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A STUDY OF GASEOUS 3-MEMBERED RING OXONIUM AND SULPHONIUM IONS

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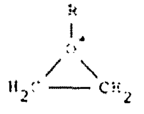
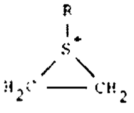
Abstract—The 1-methyl-1-thionia cyclopropane **3** and 1-phenyl-1-thionia cyclopropane **4** ions are stable, with lifetimes greater than 10^{-5} sec, and can be identified from their collisional activation spectra. Their metastable counterparts (lifetime window 10^{-6}–10^{-5} sec) have undergone ring opening to the isomeric structures $CH_3\overset{+}{S}=CHCH_3$ **9** and $C_6H_5\overset{+}{S}=CHCH_3$ **11** prior to decomposition. The 1-methyl-1-oxonia cyclopropane **1** and 1-phenyl-1-oxonia cyclopropane **2** ions could not be generated: instead acyclic structures $CH_3\overset{+}{O}=CHCH_3$ **5** and $C_6H_5\overset{+}{O}=CHCH_3$ **7** were found for both metastable and long living species. Loss of a phenoxy radical from $C_6H_5OCH_2CH_2OCH_3$ is shown to be preceded by a reciprocal hydrogen transfer and is not due to a SN_i-type reaction.

The gas phase $C_2H_5O^+$ ion structure problem[1,2] has long been a matter of considerable interest. In this context special attention has been devoted to the distinction of gaseous protonated ethylene oxide and protonated acetaldehyde isomers.[2,3b] These species exhibited similar behaviour† to a variety of ion structure probes, including collisional activation (CA).[3] Improved CA-instrumentation[5] however has recently resulted in unequivocal differentiation[4] of the two isomeric ions. The prediction that protonated ethylene sulphide species should also be among the stable $C_2H_5S^+$ species on account of reduced ring strain, was confirmed in the same study.[4] These data[4] on cyclic onium ions finally also showed that gas phase displacement reactions are only important in the production of cyclic sulphonium ions.

With regard to this revived interest in three-membered ring saturated onium ions, an investigation of higher homologs is of order. Gaseous $C_3H_7O^+$[6] and $C_4H_9O^+$[7] species have been studied in the past, but no evidence has so far been produced for the gas phase occurrence of *O*-alkylated ethylene oxide (such as **1**), even though such species are often invoked in the literature[8] and have been known in the solute phase.[9] As far as the sulphur analogs $C_3H_7S^+$ and $C_4H_9S^+$ are concerned, the scarcity of gas phase data is in striking contrast to their well-documented occurrence in solution.[10] Only one report[11] has dealt with the problem of the gas phase stability of cyclic $C_3H_7S^+$ ions **3**. Based on ICR[12] data showing different ion-molecule reactivities for $C_3H_7S^+$ species generated from $CH_3SCH_2CH_2OH$ (through protonation and loss of water) and acyclic reference species of known structures, it was concluded that cyclic ions **3** were stable in the gas phase. Although the different behaviour was shown to correlate with a cyclic structure, these results may reflect no more than differences in internal energies due to different precursors.[11] Hence more direct evidence for the gas phase occurrence of ions **3** is necessary to validate the conclusions of this ICR study.



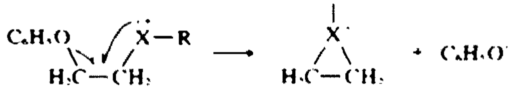
1: $R = CH_3$
2: $R = C_6H_5$



3: $R = CH_3$
4: $R = C_6H_5$

A gas phase investigation of onium species such as **1** and **3** necessitates the selection of suitable precursor molecules from which these species can be expected to be produced upon electron impact. Based on earlier studies,[14] the ω-functionalized phenetoles $C_6H_5OCH_2CH_2XR$ ($X = O, S$; $R = CH_3$) appeared to be the most logical candidates: loss of a phenoxy radical from these molecular ions was expected to be the result of a functional group interaction as depicted in Scheme 1. The present study has therefore been concerned with the application of collisional activation[3] to the structure of long living (lifetime > 10^{-5} sec) $[M-C_6H_5O]^+$ ions generated from these substituted phenetoles. Compounds in which $R = C_6H_5$ have also been included because these should produce phenylated ethylene oxide **2** and phenylated ethylene sulphide **4** species.

$C_3H_7O^+$ ions have been generated from β-methoxy phenetole (I) through loss of a phenoxy radical (*vide supra*) and from sec.butyl methyl ether (II) through



Scheme 1.

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† As has been pointed out elsewhere,[4] the contention[2c] that these species can be distinguished by reaction with PH_3 or H_2S in an ion cyclotron resonance (ICR) spectrometer, remains open to question as this criterion has only been tested on $C_2H_5O^+$ ions generated by direct protonation of ethylene oxide and acetaldehyde, and may well reflect internal energy differences.

α-fission. The CA-spectra, gathered in Table 1, are identical within error, thus demonstrating that only one long living $C_3H_7O^+$ species of $CH_3\dot{O}{=}CHCH_3$ **5** structure is produced from I. Note that the selection of a $CH_3\dot{O}{=}CHCH_3$ reference ion was motivated by the earlier report[6a] that this species is obtained from $CH_3OCH_2CH_2OCH_3$. Also note that no other $C_3H_7O^+$ reference ions of different structure have been included as these have been shown[6a] to yield substantially different CA-spectra.

At first glance the data (Table 1) on compounds I and II, could be interpreted in terms of initial formation of ions **1** (see Scheme 2) and subsequent rearrangement to the apparently more stable† species **5**. If a cyclic oxonium ion **1** does occur as an intermediate, only one deuterated $C_3H_5D_2O^+$ species of structure **1** is to be produced from labelled compounds $C_6H_5OCD_2CH_2OCH_3$ (I_a) and $C_6H_5OCH_2CD_2OCH_3$ (I_b), which consequently should yield identical CA-spectra. This obviously (Table 1) is not the case. Moreover, the non-identity of the CA-spectra of $[M-C_6H_5O]^+$ ions from I_a and I_b clearly establishes (i) that no total scrambling has occurred prior to CA-analysis, (ii) that methylene hydrogen scrambling (if occurring at all) is incomplete and (iii) that at least a substantial part of collision induced fragmentation does not involve a symmetrical transition state (e.g. **1**).

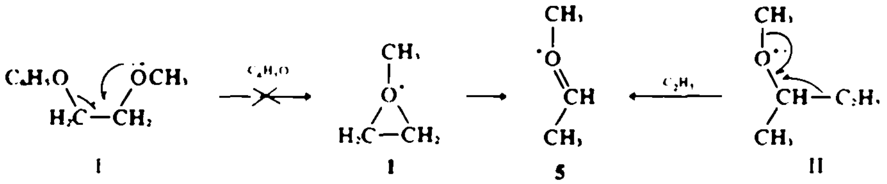
It is at this point important to note that the loss of a phenoxy radical from compounds I, I_a and I_b occurs in the ratio 1:1:0.88, as has been determined on equimolecular mixtures I + I_a and I · I_b. This points to the operation of an iostope effect at some stage in the formation of $[M-C_6H_5O]^+$ ions from I_b, more particularly to a β-hydrogen transfer. Simple cleavage of the C–O bond (as in Scheme 3) and subsequent 1,2-shift of the β-hydrogen, can account for both the observed isotope effect and the production of ions **5**. However, the absence of $[M-C_6H_5O]^+$ ions in the spectra of monofunctional phenylalkyl ethers is a strong argument against this mechanism and leaves little way but for a functional group interaction‡ in I, I_a and I_b. A plausible reaction of this type is outlined in Scheme 4. Following the concept of charge localization, an electron is removed in the phenoxy substituent.§ A β-hydrogen is then abstracted and exchanged between the two oxygen functions: the latter step should only be slightly endothermic, considering the slightly greater proton affinity of anisole with respect to dimethylether.[18] Radical site initiated[19] cleavage then results in protonated methylvinylether which is converted into ions **5** by a 1,3-hydrogen shift. According to Scheme 4, compounds I_a, I_b and I_c should yield species **5a**, **5b** and **5c** respectively, which are indeed confirmed by the data in Table 1.

$$CD_2H{-}\dot{C}H{=}\dot{O}CH_3 \qquad CH_2D{-}CD{=}\dot{O}CH_3$$

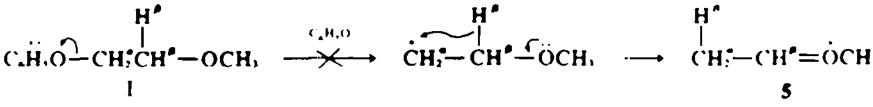
5a **5b**

$$CH_3{-}CH{=}\dot{O}CD_3$$

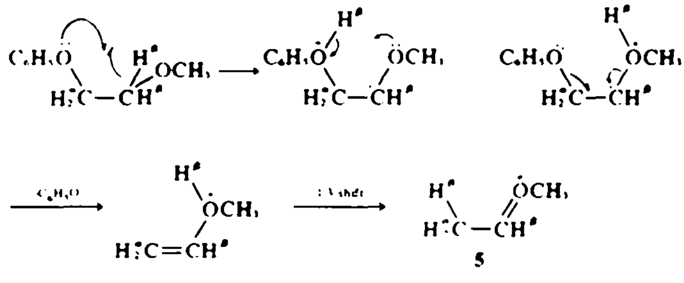
5c



Scheme 2.



Scheme 3.



Scheme 4.

The generation of a CH_3^+ fragment upon CA of ions **5** can occur by two different mechanisms as indicated in Scheme 5. Of these, process a involves a stable molecule of acetaldehyde as the lost neutral and will therefore be preferred: substantial retention consequently occurs at $m/e = 15$ for species **5a** and **5b** (from I_a, I_b), whereas predominant shift to $m/e = 18$ occurs for species **5c**

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† In analogy to $C_2H_5O^+$ data[20] indicating protonated ethylene oxide to be approximately 26 kcal · mole⁻¹ less stable than protonated acetaldehyde.

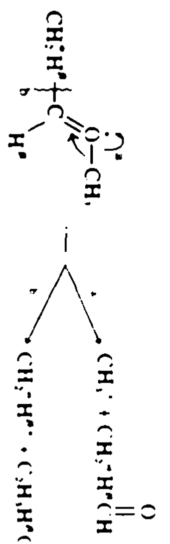
‡ Somewhat similar situations have been encountered in other α,ω-bifunctional alkanes.[21]

§ IP ($C_6H_5OCH_3$) = 8.20 eV;[16] IP (CH_3OCH_3) – 10.0 eV;[17] IP ($C_6H_5OCH_2CH_2OCH_3$) = 8.41 eV.[14a]

Table 1. Partial CA-spectra[a] of $C_3H_7O^+$ ions and labelled analogs

Precursor	Ion structure		m/e																	
			12	13	14	15	16	17	18	19	39	40	41	42	43	44	45	46	47	48
$C_6H_5OCH_2CH_2OCH_3$	(I)[b]	**5**	1.1	3.0	8.5	29.0	1.9	—	—	—	0.6	—	3.9	11.1	36.1	3.3	1.5	—	—	—
$CH_3OCH(CH_3)CH_2CH_3$	(II)[b]	**5**	0.7	2.4	7.5	27.3	1.7	—	—	—	0.8	—	4.9	12.1	37.1	3.8	1.6	—	—	—
$C_6H_5OCD_2CH_2OCH_3$	(I_a)	**5a**	0.8	1.5	4.0	17.4	6.0	12.5	0.7	—	0.2	0.7	1.1	3.5	8.3	12.8	26.0	3.0	1.4	—
$C_6H_5OCH_2CD_2OCH_3$	(I_b)	**5b**	1.0	2.0	5.1	19.4	9.6	6.4	0.6	—	0.3	0.7	1.1	3.5	9.1	22.5	14.7	2.5	1.5	—
$C_6H_5OCH_2CH_2OCD_3$	(I_c)	**5c**	0.9	1.8	5.6	11.7	3.4	1.6	19.1	0.9	—	0.6	2.7	11.1	30.4	4.7	0.8	1.9	0.9	1.7

[a] Abundances relative to the sum of all indicated fragments = 100. The *m/e* = 24-34 and *m/e* – 55–60 region has been excluded because the occurrence of peaks at *m/e* = 29 and 31 in the unimolecular metastable ion (MI) spectra: these will be partially shifted in the labelled ions and consequently interfere. All data refer to 70 eV measurements. [b] Lowering the electron energy from 70 to 15 eV does not alter this spectrum; this demonstrates that collision induced decomposition occurs from one structure only and not from a mixture of structures.



Scheme 5.

(from I_c). The other process (b) is reflected in the abundances at *m/e* = 17 (CD_2H^+) and 16 (CH_2D^+) for compounds I_a and I_b respectively. It should also be noted that the occurrence of sizeable abundances (Table 1) at *m/e* = 16 for I_a and *m/e* = 17 for I_b has not yet been accounted for. Because of the low abundances at *m/e* = 16 and *m/e* = 17 in the CA-spectrum of ions **5c** (from I_c), only a minor fraction of the $C_3H_7O^+$ ions from I can have undergone total scrambling.† Partial scrambling, involving only the $CH_2^\alpha H^\beta CH^\beta$ moiety of ions **5** will produce equal amounts of CH_2D^+ (*m/e* = 16) and CHD_2^+ (*m/e* = 17) through process b in Scheme 5. Isomerization of ions **5** to ions **1** prior to CA analysis leads to the same result (Scheme 6). Both mechanisms can account for the virtually equal abundances at *m/e* = 16 and *m/e* = 17 for I_a and I_b respectively, but are to be discarded as low electron energy (12 eV, nominal) data on $[M\text{-}C_6H_5O]^+$ ions from I_a are within error equal to the 70 eV data. The generation of *m/e* = 16 (I_a) and *m/e* = 17 (I_b) can consequently only be due to collision induced decomposition partially occurring over a symmetrical intermediate **1**.

Collision induced decomposition of $C_3H_7O^+$ ions from I also yields an abundant *m/e* = 43 fragment through loss of the elements of CH_4 (Table 1). The reaction clearly involves the original OCH_3 methyl group as indicated by the data on I_c and likely involves a mechanism as depicted in Scheme 7; accordingly a dominant shift to *m/e* = 45 and 44 is observed for ions **5a** (H^α = D) and **5b** (H^β = D), respectively, the slightly lower value of *m/e* = 44 from **5b** possibly being due to the operation of an isotope effect. The occurrence of *m/e* = 44 and *m/e* = 45 peaks in the CA-spectra of **5a** and **5b** respectively, is to be rationalized (see also discussion on the CH_3^+ fragment) by collisional induced decomposition partially occurring over a symmetrical intermediate **1**.

The preceding evidence for the structure of $C_3H_7O^+$ ions generated from I refers to long-living species (lifetimes $>10^{-5}$ sec). The slightly more energetic $C_3H_7O^+$ ions that undergo unimolecular metastable decomposition (lifetime window 10^{-6}–10^{-5} sec) need not necessarily have the same structure. MI-spectra have therefore been collected (Table 2), but indicate a similar situation: metastable $C_3H_7O^+$ ions from I also have the structure **5** of the α-fission product from II. The virtually identical data on I_a and I_b require a decomposition pathway symmetrical with respect to the α and β methylene groups in I, unless total scrambling of all hydrogens or complete scrambling of the α and β methylene hydrogens has preceded fragmentation. The latter two possibilities can be discarded as only partial scrambling (if any) was found in the less energetic, long living species analyzed by CA. The total scrambling picture is also disproved by the difference between experimental and calculated MI-spectra (Table 2). Isomerization of ions **5** to ions **1** (see Schemes 6 and 8)

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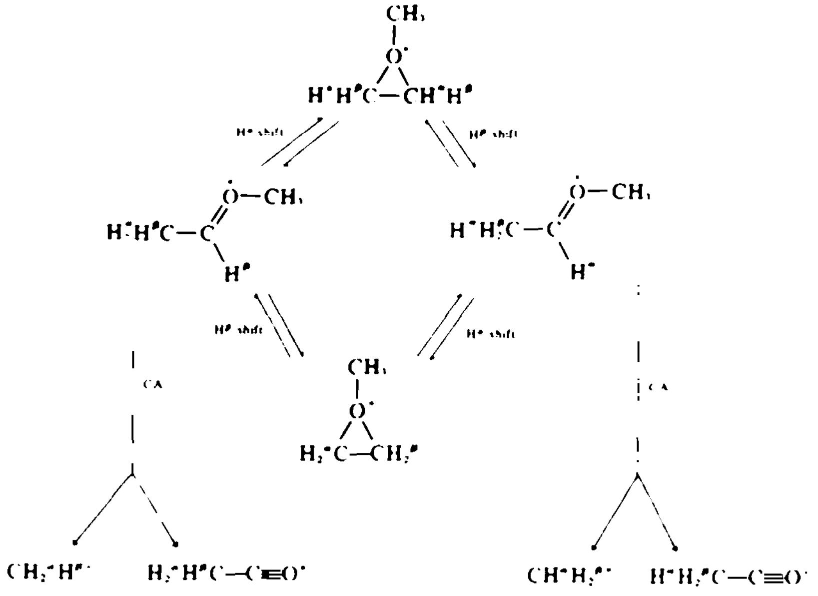
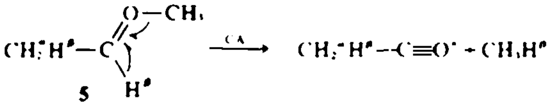
†Total scrambling in all $C_3H_4D_3O^+$ ions from I_c would yield the CH_3^+, CH_2D^+, CHD_2^+ and CD_3^+ fragments (*m/e* – 15, 16, 17 and 18, respectively) in a ratio 11 : 51 : 34 : 3.



Scheme 6.



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Scheme 7.

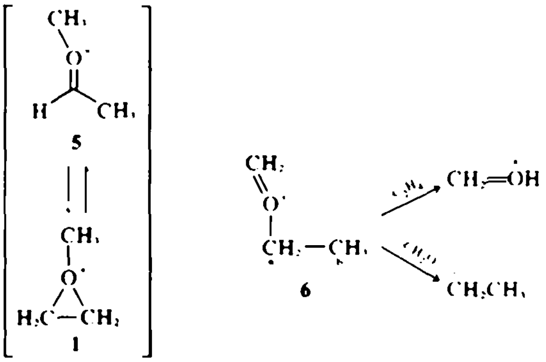
Table 2. MI-spectra[a] of $C_3H_xD_{7-x}O^+$ ions (x = 4, 5, 7)

		m/e 29	30	31	32	33	34
$CH_3O\overset{CH_3}{C}HCH_2CH_3$	(II)	18	—	82	—	—	—
$C_6H_5OCH_2CH_2OCH_3$	(I)[b]	21	—	79	—	—	—
$C_6H_5OCD_2CH_2OCH_3$	(I_a)	—	—	65	35	—	—
$C_6H_5OCH_2CD_2OCH_3$	(I_b)	—	—	67	33	—	—
$C_6H_5OCH_2CH_2OCD_3$	(I_c)[c]	—	17	1	2	66	14
Calculating for total scrambling in I_a and I_b		1	10	33	45	11	—
Calculated for total scrambling in I_c		—	3	21	47	27	2

[a] All abundances have been normalized to a sum = 100.

[b] The fragment at *m/e* = 29 must be $C_2H_5^+$ (and not CHO^+) as a complete shift occurs to *m/e* = 31 for I_a and I_b; it is therefore generated by loss of CH_2O. Loss of C_2H_4 on the other hand results in the *m/e* = 31 fragment.

[c] These data are in surprisingly good agreement with literature data[6a] on $CD_3\text{-}\dot{O}{=}CH\text{-}CH_3$ 5c ions generated through *α*-fission: (*m/e* = 33)/(*m/e* = 34) = 80/16.



Scheme 8.

consequently is the only logical explanation. Such a mechanism is still compatible with the previously reported[6a] decomposition of metastable ions **5** over structure **6** (see Scheme 8) and correlates well with the collision induced decomposition of ions **5** partially occurring (*vide supra*) over a symmetrical intermediate **1**. A quantitative analysis of the data on I_a, I_b, I_c (Table 2) indicates that in the subsequent decomposition of ions **6** to $CH_2{=}\dot{O}H$ fragments, the transferred hydrogen originates for about 33% from position a and about 67% from position b. This is in good agreement with the data† on ion source decomposing ions produced by *α*-fission of ethyl ethers, the slightly reduced specificity for position b most probably being due to increased (partial) scrambling in the less energetic metastable ions.

In an attempt to demonstrate the gas phase occurrence of 1-oxonia-1-phenyl cyclopropane ions **2**, several $C_8H_9O^+$ fragments have been generated (see Scheme 9): compounds IV and V should yield reference ions of structure **7** and **8** respectively. The two species are readily distinguished by their CA-spectra (Table 3; see, e.g. the abundances at *m/e* = 77, 105 and 120) which to some extent reflect their structures. Species **8** for instance is the only ion expected to produce abundant benzoyl ion fragments ($C_6H_5C{\equiv}O^+$, *m/e* = 105). Production of a *m/e* = 77 fragment on the other hand is favoured for ions **7** as this reaction involves loss of a much more stable neutral (acetaldehyde).

In complete analogy to the findings for the $C_3H_7O^+$ species generated from *β*-methoxy phenetole (I), loss of

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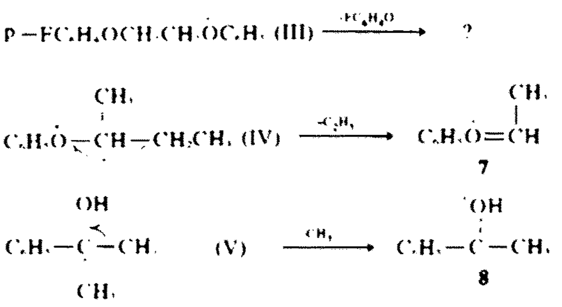
† Ion source decomposing $CH_3CH{=}\dot{O}CD_2CH_3$ ions for instance loose C_2H_4 and C_2H_3D in a ratio of 85:15.[20]



$p-FC_6H_4OCH_2CH_2\dot{O}C_6H_5$ (III) $\xrightarrow{-FC_6H_4O}$?

$C_6H_5\dot{O}-\overset{CH_3}{CH}-CH_2CH_3$ (IV) $\xrightarrow{-C_2H_5}$ $C_6H_5\overset{+}{O}=\overset{CH_3}{CH}$ **7**

$C_6H_5-\overset{OH}{\underset{CH_3}{\dot{C}}}-CH_3$ (V) $\xrightarrow{-CH_3}$ $C_6H_5-\overset{+OH}{C}-CH_3$ **8**

Scheme 9.

$FC_6H_4O^{\cdot}$ from III results in acyclic ions of structure **7** (Table 3). Their formation very likely is due to a mechanism similar to the one outlined in Scheme 4.[†] Labelling experiments have also been carried out, but, in contrast to the results on $C_3H_5D_2O^+$ species (*vide supra*, Table 1) the CA-spectra for $C_8H_7D_2O^+$ ions from p-$FC_6H_4OCH_2CD_2OC_6H_5$ (III$_b$) and p-$FC_6H_4OCD_2CH_2OC_6H_5$ (III$_a$) are surprisingly similar. The spectra are in fact superimposable, except for the m/e = 43–46 region. Apparently extensive symmetrization with respect to the α and β methylene units has occurred in most of the $C_8H_7D_2O^+$ ions prior to CA-analysis. Whether this is due to scrambling or to isomerization (to ions type **2**) prior to collision cannot be ascertained: a detailed analysis of all peak patterns is severely hampered by the important overlap of adjacent peaks and has therefore not been attempted.

The observed differences in the spectral region m/e = 43–47 (see Fig. 1) do however correlate with acyclic structure. Decomposition of $C_8H_7D_2O^+$ ions **7**, generated from III$_b$, yields fragments at m/e = 44 and 45, while those from III$_a$ seem to exhibit only a more intense fragment at m/e = 45 (see Fig. 1). This difference can be rationalized in a manner similar to Scheme 4 (see Scheme 10). Assuming (i) that the CH_3CO^+ fragment is due to hydrogen transfer from both the methine (a) and the methyl group (b) of **7**, and (ii) that process a is dominant, III$_a$ should essentially yield a m/e = 45 peak

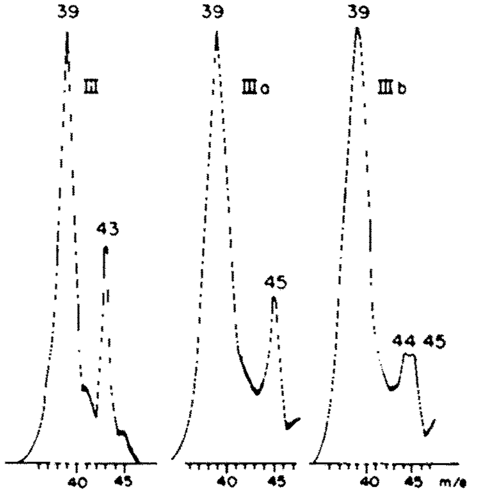


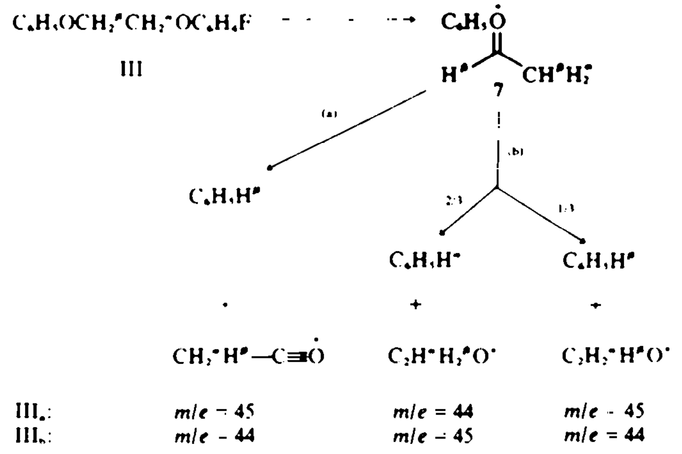
Fig. 1. Partial CA-spectra of $[M-C_6H_5O]^+$ ions from III, III$_a$ and III$_b$.

Table 3. CA-spectra[a,b] of $C_8H_9O^+$ ions (m/e = 121)

Precursor		Ion structure	m/e																		
			15	27	29	31	39	(43)	51	55	61	63	65	75	77	89	(91)	(93)	(103)	105	120
p-$FC_6H_4OCH_2CH_2OC_6H_5$	(III)	**7**	-	2.8	1.0	-	6.3	(3.8)	15.9	1.8	—	4.0	6.2	3.6	55.9	—	(11.7)	(26.7)	(23.0)	2.7	—
$C_6H_5O\underset{CH_3}{CH}CH_2CH_3$	(IV)	**7**	—	2.9	0.9	—	7.0	(2.7)	16.1	1.8	—	4.6	7.0	3.0	54.6	—	(16.0)	(49.7)	(35.9)	2.8	—
$C_6H_5\overset{OH}{\underset{CH_3}{C}}CH_3$	(V)	**8**	0.2	1.8	0.6	0.2	4.5	(80.5)	12.1	0.7	1.8	3.1	3.5	2.5	23.1	1.3	(5.1)	(1.8)	(2.5)	19.0	25.5

[a]Abundances are normalized to a sum = 100, excluding those peaks due to low energy processes as revealed by metastable ion (MI) spectra: m/e = 43 (V), m/e = 93 and 103 (IV and III). The abundance of m/e = 91 has also been excluded because of extensive overlap with the very broad m/e = 93 for III and IV. [b]CA-spectra obtained at 15 eV (nominal) were in each case identical to the above 70 eV spectra, except for the low energy processes mentioned s.v. a. This demonstrates that decomposition occurs from one structure in each case.

[†] Accordingly an equimolecular mixture of III and III$_b$ reveals an isotope effect of 0.87 for loss of FC_6H_4O from III$_b$.



Scheme 10.

and only a minor fragment at *m/e* = 44, especially as the formation of the latter is subjected to the operation of an isotope effect ($H^{\alpha} = D$). This minor contribution at *m/e* = 44 apparently is masked in the flank of *m/e* = 45 (see Fig. 1). Compound III_b however will produce a reduced (isotope effect: $H^{\beta} = D$) CA-fragment at *m/e* = 44 through processes a and b, and consequently the production of *m/e* = 45 through b becomes even more important (in comparison to *m/e* = 44 from III_a). As a result *m/e* = 45 is partially resolved (see Fig. 1).

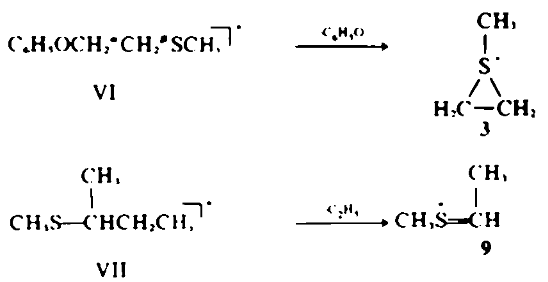
Unimolecularly decomposing metastable $C_8H_9O^+$ ions (*m/e* = 121) generated from III and IV (Scheme 9) yield identical MI-spectra (not shown): CO (*vide infra*) and H_2O are lost in the same ratio, indicating an acyclic structure 7 for the metastable $[M\text{-}C_6H_5O]^+$ ions from III. The data on labelled analogs III_a, III_b and III_c ($C_6H_5OCH_2CH_2OC_6D_5$) confirm that the *m/e* = 93 fragment is uniquely due to loss of CO. An analysis of the MI-spectra reveals that loss of H_2O (Table 4) is preceded by total scrambling of all hydrogens: it is thus impossible to verify whether metastable $C_8H_9O^+$ ions from III have isomerized to 2 prior to or upon decomposition.

Table 4. Loss of $(H,D)_2O$ from metastable $C_8H_xD_{9-x}O^+$ ions ($x = 4, 7, 9$)*

x	Precursor		$-H_2O$	$-HDO$	$-D_2O$
9	$C_6H_5OCH_2CH_2OC_6H_4F$	(III)	100	—	—
7	$C_6H_5OCH_2CD_2OC_6H_4F$	(III_a)	57	43	—
7	$C_6H_5OCD_2CH_2OC_6H_4F$	(III_b)	60	40	—
4	$C_6D_5OCH_2CH_2OC_6H_5$	(III_c)	19	54	26
7	Calculated for total scrambling in III_a and III_b		58	39	3
4	Calculated for total scrambling in III_c		17	56	28

*All abundances have been normalized to a sum = 100.

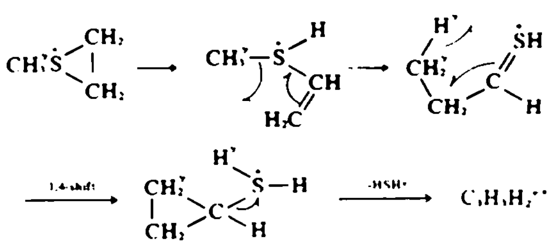
The results of our $C_3H_7O^+$ investigation (*vide supra*) prompted us to compare the CA-data on $C_3H_7S^+$ ions generated from β-methylthio-phenetole (VI) with the data on the α-fission product (Scheme 11) from sec.butyl methyl sulphide (VII). The different spectra (compare abundances at *m/e* = 46, 59, 60, 61, 73 and 74) in Table 5 clearly indicate that these $C_3H_7S^+$ species are different in contrast to their oxygen analogs (vide supra). Salient features in the CA-spectrum of $[M\text{-}C_6H_5O]^+$ ions are, e.g. the enhanced losses of CH_2 (*m/e* = 61) and C_2H_4 (*m/e* = 47) and these do correlate with a cyclic structure 3.



Scheme 11.

Deuterium labelling has once again been performed in order to further corroborate this assumption: within the limits of reproductibility identical spectra have been obtained for $C_3H_5D_2S^+$ ions (*m/e* = 77) from VI_a and VI_b (Table 5). Excluding total scrambling† of all ions (prior to CA-analysis), a cyclic structure 3 must therefore be at hand, unless collision induced decompositions are preceded by complete hydrogen scrambling in the α and β methylene units.

The diagnostically very important *m/e* = 61 fragment, generated from $C_3H_7S^+$ ions through loss of a CH_2 unit, involves the α and β methylene hydrogens only, as SCD_3 labelling in VI_c results in a quantitative shift of the fragment to *m/e* = 64 (Table 5). If the assumption of cyclic $C_3H_7S^+$ ions 3 is correct, CH_2 and CD_2 losses from $C_3H_5D_2S^+$ ions (compounds VI_a and VI_b) should occur in a 1 : 1 ratio. This is not directly visible in the CA-spectra (Table 5) as losses of CD_2 and CH_4 from $C_3H_5D_2S^+$



Scheme 12.

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† Total retention of all peaks *m/e* = 57–60 in the spectrum of $C_3H_4D_3O^+$ ions (*m/e* = 78) from VI_c, clearly rules out this possibility and of course indicates that the generation of these fragments involves the SCH_3 methyl group.

Table 5. CA-spectra[a] of $C_3H_xD_{7-x}S^+$ ions (x = 4, 5, 7)

m/e	Composition[b]	$CH_3S\overset{\overset{CH_3}{\mid}}{C}HCH_2CH_3^+$ VII	$\phi OCH_2CH_2SCH_3^+$ VI	p-$FC_6H_4OCH_2$[d] CD_2SCH_3 VI_b	p-$FC_6H_4OCD_2$[d] CH_2SCH_3 VI_a	$C_6H_5OCH_2CH_2SCD_3$ VI_c
15	CH_3	1.6	1.0	1.3	1.4	
18						2.4
26	C_2H_2	6.4	6.9			9.4
27	C_2H_3	11.5	12.8	6.3	6.4	14.1
28	C_2H_4	2.7	4.7	8.6	8.9	
29	C_2H_5	1.4	1.5	8.6	8.5	2.9
30				4.8	4.7	
31				3.1	3.1	1.4
32	S	1.7	1.7	2.0	2.1	2.5
33	SH	1.4	1.5			
35	H_3S	—	0.7	1.0	1.0	
36				0.6	0.6	
37				0.4	0.3	0.7
39	C_3H_3	3.0	1.4			
40				1.5	1.5	
(41)	C_3H_5	(29.3)	(37.1)	(1.3)	(1.4)	
(42)				(13.5)	(12.9)	(3.6)
(43)				(27.8)	(24.3)	(25.1)
(44)						(11.6)
(45)	CHS	(33.6)	(36.8)	(30.4)	(30.4)	(20.9)
(46)	CH_2S	(11.0)	(24.3)	(30.6)	(30.3)	(25.5)
(47)	CH_3S	(34.8)	(46.8)	(30.3)	(27.8)	
(48)	CH_3SH	(3.1)	(3.8)	(24.8)	(23.4)	(22.3)
(49)	CH_3SH_2	(7.6)	(8.2)	(5.5)	(5.3)	(26.3)
(50)				(5.5)	(5.3)	(13.4)
(51)				(2.1)	(1.7)	(6.2)
(52)						(9.6)
57	C_2HS	7.1	6.7	2.8	2.8	7.2
58	C_2H_2S	16.0	13.4	5.7	5.6	13.9
59	C_2H_3S	23.6	17.9	7.7	7.5	19.3
60	C_2H_4S	12.0	8.0	10.6	10.1	9.1
61	C_2H_5S	0.7	2.6	11.2	11.1	—
62				8.8	8.6	—
63				2.2	2.1	—
64						3.0
69	C_3HS	0.6	—			
71	C_3H_3S	1.0	—			
73	C_3H_5S	2.3	6.5			
74	C_3H_6S	6.8	12.7	1.5	1.2	
75				3.1	3.2	1.2
76				8.7	9.4	3.3
77						9.6

[a] Abundances have been normalized to a sum = 100 for all peaks excluding the m/e = 41–52 region. MI spectra for unlabelled compounds do indeed contain peaks at m/e = 41 and 47: these are therefore due to low energy processes which are sensitive to internal energy variations. Because of partial shifts of these peaks in the spectra obtained from labelled precursors, the entire region 41–52 was omitted in the normalization.

[b] For unlabelled precursors only.

[c] Except for the abundances at m/e = 41 and 47, no changes occur upon lowering the electron energy from 70 to 15 eV: collision induced decomposition therefore occurs from a single structure and not from a mixture of structures.

[d] The additional p-fluoro label was necessary because VI yields an appreciable peak at m/e – 77 ($C_6H_5^+$) isobaric with $C_3H_5D_2O^+$ ions. The unlabelled p-fluoro compound on the other hand could not be used (instead of VI) as $C_3H_7S^+$ and $C_6H_3^+$ (through loss of HF from $C_6H_4F^+$, m/e = 95) both occur at m/e = 75.

species coincide at $m/e = 61$, but the equal losses of CH_2 (yielding $m/e = 63$) for both VI_a and VI_b are a strong indication that this is indeed so. Moreover, $m/e = 62$ and $m/e = 63$ fragments should occur in a ratio of 6:1† if $C_3H_5D_2S^+$ ions from VI_a and VI_b are indeed identical (i.e. **3** is their structure), whereas this ratio should be as high as 23:1† if the identical results for VI_a and VI_b were due to scrambling of α and β methylene hydrogens. The actual ratio being ~4:1,‡ there cannot be any doubt concerning the cyclic structure **3** of $[M-C_6H_5O]^+$ ions generated from VI.

With regard to these striking results on long living $C_3H_7S^+$ ions, the structure of their unimolecularly decomposing metastable counterparts evidently is of interest. Apparently (see Table 6) it is not possible to distinguish metastable $[M-C_6H_5O]^+$ ions from ions **9** on the basis of the MI-spectra: both species loose H_2S ($m/e - 41$) and C_2H_4 ($m/e = 47$) in the same ratio. The MI-spectra of $C_3H_5D_2S^+$ ions on the contrary indicate that a symmetrical structure has been involved: neither total scrambling nor scrambling over the α and β methylene units can be responsible for the identical spectra obtained from VI_a and VI_b as these mechanisms have been shown to be of minor importance in the even less energetic $C_3H_7S^+$ ions sampled by CA (see also the calculated distributions for total scrambling: Table 6). It must therefore be concluded that $C_3H_7S^+$ ions, initially produced as **3** and with sufficient internal energy to undergo unimolecular metastable decomposition, isomerize to the acyclic species **9** prior to fragmentation. Such isomerization results in rapidly interconverting structures even if decomposition occurs predominantly or exclusively from only one of these, and finally leads to randomization of the α and β methylene hydrogens exactly in the manner depicted in Scheme 6. As far as loss of H_2S ($m/e = 41$) is concerned, the data in Table 6 correspond to a dominant site-specific process involving one CH_3S hydrogen and one from the original methylene groups, with an isotope effect discriminating against deuterium in the latter case. A plausible sequence of events accomodating this result is given in Scheme 12. Loss of C_2H_4 ($m/e - 47$) occurs in a more complicated fashion but can be described very accurately by assuming decomposition over ions **10** (*cf* decomposition of metastable ions $C_3H_7O^+$) and partial conversion of **10** into **10'** by a 1,3-methyl shift (Scheme 13).

The CA-data on C_8H_9S ions ($m/e - 137$) generated (Scheme 14) from β-phenylthio-phenetole (VIII) and from phenyl sec.butyl ether (IX) are contrasted in Table 7. The spectra show substantial differences (e.g. at m/e = 69, 77, 121 and 123) demonstrating that different structures are involved. In contrast to their $C_8H_9O^+$ analogs (vide supra), $C_8H_9S^+$ ions produced from VIII could therefore have cyclic structure **4**, especially as this structure correlates with some features of the CA-spectra: species **4** are the only ones to undergo loss of CH_2 (yielding $m/e - 123$), whereas loss of the elements of CH_4 ($m/e = 121$) requires much less rearrangement from structure **11**.

This structural inference based on spectral comparison is reinforced by the data on labelled compounds $VIII_a$ and $VIII_b$ (Table 7). Excluding total scrambling§ in all $C_8H_7D_2S^+$ ions, the superimposable spectra are compatible either with scrambling of α and β methylene hydrogens or with the formation of only one $C_8H_7D_2S^+$ species from both $VIII_a$ and $VIII_b$ (i.e. structure **4**). These two alternatives can be distinguished (cf. $C_3H_7S^+$ ions) by an analysis of the diagnostically very important fragment

Table 6. MI spectra* of $C_3H_xD_{7-x}\dot{S}$ ions (x = 4, 5, 7)

		m/e							
		41	42	43	44	47	48	49	50
$CH_3S\overset{\overset{CH_3}{\vert}}{C}HCH_2CH_3$	(VII)	50.8	—	—	—	49.2	—	—	—
$C_6H_5OCH_2CH_2SCH_3$	(VI)ᵇ	51.6	—	—	—	48.4	—	—	—
$C_6H_5OCD_2CH_2SCH_3$	(VI_a)	<1	13.8	32.8	—	21.7	27.7	4.0	—
$C_6H_5OCH_2CD_2SCH_3$	(VI_b)	<1	14.2	33.6	—	21.3	27.0	3.9	—
$C_6H_5OCH_2CH_2SCD_3$	(VI_c)	—	3.0	39.0	6.6	0.4	19.4	30.1	1.4
Calculated for total scrambling in VI_a and VI_b		2.5	24.5	24.5	—	13.8	27.7	6.9	—
Calculated for total scrambling in VI_c		—	7.4	29.5	14.7	5.5	24.9	16.6	1.4

*All abundances are normalized to a sum = 100.

ᵇThe MI-spectrum of $m/e = 75$ ions from VI contains an "apparent" fragment at an energy fraction 77/79 which is due to the metastable transition $m/e = 79 \rightarrow m/e = 77$ ($77^2/79 = 75$) occurring in the first field free region (i.e. prior to mass analysis).

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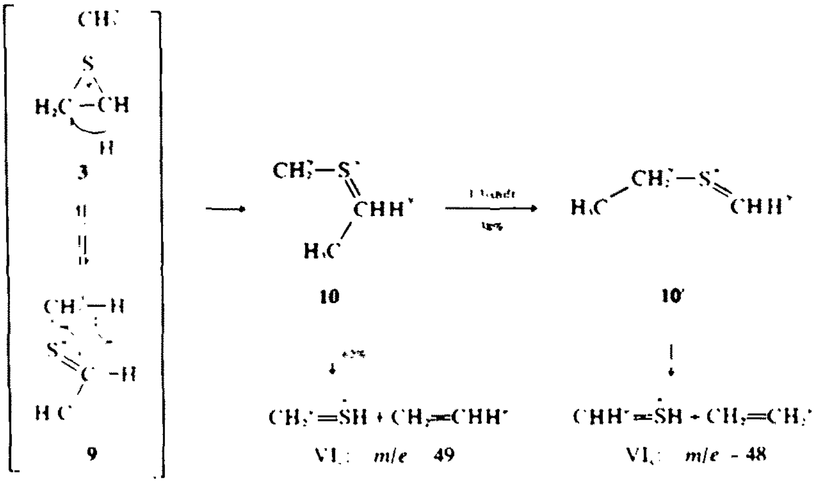
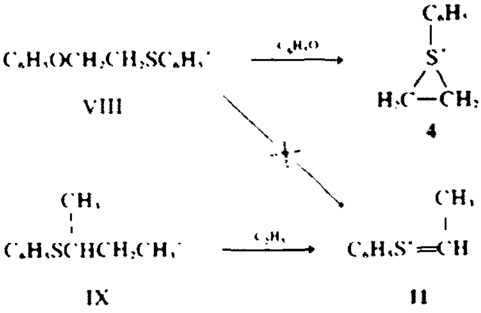
†The data on VI_c indicate that only the SCH_3 methyl group is involved in the production of the $m/e = 60$ fragment (loss of CH_3). Consequently this fragment (abundance: 8.0, see Table 5) must be quantitatively shifted to $m/e = 62$ for VI_a and VI_b. In the event of complete α and β methylene hydrogen randomization, CH_2, CHD and CD_2 will be lost in a 1:4:1 ratio, thereby contributing $2.6/6 = 0.43$ at $m/e = 61$ and 63 and $(2.6/6)4 = 1.73$ at $m/e = 62$. As a result a ($m/e = 62$): ($m/e = 63$) ratio of $(8.0 + 1.73):0.43 \sim 23:1$ is expected. If however no such scrambling occurs and a cyclic structure **3** is present, CH_2 and CD_2 should be lost from the $C_3H_5D_2S^+$ species in a 1:1 ratio, thereby contributing $2.6/2 = 1.3$ at both $m/e = 61$ and 63, and yielding a ($m/e = 62$): ($m/e = 63$) ratio of $8.0:1.3 \sim 6:1$.

‡This is slightly lower than the expected (*vide supra*) 6:1 ratio. Partial overlap of $m/e = 62$ and $m/e = 63$ results in a slightly increased peak hight for $m/e = 63$ and consequently a slightly reduced ratio.

§Such total scrambling prior to CA-analysis has not occurred to a great extent as complete retention of peaks at $m/e = 39$, 45, 51 and 65 has occurred (see Table 7).



Scheme 13.



Scheme 14.

at *m/e* = 123, generated through loss of a CH_2 unit. Assuming cyclic ions **4** to be present, equal amounts of CH_2 and CD_2 are to be lost from $C_8H_7D_2S^+$ ions generated from $VIII_a$ and $VIII_b$, thus yielding equally abundant peaks at *m/e* = 125 and 123. Some interference does however occur: loss of a CH_4 molecule (*m/e* = 121) from $C_8H_9S^+$ ions apparently involves three aliphatic hydrogens and one aromatic hydrogen and consequently results in equally abundant peaks at *m/e* – 121 and 122 for $C_8H_7D_2S^+$ ions. These peaks being more intense and also broader, partial (but important) overlap of the high mass flank of *m/e* = 122 will occur with the *m/e* = 123 peak (loss of CD_2), thus causing an increased peak height. The data in Table 7 do reveal the correct (i.e. 50%) shift of *m/e* = 123 (in $C_8H_9S^+$) to *m/e* = 125 (in $C_8H_7D_2S^+$). It should also be noted that the absence of any significant peak at *m/e* = 124 for $VIII_a$ and $VIII_b$ clearly establishes that no scrambling has occurred in the aliphatic portion of the $C_8H_7D_2S^+$ ions.†

The behaviour of metastable $C_8H_9S^+$ ions produced from VIII closely resembles (Table 8) that of the α-fission product $C_6H_5\dot{S}{=}CHCH_3$ **11** from IX, indicating the same structure **11** for both. The minor abundance variation clearly results from differences in the internal energy distribution as production of $C_8H_9S^+$ ions from VIII and IX involves loss of 93 and 29 mass units respectively: the internal energy must be less in the former case. Deuterium labelling ($VIII_a$ and $VIII_b$) results in only one MI-spectrum for $C_8H_7D_2S^+$ ions: the only

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†This would result in CH_2, CHD and CD_2 being lost in a 1:4:1 ratio, resulting in a (*m/e* – 124):(*m/e* = 125) ratio of 4:1 which evidently is not the case (Table 7).

Table 7. Partial CA-spectra[a] of $C_8H_xD_{9-x}S^+$ ions (x = 7, 9)

Precursor		*m/e* 27	39	41	45	51	63	65	69	77	82	121	122	123	124	125
$C_6H_5S\overset{CH_3}{C}HCH_2CH_3$	(IX)[b]	3.5	6.7	0.9	7.5	19.1	4.7	11.5	6.2	26.1	2.2	11.6	—	—	—	—
$C_6H_5OCH_2CH_2SC_6H_5$	(VIII)[b]	2.6	9.5	—	7.2	16.1	6.9	15.8	14.2	18.2	5.0	3.1	—	1.4	—	—
$C_6H_5OCD_2CH_2SC_6H_5$	($VIII_a$)[c,d]	2.4	10.0	—	7.6	15.9	9.4	16.4	16.5	11.9	5.9	1.4	1.4	1.2	—	0.5
$C_6H_5OCH_2CD_2SC_6H_5$	($VIII_b$)[c,d]	2.5	9.7	—	7.3	16.2	9.2	15.6	16.1	12.0	5.9	1.6	1.6	1.6	—	0.7

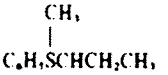
[a] All abundances have been normalized to a sum ~ 100. Unimolecular metastable decomposition to fragments at *m/e* = 59, 91, 103, 104, 109 and 135 does occur for the unlabelled compounds: these fragments are therefore due to low energy processes and have consequently been omitted. This is also the case for the peaks at one and two mass units higher in the labelled compounds.

[b] Lowering the electron energy from 70 to 15 eV (nominal) leaves this spectrum unchanged: collision induced decomposition therefore occurs from a single structure and not from a mixture of structures.

[c] The reduced abundance at *m/e* – 77 is due to a partial shift to *m/e* = 78 which peak is unresolved. Partially this reduction could also be due to methylene hydrogen transfer prior to formation of *m/e* 77 (isotope effect).

[d] As a result of the relatively high *m/e*-value of $C_8H_9S^+$ ions and the significant peak widths of CA-peaks (energy releases), partially shifted peaks in spectra of labelled ions will result in poorly resolved multiplets. Numerical evaluation is therefore often difficult and has only been performed on clearly defined peak tops.

Table 8. MI-spectra[a] of $C_8H_xD_{9-x}S^+$ ions (x = 7, 9)

		m/e												
		59	60	61	103	104	105	106	109	110	111	135	136	137
 $C_6H_5S\overset{CH_3}{\overset{\vert}{C}}HCH_2CH_3$	(IX)	23.7	—	—	26.5	10.8	—	—	39.0	—	—	(418)	—	—
$C_6H_5OCH_2CH_2SC_6H_5$	(VIII)	18.4	—	—	24.9	12.6	—	—	44.1	—	—	(980)	—	—
$C_6H_5OCD_2CH_2SC_6H_5$	($VIII_a$)	6.8	10.2	3.1	—	10.9	16.3	8.9	21.9	15.1	6.8	—	(175)	(431)
$C_6H_5OCH_2CD_2SC_6H_5$	($VIII_b$)	5.6	8.0	2.9	—	10.2	16.1	9.0	22.2	16.9	9.2	—	(193)	(482)
Calculated for total scrambling in $VIII_a$ and $VIII_b$[b]		7.7	9.2	1.5	0.7	9.7	17.3	9.8	7.4	24.5	12.3	(27)	(381)	(572)

[a] All abundances have been normalized to a sum = 100, excluding m/e = 135 (in IX and VIII) because of the large differences in intensities.

[b] Assuming no isotope effects are occurring.

logical explanation (excluding total scrambling: see Table 8) is that these more energetic (in comparison to long living $C_8H_9S^+$ ions sampled by CA) $C_8H_9S^+$ ions are initially generated as cyclic species **4**, but have subsequently undergone ring opening to **11**.

CONCLUSIONS

From the above analyses it follows that three-membered ring sulphonium ions **3**† and **4** are stable in the gas phase at lifetimes greater than 10^{-5} sec. The corresponding oxonium ions **1** and **2** however, could not be demonstrated: instead the acyclic oxonium ions $CH_3\dot{O}{=}CHCH_3$ **5** and $C_6H_5\dot{O}{=}CHCH_3$ **7** were found. These results are in perfect agreement with the earlier ICR-data[11] and validate the elegant correlations which had been drawn between gas phase reactivities and solute phase reactions. The production of stable acyclic oxygenated species **5** and **7** through loss of a phenoxy radical from $C_6H_5OCH_2CH_2OCH_3$ (I) and p-$FC_6H_4OCH_2CH_2OC_6H_5$ (III) respectively, indicates that the predicted SN_i-mechanism (Scheme 1) is outcompeted by the reciprocal hydrogen shift of Scheme 4. This is readily understood in terms of much more stringent energy requirements imposed by the highly strained transition state involved in the displacement reaction of Scheme 1 (X = O). Substitution of the oxygen atom for a sulphur, as in $C_6H_5OCH_2CH_2SCH_3$ (VI) and $C_6H_5OCH_2CH_2SC_6H_5$ (VIII), however, reduces the ring strain of this transition state and thereby effectively lowers‡ the activation energy for direct SN_i reaction. As a result the hydrogen shift is now outcompeted by the displacement reaction. This clearly illustrates that fragmentation reactions can be very sensitive to structural changes.

The unimolecularly decomposing metastable $[M-C_6H_5O]^+$ species of lifetimes in the 10^{-6}–10^{-5} sec interval, are all undistinguishable from the acyclic $R–\dot{X}{=}CHCH_3$ (X = O, S; R = CH_3, C_6H_5) reference species. The sulphur containing ions $CH_3\dot{S}{=}CHCH_3$ **9** and $C_6H_5\dot{S}{=}CHCH_3$ **11** are produced by isomerization of the initial cyclic product **3** and **4**, respectively. The oxygenated species **5** however is directly generated from the molecular ions of I, but does rearrange to **1** prior to decomposition. Metastable $C_8H_9O^+$ ions from III are also acyclic **7** but it could not be ascertained that their formation or their decomposition involves a cyclic intermediate **2**, although the latter seems more plausible on account of the data on $C_3H_7O^+$ ions.

These conclusions concerning metastable ions are the result of a careful confrontation of MI- and CA-data and would not have been possible if MI-data only had been used. The present study clearly shows the combination of the two ion structure probes (in conjunction with labelling experiments) to be extremely useful in obtaining a deeper insight in ion structure problems.

EXPERIMENTAL

Mass spectrometric measurements were performed on an AEI-MS50 double focusing instrument: ionizing energy 70 eV, emission current 300 μA, source temp. 200°. Collisional activation measurements were made on a modified Varian CH4B mass spectrometer equipped with an electric sector following the magnet (acceleration voltage 8 kV, electron energy 70 eV, electron beam 20 μA, source temp. 150°). For CA-measurements the He pressure in the collision chamber was increased until the precursor ion intensity was reduced to one third of its original value. The CA-spectra were then recorded as reported previously.[16] All CA-spectra are the means of at least two measurements.

Starting compounds for the synthesis of 1,2-bifunctional ethanes were methyl phenoxyacetate and methyl p-fluorophenoxyacetate (Scheme 15) obtained by acidic esterification of the commercial (Aldrich) acids. Their α,α-d_2 derivatives were obtained by three successive equilibrations with methanol-OD (Aldrich) to which a sodium splinter had been added: the 24 hr equilibrations were carried out at 100°C in a sealed glass tube. Further conversion of the starting materials was performed as outlined in Scheme 15. Lithium aluminum deuteride (Merck) and trideuteromethyl iodide (Aldrich) were obtained commercially. The preparation of III_a from methyl phenoxyacetate involved the use of p-FC_6H_4ONa in reaction 2. Lithium aluminum deuteride reduction of methyl methoxyacetate, tosylation and substitution with sodium phenoxide yielded I_b. These routes to I_a and III_a were preferred because of the higher isotopic purities (98% d_2 rather than ~90% d_2). Compound III_b was prepared using sodiumphenoxide-d_5 in reaction 2, whereas VI_a necessitated trideuteromethylation of 2-phenoxyethanethiol.[21] A Grignard reaction of phenylmagnesium bromide and acetone[22] afforded V. Finally, the use of sec.butanol as a substrate in reaction 1, yields

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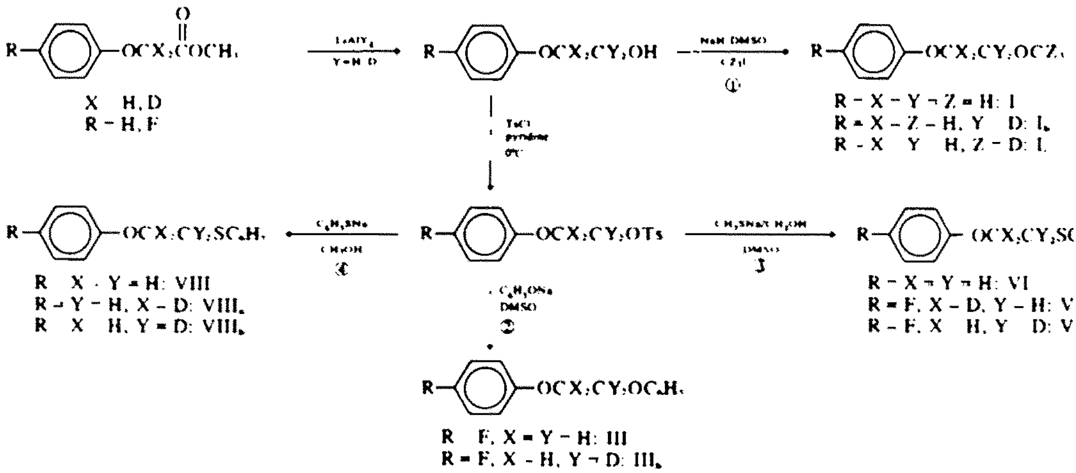
†After submission of this paper we were informed of CA-results[23] obtained in Prof. McLafferty's group and indicating that ions **3** are stable species. This is in agreement with the present data which do however provide more conclusive evidence for the cyclic structure through deuterium labelling (vide supra).

‡This is also reflected in the |AP(M-C_6H_5O)-IP| values[14a] for $C_6H_5OCH_2CH_2OC_6H_5$ (1.8 eV) and $C_6H_5OCH_2CH_2SC_6H_5$ (0.8 eV).



Scheme 15.

II, whereas its tosylate results in IV, VII and IX when subjected to reactions 2, 3 and 4, respectively. Isotopic purities of all labelled compounds have been determined by mass spectrometry: 98% d_2 for I_a, I_b, III_a, III_b, VI_b and $VIII_b$; 99% d_3 for I_c and VI_c; 91% d_2 for VI_a and $VIII_a$. No corrections for incomplete labelling are, however, necessary as mass analysis precedes CA- and MI-analysis. Positional retention of the label has also been verified for all d_2 compounds by 90 MHz ^{1}H NMR measurements on a Varian EM390 apparatus. Purity of all compounds has been checked by gas chromatography, thin layer chromatography or high pressure liquid chromatography. When necessary, purification was carried out by preparative GC or HPLC.

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