Unimolecular Reactions of Ionised Ethers

Richard D. Bowen *,†
Department of Chemistry, University of Warwick, Coventry CV4 7AL
Allan Maccoll
Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ

The 12.1 eV 75 °C electron ionisation mass spectra of 25 saturated dialkyl ethers containing between six and eight carbon atoms are reported and discussed in energetic terms. Dissociation by α-cleavage of $M^{+\bullet}$ typically gives rise to intense peaks in these spectra. However, rearrangement processes, leading to eventual 1,3-*O*-alkyl shifts and subsequent ethyl radical loss, are also important for ionised ethers in which both alkyl groups have primary structures. Other significant ions in the spectra of n-$C_nH_{2n+1}OR$ ethers include those formed by loss of ROH or $C_nH_{2n-1}^{\bullet}$ from $M^{+\bullet}$. Ionised ethers containing one secondary alkyl group tend to dissociate by α-cleavage of this group, or to a lesser extent by loss of the corresponding alkane, without undergoing such extensive rearrangements. Distonic ions and ion–molecule complexes play key roles in the isomerisation and dissociation steps involved in these fragmentations. Simple cleavages dominate the spectra of ethers containing a tertiary alkyl group. These ethers show very small or negligible $M^{+\bullet}$ peaks. Ions corresponding to rupture of the C–O σ-bond, with charge retention by the hydrocarbon fragment, appear in the spectra of some ethers. There is evidence, however, that these ions may originate, at least in part, by secondary dissociations of the primary daughter ions, rather than by direct decomposition of $M^{+\bullet}$.

The reactions undergone by ionised dialkyl ethers of relatively high internal energies were documented over thirty years ago.[1] It subsequently became apparent that a great simplification in the spectra of large dialkyl ethers could be effected by recording the mass spectra at low ionising electron energies and low temperatures.[2,3] More recent work has uncovered curious and noteworthy features of the chemistry of ionised ethers, especially at internal energies close to the threshold for fragmentation.[4–11] Thus, for example, many metastable $[\text{n-}C_nH_{2n+1}O\text{–n-}C_mH_{2m+1}]^{+\bullet}$ species expel an ethyl radical.[11] This remarkable process, which must involve extensive rearrangement, has been carefully studied using ^2H-labelling experiments for ionised ethyl butyl ethers.[4,5,7,8,10] Other intriguing reactions of ionised ethers include alkane expulsions[7,8,10] and production of protonated alcohols by elimination of a radical having one unit of unsaturation.[3,4]

The recognition that distonic[12] ions (radical-cation structures in which the formal charge and radical sites can be considered to be localised on separate atoms)[13–21] and ion–molecule complexes (IMCs)[22–25] often play important roles in the chemistry of isolated ions has led to a renewed interest in the behaviour of ionised ethers.[26–30] Very recent definitive experiments have shown that alkane loss from certain ionised ethers proceeds *via* ion–molecule complexes,[29] and that rearrangement and dissociation of n-$C_4H_9OC_2H_5^{+\bullet}$ and related species occurs *via* distonic intermediates and IMCs.[30] In view of these developments, it seemed of interest to survey the low-energy, low-temperature mass spectra of dialkyl ethers of moderate size in order to discover the extent to which rearrangements involving distonic ions and IMCs participate in the reactions of ionised ethers at these internal energies.

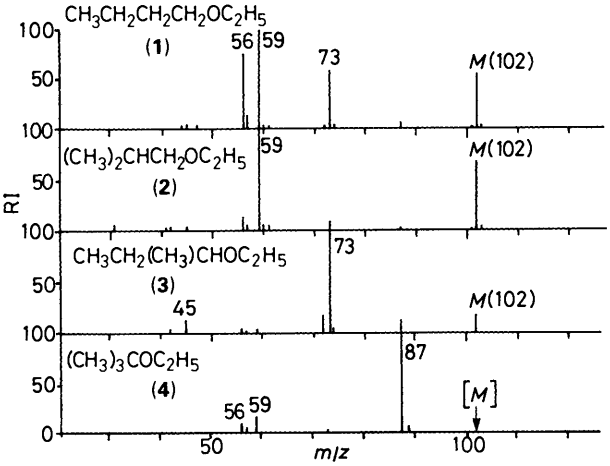


Figure 1. Mass spectra (12.1 eV, 75 °C) of $C_4H_9OC_2H_5$ ethers.

Results and Discussion

The 12.1 eV, 75 °C electron ionisation mass spectra of the four isomeric $C_4H_9OC_2H_5$ ethers, the three isomeric $C_3H_7OC_3H_7$ ethers, and eight larger ethers containing butyl or pentyl groups are shown in Figures 1, 2, and 3, respectively. The spectra of ten other ethers of diverse structure are given in Table 1.

(1) *Reactions of Metastable* $C_4H_9OC_2H_5^{+\bullet}$ *Ions*.—Since metastable $C_4H_9OC_2H_5^{+\bullet}$ radical-cations have been extensively studied,[4,5,7,8,10] it is helpful to discuss their reactions, so as to shed light on the behaviour of larger ionised ethers. The enthalpies of formation of reactants, distonic intermediates and likely combinations of products are given in Table 2. These data represent a combination of experimental values and those obtained by using estimation procedures based on group equivalent methods, hydrogen atom and hydride anion abstraction energies, and proton affinity measurements.[8,31–38] Where comparisons are possible, the agreement between the values given in Table 2 and those utilised in earlier[8,10] work is good.

---

† SERC Advanced Fellow.

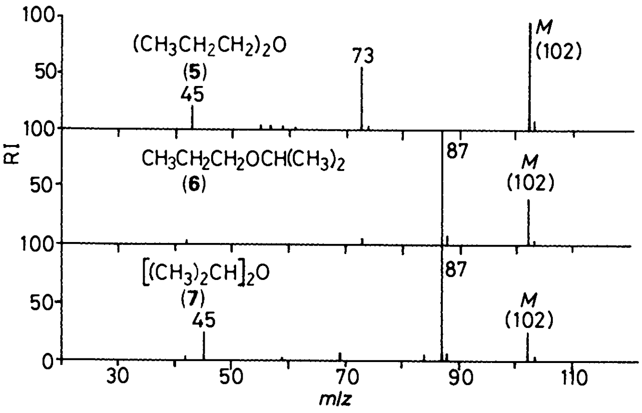


Figure 2. Mass spectra (12.1 eV, 75 °C) of $C_3H_7OC_3H_7$ ethers.

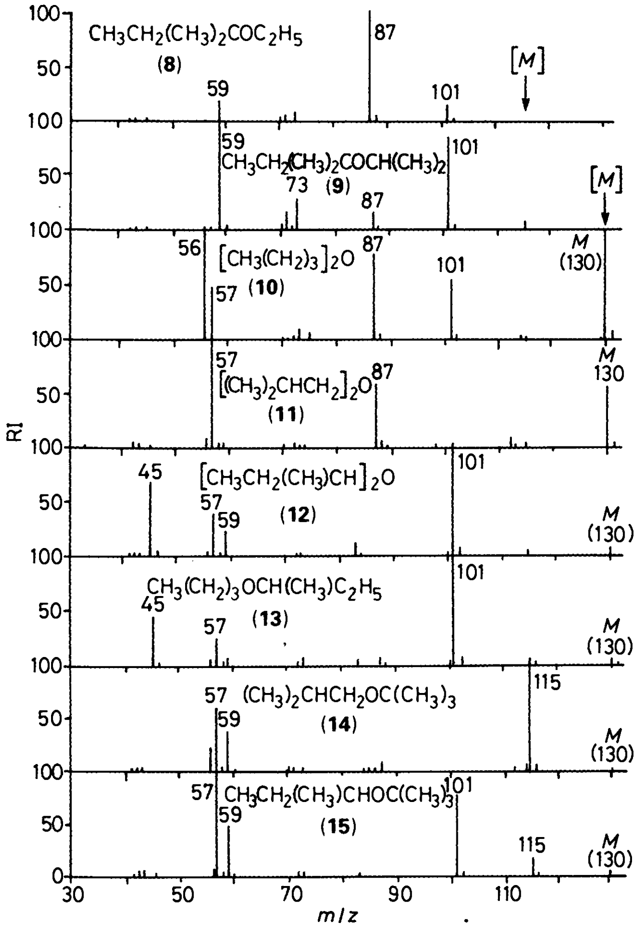


Figure 3. Mass spectra (12.1 eV, 75 °C) of selected $C_7H_{16}O$ and $C_8H_{18}O$ ethers.

The mechanisms whereby low-energy $C_4H_9OC_2H_5^{+\bullet}$ species are thought to rearrange and dissociate are given in Schemes 1[7,8,10,26–30] and 2. Starting from $(\mathbf{1})^{+\bullet}$, a 1,4-hydrogen shift yields the distonic ion (**1δ**); a similar process in $(\mathbf{2})^{+\bullet}$ gives (**2δ**). Both these processes are approximately thermoneutral. Interconversion of (**1δ**) and (**2δ**) can occur by 1,2-shifts in the radical chains. Alternatively, this rearrangement can be envisaged as occurring *via* an IMC, (**A**), comprising ionised methyl cyclopropane and ethanol. The total enthalpy of formation of these components is 700[31] kJ mol^{-1}; the IMC (**A**) ought to be significantly stablised by ion–dipole and related interactions,[25] possibly by 50 kJ mol^{-1} or more.[39,40] All the species (**1δ**), (**2δ**), and (**A**) should, therefore, be energetically accessible to $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ at energies below those needed to effect dissociation of either by simple cleavage ($CH_3^\bullet$ and $C_3H_7^\bullet$ losses), Table 2. Rearrangement of (**A**) to (**3δ**), followed by hydrogen transfer from oxygen to carbon, affords $(\mathbf{3})^{+\bullet}$. This provides a mechanism for $C_2H_5^\bullet$ loss from $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$, since $(\mathbf{3})^{+\bullet}$ can undergo simple cleavage to form a favourable daughter ion.

The isomerisation steps converting the distonic ions (**1δ**), (**2δ**), and (**3δ**) into the complex (**A**) (or *vice versa*) are more readily visualised if it is kept in mind that ionised methylcyclopropane shows some of the characteristics that would be expected for the ring opened distonic isomers $[CH_3\overset{+}{C}HCH_2\overset{\bullet}{C}H_2$ and $\overset{+}{C}H_2(CH_3)CH\overset{\bullet}{C}H_2]$ of $C_4H_8^{+\bullet}$. Whilst these species, if regarded as classical cation-radicals, are almost certainly inaccessibly high in energy [ΔH_f(est) for $CH_3\overset{+}{C}HCH_2\overset{\bullet}{C}H_2$ = 965 kJ mol^{-1}, compared with ΔH_f $(CH_3CHCH_2CH_2)^{+\bullet}$ = 935 kJ mol^{-1}], they are helpful in describing the reactivity of the $C_4H_8^{+\bullet}$ species.

Loss of H_2O from $CH_3CH_2CH_2OH^{+\bullet}$ has been explained in terms of isomerisation to an IMC comprising ionised cyclopropane attached to a water molecule.[41] This is consistent with CID measurements,[42] which show that the structure of the resultant daughter ion is ionised cyclopropane. *ab initio* Molecular orbital calculations revealed that the most stable geometry of this IMC corresponds to a structure in which one C–C bond in the $C_3H_6^{+\bullet}$ moiety is substantially longer (1.868 Å) compared with the other two (1.476 Å). These conclusions support the view that the ionised cyclopropane entities in IMCs of this kind show some structural resemblance to their ring-opened distonic counterparts.

Further evidence in favour of a unified mechanism for the decomposition of $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ involving isomerisation to a common intermediate such as (**A**), as outlined in Scheme 1, is as follows.

(i) The MIKES[43] spectra of $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ are essentially identical.[10]

(ii) The behaviour of $CH_3CH_2CH_2CD_2OC_2H_5^{+\bullet}$ and $CH_3CH_2CD_2CH_2OC_2H_5^{+\bullet}$, both of which expel $C_2H_3D_2^\bullet$ with high specificity[8,10] (>98%) in ethyl losses, suggests that the methylene groups in positions 1 and 2 of the butyl chain of $(\mathbf{1})^{+\bullet}$ become equivalent prior to dissociation. The intermediacy of (**A**) naturally accommodates this observation. Similarly, the finding that $CH_3CD_2CH_2CH_2OC_2H_5^{+\bullet}$ loses mainly $C_2H_4D^\bullet$ and that $CD_3CH_2CH_2CH_2OC_2H_5^{+\bullet}$ expels almost exclusively $C_2H_5^\bullet$ is also rationalised using Scheme 1. Similar remarks apply to the behaviour of $(CH_3)_2CHCD_2OC_2H_5^{+\bullet}$, $(CH_3)_2CDCD_2OC_2H_5^{+\bullet}$, and $(CD_3)_2CHCH_2OC_2H_5^{+\bullet}$, which respectively lose $C_2H_3D_2^\bullet$ (essentially exclusively), mainly $C_2H_3D_2^\bullet$ (90% specificity), and mostly $C_2H_2D_3^\bullet$ (59% specificity),[10] in ethyl eliminations.

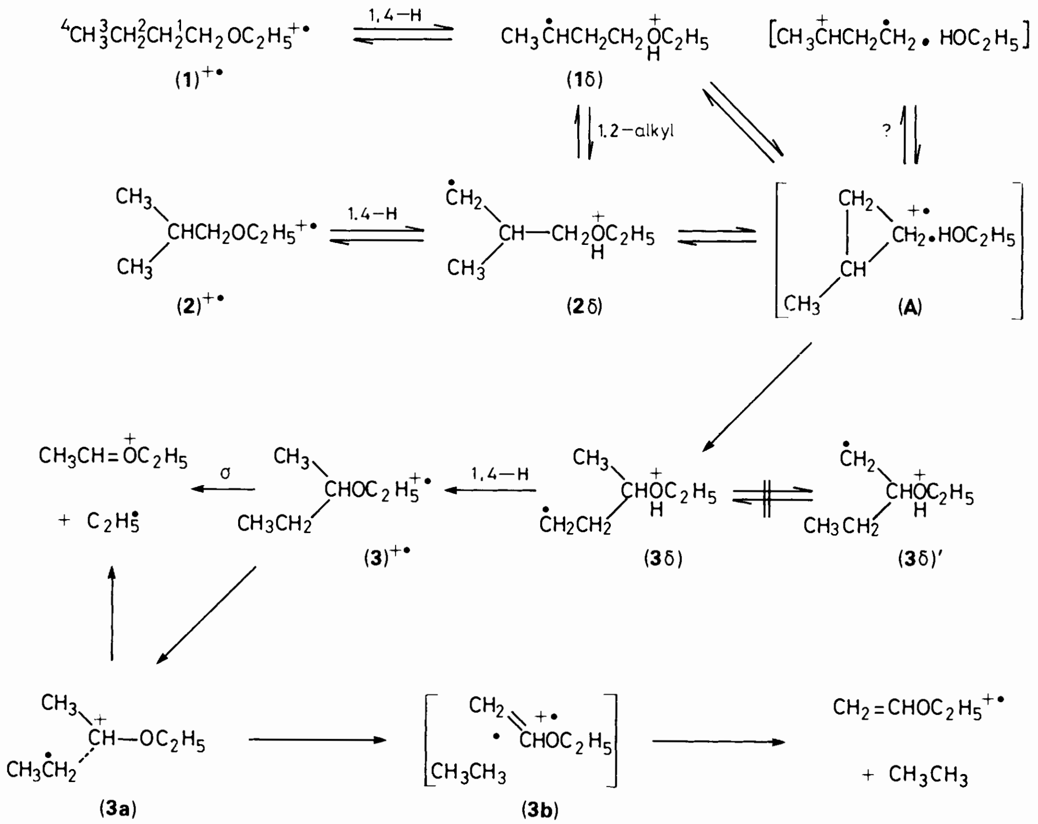
(iii) Studies of $CH_3CH_2CH_2OCH_3^{+\bullet}$ and $CH_3CH_2CH_2OCH_2CH_3^{+\bullet}$ show that losses of ethyl and allyl radicals take place after extensive or complete interchange of the hydrogen atoms in the propyl chain has occurred.[30] Moreover, collision-induced dissociation of non-decomposing $CH_3CD_2CH_2OCH_2CH_3^{+\bullet}$ ions results in the production of $CD_2{=}O^+CH_2CH_3$ as well as the expected $CH_2{=}O^+CH_2CH_3$.[30] All these results can be logically interpreted given the intermediacy of the complex $[CH_2CH_2CD_2{\cdot}HOC_2H_5]^{+\bullet}$.

(iv) The estimated energetics of the steps postulated in Scheme 1 are in accord with the finding that $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ interconvert or rearrange to a common intermediate before isomerising irreversibly to $(\mathbf{3})^{+\bullet}$; the rate-determining step is probably $(\mathbf{A}) \longrightarrow (\mathbf{3\delta})$. In contrast, $(\mathbf{3})^{+\bullet}$ dissociates *via* α-cleavage, or α-cleavage and associated hydrogen transfer, in preference to isomerising to $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$. The effects of this rate-determining isomerisation of $(\mathbf{1})^{+\bullet}$ and $(\mathbf{2})^{+\bullet}$ to $(\mathbf{3})^{+\bullet}$ are manifested in the greater tendency of rearranged ions of

Table 1. Mass spectral (12.1 eV, 75 °C) of the ethers (**16**)–(**25**).

	Compound	*m*/*z* and relative abundance[a]
(**16**)	n-$C_5H_{11}OCH_3$	103 (3), 102 (*M*, 29), 74 (7), 71 (6), 70 (100), 59 (15), 55 (7), 45 (25), 42 (13), 33 (18)
(**17**)	$CH_3CH_2CH_2(CH_3)CHOCH_3$	102 (*M*, 12), 87 (17), 70 (12), 60 (5), 59 (100), 58 (20), 57 (3), 56 (30), 45 (21)
(**18**)	$(CH_3)_3CCH_2OCH_3$	103 (6), 102 (*M*, 94), 87 (20), 70 (17), 57 (48), 56 (100), 47 (27), 45 (3)
(**19**)	$CH_3(C_2H_5)_2COCH_3$	101 ($M - CH_3$, 7), 88 (7), 87 ($M - C_2H_5$, 100), 85 (5), 84 (7)
(**20**)	$CH_3CH_2CH_2OC(CH_3)_3$	102 (7), 101 ($M - CH_3$, 100), 87 (4), 59 (37), 57 (18), 56 (5)
(**21**)	n-$C_4H_9OCH(CH_3)_2$	117 (2), 116 (*M*, 23), 102 (7), 101 (100), 87 (3), 83 (5), 73 (16), 57 (11), 56 (4)
(**22**)	n-$C_5H_{11}OCH(CH_3)_2$	131 (4), 130 (*M*, 34), 116 (8), 115 (100), 97 (5), 73 (21), 72 (5), 71 (51), 70 (16), 57 (21), 45 (22), 43 (11), 42 (8)
(**23**)	$(CH_3)_2CHCH_2CH_2OCH(CH_3)_2$	130 (*M*, 8), 116 (6), 115 (59), 73 (14), 72 (4), 71 (51), 70 (100), 60 (6), 59 (4), 58 (18), 45 (8), 43 (6), 42 (6)
(**24**)	$(CH_3CH_2CH_2)_2CHOCH_3$	130 (*M*, 8), 98 (3), 88 (7), 87 (100), 86 (21)
(**25**)	$[(CH_3)_2CH]_2CHOCH_3$	130 (*M*, 5), 88 (7), 87 (100), 86 (36)

[a] Values measured by peak heights and normalised to a value of 100 for the most abundant ion. Apart from isotope peaks and other significant ions, values of < 5 units were omitted.



Scheme 1.

structure $(3)^{+\bullet}$ [formed from $(1)^{+\bullet}$ and $(2)^{+\bullet}$] to undergo the higher energy decay route ($C_2H_5^\bullet$ loss) available to $(3)^{+\bullet}$. In addition, the kinetic energy releases accompanying $C_2H_5^\bullet$ loss from $(1)^{+\bullet}$ and $(2)^{+\bullet}$ are very similar and slightly greater than that found for $(3)^{+\bullet}$.[10] These trends are typical of those which are found when rate-determining isomerisations occur.[44–46]

(v) In contrast to $(3)^{+\bullet}$, $(1)^{+\bullet}$ and $(2)^{+\bullet}$ eliminate a small percentage of $CH_3^\bullet$. This indicates that $(1)^{+\bullet}$ and $(2)^{+\bullet}$ are able to reach transition states and product combinations which are inaccessible to $(3)^{+\bullet}$; this is consistent with the view that $(1)^{+\bullet}$ and $(2)^{+\bullet}$ rearrange to $(3)^{+\bullet}$ through a transition state higher in energy than that involved in direct dissociation of $(3)^{+\bullet}$. Similar arguments apply to C_2H_5OH expulsion, which occurs to an appreciable extent for $(1)^{+\bullet}$ and $(2)^{+\bullet}$, but not for $(3)^{+\bullet}$.

(iv) Other reactions of $(1)^{+\bullet}$, $(2)^{+\bullet}$ and higher homologues can be interpreted in terms of IMCs such as (**A**). The loss of ROH is explained by separation of these IMCs to give $C_nH_{2n}^{+\bullet}$ ions. Rearrangement of the $C_nH_{2n}^{+\bullet}$ species within the IMC probably may occur at energies below the threshold for dissociation, thus permitting the production of the thermodynamically most favourable product structure.[47] The related fragmentation by $C_nH_{2n-1}^\bullet$ expulsion with formation of ROH_2^+ is readily rationalised by invoking a hydrogen transfer between the developing $C_nH_{2n}^{+\bullet}$ and ROH products. Finally, the loss of $C_2H_5^\bullet$ from $[\text{n-}C_nH_{2n+1}O\text{-n-}O\text{-}C_mH_{2m+1}]^{+\bullet}$ species may be understood: an isomerisation analogous to $(1)^{+\bullet} \longrightarrow (3)^{+\bullet}$ affords an ionised secondary ether, from which $C_2H_5^\bullet$ is lost by simple cleavage.

In contrast to $(1)^{+\bullet}$ and $(2)^{+\bullet}$, which lose mainly $C_2H_5^\bullet$ together with minor amounts of $CH_3^\bullet$ and C_2H_5OH in metastable transitions, $(3)^{+\bullet}$ expels predominantly C_2H_6, with only a smaller contribution from $C_2H_5^\bullet$ elimination. Furthermore, ^{2}H-labelling experiments reveal that the expelled ethane originates from the ethyl group of the *sec*-butyl chain, with

Table 2. Energy data[a] relevant to the decomposition of $C_4H_9OC_2H_5^{+\bullet}$ radical-cations.

Reactant and ΔH_f	Intermediate and ΔH_f	Products and ΔH_f	$\Sigma\Delta H_f$
$CH_3CH_2CH_2CH_2OC_2H_5^{+\bullet}$ 615^{c}	$CH_3\dot{C}HCH_2CH_2\overset{+}{O}HC_2H_5$ 595^{d}	$CH_3CH_2CH_2CH_2\overset{+}{O}{=}CH_2 + CH_3^{\bullet}$ 580^{b} 140^{f}	720
		$CH_3CH_2CH_2^{\bullet} + CH_2{=}\overset{+}{O}C_2H_5$ 90^{f} 615^{g}	705
		$CH_3CH{=}\overset{+}{O}C_2H_5 + C_2H_5^{\bullet}$ 520^{b} 110^{f}	630
$(CH_3)_2CHCH_2OC_2H_5^{+\bullet}$ 605^{c}	$^{\bullet}CH_2(CH_3)CHCH_2^{+}OHC_2H_5$ 580^{d}	$(CH_3)_2CHCH_2\overset{+}{O}{=}CH_2 + CH_3^{\bullet}$ 575^{b} 140^{f}	715
		$(CH_3)_2CH^{\bullet} + CH_2{=}\overset{+}{O}C_2H_5$ 70^{f} 615^{g}	685
		$CH_3CH{=}\overset{+}{O}C_2H_5 + C_2H_5$ 520^{b} 110^{f}	630
$CH_3CH_2(CH_3)CHOC_2H_5^{+\bullet}$ 605^{c}	$^{\bullet}CH_2CH_2(CH_3)CH\overset{+}{O}HC_2H_5$ 605^{d}	$CH_3CH_2(CH_3)CH\overset{+}{O}{=}CH_2 + CH_3^{\bullet}$ 565^{b} 140^{f}	705
		$C_2H_5^{\bullet} + CH_3CH{=}\overset{+}{O}C_2H_5$ 110^{f} 520^{b}	630
		$C_2H_6 + CH_2{=}CHOC_2H_5^{+\bullet}$ -85^{f} 630^{h}	545
		$CH_3^{\bullet} + CH_3CH_2CH{=}\overset{+}{O}C_2H_5$ 140^{f} 495^{b}	635
		$CH_4 + CH_3CH{=}CHOC_2H_5^{+\bullet}$ -75^{f} 525^{e}	450
		$CH_3CH{=}CHCH_3^{+\bullet} + C_2H_5OH$ 870^{f} -235^{f}	635
		$C_4H_7^{\bullet} + C_2H_5OH_2^{+}$ 120^{j} 520^{k}	640
$(CH_3)_3COC_2H_5^{+\bullet}$ 585^{c}	$^{\bullet}CH_2(CH_3)_2C\overset{+}{O}HC_2H_5$ 590^{d}	$(CH_3)_3C\overset{+}{O}{=}CH_2 + CH_3^{\bullet}$ 555^{b} 140^{f}	695
		$(CH_3)_3C^{+} + {}^{\bullet}OC_2H_5$ 695^{i} -25^{f}	670
		$CH_3^{\bullet} + (CH_3)_2C{=}\overset{+}{O}C_2H_5$ 140^{f} 435^{b}	575
		$CH_4 + CH_2{=}(CH_3)COC_2H_5^{+\bullet}$ -75^{f} 525^{e}	450
		$(CH_3)_2C{=}CH_2^{+\bullet} + C_2H_5OH$ 875^{f} -235^{f}	640
		$C_4H_7^{\bullet} + C_2H_5OH_2^{+}$ 120^{j} 520^{k}	640

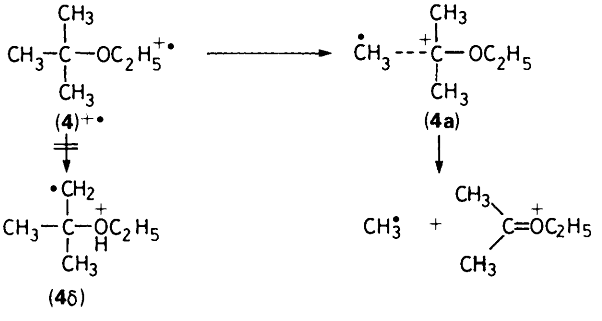
[a] All values in kJ mol^{-1} and rounded to the nearest 5 kJ mol^{-1}. [b] Value calculated from that of the corresponding carbonium ion using the equation $\Delta H_f(R^1OC^+R^2R^3) = -159 + 0.931\ [\Delta H_f(R^1CH_2C^+R^2R^3)]$; this algorithm is derived from the correlation between the known enthalpies of formation of lower members of the homologous series of oxonium and carbonium ions. The structures of these oxonium ions are represented in the text and schemes as $R^{1+}O{=}CR^2R^3$, so as to emphasise that they contain an incipient carbonyl compound $O{=}CR^2R^3$. The alternative canonical form, $R^1O{-}C^+R^2R^3$, emphasises the resemblance between the oxonium ions and the corresponding carbonium ions $R^1CH_2C^+R^2R^3$. [c] Value estimated from those known (ref. 31) for related ionised ethers using a group equivalent approach (ref. 32). [d] Value obtained using the proton affinity (ref. 33) of $C_4H_9OC_2H_5$ and known values for hydrogen abstraction energies (ref. 34). [e] Value estimated from that reported (ref. 8) for $CH_2{=}CHOC_2H_5^{+\bullet}$ on the assumption that homologation confers the same stabilisation as is found for ionised alkenes (ref. 31). [f] Ref. 31. [g] Ref. 35. [h] Ref. 8. [i] Refs. 36, 37. [j] Ref. 38. [k] Ref. 33.

abstraction of a hydrogen atom from the adjacent methyl group. Thus, $CH_3CH_2(CD_3)CHOC_2H_5^{+\bullet}$ loses C_2H_5D with high specificity, whereas $CH_3CH_2(CH_3)CHOCD_2CH_3^{+\bullet}$ eliminates mainly C_2H_6.[8] This may be interpreted as a 1,2-elimination, occurring with a low degree of concert [**(3)**$^{+\bullet} \longrightarrow$ **(3a)** $\longrightarrow$ products].[26] The species **(3a)** can be regarded as an IMC of ethyl radical and $C_4H_9O^+$. Hydrogen transfer between the developing products to form ethane and $CH_2{=}CHOC_2H_5^{+\bullet}$ is significantly exothermic and irreversible, thus allowing no opportunity for exchange of hydrogen atoms as **(3a)** decomposes.

Further evidence for the intermediacy of IMCs in alkane loss from ionised ethers is found in the dissociation of higher homologues of **(3)**$^{+\bullet}$ for which the complexes corresponding to **(3a)** and **(3b)** are of comparable energy. In such circumstances, specific hydrogen exchange occurs owing to the interconversion of the complexes containing a radical and an alkane.[29] There is also a distinct diminution in the kinetic energy release associated with alkane loss in these cases.[29] These observations are consistent with the intermediacy of interconverting pairs of IMCs in loss of alkanes from certain ionised ethers.

Three other points concerning the decomposition of **(3)**$^{+\bullet}$ deserve mention. First, if hydrogen migration **(3)**$^{+\bullet} \longrightarrow$ **(3δ)** occurs, then reversion of **(3δ)** to **(3)**$^{+\bullet}$ must be fast compared with the rate of hydrogen exchange between the methyl and radical site in the C_4H_8 chain of **(3δ)**. If this were not so, then **(3δ)** $\rightleftharpoons$ **(3δ′)** would destroy the positional integrity of the CD_3 group in $CH_3CH_2(CD_3)CHOC_2H_5^{+\bullet}$ and lead to $C_2H_4D_2$ loss; experimentally, only a very small amount of $C_2H_4D_2$ loss is observed.[8] Secondly, the expulsion of CH_4 from **(3)**$^{+\bullet}$ appears to be energetically favourable, especially when assessed in terms of product stability. Yet CH_4 loss does not occur to an appreciable extent from metastable (**3**)$^{+\cdot}$. This discrimination against CH_4 loss from ionised ethers containing a 2-alkoxy group appears to be general.[8] A probable explanation is that formation of the developing IMCs containing methyl radicals is less favourable than production of their counterparts containing ethyl and larger radicals.

Loss of CH_4 and $CH_3^{\cdot}$ occur in competition from metastable $(CH_3)_3COR^{+\cdot}$ species.[28] However, $CH_3^{\cdot}$ expulsion (*via* α-cleavage) rapidly outstrips CH_4 elimination [occurring *via* hydrogen transfer within an IMC such as (**4a**)] in importance as R becomes larger or the internal energy of the $(CH_3)_3COR^{+\cdot}$ ions increases, even though CH_4 loss yields the energetically more favourable products.



Scheme 2.

(2) *Mass Spectra* (12.1 eV, 75 °C) *of* $C_4H_9OC_2H_5$ *Ethers.*—The conventional 70 eV spectra of dialkyl ethers typically contain prominent peaks corresponding to α-cleavage of $M^{+\cdot}$; ions arising by further decomposition of the primary $[M - \text{alkyl}]^+$ fragments are also commonly of high abundance.[1] It is clear from Figure 1 that α-cleavage processes remain characteristically important in the 12.1 eV, 75 °C spectra of $C_4H_9OC_2H_5$ ethers. Nevertheless, a significant percentage of the molecular ions in the 12.1 eV spectra are produced with very low internal energies. These ions tend to undergo the rearrangement and fragmentation processes which are characteristic of metastable $C_4H_9OC_2H_5^{+\cdot}$species. This generalisation is illustrated by the following specific points:

(i) The spectra of (**1**) and (**2**) show peaks at *m*/*z* 73 corresponding to $C_2H_5^{\cdot}$ loss from $M^{+\cdot}$. The formation of this ion can be explained using the mechanism of Scheme 1.

(ii) Similar remarks apply to the ions at *m*/*z* 56 ($[M - C_2H_5OH]^{+\cdot}$) in the spectra of (**1**) and (**2**). Since the $[M - C_2H_5]^+$ and $[M - C_2H_5OH]^{+\cdot}$ peaks are of greater intensity in the spectrum of (**1**), it is evident that rearrangement of $C_4H_9OC_2H_5^{+\cdot}$ to (**A**) occurs more readily in the spectrum of n-butyl ethyl as opposed to isobutyl ethyl ether. Indeed, in the spectrum of (**1**), the intensity of the peaks at *m*/*z* 56 and 73 rivals that of the peak at *m*/*z* 59 arising by α-cleavage.

(iii) A peak of moderate intensity is present at $[M - C_2H_6]^{+\cdot}$ (*m*/*z* 72) in the spectrum of (**3**). The production of this ion may be rationalised using the mechanism of Scheme 1.

Both (**1**) and (**2**), which contain primary butyl groups, show prominent $M^{+\cdot}$ peaks in their spectra. The relative intensity of the $M^{+\cdot}$ peak in the spectrum of (**3**), which contains a *sec*-butyl group, is considerably reduced. The spectrum of (**4**), in which a t-butyl group is present, does not contain an appreciable molecular ion. This reflects changes in the energetics [(**4**)$^{+\cdot}$ is of comparable energy to the products of simple cleavage] and the shorter chain length [rearrangement to the distonic ion (**4**) requires a 1,3-hydrogen shift, which is infeasible geometrically]. There is no appreciable $[M - CH_4]^{+\cdot}$ peak, even though CH_4 loss produces lower energy products than those derived from $CH_3^{\cdot}$ expulsion.

The abundance of ions formed by C–O cleavage of $C_4H_9OC_2H_5^{+\cdot}$ is extremely low. Even for the most favourable case, (**4**)$^{+\cdot}$, the peak at *m*/*z* 57 ($C_4H_9^+$) is only weak. There is, however, a peak of moderate intensity at *m*/*z* 59 ($C_3H_7O^+$) in the spectrum of (**4**). This is logically interpreted as arising by C_2H_4 loss from $[M - CH_3]^+$, since there is metastable peak (*m** 40.0, $87^+ \longrightarrow 59^+ + 28$) for this process.

(3) *Mass Spectra* (12.1 eV, 75 °C) *of* $C_3H_7OC_3H_7$ *and Larger Ethers.*—(*a*) *Ethers containing only primary alkyl groups.* The main features of the mass spectra of these ethers are as follows:

(i) Molecular ion peaks of medium to very high intensity are present.

(ii) The abundance of ions formed by α-cleavage of $M^{+\cdot}$ is also great.

(iii) Elimination of R^1OH from $[R^1OR^2]^{+\cdot}$ becomes important when R^2 contains a linear chain of at least four carbon atoms attached at one end to oxygen.[7,8] Thus, for example, n-$C_5H_{11}OCH_3^{+\cdot}$, (**16**)$^{+\cdot}$, expels CH_3OH in both relatively fast (ion-source) and slow (metastable ion) dissociations.[11] Other $C_5H_{11}OR$ compounds exhibit $[M - ROH]^{+\cdot}$ as the base peak in their spectra.[11] Similarly (n-$C_4H_9)_2O^{+\cdot}$, (**10**)$^{+\cdot}$, shows $[M - C_4H_9OH]^{+\cdot}$ as an intense peak.

(iv) The third common decomposition pathway for $[R^1OR^2]^{+\cdot}$ radical-cations is ethyl elimination. Again, this process is preferentially associated with ethers containing at least four contiguous carbon atoms attached to oxygen (except for n-propyl ethers, for which $[M - C_2H_5]^{+\cdot}$ arises, with or without prior rearrangement, by nominal α-cleavage). Ethyl loss becomes more important as the average internal energy of the ionised ethers decreases; indeed, for metastable ions, it is often the dominant fragmentation. Thus, (n-$C_4H_9)_2O^{+\cdot}$ and [n-$C_5H_{11}O$–n-$C_mH_{2m+1}]^{+\cdot}$ (m = 1—5) all expel $C_2H_5^{\cdot}$ in slow dissociations.[7,8,11]

(v) Loss of a radical having one unit of unsaturation ($C_mH_{2m-1}^{\cdot}$) occurs for some $C_nH_{2n+1}OC_mH_{2m+1}$ species, especially at very low internal energies. Thus, metastable (n-$C_3H_7)_2O^{+\cdot}$ and (iso-$C_4H_9)_2^{+\cdot}$ lose $C_3H_5^{\cdot}$ (*m** 36.5, $102^+ \longrightarrow 61^+ + 41$) and $C_4H_7^{\cdot}$ (*m** 43.3, $130^+ \longrightarrow 75^+ + 55$), respectively; moreover, the spectrum of n-$C_5H_{11}OCH_3$ contains a moderately intense peak at *m*/*z* 33 (18%).

Processes (iii), (iv), and (v) may be explained using mechanisms involving distonic ions and IMCs. The abundances of $[M - \text{alcohol}]^{+\cdot}$ and $[M - C_2H_5]^+$ ions in the spectra of isobutyl alkyl ethers is noticeably smaller than those found for the isomeric n-butyl compounds. This indicates that the ionised n-butyl ethers rearrange to the IMCs more readily at relatively high internal energies than do the corresponding isobutyl species. The enhanced abundance of $[M - C_2H_5]^+$ and $[M - ROH]^{+\cdot}$ ions in the spectra of n-$C_nH_{2n+1}OR^{+\cdot}$ is analytically useful since it allows a clear differentiation to be made between n-C_4H_9OR and iso-C_4H_9OR compounds. Nevertheless, at energies appropriate to decomposition of metastable ions, $C_2H_5^{\cdot}$ loss from iso-$C_4H_9OR^{+\cdot}$ radical-cations becomes more pronounced, as shown by the behaviour of (iso-$C_4H_9)_2O^{+\cdot}$ (*m** 78.5, $130^+ \longrightarrow 101^+ + 29$).

(iv) Ions produced by dissociation of the primary fragmentation products become increasingly prominent in the spectra of larger ethers. Thus, both (n-$C_4H_9)_2O$ and (iso-$C_4H_9)_2O$ display intense peaks at *m*/*z* 57. This peak is probably not always produced directly from $M^{+\cdot}$; instead, *m*/*z* 57 may arise by CH_2O expulsion from the $C_4H_9^+O{=}CH_2$ ions (*m*/*z* 87) formed by α-cleavage of (n-$C_4H_9)_2O^{+\cdot}$ and (iso-$C_4H_9)_2O^{+\cdot}$. This explanation is supported by the observation of the associated metastable peak (*m** 37.3, $87^+ \longrightarrow 57^+ + 30$) and by the known behaviour of $C_4H_9^+O{=}CH_2$ ions, each of which expels CH_2O in slow dissociations.[47] Other ions which may be ascribed to the secondary decomposition of primary daughter ions include *m*/*z* 83 in the spectrum of (n-$C_4H_9)_2O$ (H_2O

loss from $[M - C_2H_5]^{\bullet}$), and m/z 55 in the spectrum of n-$C_5H_{11}OCH_3$ ($CH_3^{\bullet}$ loss from $[M - CH_3OH]^{+\bullet}$). The presence of these peaks is consistent with the reported reactions of n-$C_4H_9^+O{=}CHCH_3$[48,49] and $C_5H_{10}^{+\bullet}$[50] ions, respectively.

Certain $ROCH_3^{+\bullet}$ radical-cations undergo another reaction in which an allyl radical is lost and $(CH_3)_2OH^+$ (m/z 47) is produced. Whilst this fragmentation is not of general importance, it can be energetically very favourable for ionised ethers in which the principal alkyl group is branched at the β-carbon atom. Thus, both $(CH_3)_2CHCH_2OCH_3$[9] and $(CH_3)_3CCH_2OCH_3$[51] show appreciable peaks at m/z 47 ($C_3H_5^{\bullet}$ and $C_4H_7^{\bullet}$ expulsion, respectively, from $M^{+\bullet}$) in their spectra; furthermore, $(CH_3)_2CHCH_2OCH_3^{+\bullet}$ eliminates $C_3H_5^{\bullet}$ in slow dissociations (m^* 25.1, $88^+ \longrightarrow 47^+ + 41$).[9] The general mechanism of this process has been the subject of controversy,[9,51,52] but it now seems clear that the related loss of CH_3OCH_3 from metastable $(CH_3)_3CCH_2OCH_3^{+\bullet}$ does involve two IMCs containing incipient $(CH_3)_3C^+$ attached to $^{\bullet}CH_2OCH_3$ and $(CH_3)_2C{=}CH_2^{+\bullet}$ co-ordinated to CH_3OCH_3.[29]

Ionised neopentyl methyl ether is unique amongst the species studied in this work in showing an abundant ion ($C_4H_9^+$ at m/z 57) which apparently arises from C–C σ-cleavage of $M^{+\bullet}$ with charge retention by the hydrocarbon fragment. This reflects the energetic factors which come into play in this system in which the β-carbon atom possesses a quaternary substitution pattern.

(*b*) *Ethers containing at least one secondary alkyl group.* The spectra of these ethers are somewhat different from those of the isomeric ethers containing only primary alkyl groups. The principal features are as follows.

(i) Molecular ion peaks are present, but they are usually of only moderate intensity. For example, the relative abundance of $M^{+\bullet}$ in the spectrum of $CH_3CH_2CH_2(CH_3)CHOCH_3$ is only 12%, compared with 29% in the spectrum of n-$C_5H_{11}OCH_3$. Even ethers in which both alkyl groups are secondary, however, show appreciable $M^{+\bullet}$ peaks. Thus, $[CH_3CH_2(CH_3)CH]_2O$ exhibits $M^{+\bullet}$ ions at a relative abundance of 8%.

(ii) The dominant primary daughter ions arise by α-cleavage with loss of the larger alkyl group from the branch point. Expulsion of $C_2H_5^{\bullet}$ from $[CH_3CH_2(CH_3)CH]_2O^{+\bullet}$ (m/z 101), and loss of $C_3H_7^{\bullet}$ from $CH_3CH_2CH_2(CH_3)CHOCH_3^{+\bullet}$ (m/z 59) accounts for the base peak in the spectra of these ethers. Loss of the smaller radical from $M^{+\bullet}$ is responsible for only a minor peak (5% and 17%, respectively, of the peak attributable to loss of the larger alkyl group).

(iii) A related fragmentation of $M^{+\bullet}$, which occurs to a limited extent in source reactions, is loss of an alkane derived from the larger alkyl group at the branch point together with a hydrogen atom from the α-carbon atom of the smaller alkyl group. For instance, n-$C_4H_9OCH(CH_3)C_2H_5$ and $[C_2H_5(CH_3)CH]_2O$ both show minor peaks (4 and 3% relative intensity, respectively) at $[M - C_2H_6]^{+\bullet}$. Similarly, the spectra of the larger ethers, $(CH_3CH_2CH_2)_2CHOCH_3$ and $[(CH_3)_2CH]_2CHOCH_3$, both contain sizeable (21 and 36%, respectively) peaks at m/z 86 ($[M - C_3H_8]^{+\bullet}$). Alkane loss often dominates the chemistry of metastable ionised ethers. This is illustrated by the behaviour of metastable n-$C_4H_9OCH(CH_3)C_2H_5^{+\bullet}$ and $[C_2H_5(CH_3)CH]_2O^{+\bullet}$, both of which expel C_2H_6 (m^* 76.9, $130^+ \longrightarrow 100^+ + 30$) with high specificity.

(iv) Alcohol expulsion occurs from ionised ethers which have a chain of at least four carbon atoms attached to oxygen in the principal alkyl group. For instance, $(CH_3CH_2CH_2)_2CHOCH_3$ shows a small peak (3%) at $[M - CH_3OH]^{+\bullet}$ (m/z 98) and a metastable peak at m/z 73.9 ($130^+ \longrightarrow 98^+ + 32$) corresponding to CH_3OH loss from $M^{+\bullet}$. In contrast, $[(CH_3)_2CH]_2CHOCH_3^{+\bullet}$ does not expel CH_3OH to an appreciable extent, either in source reactions or in metastable transitions.

(v) Ions corresponding to elimination of H_2O, alkenes or carbonyl compounds from the $[M - \text{alkyl}]^+$ ions produced by α-cleavage of $M^{+\bullet}$ appear with increasing frequency in the spectra of larger secondary ethers. Thus, the ions at m/z 83, 59, 57, and 45 in the spectrum of $[CH_3CH_2(CH_3)CH]_2O$ can be ascribed to loss of H_2O, C_3H_6, CH_3CHO, and C_4H_8, respectively, from $[M - C_2H_5]^+$. These reactions are consistent with the known behaviour of metastable $C_4H_9^+O{=}CHCH_3$ ions.[48,49]

The ionised ethers containing a secondary alkyl group show less tendency to undergo skeletal rearrangement than do their primary isomers. This is not unexpected in view of their inferior stability with respect to dissociation by α-cleavage. Nevertheless, some ionised secondary ethers do undergo isomerisation of the carbon and oxygen framework at low internal energies. This is shown by the loss of a methyl radical from C_1 or C_5 from metastable $CH_3CH_2CH_2(CH_3)CHOC_2H_5^{+\bullet}$ ions,[30] which indicates that a formal 1,3-alkoxy shift competes with simple cleavage in this system. Metastable n-$C_4H_9OCH(CH_3)_2^{+\bullet}$ ions expel an ethyl radical as well as the expected methyl radical (α-cleavage). The ethyl radical loss probably occurs by rearrangement to $CH_3CH_2(CH_3)CHOCH(CH_3)_2^{+\bullet}$, which then expels $C_2H_5^{\bullet}$ by α-cleavage. Similarly, the base peak at m/z 70 ($C_5H_{10}^{+\bullet}$) in the spectrum of $(CH_3)_2CHCH_2CH_2OCH(CH_3)_2$ corresponds to $[M - C_3H_7OH]^{+\bullet}$. It may be seen, therefore, that in some circumstances, isomerisation processes involving distonic ions and IMCs are able to compete with α-cleavages for metastable ionised ethers containing secondary alkyl groups.

(*c*) *Ethers containing a tertiary alkyl group.* The spectra of these ethers do not show several of the general features which are observed for their counterparts with primary and secondary alkyl groups. The following trends are evident.

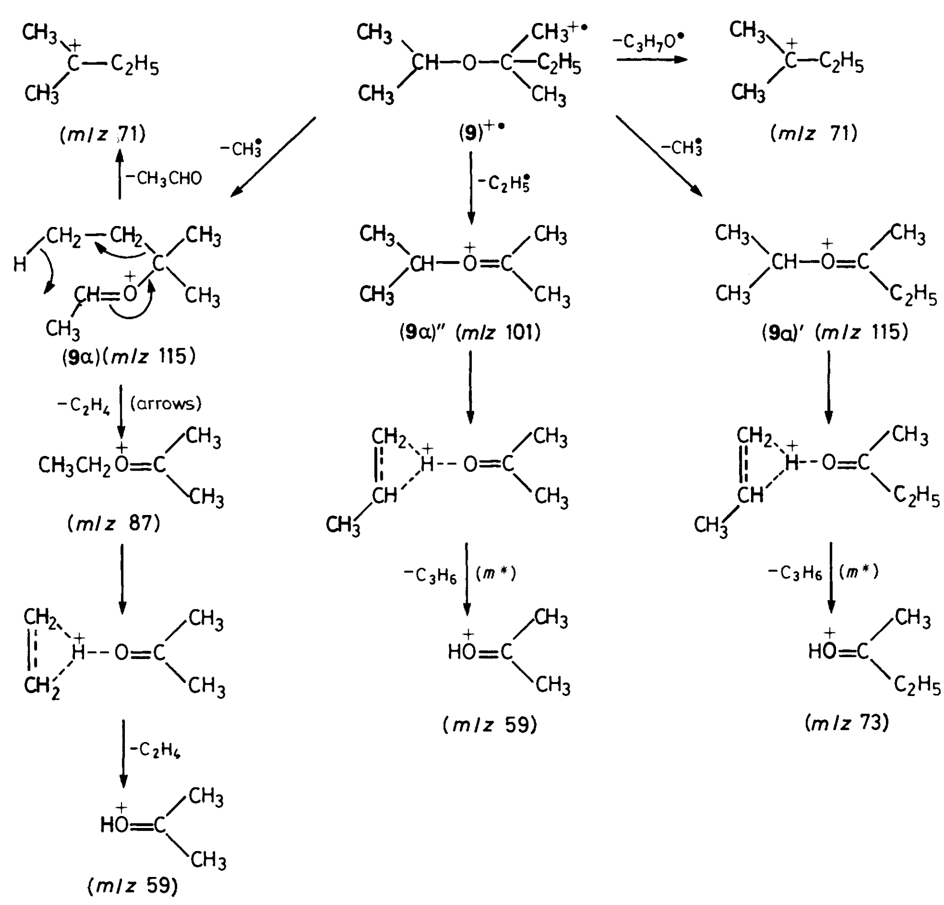
(i) Molecular ion peaks are of very weak (< 1%) or negligible relative intensity.

(ii) Ions arising by α-cleavage account for almost all the peaks produced by fragmentation of $M^{+\bullet}$. Other reactions, which are sometimes observed for ionised ethers with only primary and secondary alkyl groups, are no longer able to compete effectively. This effect originates from the reduced stability of $M^{+\bullet}$, the enhanced ease of α-cleavage, and the shortened chain lengths of the tertiary alkyl groups which renders hydrogen transfers to oxygen from carbon more difficult.

In general, the dominant α-cleavage takes place in the tertiary alkyl group. Thus, for example, $[M - C_2H_5]^+$ is only 4% of the relative intensity of $[M - CH_3]^+$ in the spectrum of $CH_3CH_2CH_2OC(CH_3)_3$. There is also a strong preference for eliminating the larger alkyl group, when such a choice exists, from the tertiary alkyl function. Thus, $CH_3(C_2H_5)_2COCH_3$, $C_2H_5OC(CH_3)_2C_2H_5$, and $(CH_3)_2CHOC(CH_3)_2C_2H_5$ display peaks at $[M - C_2H_5]^+$ which are much more intense than those at $[M - CH_3]^+$ (ratio of relative intensities 14:1, 7.3:1, and 11:1, respectively).

(iii) Peaks formed by secondary fragmentation of the primary daughter ions are present in many of these spectra. These peaks usually correspond to alkene or aldehyde loss from the primary oxonium ions $C_nH_{2n+1}O^+$; there are, however, smaller peaks produced by water elimination from the oxonium ions.

For example, the peaks at m/z 57 and 59 in the spectrum of $(CH_3)_3COCH_2CH(CH_3)_2$ are attributable to $[M - C_3H_7 - CH_2O]^+$ and $[M - CH_3 - C_4H_8]^+$, respectively. Similarly, in the spectrum of $(CH_3)_2CHOC(CH_3)_2C_2H_5$, the ions at m/z 87 ($[M - CH_3 - C_2H_4]^+$), 73 ($[M - C_2H_5 - C_2H_4]^+$), 71 ($[M - CH_3 - CH_3CHO]^+$, and 59 ($[M - C_2H_5 - C_3H_6]^+$) can all be ascribed to secondary dissociations of the primary daughter ions. Several of the secondary fragmentations give rise to metastable peaks; for instance, $115^+ \longrightarrow 73^+ + 42$ (m^* 46.3) and $101^+ \longrightarrow 59^+ + 42$ (m^* 34.5) in the spectrum of $(CH_3)_2CHOC(CH_3)_2C_2H_5$, and $101^+ \longrightarrow 57^+ + 44$ (m^* 32.2) in the spectrum of $(CH_3)_3COCH(CH_3)C_2H_5$.



Scheme 3.

An example of a peak of lower intensity which originates from water loss from $C_nH_{2n+1}O^+$ oxonium ions is *m/z* 83 $[M - C_2H_5 - H_2O]^+$ in the spectrum of $(CH_3)_3COCH(CH_3)C_2H_5$. Metastable $(CH_3)_3C^+O{=}CHCH_3$ ions are known to eliminate predominantly (97%) H_2O;[49] it is clear, however, that water loss competes only poorly with aldehyde and alkene expulsion when these $C_nH_{2n+1}O^+$ oxonium ions dissociate in reactions occurring in the ion source.

Alkene and aldehyde losses are thought to occur from at least some of these oxonium ions *via* IMCs.[23,47,49] This is illustrated for the decomposition of ions derived from $(CH_3)_2CHOC(CH_3)_2C_2H_5^{+\cdot}$ in Scheme 3. Thus, (**9α′**) and (**9α″**), which are derived from $(\mathbf{9})^{+\cdot}$ by expulsion of $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$, respectively, both lose C_3H_6 in a way that is logically interpreted as involving IMCs in which propene and acetone or butanone are co-ordinated to a common proton. Since these ketones have a much greater proton affinity than propene,[33] the IMCs break down with retention of the proton by the carbonyl compound. In contrast, the ion, (**9α**), produced by cleavage in the isopropyl group in $(\mathbf{9})^{+\cdot}$, expels acetaldehyde; this reflects the lower proton affinity[33] of aldehydes compared with ketones and heavily substituted alkenes.

A final general point concerns the presence of peaks corresponding to $C_nH_{2n+1}^+$ carbonium ions. These ions may be formed from $M^{+\cdot}$ by cleavage of the appropriate C–O bond [*e.g. m/z* 71, $C_5H_{11}^+$, from $(\mathbf{9})^{+\cdot}$, Scheme 3]. It is unlikely that these ions originate wholly in this fashion, since formation of $C_nH_{2n+1}^+$ ions would then be expected to be particularly favoured for tertiary ethers; however, this is not the case. Thus, the spectrum of $(CH_3)_3COCH_2CH_2CH_3$ shows only a moderate peak (relative intensity 18%) at *m/z* 57, $(CH_3)_2CHOC(CH_3)_2C_2H_5$ and $CH_3CH_2OC(CH_3)_2C_2H_5$ display ions of only low abundance at *m/z* 71 ($[C_5H_{11}]^+$) in their spectra, and the ion at *m/z* 85 ($[C_6H_{13}]^+$) in the spectrum of $CH_3(C_2H_5)_2COCH_3$ is of minor importance. It is likely, therefore, that at least some of the $C_nH_{2n+1}^+$ ions in these spectra usually arise from secondary dissociations of the oxonium ions produced by α-cleavage of $M^{+\cdot}$. For instance, part of the moderate intensity peak at *m/z* 71 in the spectrum of (**9**) probably originates *via* the sequence $(\mathbf{9})^{+\cdot} \longrightarrow (\mathbf{9\alpha}) \longrightarrow C_5H_{11}^+ + CH_3CHO$ (Scheme 3).

Conclusions

Rearrangements involving distonic ions and IMCs play a significant role in the 12.1 eV, 75 °C mass spectra of dialkyl ethers. These isomerisations provide a unifying mechanism for interpreting various fragmentations of ionised ethers which cannot be explained as simple cleavages of the molecular ions. The rearrangements are most noticeable in the spectra of di-n-alkyl ethers, but they also occur to a lesser extent in the spectra of other ethers in which the alkyl groups are primary or secondary in structure. Ionised ethers derived from tertiary alcohols show essentially exclusive α-cleavage.

Isomerisations compete much more effectively with α-cleavages in the reactions of metastable $R^1R^2O^{+\cdot}$ species. This effect is most clearly evident for metastable ionised ethers containing two primary alkyl groups, but it is also apparent when one or both of the alkyl groups has a secondary structure.

Experimental

The 12.1 eV, 75 °C mass spectra were recorded on a modified AEI MS9 double-focussing mass spectrometer equipped with a water-cooled source. Details of the experimental procedure,

$$(CH_3)_2CHCH_2OH \xrightarrow{\text{i,ii}} (CH_3)_2CHCH_2OC_2H_5 \quad (1)$$

$$(CH_3)_2CHOH \xrightarrow[\text{v}]{\text{iii,iv}} (CH_3)_2CHOC(CH_3)_2C_2H_5 \quad (2)$$

$$(CH_3)_3COH \xrightarrow{\text{vi}} (CH_3)_3COC_2H_5 \quad (3)$$

$$(CH_3)_2CHCH_2Br \xrightarrow{\text{vii,viii}} (CH_3)_2CHCH_2OC(CH_3)_3 \quad (4)$$

Scheme 4. *Reagents:* i, NaH; ii, C_2H_5I; iii, $Hg(OCOCF_3)_2$; iv, $(CH_3)_2C{=}CHCH_3$; v, NaOH, $NaBH_4$, H_2O; vi, C_2H_5OH, $KHSO_4$, slow distillation; vii, Mg, $(C_2H_5)_2O$; viii, $PhCO_3C(CH_3)_3$.

including the method of accurately calibrating the ionising electron energy, have been published elsewhere.[53]

Di-n-butyl ether was commercially available. The other ethers were synthesised by one of four routes depending on the nature of the constituent alkyl groups. These routes involved condensation of the sodium alkoxide and the appropriate alkyl iodide or bromide,[54] reductive solvodemercuration,[55] slow distillation of a mixture of t-butyl alcohol and a second alcohol, [56] and reaction of an alkyl Grignard reagent with t-butyl perbenzoate.[57] Illustrative examples are given in Scheme 4. The crude ethers were isolated either by distillation of the reaction mixture or by extraction into pentane after aqueous work-up. Careful refractionation then afforded samples of the ethers containing no detectable impurities. The redistillation of the heavily branched ethers, particularly those containing t-butyl groups synthesised from t-butyl perbenzoate, was conducted with special care under a nitrogen atmosphere behind a safety screen. **CAUTION!** An explosion occurred during the distillation of one sample of t-butyl isobutyl ether, even though the usual tests on the material in the distillation flask did not reveal the presence of peroxides. It is advisable to conduct these distillations behind a safety screen and to distil a maximum of only three-quarters of the crude material.

Acknowledgements

Financial support from the SERC (an Advanced Fellowship to R. D. B.) is gratefully acknowledged. Drs. S. Hammerum and D. J. McAdoo kindly communicated results prior to publication; Dr. Hammerum also exchanged ideas during many stimulating discussions; their assistance in this respect is acknowledged with thanks. Special thanks are due to Mrs. M. Callaway for her care in preparing and revising the typescript.

References

1 F. W. McLafferty, *Anal. Chem.*, 1957, **29**, 1782.
2 M. Spiteller-Friedmann and G. Spiteller, *Chem. Ber.*, 1967, **100**, 79.
3 G. Spiteller and M. Spiteller-Friedmann, in 'Some Newer Physical Methods in Structural Chemistry,' eds. R. Bonnett and J. G. Davies, United Trade Press, London, 1967, pp. 121.
4 R. G. Cooks, A. N. H. Yeo, and D. H. Williams, *Org. Mass Spectrom.*, 1969, **2**, 985.
5 S. L. Bernasek and R. G. Cooks, *Org. Mass Spectrom.*, 1970, **3**, 127.
6 S. Tajima, J. van der Greef, and N. M. M. Nibbering, *Org. Mass Spectrom.*, 1978, **13**, 551.
7 C. E. Hudson and D. J. McAdoo, *Org. Mass Spectrom.*, 1979, **14**, 109.
8 C. E. Hudson, R. D. Lerner, R. Aleman, and D. J. McAdoo, *J. Phys. Chem.*, 1980, **84**, 155.
9 R. D. Bowen and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 836.
10 H. E. Audier, G. Bouchoux, Y. Hoppilliard, and A. Milliet, *Org. Mass Spectrom.*, 1982, **17**, 382.
11 R. D. Bowen and A. Maccoll, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1101.
12 B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5805.
13 S. Hammerum, *Tetrahedron Lett.*, 1981, **22**, 157.
14 J. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *J. Am. Chem. Soc.*, 1982, **104**, 2931.
15 S. Hammerum, J. B. Christensen, H. Egsgaard, E. Larsen, K. F. Donchi, and P. J. Derrick, *Int. J. Mass Spectrom. Ion Phys.*, 1983, **47**, 351.
16 S. Hammerum, D. Kuch, and P. J. Derrick, *Tetrahedron Lett.*, 1984, **25**, 893.
17 C. Wesdemiotis, P. O. Davis, R. Feng, J. Tso, and F. W. McLafferty, *J. Am. Chem. Soc.*, 1985, **107**, 8059.
18 H. E. Audier, G. Sozzi, and J. P. Denhez, *Tetrahedron*, 1986, **42**, 1179.
19 For reviews on the importance of distonic ions in the chemistry of $C_nH_{2n}O^{+\bullet}$ species, see: G. Bouchoux, *Mass Spectrom. Rev.*, 1988, **7**, 1; 1988, **7**, 203.
20 For a review of distonic ions, see: S. Hammerum, *Mass Spectrom. Rev.*, 1988, **7**, 123.
21 T. Bjornholm, S. Hammerum, and D. Kuch, *J. Am. Chem. Soc.*, 1988, **110**, 3862.
22 T. H. Morton, *J. Am. Chem. Soc.*, 1980, **102**, 1596.
23 R. D. Bowen and D. H. Williams, *J. Am. Chem. Soc.*, 1980, **102**, 2752; see also references cited therein.
24 T. H. Morton, *Tetrahedron*, 1982, **38**, 3195.
25 For a review on ion–molecule complexes see: D. J. McAdoo, *Mass Spectrom. Rev.*, 1988, **7**, 363.
26 C. E. Hudson and D. J. McAdoo, *Adv. Mass Spectrom.*, 1985, 797.
27 D. J. McAdoo, J. C. Traeger, C. E. Hudson, and L. L. Griffin, *J. Phys. Chem.*, 1988, **92**, 1524.
28 D. J. McAdoo, C. E. Hudson, J. C. Traeger, A. Grose, and L. L. Griffin, *Adv. Mass Spectrom.*, in press; J. C. Traeger, C. E. Hudson, and D. J. McAdoo, submitted for publication.
29 S. Hammerum, *J. Chem. Soc., Chem. Commun.*, 1988, 858; S. Hammerum and H. E. Audier, *J. Chem. Soc., Chem. Commun.*, 1988, 860.
30 H. E. Audier, A. Millet, G. Sozzi, and S. Hammerum, presented at the triennial mass spectrometry meeting, Bordeaux, France, 1988; see also *Adv. Mass Spectrom.*, in press.
31 H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, 1976, 6.
32 J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; *J. Chem. Phys.*, 1953, **21**, 2029.
33 S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
34 F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 6917.
35 F. P. Lossing, *J. Am. Chem. Soc.*, 1977, **99**, 7526.
36 F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, 1970, **48**, 955.
37 F. P. Lossing and A. Maccoll, *Can. J. Chem.*, 1976, **54**, 990.
38 F. P. Lossing, *Can. J. Chem.*, 1972, **50**, 3973.
39 R. D. Bowen and D. H. Williams, *Int. J. Mass Spectrom. Ion Phys.*, 1979, **29**, 47.
40 H. Schwarz and D. Stahl, *Int. J. Mass Spectrom. Ion. Phys.*, 1980, **36**, 285.
41 J. L. Holmes, A. A. Mommers, J. E. Szulejko, and J. K. Terlouw, *J. Chem. Soc., Chem. Commun.*, 1984, 165.
42 J.-D. Shao, T. Baer, J. C. Morrow, and M. L. Frazer-Monteiro, *J. Chem. Phys.*, 1987, **87**, 5242.
43 J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger, and T. Y. Ridley, *Anal. Chem.*, 1973, **45**, 1023A.
44 D. H. Williams and G. Hvistendahl, *J. Am. Chem. Soc.*, 1975, **97**, 3097.
45 R. D. Bowen, D. H. Williams, and H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 451.
46 R. D. Bowen and D. H. Williams, in 'Rearrangements in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, ch. 2.
47 R. D. Bowen, B. J. Stapleton, and D. H. Williams, *J. Chem. Soc., Chem. Commun.*, 1978, 24.
48 G. A. Smith and D. H. Williams, *J. Am. Chem. Soc.*, 1969, **91**, 5254.
49 R. D. Bowen and D. H. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1411.
50 R. D. Bowen and D. H. Williams, *Org. Mass Spectrom.*, 1977, **12**, 453.

51 R. D. Bowen and A. Maccoll, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1005.
52 S. Hammerum and P. J. Derrick, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1577.
53 R. D. Bowen and A. Maccoll, *Org. Mass Spectrom.*, 1984, **19**, 379.
54 For a review of the Williamson synthesis, see: H. Feuer and J. Hooz in 'The Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, New York, 1967, pp. 446–450, 460–468.
55 H. C. Brown, J. T. Kurek, M.-H. Rei, and K. L. Thompson, *J. Org. Chem.*, 1985, **50**, 1171.
56 J. F. Norris and G. W. Rigby, *J. Am. Chem. Soc.*, 1932, **54**, 3088.
57 S.-O. Lawesson and N. C. Yang, *J. Am. Chem. Soc.*, 1959, **81**, 4230.

Paper 9/01769K
Received 26th *April* 1989
Accepted 3rd *August* 1989