Isomerization and Fragmentation of Aliphatic Thioether Radical Cations in the Gas Phase: Ion–Neutral Complexes in the Reactions of Metastable Ethyl Propyl Thioether Ions

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The dominant unimolecular reactions of the molecular ion of ethyl propyl thioether are (*i*) loss of a methyl radical from the ethyl or the propyl group, (*ii*) loss of an ethyl radical from the propyl group and (*iii*) elimination of a propene molecule and an allyl radical by transfer of one or two hydrogen atoms, respectively, from the propyl group to the sulphur atom. The loss of a methyl radical on the μs timescale involves only the propyl entity and is preceded by an isomerization of this group to an isopropyl group. Partial loss of the positional identity of the hydrogen atoms of the propyl group occurs during the reactions of the metastable ions, but incorporation of hydrogen or carbon atoms from the ethyl group into the formed neutral species does not occur. The reactions of the metastable ions are discussed in terms of cleavage of a C–S bond assisted by a 1,2-hydride shift in the incipient carbenium ion leading to an ion–neutral complex of a thioethoxy radical and a secondary propyl carbenium ion. The ion–neutral complex can recombine to form the molecular ion of ethyl isopropyl thioether prior to methyl radical loss, or react by proton transfer to give a complex of $CH_3CH_2SH^{+\bullet}$ and $CH_2{=}CH{-}CH_3$, which may dissociate or undergo hydrogen atom transfer followed by elimination of an allyl radical. The partial loss of positional identity of the hydrogen atoms during the decomposition of the metastable ions is mainly a result of reversible proton transfer between the constituents, which competes favourably with 1,2-hydride shifts within the carbenium ion entity of the complex.

The study of the unimolecular chemistry of organic (radical) cations in the gas phase continues to be an active field of research in which new concepts are being advanced for the mechanistic details of apparently simple reactions. In recent years, the fragmentations of isolated metastable (radical) cations have been discussed repeatedly in terms of models which assume the formation of intermediate ion–neutral complexes weakly bound by electrostatic forces.[1–20] These ion–neutral complexes normally evade direct experimental observation, but their intermediacy is deduced from the occurrence of hydrogen exchange in the ionic part of the complex and/or by reversible proton/hydrogen atom transfer between the constituents of the complex. Particular attention has been addressed to the loss of propene from the molecular ion of phenyl propyl ether,[2,4,6,13,15] which is proposed to proceed by heterolytic cleavage followed by a 1,2-hydride shift in the incipient propyl carbenium ion under formation of an electrostatically bound complex of $C_6H_5O^\bullet$ and $(CH_3)_2CH^+$. Reversible 1,2-hydride shifts in the propyl carbenium ion have been proposed to account for the loss of the positional identity of the hydrogen atoms prior to proton transfer yielding the observed $C_6H_5OH^{+\bullet}$ ion.[2,4,15]

Conversely, the loss of positional identity of hydrogen atoms during the unimolecular reactions of radical cations in the gas phase has been demonstrated in many instances to be initiated by intramolecular hydrogen shifts leading to distonic isomers† of the conventional ions.[21–24] The role of ion–neutral complexes and distonic ions in the unimolecular reactions of radical cations in the gas phase has been discussed mainly for simple nitrogen- or oxygen-containing species. Comparatively less work has been devoted to testing whether these concepts apply to the gas phase unimolecular chemistry of the radical cations derived from organic sulphur compounds, such as thioethers.

The present work was initiated in order to take a fresh look at the mechanistic details of the decomposition of thioether radical cations in the gas phase[25–30] and in particular the elimination of an alkene molecule, which is a common reaction of simple thioether molecular ions. The molecular ion of ethyl propyl thioether was selected for a closer study in order to determine the origin of the hydrogen atom transferred in the loss of propene, which is strongly preferred over the loss of ethene, and the possible role of ion–neutral complexes and/or distonic ions in this reaction.

Results

Simple thioether radical cations are known to exhibit a wider variety of unimolecular reactions than their oxygen analogues.[28] This is mainly a result of the higher critical energy for α-cleavage of the thioether molecular ions than of ether radical cations, which allows other reactions to compete with α-cleavage.[28] In the ion-source the dominant reactions of the molecular ion of ethyl propyl thioether are: loss of an ethyl radical, loss of a methyl radical, elimination of a propene molecule [eqn. (1)] and heterolytic cleavage of the carbon–sulphur bonds leading to carbenium ions. Loss of an ethyl radical by α-cleavage is the main process and dominates over loss of methyl radical, which involves competing pathways (*vide infra*). Propene loss is the second main reaction in the ion-source whereas ethene loss is hardly observed.

$$\underset{m/z\ 104}{CH_3CH_2\overset{+\bullet}{S}CH_2CH_2CH_3} \longrightarrow \underset{m/z\ 62}{CH_3CH_2\overset{+\bullet}{S}H} + CH_3CH{=}CH_2 \quad (1)$$

The metastable ethyl propyl thioether molecular ions frag-

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† Distonic ions arise (formally) by ionization of diradicals or zwitterions and have the charge and radical sites located at separate atoms (see refs. 21–24).

Table 1 Relative abundances (%) of the ions formed by methyl radical loss from the molecular ion of ethyl propyl thioether (*m*/*z* 104) and labelled analogues[a]

		Ion-source[b] *m*/*z*				2nd FFR *m*/*z*				Statistical distribution[c] *m*/*z*			
Compound		89	90	91	92	89	90	91	92	89	90	91	92
$CH_3CH_2SCD_2CH_2CH_3$	**1a**	14		86		34	26	40		14	57	29	
$CH_3CH_2SCH_2CD_2CH_3$	**1b**		14	86		5	44	51		14	57	29	
$CH_3CH_2SCH_2CH_2CD_3$	**1c**	19			81	19	24	25	32	3	34	51	12
$CH_3CD_2SCH_2CH_2CH_3$	**1d**			100				100				100	
$CD_3CH_2SCH_2CH_2CH_3$	**1e**	59			41				100				100
$CH_3CH_2S^{13}CH_2CH_2CH_3$	**1f**	21	79			50	50			50	50		

[a] Corrected for contributions from the natural isotopes of sulphur and carbon. [b] Corrected for incomplete labelling (see Experimental section). [c] Label retention calculated for random distribution of the seven hydrogen atoms of the propyl group and equivalence of the α- and γ-C-atom before loss of a methyl radical.

Table 2 Relative abundances of the ions formed by loss of propene or an allyl radical from the ethyl propyl thioether radical cation (*m*/*z* 104) and labelled analogues[a]

		Ion-source[b] *m*/*z*						2nd FFR *m*/*z*				
Compound		62	63	64	65	66	Σ_i[c]	62	63	64	65	66
$CH_3CH_2SCH_2CH_2CH_3$	**1**	79	18				61	23	77			
$CH_3CH_2SCD_2CH_2CH_3$	**1a**	68	25	6	1		69	29	48	21	2	
$CH_3CH_2SCH_2CD_2CH_3$	**1b**	24	55	18	3		33	16	43	40	1	
$CH_3CH_2SCH_2CH_2CD_3$	**1c**	73	11	14	1		70	27	24	43	7	
$CH_3CD_2SCH_2CH_2CH_3$	**1d**			71	24		75			22	78	
$CD_3CH_2SCH_2CH_2CH_3$	**1e**				74	26	68			25	75	
$CH_3CH_2S^{13}CH_2CH_2CH_3$	**1f**	75	17	7			69	26	74			

[a] Corrected for contributions from the natural isotopes of sulphur and carbon. [b] Corrected for incomplete labelling (see Experimental section). [c] Sum of the abundances of the *m*/*z* 62–66 ions formed in the ion-source and normalized with respect to the main product ion, which corresponds in all cases to the loss of an ethyl radical from the molecular ion.

Table 3 Partial Collision Induced Dissociation (CID) spectra of the molecular ion of ethyl propyl thioether (*m*/*z* 104) and labelled analogues[a]

		m/*z*																		
Compound		58	59	60	61	62	63	64	65	73	74	75	76	77	78	79	89	90	91	92
$CH_3CH_2SCH_2CH_2CH_3$	**1**	1	2	3	6	23	14			1	1	39	3				7			
$CH_3CH_2SCD_2CH_2CH_3$	**1a**	1	1	2	5	24	13	2				2	2	37	3		2	1	5	
$CH_3CH_2SCH_2CD_2CH_3$	**1b**	1	2	3	5	6	19	10			2	37	2	3	3			1	6	
$CH_3CH_2SCH_2CH_2CD_3$	**1c**	1	2	3	5	23	5	9	1		1	33	1	2	3	2	2	1	1	5
$CH_3CH_2S^{13}CH_2CH_2CH_3$	**1f**	1	2	3	5	24	14				1	2	38	3			2	5		

[a] Corrected for contributions from the natural isotopes of sulphur and carbon.

ment predominantly by elimination of a methyl radical (20%), an allyl radical [eqn. (2)] (60%) and a propene molecule (20%).

$$\underset{m/z\ 104}{CH_3CH_2\overset{+\bullet}{S}CH_2CH_2CH_3} \longrightarrow \underset{m/z\ 63}{CH_3CH_2SH_2{}^+} + CH_2{=}CH{-}CH_2{}^{\bullet} \quad (2)$$

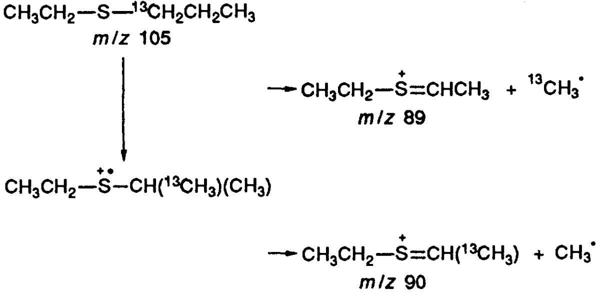
The reactions of the metastable ions give rise to Gaussian-shaped peaks.[31] The kinetic energy release as derived from the half-height width of the peaks ($T_{0.5}$) is 2.22 kJ mol^{-1} for methyl radical loss, 1.74 kJ mol^{-1} for allyl radical loss and 1.93 kJ mol^{-1} for propene loss.[31] Loss of an ethyl radical by α-cleavage is negligible in the reactions of the metastable molecular ions in contrast to the loss of a methyl radical, which competes effectively with the loss of propene and an allyl radical.

The results for the loss of a methyl radical from a series of isotopomers of the ethyl propyl thioether ion are collected in Table 1. The results for the loss of propene and an allyl radical from the molecular ions of the labelled compounds are summarized in Table 2.

The Collision Induced Dissociation (CID) spectra[32] of the ethyl propyl thioether molecular ion and the isotopomers (Table 3) are dominated by peaks caused by the loss of an ethyl radical or a propene molecule and resemble the 70 eV electron impact (EI) ion-source spectra of the compounds (see Tables 1 and 2 for selected parts of the EI spectra). The similarity between the CID results and the 70 eV EI spectra indicate that the main part of the non-decomposing ethyl propyl thioether molecular ions with lifetimes of μs have not isomerized to more stable structures.

Methyl Radical Loss.—In the ion-source α-cleavage of the ethyl group is the main pathway for the loss of a methyl radical as indicated by the dominant loss of $CH_3{}^{\bullet}$ from the molecular ion of **1c** and the preference for $CD_3{}^{\bullet}$ loss from ionized **1e** (Table 1). Other mechanisms are operative in the loss of a methyl radical as indicated by the 19% loss of $CD_3{}^{\bullet}$ from the molecular ion of **1c** and the competing elimination of $^{13}CH_3^{\bullet}$ and $CH_3^{\bullet}$ from the molecular ion of **1f** (Table 1).

Methyl radical loss from the metastable ions (column 2nd FFR in Table 1) involves only the propyl group as can be seen from the exclusive loss of $CH_3^{\bullet}$ from the radical cations of **1e** and **1d**. The equal loss of $^{13}CH_3^{\bullet}$ and $CH_3^{\bullet}$ from the metastable molecular ions of **1f** strongly suggests that methyl radical loss on the μs timescale is preceded by an isomerization of the propyl group to an isopropyl group [eqn. (3)].



$$CH_3CH_2{-}\overset{+\bullet}{S}{-}^{13}CH_2CH_2CH_3 \quad m/z\ 105$$

$$\longrightarrow CH_3CH_2{-}\overset{+}{S}{=}CHCH_3 + {}^{13}CH_3^{\bullet} \quad m/z\ 89 \qquad (3a)$$

$$CH_3CH_2{-}\overset{+\bullet}{S}{-}CH(^{13}CH_3)(CH_3)$$

$$\longrightarrow CH_3CH_2{-}\overset{+}{S}{=}CH(^{13}CH_3) + CH_3^{\bullet} \quad m/z\ 90 \qquad (3b)$$

The elimination of a methyl radical from the metastable ions is associated with loss of the positional identity of the hydrogen atoms of the propyl group as illustrated by the competing loss of $CH_3^{\bullet}$, $CH_2D^{\bullet}$, $CHD_2^{\bullet}$ and $CD_3^{\bullet}$ from the molecular ions of **1c** (Table 1). The relative abundances of the ions formed by methyl radical loss from the radical cation of **1c** (19:24:25:32) is different from the distribution (3:34:51:12) estimated upon the assumption that all seven hydrogen atoms of the propyl group become equivalent prior to reaction and that the α- and γ-carbon atoms become indistinguishable before fragmentation occurs.

Loss of an Ethyl Radical and Ethene.—The elimination of an ethyl radical proceeds by α-cleavage in the propyl group and to a minor extent by heterolytic cleavage of a sulphur–carbon bond as exemplified by the 95:5 ratio between the loss of $C_2H_3D_2^{\bullet}$ and $C_2H_5^{\bullet}$ in the ion-source reactions of the molecular ion of **1b**. The ethene molecule expelled to a very minor extent in the 2nd FFR originates mainly from the ethyl part of the ions as indicated by a more pronounced loss of C_2H_4 than of deuterium-containing ethene molecules in the reactions of the radical cations of **1a**–**c**.

Loss of Propene and an Allyl Radical.—The absence of incorporation of deuterium atoms into these neutral species during the fragmentation of the molecular ions of **1d** and **1e** (Table 2) provide evidence that propene and allyl radical loss involve only the propyl group. The distributions of the ions with *m*/*z* 62–65 formed by decomposition of the molecular ions of the isotopomers **1a**–**c** reveal that considerable loss of positional identity of the hydrogen atoms occurs during fragmentation in the ion-source and in the 2nd FFR of the instrument. Complete randomization of the hydrogen atoms of the propyl entity is not occurring as indicated by the different distribution of the abundances of the ions with *m*/*z* 62–65 formed in the ion-source as well as in the 2nd FFR by loss of propene or an allyl radical from the molecular ions of **1a** and **1b** (Table 2; see also Appendix).

The radical cation, $CH_3CH_2SH^{+\bullet}$ (*m*/*z* 62), which is the product of propene elimination [eqn. (1)], is formed in nearly equal abundance by fragmentation of the molecular ions of **1**, **1a**, **1c*** and **1f** in the ion-source. Furthermore, the abundances of the *m*/*z* 64 and *m*/*z* 65 ions from fragmentation of the radical cations from **1d** and **1e**, respectively, are nearly the same. In contrast, the molecular ion of the β-labelled compound, **1b**, shows a marked preference for the formation of *m*/*z* 63 ions over the formation of *m*/*z* 62 ions in the ion-source reactions (Table 2). These observations imply that there is a certain specificity for the β-position in the hydrogen transfer associated with propene loss in the ion-source. Propene elimination by transfer of a hydrogen atom from the β-position may be associated with a significant hydrogen isotope effect as indicated by the observation that the sum of the abundances of the *m*/*z* 62–66 ions is lower for **1b** than for the molecular ions of the other compounds studied (Table 2).

Discussion

Small sulphur-containing distonic ions, *e.g.* $^{\bullet}CH_2\overset{+}{S}H_2$ and $^{\bullet}CH_2\overset{+}{S}(H)CH_3$, are estimated to be less stable than their conventional counterparts, $CH_3SH^{+\bullet}$ and $CH_3SCH_3^{+\bullet}$, respectively.[22,23] By comparison, the distonic isomers of simple oxygen-containing radical cations are often the more stable species, and have been shown to play an important role in the decomposition of metastable aliphatic ether molecular ions.[34] The results for the reactions of the metastable ions of the labelled ethyl propyl thioether radical cations reveal that the neutral species eliminated do not incorporate hydrogen atoms from the ethyl group. Such a hydrogen atom interchange between the alkyl moieties could be expected if the reactions of the metastable ions were initiated by formation of distonic isomers of the molecular ion of ethyl propyl thioether in analogy with the reactions of metastable ethyl propyl ether ions.[34] The initial step in the reactions of the ether molecular ion was described as (reversible) transfer of a hydrogen atom from the methyl group of the propyl chain to the oxygen atom leading to formation of a γ-distonic ion, $CH_3CH_2\overset{+}{O}(H)CH_2CH_2CH_2^{\bullet}$, which in part reacts further by intramolecular hydrogen shifts involving the ethyl group.[34,35] The present results for the ethyl propyl thioether radical cation do not provide evidence for the formation of intermediates that are capable of undergoing hydrogen atom shifts between the hydrocarbon chains of the ions. The results do not completely exclude the occurrence of hydrogen shifts leading to distonic isomers of the molecular ion of ethyl propyl thioether, but the intermediacy of distonic ions appears unnecessary for a mechanistic explanation of the results even though the elimination of propene in the ion-source by transfer of a hydrogen atom from the β-position of the propyl group could be viewed as a step-wise process with a distonic intermediate.

The observation that the methyl radicals eliminated from the metastable ions originate entirely from the propyl chain, in combination with the equal probability for loss of $^{13}CH_3^{\bullet}$ and $CH_3^{\bullet}$ [eqn. (3) and Table 1] from the metastable ions of **1f** provide evidence for the isomerization of the propyl group to an isopropyl group. This isomerization may be accounted for by elongation of the bond between the sulphur atom and the α-carbon atom of the propyl group concomitant with a 1,2-hydride shift in the incipient primary propyl carbenium ion, and with covalent bond formation between the sulphur atom and the original β-carbon of the propyl chain. Methyl radical loss, however, is accompanied by extensive loss of the positional identity of the hydrogen atoms of the propyl chain implying that the isomerization involves an intermediate with a lifetime sufficiently long to allow for this exchange to compete with fragmentation. A simple mechanistic picture which accommodates the main features of the observations is shown in Scheme 1. The key intermediate in this scheme is an ion–neutral

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* The presence of three deuterium atoms in **1c** will obviously cause the probability of forming $CH_3CH_2SH^{+\bullet}$ (*m*/*z* 62) to be lower than the probability of formation of this product ion from **1a**, which contains two deuterium atoms. This statistical effect, however, is not large enough to interfere with the qualitative conclusion reached.

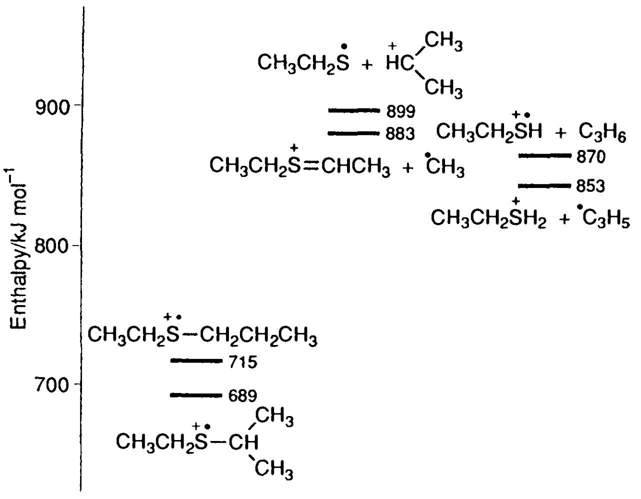
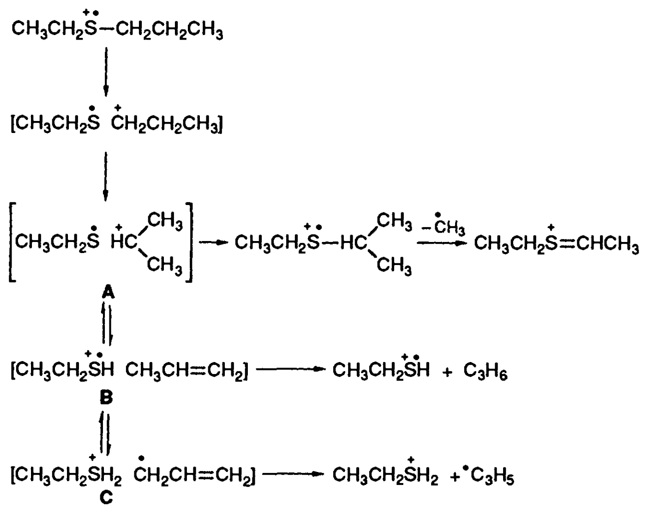


Fig. 1 Enthalpy diagram for the reactions of the metastable radical cation of ethyl propyl thioether (see Appendix).

complex composed of a thioethoxy radical and a secondary propyl carbenium ion formed by heterolytic cleavage of the appropriate sulphur–carbon bond assisted by a 1,2-hydride shift in the incipient ion. The ion–neutral complex can react to form the molecular ion of ethyl isopropyl thioether, which then eliminates a methyl radical by α-cleavage. Proton transfer between the constituents can lead to a complex of the ethanethiol radical cation and propene, which subsequently dissociates or reacts by hydrogen atom transfer prior to elimination of an allyl radical (see Scheme 1).



Scheme 1 Mechanism for the reactions of the metastable radical cation of ethyl propyl thioether.

The thermochemistry associated with the overall reactions of the metastable ions is indicated in Fig. 1 for the formation of the ion structures given in eqns. (1)–(3) (see Appendix).[36–39] Methyl radical loss is estimated to be 13 kJ mol⁻¹ more endothermic than propene loss, which in turn is 17 kJ mol⁻¹ more endothermic than elimination of an allyl radical. Heterolytic cleavage leading to free secondary $\mathrm{C_3H_7}^+$ ions is estimated to be only *ca.* 16 kJ mol⁻¹ more endothermic than methyl radical loss. The former process does not occur on the μs timescale revealing that the ion–neutral complex **A** in Scheme 1 is formed with insufficient internal energy to allow simple dissociation to compete with the other pathways shown in the scheme.

ab initio Calculations indicate that the primary propyl carbenium ion does not correspond to a minimum on the $\mathrm{C_3H_7}^+$ potential energy surface,[40] but undergoes a 1,2-hydride shift without an energy barrier to the secondary ion, which is calculated to be about 80 kJ mol⁻¹ more stable than the primary propyl carbenium ion in agreement with experimental results.[36,41] The formation of an assumed primary carbenium ion by heterolytic cleavage of the appropriate sulphur–carbon bond is thus estimated to be 80 kJ mol⁻¹ more endothermic than formation of a secondary propyl carbenium ion. The heats of formation of the intermediate complexes in Scheme 1 are unknown, but a similar stabilization energy with respect to the separated reactants is anticipated for complex **A** in Scheme 1 and a complex consisting of a thioethoxyl radical and a primary propyl carbenium ion.* This suggests that the difference in the overall endothermicities of the formation of a primary and a secondary propyl carbenium ion is maintained in the relative energies of the possible intermediate complexes. Cleavage of a sulphur–carbon bond into a complex of a thioethoxyl radical and a primary carbenium ion, which subsequently undergoes a 1,2-hydride shift into a secondary carbenium ion, may be expected on these grounds to result in a $[\mathrm{RS}^{\bullet} + (\mathrm{CH_3})_2\mathrm{CH}^+]$ complex with sufficient internal energy to allow simple dissociation into free secondary $\mathrm{C_3H_7}^+$ ions to compete with the other reactions, in contrast to observation. The initial step in the reaction of the metastable ions is viewed, therefore, as a 1,2-hydride-shift-assisted heterolytic cleavage[42] of a sulphur–carbon bond leading directly to the proposed ion–neutral complex, **A**.

An implication of the above reasoning is that reversible 1,2-hydride shifts in the carbenium ion part of the ion–neutral complexes play a minor role in the hydrogen atom exchange associated with the reactions of the metastable ions. The minor loss of $\mathrm{CHD_2}^{\bullet}$ (5%) from the metastable ions of **1b** could be rationalized by a large primary isotope effect on the 1,2-hydride shift in the carbenium ion, but this is difficult to reconcile with the extensive loss of positional integrity of the hydrogen/deuterium atoms before a methyl radical is eliminated from the metastable ions of **1a** and **1c** (see Table 1). In addition to the energetic considerations, the minor extent of $\mathrm{CHD_2}^{\bullet}$ loss from the metastable ions of **1b** and the pronounced difference between the distribution of the abundances of the ions formed by methyl radical loss from the metastable ions of **1a** and **1b** indicate that the hydrogen exchange cannot be fully accounted for by reversible 1,2-hydride shifts in the carbenium ion part of the complex.[46]

The proton affinity of the thioethoxy radical is estimated to be at most 30 kJ mol⁻¹ higher than the value for propene (see Appendix),[36] which may be a sufficiently small difference to allow for interconversion between complexes **A** and **B*** by reversible proton transfer to compete with the propene loss or the subsequent hydrogen atom abstraction leading to complex **C** in Scheme 1.[46] However, complete loss of the positional identity of the hydrogen atoms of the two methyl groups in the secondary propyl carbenium ion in complex **A** does not occur prior to methyl radical loss implying that a certain part of these complexes does not undergo proton transfer to complex **B**, but

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* The stabilization energy of an ion–neutral complex can be crudely approximated by an estimation of the pure long range ion–dipole and ion-induced dipole interactions between the particles (see for example refs. 4 and 8). The ion-neutral complex **A** in Scheme 1 is estimated to 47 kJ mol⁻¹ more stable than the separated reactants assuming a distance of 4 Å (*ca.* the sum of the van der Waals radii of ethanethiol and propene) and with the use of the dipole moment (1.48 D)[43] and polarizability (7.38 Å³)[44] of ethanethiol. The ion–neutral complex **A** is estimated to be 25 kJ mol⁻¹ more stable than the separated components assuming a distance of 4 Å and with the use of the dipole moment (0.36 D)[43] and polarizability (7.02 Å³, calculated from the molar refractivity)[45] of propene.

may react directly to form the molecular ion of ethyl isopropyl thioether.

The occurrence of only partial hydrogen exchange on the μs time-scale is also manifested in the loss of propene or an allyl radical as can be seen from the different distributions of the abundances of the *m/z* 62–65 ions from the metastable ions of **1a** and **1b** (Table 2). The obtained distributions are inconsistent with complete equilibration of the five hydrogen atoms and two deuterium atoms and also with a model which assumes irreversible formation of the secondary propyl carbenium ion followed by equilibration of four hydrogen atoms and two deuterium atoms in the case of the molecular ion of **1a** and five hydrogen atoms and one deuterium atom in the case of the molecular ion of **1b** (see Appendix). A pronounced preference for formation of $CH_3CH_2SHD^+$ ions (*m/z* 64) is observed for the metastable ions of **1b**, which also form fewer $CH_3CH_2SH^{+\bullet}$ ions (*m/z* 62) than the metastable ions of **1a**. These results indicate that the preference for transfer of a hydrogen atom from the β-position noted in the ion-source reactions is maintained to some extent in the loss of propene and an allyl radical from the metastable ions. Although the critical energy for a specific 1,3-hydrogen shift in thioether radical cations is unknown, the present experimental results strongly suggest that such a shift followed by cleavage of the appropriate sulphur–carbon bond leading directly to complex **B** can compete with the reaction pathway shown in Scheme 1.

Conclusions

The metastable ethyl propyl thioether radical cations react by loss of a methyl radical, a propene molecule and an allyl radical. The neutral species eliminated originate entirely from the propyl moiety of the molecular ions and no evidence for the intermediacy of distonic ions is obtained. The reaction of the metastable ions may be described as initial cleavage of the bond between the sulphur atoms and the α-carbon atom of the propyl group assisted by a 1,2-hydride shift in the incipient carbenium ion. This results in an ion–neutral complex of the thioethoxy radical and a secondary propyl carbenium ion (complex **A**), which can react to form the molecular ion of ethyl isopropyl thioether prior to methyl radical loss. Proton transfer between the constituents results in a complex of the ethanethiol radical cation and propene (complex **B**), which dissociates or reacts by hydrogen atom transfer before an allyl radical is expelled. The partial loss of positional identity of the hydrogen atoms of the propyl entity associated with the fragmentation of the metastable ions is ascribed to reversible proton transfer between complexes **A** and **B**, which compete favourably with 1,2-hydride shifts in the carbenium ion part of complex **A** and to some extent with the reactions leading to elimination of a methyl radical, a propene molecule and an allyl radical. This mechanistic scheme advanced for the reactions of the metastable ions is incomplete as manifested in a certain preference for transfer of a β-hydrogen atom from the propyl group to the sulphur atom in the loss of propene and an allyl radical. The results illustrate that many mechanistic details of the fragmentations of apparently simple radical cations in the gas phase are yet to be resolved and understood.

Experimental

The Electron Impact (EI), the Mass Analyzed Ion Kinetic Energy (MIKE)[31] and Collision Induced Dissociation (CID)[32] mass spectra were recorded with the use of a VG ZAB-2HFqQ reverse geometry double focussing quadrupole hybrid mass spectrometer. The ethyl propyl thioether and the isotopomers were introduced into the ion-source through a septum inlet heated to 150 °C. The ion-source conditions were: acceleration voltage 8 kV, electron energy 70 eV, repeller voltage 0 V, ion-source temperature 180 °C. The CID spectra were recorded with a 10% reduction in the main ion beam and with He as the collision gas. Ethyl propyl thioether was prepared by a reaction between CH_3CH_2SNa and propyl bromide.[47] The isotopomers **1a–c** and **1f** (see Tables) were prepared from the appropriately labelled propyl bromide compounds. The $CH_3CH_2{}^{13}CH_2Br$ compound was synthesized by a Grignard reaction between CH_3CH_2MgI and $^{13}CO_2$, subsequent reduction of the acid to the alcohol with $LiAlH_4$ and conversion of the alcohol to the bromide.[47] The labelled isotopomers **1d** and **1e** were prepared by reaction between $CH_3CH_2CH_2SNa$ and a suitably labelled ethyl bromide. The thioethers were purified by preparative gas chromatography prior to use (column: SE 30; temperature: 70 °C) and their identity was confirmed by NMR and mass spectrometry. The compounds **1a–e** were more than 98% isotopically pure as determined by mass spectrometry. The sample of **1f** contained 7% unlabelled ethyl propyl thioether.

Appendix

Thermochemistry.—Most of the ΔH_f° data and the bond dissociation energies (E_D) were taken or estimated from data in refs. 36 and 37. The heat of formation of the $CH_3CH_2S^\bullet$ radical is estimated to be 100 kJ mol^{-1} on the basis of an E_D of 364 kJ mol^{-1} of the S–H bond in ethanethiol taken from ref. 37. The proton affinity of $CH_3CH_2S^\bullet$ is estimated to be 784 kJ mol^{-1} from data in ref. 36. Considerable uncertainty exists as to the heats of formation of sulphonium ions in the gas phase. The heat of formation of the ion $CH_3CH_2\overset{+}{S}{=}CHCH_3$ is estimated to be about 737 kJ mol^{-1} with the use of $\Delta H_f^\circ(CH_3\overset{+}{S}{=}CH_2)$ = 812 kJ mol^{-1} taken from ref. 36 as the anchor point. The estimation is based upon the assumption that the difference between the heats of formation of $CH_3\overset{+}{S}{=}CH_2$ and $CH_3\overset{+}{S}{=}CHCH_3$ is the same as the difference in heats of formation between $CH_3CH_2\overset{+}{S}{=}CH_2$ and $CH_3CH_2\overset{+}{S}{=}CHCH_3$. The heats of formation of the three former sulphonium ions are given in refs. 38 and 39 as: $\Delta H_f^\circ(CH_3\overset{+}{S}{=}CH_2)$ = 828 kJ mol^{-1}, $\Delta H_f^\circ(CH_3\overset{+}{S}{=}CHCH_3)$ = 778 kJ mol^{-1} and $\Delta H_f^\circ(CH_3CH_2\overset{+}{S}{=}CH_2)$ = 803 kJ mol^{-1}. The lower value for $\Delta H_f^\circ(CH_3\overset{+}{S}{=}CH_2)$ of 812 kJ mol^{-1} was used as the reference point, since the higher value results in a similar ΔH_f° for the loss of a methyl radical and the formation of secondary $C_3H_7{}^+$ ions from the molecular ion of ethyl propyl thioether, a reaction which is not observed. Furthermore, the values in refs. 38 and 39 are based upon appearance energy measurements and are likely to represent upper limits to the true values.

Randomization of the Isotopic Labels.—The ratio between the abundances of the *m/z* 62 and 63 ions formed in the 2nd FFR is 1:3 (see Results and Table 2). This ratio between loss of propene and an allyl radical, respectively, is assumed to be maintained for the isotopomers of the ethyl propyl thioether molecular ion. Complete equilibration of the five hydrogen atoms and the two deuterium atoms of the propyl group in the molecular ions of **1a** and **1b** is calculated to result in a distribution of the abundances of the *m/z* 62–65 ions of 17:43:36:4, respectively, on the basis of the 1:3 ratio between propene and allyl radical loss and with the implicit assumption that no isotope effect accompanies the reactions. The distribution of abundances of the *m/z* 62–65 ions is calculated to be 17:38:40:5 for the molecular ion of **1a** on the basis of a model which assumes the 1,2-hydrogen shift leading to the complex of the thioethoxy radical and a secondary carbenium ion (see Scheme 1) to be irreversible and that complete equilibration of the four hydrogen atoms and the two deuterium atoms at the methyl groups of the carbenium ion occurs before propene or an allyl radical is eliminated. With the same model the distribution of the abundances of the m/z 62–65 ions is calculated to be 20:55:25:0 for the molecular ion of **1b**.

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