An Attempt to Detect Thiirenium Ions in the Gas Phase

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$C_nH_{2n-1}S^+$ ions (*n* 3—5, 7, 11) were generated in the gas phase from several $CH_3SCR^1{=}CR^2X$ precursors (R^1,R^2 = H, alkyl; X = Cl, Br) *via* electron-impact-induced X$^•$ loss. Their reactions, unimolecular and collision induced, were studied by ion kinetic energy spectrometry. The major fragmentations are identified and the thermochemistry considered. Of particular interest were unimolecular alkene elimination reactions, observed for n = 3—5, which lead to product ions of composition $R^1(R^2)CS^+$. $C_4H_7S^+$ ions undergo elimination of C_2H_4 and C_3H_6 to give $C_2H_3S^+$ and HCS^+, respectively. Metastable peak shape analysis, analysis of model ions, and deuterium labelling experiments show that the two reactions occur *via* two different mechanisms. A general scheme is proposed for unimolecular decomposition of $C_nH_{2n-1}S^+$ ions. Thiirenium ions could not be detected nor need be invoked as intermediates in the extensive rearrangements that precede some of the major reactions.

Organosulphur chemistry plays a fundamental role in biological systems as well as in synthetic applications. Interest has now extended to the energetics, structures, and reactivities of organosulphur ions in the gas phase. Thus, species known in solution, such as thiiranium ions, have been identified and studied in the gas phase by means of various techniques.[1–3] On the other hand, gas-phase studies have led to the characterization of ions which have so far eluded detection in solution, such as thioacylium ions.[4]

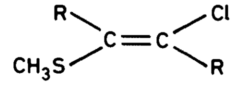
Thiirenium ions are interesting species which have been fully characterized in solution, in the solid state as stable salts, and in theoretical investigations.[5] In solution thiirenium ions form during addition reactions of sulphenyl derivatives to alkynes and solvolysis of, *e.g.*, β-thiovinyl sulphonates.[5]

We report in this paper the results of an investigation carried out with the purpose of characterizing various $C_nH_{2n-1}S^+$ ions in the gas phase through the study of their reactivity. Particular attention was given to the possibility of observing thiirenium species. Criteria used to this end are based on experiments involving analysis of the energy released in the fragmentation of the precursor molecular ions $M^{+•}$ to $[M - \text{Hal}]^+$ species, and analysis of the unimolecular as well as collision-induced decompositions of the latter ions.[6]

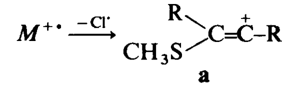
Results and Discussion

Thiirenium ions can conceivably form in the gas phase from ionized β-methylthiovinyl halides *via* loss of halogen radical. This process can be formally viewed as the gas-phase version of an ionization step in solution, in which an ionized substrate and a radical leaving group are involved. We have therefore explored the possibility of generating thiirenium ions *via* this route.

Analysis of $M^{+•}$ *Ions.*—Under electron impact (e.i.) conditions (70 eV) compounds (**1**)—(**4**) lose Cl$^•$, this process being most favourable for (**1**) and (**4**).[7] Exactly the same trend is observed for unimolecular Cl$^•$ loss occurring in the second field-free region of the mass spectrometer. The MIKE spectra of the molecular ions of (**1**) and (**4**) consist almost exclusively of the peak due to $[M - \text{Cl}]^+$ species, whereas loss of $CH_3^•$ predominates over loss of Cl$^•$ for $[(\mathbf{2})]^{+•}$ and, particularly, for $[(\mathbf{3})]^{+•}$. In all cases fragmentation of the C–Cl bond leads to narrow gaussian metastable peaks. The corresponding average kinetic energy release data, estimated as $T_{0.5}$/kJ mol^{-1} from the width of the peak at half-height, are 4.1 (**1**), 3.5 (**2**), 4.1 (**3**), and 2.8 (**4**). These are modest amounts of energy. Simple cleavage of the C–Cl bond in ionized (**1**)—(**4**) should lead to vinyl cations **a** [equation (1)] and have *ca.* 0 reverse activation energy.



(**1**) R = H
(**2**) R = CH$_3$
(**3**) R = CH$_2$CH$_3$
(**4**) R = C(CH$_3$)$_3$

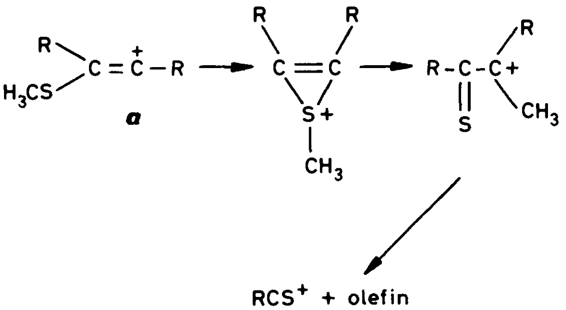


$$M^{+•} \xrightarrow{-\text{Cl}^•} \text{R}(\text{CH}_3\text{S})\text{C}{=}\overset{+}{\text{C}}\text{–R} \qquad (1)$$

a

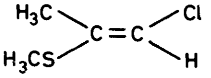
Stabilization of the incipient carbocation could be achieved through anchimeric participation by sulphur. The product of fragmentation would be, in this case, the thiirenium ion, a species more stable than the corresponding vinyl cation **a** by 88—99 kJ mol^{-1}.[5] Part of this isomerization energy would be available at the transition state and, to some extent, could be released as kinetic energy of the products,[8,9] It is estimated that, for activation complexes of three-membered-ring geometry, between 60 and 100% of the reverse activation energy would normally be released as kinetic energy of the fragments.[10] According to these estimates, bridging by sulphur in the present case should release 50 kJ mol^{-1} or more, far above the observed $T_{0.5}$ values. Thus, metastable peak analysis fails to reveal the occurrence of significant molecular reorganization during fragmentation of the molecular ions of compounds (**1**)—(**4**) *via* Cl$^•$ loss.

Analysis of $[C_nH_{2n-1}S]^+$ *Ions.—Unimolecular fragmentation reactions.* The MIKE spectra are reported in the Experimental section. The type of substituent R determines the mode of unimolecular fragmentation of ions **a** from precursors (**1**)—(**4**). Thus, for (**3**) and (**4**) loss of CH$_4$S is the dominant process, whereas for (**1**) and (**2**) loss of C_mH_{2m} (*m* 2 and 3, respectively) occurs predominantly [exclusively for (**1**)], and leads to ions with composition RCS^+. Metastable $C_5H_9S^+$ ions also undergo loss of C_3H_4, H_2S, and CH_2S. For the olefin-elimination reaction of $C_3H_5S^+$ and $C_5H_9S^+$ ions, it is noteworthy that only HCS^+ (and no $C_2H_3S^+$) forms for (**1**) and only $C_2H_3S^+$ (and no HCS^+) for (**2**). This suggests that one of the R groups originally on the C–C double bond becomes part of the product RCS^+. An attractive route to arrive at RCS^+ from **a** involves the intermediacy of thiirenium ions as in Scheme 1. A 1,2-methyl shift from S to C and ring opening lead to an α-thiocarbonyl cation which fragments to RCS^+ and olefin. This mechanism would account for the fact that ions **a** from precursors (**1**) and (**2**) lead only to HCS^+ and CH_3CS^+, respectively, and predicts that a thiirenium ion bearing two different R substituents on the ring will produce two different RCS^+ species.



Scheme 1.

To test for this mechanism we have analysed $C_4H_7S^+$ ions generated from precursors (**5**)—(**7**) *via* e.i.-induced halogen loss. Compound (**8**), the deuterium-labelled analogue of (**5**), was also studied, and so were the isomeric C_4H_8S sulphides (**9**)—(**13**), chosen as structural models. Compounds (**9**)—(**13**) form $C_4H_7S^+$ ions *via* e.i.-induced hydrogen loss.



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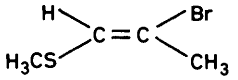

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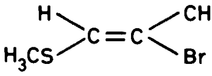

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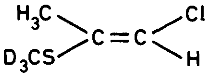

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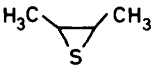

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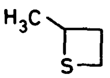

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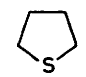


(11)

$H_3CSCH=CHCH_3$

(12)

$H_3CSCH_2CH=CH_2$

(13)

The MIKE spectra of $C_4H_7S^+$ ions are reported in Table 1, that of the $C_4H_4D_3S^+$ ion in Table 2. The data show that (1) all $C_4H_7S^+$ ions examined fragment according to a common pattern which comprises losses of H˙, H_2, C_2H_4, H_2S, and C_3H_6. In addition to these processes, $C_4H_7S^+$ ions generated from methyl prop-1-enyl sulphide (**12**) and allyl methyl sulphide (**13**) undergo loss of CH_3˙ and of CH_3˙ and CH_4, respectively. (2) The spectra of ions **a** from (**5**)—(**7**) are very similar in their peak relative intensities. They differ from all other spectra by a conspicuously abundant fragment at *m/z* 45 (HCS^+). The spectra of $C_4H_7S^+$ ions from (**9**) and (**10**) are also similar. (3) The ion $C_4H_4D_3S^+$ from (**8**) fragments according to the general pattern of ions **a** from (**5**)—(**7**) and for each process leads to product ions of all possible isotopic compositions. The isotopic distributions within each family of ions formed in olefin-elimination reactions, *i.e.* CXS^+ and $C_2X_3S^+$ (X = H,D), is very close to that calculated for complete randomization of the label within the fragmenting species. By contrast, some specificity is retained in processes involving elimination of X_2 and X_2S (X = H,D). Thus, more H is lost in the neutral than is predicted for complete randomization of the label.

According to the mechanism in Scheme 1 ions **a** from (**5**)—(**7**) must give HCS^+ and CH_3CS^+ in constant relative abundances irrespective of the original precursor. The experimental results conform to these expectations, since both $C_2H_3S^+$ and HCS^+ are produced from ions **a** from (**5**)—(**7**) in nearly constant ratio, namely 1:3—4.

Table 1. Relative abundances of ions formed in unimolecular reactions of $C_4H_7S^+$ ions (*m/z* 87)[a,b]

	m/z						
	86	85	72	71	59	53	45
M	(H˙)	(H_2)	(CH_3˙)	(CH_4)	(C_2H_4)	(H_2S)	(C_3H_6)
(**5**)	14	32			6	32	17
(**6**)	10	30			7	27	26
(**7**)	10	37			6	24	23
(**9**)	13	41			9	34	2
(**10**)	13	55			6	25	2
(**11**)	8	83			2	5	1
(**12**)	14	51	2		6	18	9
(**13**)	1	38	19	5	6	26	5

[a] Peak heights have been normalized to a sum = 100. [b] Neutral fragments lost are shown in parentheses.

Table 2. Products of unimolecular decomposition of the ion $C_4H_4D_3S^+$ (*m/z* 90) from precursor (**8**)

m/z	Abundance[a]		Composition[b]		Isotopic distribution[c]
89	5.7	10	$C_4X_6S^{+\cdot}$	$C_4H_3D_3S^{+\cdot}$	*d* (1.0)
	4.3[d]			$C_4H_4D_2S^{+\cdot}$	*d* (0.75)
88	20.6				
	16.3	34.5	$C_4X_5S^+$	$C_4H_2D_3S^+$	9.1 (1.8)
87	16.4			$C_4H_3D_2S^+$	9.1 (2.7)
86	1.8			$C_4H_4DS^+$	1.0 (1.0)
62	0.7[e]	8	$C_2X_3S^+$	$C_2D_3S^+$	0.2 (0.4)
61	2.5[e]			$C_2HD_2S^+$	1.6 (1.6)
60	3.6[e]			$C_2H_2DS^+$	2.1 (2.2)
59	1.4[e]			$C_2H_3S^+$	1.0 (1.0)
56	12.1	30	$C_4X_5{}^+$	$C_4H_2D_3{}^+$	4.8 (1.8)
55	15.7			$C_4H_3D_2{}^+$	6.3 (2.7)
54	2.5			$C_4H_4D^+$	1.0 (1.0)
46	6.4	16	CXS^+	CDS^+	0.7 (0.8)
45	9.3			CHS^+	1.0 (1.0)

[a] See footnote *a* of Table 1. [b] X = H,D. [c] Within each family of ions. Calculated values for complete statistical distribution of the label within the fragmenting species are given in parentheses. [d] Calculated assuming equal probability for H˙ and D˙ loss. [e] From deconvolution of complex signal.

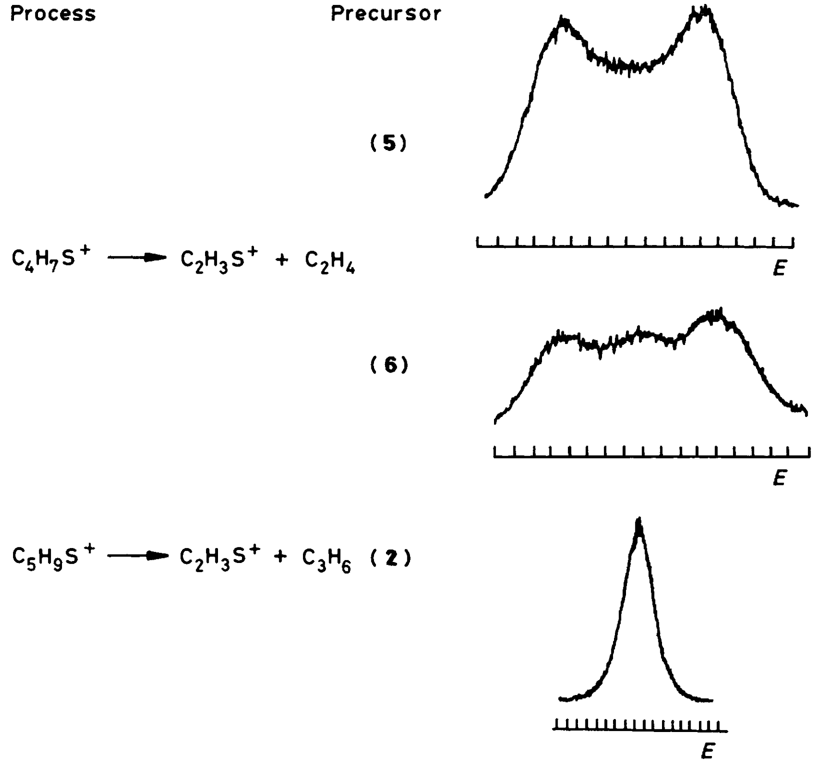
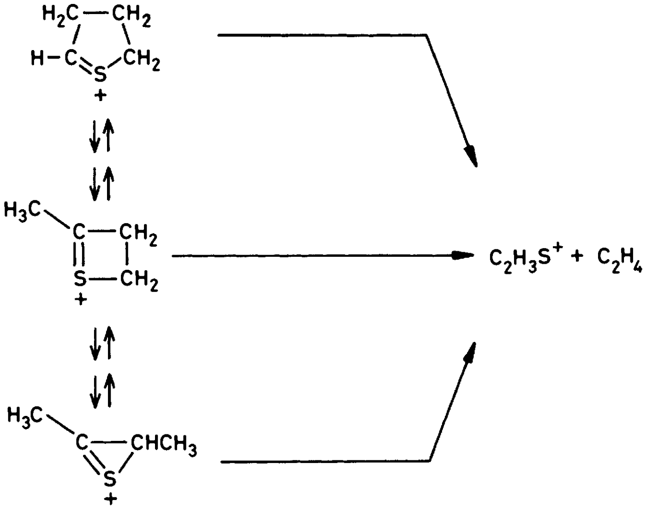


Figure. Peaks observed in the MIKE spectra for the processes indicated

The mechanism in Scheme 1, however, is not compatible with other observations based mainly on peak shape analysis. Elimination of C_2H_4 from all $C_4H_7S^+$ ions examined occurs with a large, specific release of kinetic energy and gives rise to diffuse dish-topped peaks ($T_{0.5}$ *ca.* 38 kJ mol^{-1}).* Contrary to ethylene loss, elimination of C_3H_6 from $C_4H_7S^+$ and $C_5H_9S^+$ ions gives rise to narrow gaussian peaks ($T_{0.5}$ < 4.2 kJ mol^{-1}). A narrow peak and a small release of kinetic energy ($T_{0.5}$ < 4.2 kJ mol^{-1}) is also observed for the elimination of C_2H_4 from $C_3H_5S^+$ [from (**1**)]. Representative peaks for alkene loss from $C_nH_{2n-1}S^+$ ions are shown in the Figure.

Metastable peak analysis provides useful insights into the mechanisms of unimolecular olefin elimination from $C_nH_{2n-1}S^+$ ions from precursors (**1**), (**2**), and (**5**)—(**7**). It is to be noted that loss of C_2H_4 from $C_4H_7S^+$ presents common and very characteristic features for all the different precursors examined. The similarity of peak shapes and corresponding $T_{0.5}$ magnitudes suggests that all these species fragment *via* a common reaction mechanism. The large amount of energy released is typical of processes with large energy barriers for the reverse reaction, in this case the addition of $C_2H_3S^+$ to C_2H_4. By contrast, loss of C_3H_6 does not appear to have significant activation energy for the reverse reaction, the addition of HCS^+ to C_3H_6. This suggests that HCS^+ and $C_2H_3S^+$ are formed according to two different routes in contrast with the mechanism in Scheme 1. Indeed, according to this mechanism, C_2H_4 elimination should occur *via* a simple bond-cleavage step, as shown in equation (2). A large release of kinetic energy can result from simple bond cleavage provided the process is an exothermic one. This was shown to be the case for the ethylene elimination reaction of some iminium ions.[11] The fragmentation step of equation (2), however, is not estimated to be exothermic on the basis of available data.† Thus, elimination of C_2H_4 from $C_4H_7S^+$ ions presumably does not occur *via* the path of equation (2) and the mechanism of Scheme 1 is invalidated.



Scheme 2.

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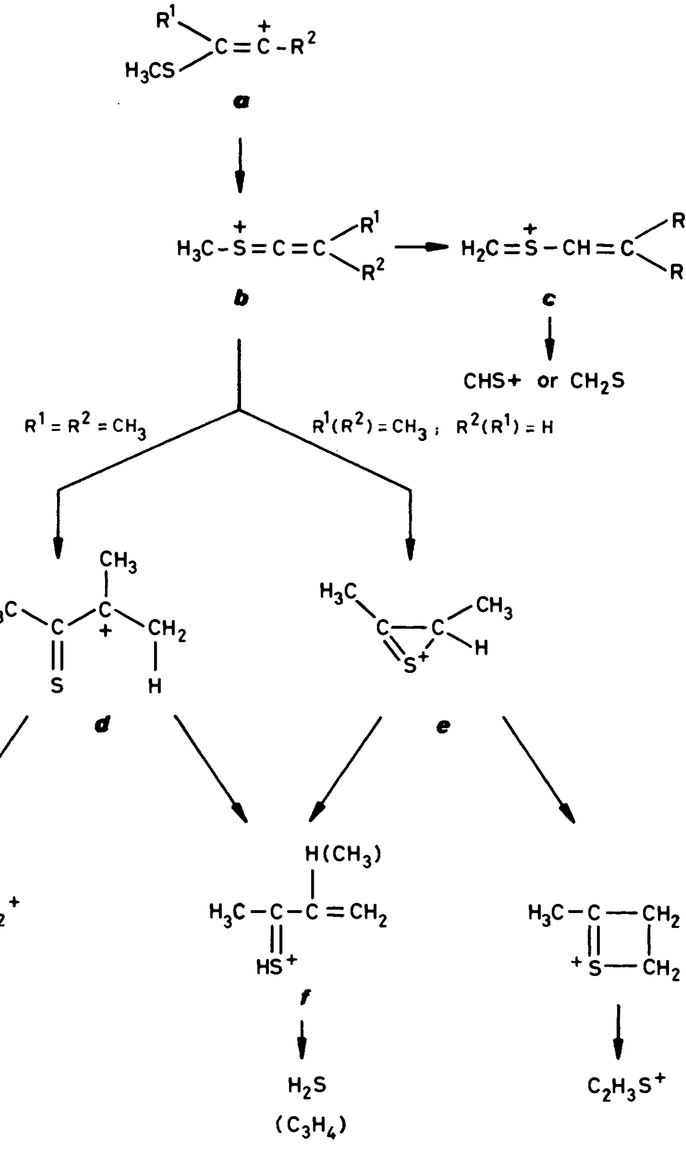
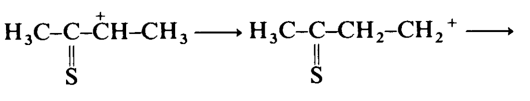
* A composite metastable peak is observed for ethylene elimination from $C_4H_7S^+$ ions from precursors (**6**) and (**7**). A very minor narrow component is superimposed on the large diffuse peak common to all other spectra. The former is likely due to the reaction of a distinct decomposing structure.

† $\Delta H_{(2)} = \Delta H_f(C_2H_4) + \Delta H_f(CH_3CS^+) - \Delta H_f$(reactant ion) = 52.3 (ref. 12*a*) + 878.6 (ref. 4) − $\Delta H_f(CH_3CSCH_2CH_2^+)$. For the reaction to be exothermic, the heat of formation of the fragmenting ion, not known, should be >931 kJ mol^{-1}. This seems an unlikely high value, considered, for example that the heat of formation of the unsubstituted ethyl cation is 903.7 kJ mol^{-1} [12b] and that the CH_3CS group should not be strongly electron withdrawing.



Scheme 3.



$$\mathrm{H_3C{-}\underset{\underset{S}{\|}}{C}{-}\overset{+}{C}H{-}CH_3 \longrightarrow H_3C{-}\underset{\underset{S}{\|}}{C}{-}CH_2{-}CH_2^+ \longrightarrow CH_3CS^+ + C_2H_4} \quad (2)$$

The origin of the large release of kinetic energy and the diffuse shape of the peak for the C_2H_4 elimination from $C_4H_7S^+$ ions probably resides in a tight transition state.[10] The most reasonable possibility is that of a concerted 1,2 (and/or 1,3) elimination from a cyclic structure as shown in Scheme 2. Such processes can be viewed as symmetry-forbidden concerted eliminations and as such are expected to occur with release of significant amounts of kinetic energy.[13] Kinetic energy release has indeed been used in this respect as a mechanistic probe for a number of H_2-elimination reactions.[14,15] We note that unimolecular elimination of H_2 from all $C_4H_7S^+$ ions examined in this study also occurs with large specific release of kinetic energy ($T_{0.5}$ *ca.* 84 kJ mol^{-1}) and thus probably falls into the same category of symmetry-forbidden reactions.

A general mechanism for the unimolecular decomposition of $C_nH_{2n-1}S^+$ions **a** from precursors (**1**), (**2**), and (**5**)—(**7**) is proposed in Scheme 3. The original vinyl cation **a** undergoes 1,2-hydride or -methyl shift to (**b**), the key intermediate in the Scheme. Ions **a** from (**5**)—(**7**) all lead to the unique species **b** with $R^1(R^2) = H$ and $R^2(R^1) = CH_3$. Species **b** can undergo 1,3-H shift to **c** which in turn can react along either of the paths shown in equation (3). Path (b), a simple cleavage step, is observed in the case *n* 5 [precursor (**2**)]. Path (a), which involves 1,3-H shift and elimination of an alkene neutral, prevails in the cases *n* 3 [(**1**)] and 4 [(**5**)—(**7**)]. From available heat of formation data* one can calculate the difference in enthalpies for each pair of reactions (**3a** and **b**), namely ΔH(3a) $-$ ΔH(3b). These are +172, +40, and -5 kJ mol^{-1}, respectively for *n* 3—5. Interestingly, in all cases the thermochemically preferred process is the one that actually takes place.

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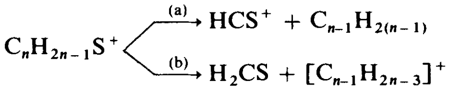
* ΔH_f/kJ mol^{-1} of neutral products are: 90.0 (CH_2S),[16] 51.9 (C_2H_4),[12a] 20.5 (C_3H_6, propene),[12a] and -18.0 (C_4H_8, 2-methylpropene).[12a] ΔH_f of ions are: 975 (HCS^+),[17] 1 109 ($C_2H_3^+$),[18] 946 ($C_3H_5^+$, allyl),[19] and 862 ($C_4H_7^+$, 1-methylallyl).[19]

Table 3. CA spectra of $C_4H_7S^+$ ions (m/z 87) from several precursors M^a

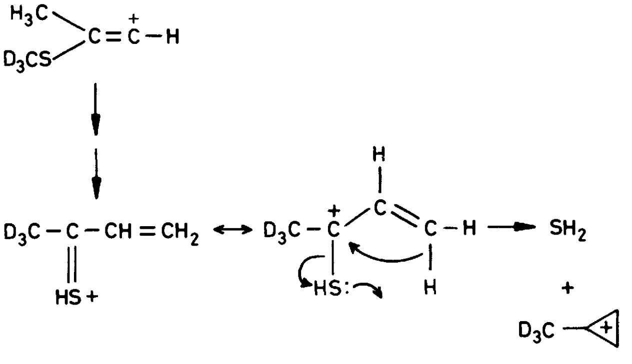
M	86	85	72	71	70	69	68	61	59	58	57	53	51	50	48	47	46	45	41	39	38	37	32	27	26
(5)	(4.6)	(51.7)	6.7	14.8	1.9	4.9	0.0	1.0	(16.7)	8.1	4.3	(27.2)	1.9	1.4	1.0	11.5	9.6	(49.3)	7.7	13.4	3.8	1.9	1.0	3.8	1.4
(6)	(5.4)	(11.3)	9.0	21.4	4.2	9.0	0.0	0.8	(4.2)	1.8	1.6	(13.0)	0.6	0.4	8.5	12.1	5.1	(42.3)	2.5	12.7	4.8	2.8	0.6	1.3	0.7
(7)	(6.1)	(13.4)	8.6	20.1	3.8	8.6	0.0	1.0	(4.8)	2.3	1.7	(12.0)	0.9	0.6	9.2	12.4	4.6	(41.1)	2.5	13.4	5.2	2.9	0.6	1.2	0.6
(9)	(25.5)	(131.9)	1.7	10.2	0.9	3.4	3.4	0.9	(26.0)	11.1	5.1	(95.7)	4.7	4.3	0.0	14.0	0.0	(59.6)	4.7	11.9	4.3	2.6	1.7	11.9	3.4
(10)	(15.5)	(69.4)	1.6	7.3	1.3	2.2	1.3	0.6	(22.7)	14.2	6.3	(34.7)	3.2	3.2	0.0	11.7	6.0	(59.9)	7.3	12.6	4.4	2.8	1.3	9.8	3.2
(11)	(26.9)	(116.6)	0.9	3.1	0.0	2.2	0.0	0.9	(31.4)	21.5	6.7	(31.4)	2.8	2.7	0.0	9.0	5.4	(58.3)	6.7	13.0	4.0	2.6	1.3	12.6	4.5
(13)	(0.5)	(143.2)	(24.3)	(23.0)	2.0	7.7	0.0	2.3	(30.7)	6.4	2.6	(72.9)	0.9	1.0	0.0	15.3	5.1	(87.0)	7.7	26.9	7.6	3.8	0.8	7.6	2.0

[a] Abundances have been normalized to a sum = 100, excluding those peaks due to low-energy processes as revealed by MIKE spectra.



$$C_nH_{2n-1}S^+ \begin{cases} \xrightarrow{(a)} HCS^+ + C_{n-1}H_{2(n-1)} \\ \xrightarrow{(b)} H_2CS + [C_{n-1}H_{2n-3}]^+ \end{cases} \qquad (3)$$

A 1,2-methyl shift from C to S leads from **b** to **d** in the case of $C_5H_9S^+$ ions ($R^1 = R^2 = CH_3$) and to **e** in the case of $C_4H_7S^+$ ions [$R^1(R^2) = H$, $R^2(R^1) = CH_3$]. Species **d** and **e** are responsible for loss of C_3H_6 and C_2H_4, respectively, according to the two different routes shown in Scheme 3. These involve a 1,2-H shift and fragmentation for the former and, as discussed earlier, concerted elimination for the latter. Species **d** and **e** also undergo loss of H_2S and, for **d**, of C_3H_4 *via* structure **f**. Elimination of H_2S from **f** most likely involves a five-membered transition state as shown in Scheme 4 for the deuteriated ion **a** from (**8**). This mechanism, which accounts for the deuterium-labelling results, has been proposed for the elimination of H_2S from $C_3H_7S^+$ ions.[20]



Scheme 4.

Interestingly, the behaviour of ions **a**, with a methylthio substituent, differs markedly from that of analogous species of composition $C_8H_7S^+$ with a phenylthio group. The latter species undergo rearrangement to the $PhCH_2CS^+$ thioacylium ion, which eliminates CS in the only unimolecular process observed.[8]

Collisional Activation (*CA*) *Experiments*.—The CA spectra of $C_4H_7S^+$ ions from precursors (**5**)—(**7**), (**9**)—(**11**), and (**13**) are reported in Table 3. Ions from (**6**) and (**7**) produce spectra which are equal within experimental error. They differ significantly, however, from that given by (**5**) (compare abundances at m/z 69—72, 58, 48, and 47). Thus, contrary to MIKE analysis, CA spectroscopy, which samples a wider population of ions, mainly long-lived ones (lifetime $>10^{-5}$ s), reveals structural differentiation still existing in $C_4H_7S^+$ ions of lower internal energies. The $C_4H_7S^+$ species from precursors (**5**)—(**7**), moreover, appear to be distinct, insofar as their CA spectra are concerned, from all other species examined.

Conclusions.—$C_nH_{2n-1}S^+$ ions, formed *via* e.i.-induced halide loss from β-methylthiovinyl halides, undergo different unimolecular reactions depending on the value of n. Of particular interest are olefin-elimination reactions which take place when n 3—5. $C_4H_7S^+$ ions undergo elimination of C_2H_4 and C_3H_6 according to two different mechanisms. Loss of C_2H_4 probably occurs from a cyclic structure *via* a concerted 1,2- or 1,3-elimination step.

No evidence was found that these cations assume a thiirenium structure under the conditions employed in this study. Ionic species which should lead to the same thiirenium ion produce different CA spectra. While their MIKE spectra are the same, the intermediacy of a thiirenium species along the fragmentation pathways is not implied by this result.

Experimental

Materials.—Compounds (**1**)—(**8**) were prepared and purified as previously described.[7] Commercial samples of tetrahydrothiophene (**11**) and allyl methyl sulphide (**13**) were distilled before use. 2,3-Dimethylthiirane (**9**),[21] 2-methylthietane (**10**),[22] and methyl prop-1-enyl sulphide (**12**)[23] were prepared and purified according to published procedures.

Mass Spectrometric Determinations.—All measurements were performed on a VG ZAB-2F instrument, operated in the e.i. mode (70 eV, 200 μA) and a source temperature of 200 °C. Samples were introduced *via* a septum inlet, heated at 150 °C. CA spectra were obtained by collisions of 8 kV ions with air in the second field-free region. The pressure in the collision cell was such as to reduce the main beam intensity to 60% of its usual value. Kinetic energy release data, $T_{0.5}$, were calculated from peak width at half height according to standard formulae.[24]

The MIKE spectra of $[M - Cl]^+$ ions from compounds (**1**)—(**4**) are (neutral lost, relative abundance %): (**1**): C_2H_4, 100. (**2**): H_2S, 26; CH_2S, 8; C_3H_4, 11; C_2H_4, 55. (**3**): CH_2S, 11; CH_4S, 89. (**4**): $CH_3^\bullet$, 3; $CH_3S^\bullet$, 5; CH_4S, 92.

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Received 18*th February* 1986; *Paper* 6/347