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Low-energy, Low-temperature Mass Spectra. Part 3.† n-Pentyl n-Alkyl Ethers

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The 12.1 eV electron-impact-induced mass spectra of five homologous pentyl alkyl ethers (n-$C_5H_{11}OR$; R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_5H_{11}) are reported. The trends in these spectra are discussed in energetic terms and compared with the spectrum of the parent alcohol. Ethyl radical loss occurs from the molecular ion of each ether; a mechanism for this unusual reaction is suggested and discussed.

The main decomposition routes of ionised ethers were documented early in the development of organic mass spectrometry.[1] However, it was not until some ten years later that the simplification effected by using low-energy (*ca.* 12 eV) ionising electrons was reported.[2] Moreover, relatively little work on the reactions of ether molecular ions has been published, although the derived oxonium ions, $C_nH_{2n+1}O^+$, have been the subject of numerous mechanistic studies.

More recent work has uncovered unusual rearrangements in ionised ethers, especially at low internal energies.[3–5] In the course of a systematic investigation of the low-energy, low-temperature mass spectra of saturated ethers,[6] several interesting phenomena became evident in the homologous series $[\text{n-}C_5H_{11}OR]^{+\cdot}$. These results are reported and discussed in this paper.

Table 1. 12.1 eV, 75 °C Mass spectra of pentyl alkyl ethers

Compound	*m*/*z* (relative abundance)[a]
$C_5H_{11}OH$	71 (5), 70 (*M* − H_2O, 100), 56 (5), 55 (25), 42 (40)
$C_5H_{11}OCH_3$	103 (3), 102 (*M*, 29), 74 (7), 71 (6), 70 (100), 59 (15), 55 (7), 45 (25), 42 (13), 33 (18)
$C_5H_{11}OC_2H_5$	117 (4), 116 (*M*, 44), 74 (9), 71 (11), 70 (100), 59 (50), 47 (24), 42 (7)
$C_5H_{11}OC_3H_7$	131 (9), 130 (*M*, 70), 102 (7), 101 (18), 87 (9), 73 (23), 71 (21), 70 (100), 61 (14), 43 (9)
$C_5H_{11}OC_4H_9$	145 (10), 144 (*M*, 91), 129 (5), 115 (15), 101 (16), 87 (19), 75 (11), 71 (19), 70 (100), 57 (13), 56 (22)
$C_5H_{11}OC_5H_{11}$	159 (7), 158 (*M*, 55), 140 (27), 129 (9), 115 (9), 111 (5), 101 (13), 98 (6), 97 (6), 89 (8), 87 (5), 84 (7), 71 (37), 70 (100)

[a] Abundances normalised to 100 units for the base peak. Apart from *M* + 1 ions, ions with a relative abundance lower than 5 units were ignored.

Results and Discussion

Table 1 gives the low-energy, low-temperature mass spectra of n-alkyl n-pentyl ethers; the spectrum of n-pentyl alcohol is also reproduced for comparison.

As would be expected, variation of the temperature of the ion source or the energy of the ionising electrons has a marked effect on the spectra. More drastic changes are produced by varying the ionising electron energy; however, increasing the source temperature or the electron energy gives rise to similar systematic changes in the mass spectra. The relative abundance of the molecular ion decreases, but the peaks corresponding to $[C_nH_{2n+1}]^+$ increase rapidly in intensity. Thus, for n-butyl n-pentyl ether, *m*/*z* 70 is the base peak at 12.1 eV for source temperatures between 75 and 200 °C, but the relative abundance of M^+ at 200 °C is only one fifth of the value at 75 °C. At a source temperature of 75 °C, *m*/*z* 70 is the base peak at 12.1 eV, but *m*/*z* 57 is significantly more abundant than *m*/*z* 70 at ionising electron energies above 15 eV; moreover, at electron energies greater than 20 eV, *m*/*z* 71 exceeds *m*/*z* 70 in relative abundance.

The 12.1 eV, 75 °C spectra of the ethers differ from that of the parent alcohol in that they show appreciable molecular ions. Moreover, the intensity of the molecular peak increases steadily in progressing from $C_5H_{11}OCH_3$ to $C_5H_{11}OC_4H_9$. The reduction in continuing to $C_5H_{11}OC_5H_{11}$ is possibly an artefact, but might merely reflect the symmetry of the molecule: $[C_5H_{11}OC_5H_{11}]^{+\cdot}$ can lose $C_5H_{11}OH$ in two ways (whereas there is only one route for ROH loss from the lower ethers), thus enhancing the abundance of *m*/*z* 70 at the expense of the molecular ion.

The presence of molecular ions for small saturated ethers appears to be quite general,[6] even when the parent alcohol exhibits no molecular ion. This effect has an energetic origin (Table 2). Water has a much lower heat of formation than would be expected from simple extrapolation of the heats of formation of low molecular weight alcohols.[7] However, ionised alcohols have higher heats of formation than those which would be predicted from the data for the corresponding ionised ethers.[8–10] Consequently, ROH loss from $[ROC_5H_{11}]^{+\cdot}$ is *ca.* 80—90 kJ mol⁻¹ more demanding than H_2O elimination from $[HOC_5H_{11}]^{+\cdot}$. Indeed, on this simple energetic model, the expulsion of H_2O from $[HOC_5H_{11}]^{+\cdot}$ would be continuously exothermic if it occurred without reverse critical energy. Other factors may favour water loss from ionised n-pentyl alcohol: it has been proposed that dissociation under electron impact arises *via* an optical excited state of the alcohol,[11,12] rather than in the normal manner of decomposition of the molecular ion.

The precise mechanism whereby $[ROC_5H_{11}]^{+\cdot}$ loses ROH cannot be elucidated from the present data. It is possible that species containing incipient pentyl cations and co-ordinated alkoxyl radicals are involved. Similar species have been implicated as intermediates in the decomposition of 'onium' ions of several classes[13,14] and the reactions of ionised alkanes[15] and ethers;[4] and a recent review[16] highlights the importance of such species in the reactions of isolated ions. Isomerisation of incipient cations takes place readily in such

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† Part 2, ref. 6.

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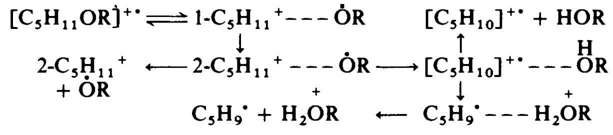
Table 2. Energy data relevant to decomposition of $[C_5H_{11}OR]^{+\cdot a}$

Ion	ΔH_f	Products and ΔH_f	$\Sigma\Delta H_f$	$\Delta\Delta H_f$
$[C_5H_{11}OH]^{+\cdot}$	665^b	$[1\text{-}C_5H_{10}]^{+\cdot c}$ (895^d) + H_2O (-240^e)	655	(−10)
$[C_5H_{11}OCH_3]^{+\cdot}$	615^b	$[1\text{-}C_5H_{10}]^{+\cdot}$ (895^d) + CH_3OH (-200^e)	695	80
$[C_5H_{11}OC_2H_5]^{+\cdot}$	585^b	$[1\text{-}C_5H_{10}]^{+\cdot}$ (895^d) + C_2H_5OH (-235^e)	660	75
$[C_5H_{11}OC_3H_7]^{+\cdot}$	560^b	$[1\text{-}C_5H_{10}]^{+\cdot}$ (895^d) + C_3H_7OH (-260^e)	635	75
$[C_5H_{11}OC_4H_9]^{+\cdot}$	530^b	$[1\text{-}C_5H_{10}]^{+\cdot}$ (895^d) + C_4H_9OH (-275^e)	620	90
$[C_5H_{11}OC_5H_{11}]^{+\cdot}$	510^b	$[1\text{-}C_5H_{10}]^{+\cdot}$ (895^d) + $C_5H_{11}OH$ (-305^f)	590	80

[a] All values in kJ mol^{-1} rounded to the nearest 5 kJ mol^{-1}. [b] Ref. 10. [c] Recent results (M. N. Mruzek and A. Maccoll, unpublished work) suggest that the $[C_5H_{10}]^{+\cdot}$ ion in the mass spectrum of n-pentyl alcohol may have the structure of ionised ethylcyclopropane. This would correspond to a 1,4-elimination of water occurring essentially at the thermochemical threshold; however, the major energetic trends apply regardless of whether ionised pent-1-ene or ionised ethylcyclopropane is produced. [d] Ref. 8. [e] Ref. 7. [f] Ref. 9.



Scheme 1.

intermediates, and must occur in the present series because formation of pentyl rather than 1-methylbutyl cation is energetically unfavourable. Scheme 1 gives an outline mechanism and explains much of the chemistry of $[C_5H_{11}OR]^{+\cdot}$.

Thus, after isomerisation of the incipient pentyl cation has occurred, simple cleavage produces $C_5H_{11}{}^{+}$ (*m*/*z* 71), whereas hydrogen transfer between the incipient products leads eventually to $[C_5H_{10}]^{+\cdot}$ and ROH. The precise structure of the pentyl cation and the $[C_5H_{10}]^{+\cdot}$ ion cannot be defined reliably, but primary cations can be excluded.

A second hydrogen transfer would produce $ROH_2{}^{+}$ and $C_5H_9{}^{\cdot}$, giving rise to a peak at $M - 69$. The occurrence of such peaks is the second general reaction of $[ROC_5H_{11}]^{+\cdot}$ ions; it has been found that analogous peaks occur in the spectra of higher molecular weight ethers at low internal energies,[2] and a detailed analysis has been given for ionised isobutyl methyl ether.[4] In the present series, doubts exist as to the structure and heat of formation of the $C_5H_9{}^{\cdot}$ radical; however, the heats of formation of dimethylallyl radicals are *ca.* 100—120 kJ mol^{-1}.[17] By using this range, together with the heat of formation [575 kJ mol^{-1} (ref. 18)] of $CH_3OH_2{}^{+}$, the energy needed to form these products can be estimated as 675—700 kJ mol^{-1}. This compares favourably with the total heat of formation (695 kJ mol^{-1}) of CH_3OH and $[1\text{-}C_5H_{10}]^{+\cdot}$. Similar calculations for the other $[C_5H_{11}OR]^{+\cdot}$ homologues reveal that $C_5H_9{}^{\cdot}$ elimination is energetically feasible, when assessed in terms of product stability.

The third major trend in the spectra is the generally low abundance of ions produced by α-cleavage. Whilst α-cleavage does take place, it does not give rise to peaks which dominate the spectra; elimination of ROH always produces the base peak at *m*/*z* 70. Neither is α-cleavage the energetically most favourable reaction: the decomposition routes of metastable $[C_5H_{11}OR]^{+\cdot}$ ions (Table 3) are loss of ROH and/or $C_2H_5{}^{\cdot}$.

Thus, the ionised ethers resemble, to some degree, the analogous alkanes, which lose alkyl radicals and alkanes in metastable transitions.[15,19] However, this analogy is only weak and must be qualified: the position of cleavage clearly is determined by the oxygen atom, although the positive charge is retained by the hydrocarbon fragment.

On the assumption that the peaks corresponding to α-cleavage arise wholly in this fashion, the competition between eliminating the larger and the smaller radical may be studied.

Table 3. Reactions of metastable $[C_5H_{11}OR]^{+\cdot}$ ions

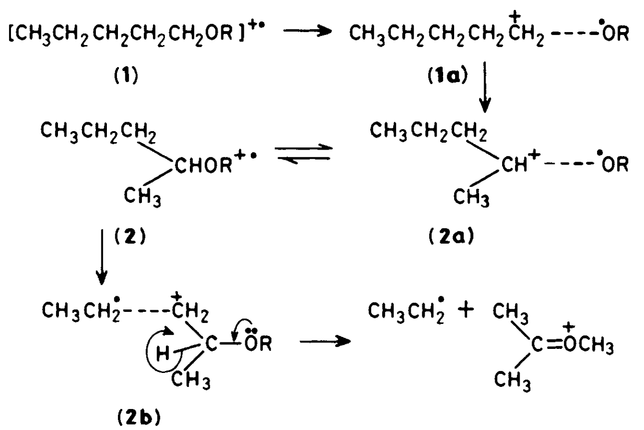
	Neutral lost[a]	
Ion	ROH	$C_2H_5{}^{\cdot}$
$[C_5H_{11}OCH_3]^{+\cdot}$	27	73
$[C_5H_{11}OC_2H_5]^{+\cdot}$	39	61
$[C_5H_{11}OC_3H_7]^{+\cdot}$	8	92
$[C_5H_{11}OC_4H_9]^{+\cdot}$	0	100
$[C_5H_{11}OC_5H_{11}]^{+\cdot}$	0	100

[a] Relative abundances measured by metastable peak areas, for ions decomposing in the second field-free region, and normalised to a total of 100 units.

The ratios of larger to smaller radical lost are 30:1 for $[C_5H_{11}OC_2H_5]^{+\cdot}$, 1.4:1 for $[C_5H_{11}OC_3H_7]^{+\cdot}$, 1.2:1 for $[C_5H_{11}OC_4H_9]^{+\cdot}$, and 1:1 for the symmetrical $[C_5H_{11}OC_5H_{11}]^{+\cdot}$. These values are similar to those reported[20] for some of the ionised ethers; it is difficult to devise an explanation based on energetics for these ratios, which show considerable dependence on the ionising electron energy close to threshold.

The final, and perhaps most surprising, feature of the mass spectra concerns the ease of $C_2H_5{}^{\cdot}$ loss from metastable $[C_5H_{11}OR]^{+\cdot}$ ions. A similar loss of $C_2H_5{}^{\cdot}$ has been found for certain small butyl ether molecular ions.[5] Since $C_2H_5{}^{\cdot}$ loss is observed from each ionised pentyl ether, it seems reasonable to conclude that it must involve the pentyl chain.

A possible mechanism is depicted in Scheme 2. After rearrangement of (**1**) to (**2**), *via* (**1a**) and (**2a**), stretching of a C–C σ-bond leads to (**2b**); a 1,2-hydride shift in the incipient cation of this complex can yield exceptionally stable products [for R = CH_3, $\Sigma\Delta H_f$ = 600 kJ mol^{-1} for $C_2H_5{}^{\cdot}$[21] and $(CH_3)_2C{=}OCH_3{}^{+}$[22]]. Comparison with Table 2 reveals that the eventual formation of the stable tertiary cation $[(CH_3)_2C{=}\overset{+}{O}CH_3 \longleftrightarrow (CH_3)_2\overset{+}{C}{-}OCH_3]$ provides a powerful driving force for the extensive rearrangement postulated in Scheme 2. Production of a secondary cation [for example, $CH_3CH_2CH{=}\overset{+}{O}CH_3 \longleftrightarrow CH_3CH_2\overset{+}{C}H{-}OCH_3$, *via* isomerisation of (**2a**) to 1-ethylpropyl methyl ether] would be only marginally preferable to ROH loss; however, this cannot be excluded on the basis of the present data. In any event, extensive isomerisation is needed before $C_2H_5{}^{\cdot}$ loss may occur; consequently, this process competes effectively only at the lowest internal energies. In addition, much more extensive rearrangement is required to permit $CH_3{}^{\cdot}$ loss to take place with concomitant formation of $CH_3CH_2(CH_3)C{=}\overset{+}{O}R$. Thus, the absence of $CH_3{}^{\cdot}$ loss from metastable $[C_5H_{11}OR]^{+\cdot}$ ions can be explained. If intermediates such as $[CH_3CH_2(CH_3)_2COR]^{+\cdot}$ were involved in $C_2H_5{}^{\cdot}$ loss, additional $CH_3{}^{\cdot}$ loss might be expected.



Scheme 2.

An alternative mechanism, involving 1,4- and 1,5-hydrogen shifts and skeletal rearrangements to give isomerisation to $[CH_3CH_2(CH_3)_2COR]^{+\cdot}$, could be put forward. Similar radical cations in which the heteroatom is protonated and the hydrocarbon chain contains a radical site are now well established,[22–26] and there is precedence for analogous mechanisms in the decomposition of ionised amines.[23,24] However, in this case, a possible objection to such a mechanism is that loss of a methyl radical might be expected to compete with elimination of an ethyl radical from the $[CH_3CH_2(CH_3)_2COR]^{+\cdot}$ formed by rearrangement of $[C_5H_{11}OR]^{+\cdot}$.

Conclusions

The low-energy, low-temperature mass spectra of pentyl alkyl ethers are both structurally informative and mechanistically interesting. In addition to the expected α-cleavage and alcohol elimination reactions, loss of $C_5H_9^{\cdot}$ and $C_2H_5^{\cdot}$ radicals occurs. Elimination of $C_2H_5^{\cdot}$ involves extensive rearrangement and must, for energetic reasons, give rise to a very stable daughter ion such as $(CH_3)_2C{=}OR^+$.

Experimental

All mass spectra were recorded with a modified A.E.I. MS 9 double-focusing spectrometer. An ionising electron energy of 12.1 eV and a source temperature of 75 °C were employed; the method has been previously described.[6]

Di-n-pentyl ether was commercially available and was fractionated before use; the other ethers were prepared by reactions of sodium pentoxide in n-pentyl alcohol with the appropriate alkyl bromide or iodide; the synthesized ethers were purified by careful refractionation after storage over sodium hydride. The purity of the ethers, checked by gas chromatography, was satisfactory.

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