in agreement with the findings of Harrison and Tsang.[9] This loss of ethylene occurs in competition with considerable scrambling of the hydrogens in the C_3 chain, thus causing extensive loss of C_2H_3D from (*39*) and (*40*). Secondly, loss of 30 m.u. (CH_2O) involves only the methoxy-group, with transfer of one of the hydrogens to the C_3 chain. Thus (*41*) loses CD_2O (32 m.u.). Thirdly, loss of 32 m.u. (CH_4O) is loss of methanol, involving the intact methoxy-group and one hydrogen from the C_3 chain. This is seen in ion (*41*), losing 35 m.u., CD_3OH.

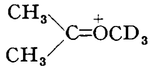
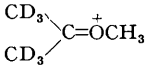
TABLE 6

^2H Labelling results for loss of 28, 30 and 32 m.u. from ions (*9*) and (*10*) ($^1m^*$)

Origin	Ion no.	Percentage loss of							
		28 CO C_2H_4	29 C_2H_3D	30 $C_2H_2D_2$ CH_2O	31 C_2HD_3 CHDO	32 CD_2O CH_4O	33 CH_3DO	34 CH_2D_2O	35 CHD_3O
$(CH_3CH_2)_2CDOCH_3\,]^{+\cdot} \longrightarrow CH_3CH_2CD{=}\overset{+}{O}CH_3$	(*39*)	17	39	8·5		32·5	3		
$(CH_3CD_2)_2CHOCH_3\,]^{+\cdot} \longrightarrow CH_3CD_2CH{=}\overset{+}{O}CH_3$	(*40*)	3	32	33·5		28	3·5		
$CH_3CH_2CH(OCD_3)_2\,]^{+\cdot} \longrightarrow CH_3CH_2CH{=}\overset{+}{O}CD_3$	(*41*)	60·5				5·5			34

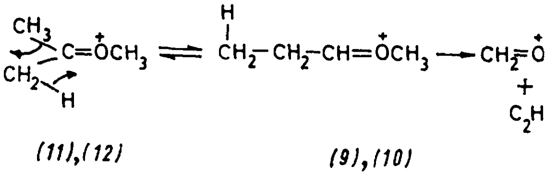
TABLE 7

^2H Labelling results for loss of 28, 30 and 32 m.u. from (*11*) and (*12*) ($^1m^*$)

Origin	Ion no.	Percentage loss of							
		28 CO C_2H_4	29 C_2H_3D	30 $C_2H_2D_2$ CH_2O	31 C_2HD_3 CHDO	32 C_2D_4 CD_2O CH_4O	33 CH_3DO	34 CH_2D_2O	35 CHD_3O
$CH_3CH_2C(CH_3)_2OCD_3\,]^{+\cdot} \longrightarrow$  $(CH_3)_2C{=}\overset{+}{O}CD_3$	(*42*)	22	1	7	4	39			27
$CH_3CH_2C(CD_3)_2OCH_3\,]^{+\cdot} \longrightarrow$  $(CD_3)_2C{=}\overset{+}{O}CH_3$	(*43*)			54·5	5·5	24	16		

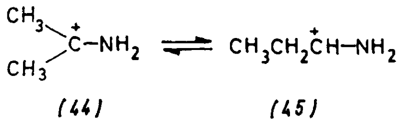
Three conclusions are evident from the data presented in Table 7. First, loss of 28 m.u. is exclusively loss of ethylene, and comes almost entirely from the C_3 chain as has been found by previous workers.[9] Thus no C_2H_3D or CO loss is observed from (*43*), but small amounts of C_2H_3D and possibly of $C_2H_2D_2$ and C_2HD_3 are lost from (*42*). Secondly, loss of formaldehyde is most probably occurring from the methoxy-group in competition with scrambling of hydrogen. Thus, mainly CH_2O loss is observed from (*43*), although small amounts of CHDO and possibly CD_2O are also lost. Also, from (*42*) mainly CD_2O loss is observed. Thirdly, loss of methanol involves only the methoxy-group and one hydrogen from the C_3 chain. Thus only CD_3OH and CH_3OD loss is observed from (*42*) and (*43*) respectively.

The sets of conclusions set out above may be interpreted in terms of ethylene loss from structures (*9*) and (*10*), and formaldehyde and methanol loss involving an intact methoxy-group attached to the C_3 chain. Ethylene loss is the dominant reaction from (*9*) and (*10*), but is not so important from (*11*) and (*12*), probably reflecting a potential isomerisation of (*11*) [(*12*)] to (*9*) [(*10*)] prior to ethylene loss (Scheme 6). From ions (*11*) and (*12*) the most important reaction is one that can proceed without rearrangement, *i.e.* formaldehyde loss. We conclude that the rate of interconversion of (*9*) and (*11*) is comparable to the rate of loss of ethylene from (*9*) and of formaldehyde from (*11*) at the internal energies appropriate to metastable transitions. In the case of the analogous $C_3H_8N^+$ ions, (*44*) and (*45*), it was found that interconversion was complete prior to metastable ethylene and ammonia loss.[3] Loss of 42 m.u. from



SCHEME 6

(*9*)—(*12*) was established to be C_3H_6 rather than CH_2CO. Ion (*40*) loses mainly 44 m.u. ($C_3H_4D_2$), no loss of 42 m.u.



being observed. Ion (*43*) loses a mixture of 46 and 47 m.u. ($C_3H_2D_4$ and C_3HD_5), and again no loss of 42 m.u. is observed.

Conclusions.—The 12 isomeric $C_4H_9O^+$ ions generated have been classified into five structurally distinct groups. In each of these groups, hydrogen scrambling reactions proceed in competition with fragmentation, and in no case reach completion before fragmentation. Only in two cases [ions (*2*) and (*3*) and (*4*)—(*6*)] do isomerisation reactions appear to be complete before fragmentation and in one other group [ions (*9*), (*10*), (*11*), and (*12*)] isomerisation proceeds in competition with fragmentation. When present, the O–H bond remains substantially intact. It is therefore apparent that the presence of an oxygen atom severely limits scrambling and isomerisation reactions compared with hydrocarbon ions.

The classification of these $C_4H_9O^+$ isomers into such distinct groups suggests that the metastable transitions from *m/e* 73 ($C_4H_9O^+$) may be of use in identifying structural entities in unknown molecules. For example, a molecule that gives rise to a $C_4H_9O^+$ fragment which decomposes in the metastable regions by loss of H_2O and C_2H_4 in the approximate ratio 1 : 24 most probably contains the $CH_3CHXOCH_2CH_3$ group [(*7*), (*8*)].

EXPERIMENTAL

All mass spectra were determined on an AEI MS-9 double-focusing mass spectrometer, with an electron beam energy of 70 eV (nominal) and source temperature *ca.* 250°. Samples were introduced *via* the heated inlet system. Metastable transitions in the first drift region were observed using the modification described by Jennings.[11]

Unlabelled samples were either available commercially or synthesised by unexceptional methods. All *O*-deuteriated alcohols were obtained by exchange of the O–H compound with D_2O, and their mass spectra were determined after equilibrating the inlet system and source of the mass spectrometer with D_2O. Other ^{2}H-labelled compounds were synthesised as described schematically below. Fuller details may be obtained from the authors. All samples were purified by g.l.c. before use. The authors are grateful to Dr. G. A. Smith for the synthesis of the labelled butyl isopropyl ethers [precursors of (*31*) and (*32*)].[7b]

(*14*)

$$CH_3CH_2COCH_2CH_2CH_3 \xrightarrow[\text{Ether}]{LiAlD_4} CH_3CH_2CD(OH)CH_2CH_2CH_3$$

(*16*)

$$CH_3CH_2COCH_2CH_2CH_3 \xrightarrow[D_2O]{K_2CO_3} CH_3CD_2COCD_2CH_2CH_3 \xrightarrow[\text{ether}]{LiAlH_4} CH_3CD_2CH(OH)CD_2CH_2CH_3$$

(*18*)

$$(CH_3CH_2)_2CO \xrightarrow[D_2O]{K_2CO_3} (CH_3CD_2)_2CO \xrightarrow[CH_2Cl_2]{CF_3CO_3H} CH_3CD_2CO_2CD_2CH_3 \xrightarrow{\overset{-}{O}H} CH_3CD_2OH + CH_3CD_2CO_2H$$

$$\xrightarrow[\text{(ii) }CH_3OH]{\text{(i) }SOCl_2} CH_3CD_2CO_2CH_3 \xrightarrow[\text{ether}]{LiAlH_4} CH_3CD_2CH_2OH \xrightarrow{PBr_3} CH_3CD_2CH_2Br \xrightarrow[\text{(ii) }CH_3CH_2CHO]{\text{(i) Mg, ether}} CH_3CH_2CH(OH)CH_2CD_2CH_3$$

(*19*)

$$CD_3CD_2OD \xrightarrow{P/I_2} CD_3CD_2I \xrightarrow[\text{(ii) }CH_3CH_2\underset{O}{CH{-}CH_2}]{\text{(i) Mg, ether}} CH_3CH_2CH(OH)CH_2CD_2CD_3$$

(*21*)

$$(CH_3CD_2)_2CO \xrightarrow[\text{ether}]{CH_3MgI} (CH_3CD_2)C(OH)CH_3$$

[see (*18*)]

(*23*)

$$(CH_3CH_2)_2CO \xrightarrow[\text{ether}]{CD_3MgI} (CH_3CH_2)_2C(OH)CD_3$$

(*26*)

$$(CD_3)_2CO \xrightarrow[\text{ether}]{LiAlH} (CD_3)_2CHOH \xrightarrow{PBr_3} (CD_3)_2CHBr \xrightarrow[\text{(ii) }(CH_3)_2CHCHO]{\text{(i) Mg, ether}} (CD_3)_2CHCH(OH)CH(CH_3)_2$$

(*29*)

$$CH_3CH_2CO_2CH_3 \xrightarrow[\text{ether}]{LiAlD_4} CH_3CH_2CD_2OH \xrightarrow[\text{(ii) }CH_3CH_2CH_2Br]{\text{(i) NaH}} CH_3CH_2CD_2OCH_2CH_2CH_3$$

(*30*)

$$CH_3CH_2CH_2CO_2CH_2CH_3 \xrightarrow[\text{ether}]{LiAlD_4} CH_3CH_2CH_2CD_2OH \xrightarrow{PBr_3} CH_3CH_2CH_2CD_2Br \xrightarrow{CH_3CH_2CH_2\overset{-}{O}\overset{+}{Na}} CH_3CH_2CH_2CD_2OCH_2CH_2CH_3$$

(*34*)

$$CH_3CH_2COCH_3 \xrightarrow[\text{ether}]{LiAlD_4} CH_3CH_2CD(OH)CH_3 \xrightarrow[\text{(ii) }CH_3CH_2Br]{\text{(i) NaH}} CH_3CH_2CD(CH_3)OCH_2CH_3$$

(*35*)

$$CH_3CH_2COCH_3 \xrightarrow[D_2O]{K_2CO_3} CH_3CD_2COCD_3 \xrightarrow[\text{ether}]{LiAlH_4} CH_3CD_2CH(OH)CD_3 \xrightarrow[\text{(ii) }CH_3CH_2Br]{\text{(i) NaH}} CH_3CD_2CH(CD_3)OCH_2CH_3$$

(*36*)

$$CH_3CD_2OH \xrightarrow[CaCl_2]{CH_3CHO} CH_3CH(OCD_2CH_3)_2$$

[from (*18*)]

(*37*)

$$CD_3CO_2H \xrightarrow[\text{(ii) }CH_3OH]{\text{(i) }SOCl_2} CD_3CO_2CH_3 \xrightarrow[\text{ether}]{LiAlH_4} CD_3CH_2OH \xrightarrow[CaCl_2]{CH_3CHO} CH_3CH(OCH_2CD_3)_2$$

(*39*)

$$(CH_3CH_2)_2CO \xrightarrow[\text{ether}]{LiAlD_4} (CH_3CH_2)_2CDOH \xrightarrow[\text{(ii) }CH_3I]{\text{(i) NaH}} (CH_3CH_2)_2CDOCH_3$$

(*40*)

$$(CH_3CD_2)_2CO \xrightarrow{LiAlH_4} (CH_3CD_2)_2CHOH \xrightarrow[\text{(ii) }CH_3I]{\text{(i) NaH}} (CH_3CD_2)CHOCH_3$$

[see (*18*)]

(*41*)

$$CH_3CH_2CHO \xrightarrow[CaCl_2]{CD_3OD} CH_3CH_2CH(OCD_3)_2$$

(*42*)

$$CH_3CH_2C(CH_3)_2OH \xrightarrow[\text{(ii) }CD_3I]{\text{(i) NaH}} CH_3CH_2C(CH_3)_2OCD_3$$

(*43*)

$$(CD_3)_2CO \xrightarrow[\text{ether}]{CH_3CH_2MgI} CH_3CH_2C(CD_3)_2OH \xrightarrow[\text{(ii) }CH_3I]{\text{(i) NaH}} CH_3CH_2C(CD_3)_2OCH_3$$

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[11] K. Jennings in 'Some Newer Physical Methods in Structural Chemistry,' eds. R. Bonnett and J. G. Davies, United Trade Press, London, 1967, p. 105.