Isomerization of $(C_2H_4S)^{+\cdot}$ Ions; Thioacetaldehyde as the Only Species Fragmenting by Hydrogen Atom Loss

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Summary The molecular ions of MeCHS and $CH_2{=}CHSH$ interconvert, possibly *via* a ring opened ethylene sulphide-type intermediate; it is however only the MeCHS radical cation which fragments by hydrogen atom loss in the microsecond time-scale.

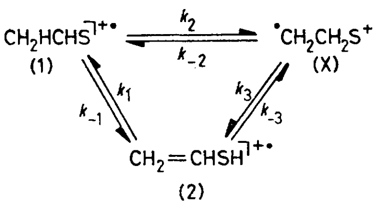
RECENTLY it was demonstrated that radical cations of MeCHS (**1**) and $CH_2{=}CHSH$ (**2**) having lifetimes of *ca.* 10^{-3} s (ion cyclotron resonance conditions) do not appreciably interconvert.[1] Here we present results on $(C_2H_4S)^{+\cdot}$ species, which decompose by H· atom loss in the microsecond time frame.

In the isoelectronic series $(C_2H_4X)^{+\cdot}$ (X = CH_2, NH, or O), decomposing C_3H_6 radical cations (lifetimes *ca.* 10^{-6} s) are structurally indistinguishable,[2] although structural integrity is retained for non-decomposing ions of low internal energy.[3] In contrast, decomposing C_2H_5N and C_2H_4O radical cations retain their structural identities. Four $(C_2H_5N)^{+\cdot}$ species have been identified[4] while $(C_2H_4O)^{+\cdot}$ ion structures have been thoroughly characterised (MeCHO, $CH_2{=}CHOH$, and $\overline{CH_2CH_2O}$).[5]

Metastable peak characteristics for hydrogen atom loss were used as a probe for the $(C_2H_4S)^{+\cdot}$ ions (m/e 60 → m/e 59 + H·). Radical cations of the MeCHS structure and of the $CH_2{=}CHSH$ structure were generated unambiguously from the molecular ions of *trans*-2,4,6-trimethyl-1,3,5-trithian,[6]† and cyclobutanethiol,[1] respectively. The metastable peak shapes for (**1**) and (**2**) were closely similar; $T_{0\cdot5}$ values were 133 ± 3 and 127 ± 4 meV, respectively. Therefore the hydrogen atom loss must be preceded by the isomerization of (**1**) to (**2**) (or *vice versa*), or isomerization of (**1**) and (**2**) can lead to a common fragmenting ion. Tomer and Djerassi[1] found that non-decomposing $(C_2H_4S)^{+\cdot}$ ions, generated from the molecular ion of n-pentyl vinyl sulphide, consisted of a 1 : 1 mixture of (**1**) and (**2**). We found the metastable characteristics for this compound to be identical with those of (**1**) ($T_{0\cdot5}$ = 134 ± 7 meV). In addition, the molecular ion of ethylene sulphide (generated by direct ionization thereof) yielded a closely similar metastable peak ($T_{0\cdot5}$ = 152 ± 3 meV) as indeed did further $(C_2H_4S)^{+\cdot}$ ions generated from thiophen, thioglycol, propane-2-thiol, and ethyl methyl sulphide, ($T_{0\cdot5}$ values 128 ± 4, 132 ± 6, 126 ± 6, and 126 ± 6 meV, respectively). Thus all $(C_2H_4S)^{+\cdot}$ ions

† Pyrolysis of this compound in the gas-phase yields monomeric MeCHS (H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Letters*, 1974, **29**, 265).

decompose over the same potential surface regardless of their initial structure. It now remains to show that MeCHS is the decomposing species.



The hydrogen *vs.* deuterium atom loss from the radical cations of the thioaldehydes CH_3CDS (**3**) and CD_3CHS (**4**) (see Table) shows that (i) the hydrogen atom of position 1 is lost predominantly (if not exclusively), (ii) the significant positional exchange of hydrogen–deuterium requires a third ion structure (**X**) [a reversible 1,3-hydrogen shift isomerization between (**1**) and (**2**) would not afford loss of positional identity], and (iii) the exchange process involves a deuterium isotope effect.[8] The almost exclusive loss of hydrogen from the radical cation of $CH_2{=}CHSD$ (**5**) shows that the thiol hydrogen (deuterium) atom is retained (compare the oxy-analogue[5]), and consequently (**5**) must have isomerized to $(CH_2DCHS)^{+\cdot}$. The deuterium atom loss from the radical cation of $CH_2{=}CDSH$ (**6**) is however only *ca.* one quarter of that expected assuming complete isomerization (1,3-hydrogen shift) to (**3**). This further illustrates the need for the isomerization route to proceed *via* (**X**). We suggest that (**X**) is the ring opened form of the ethylene sulphide molecular ion.

The relative rates of the various isomerization steps can be qualitatively assessed from the observed metastable peak abundances. The hydrogen–deuterium atom losses from (**3**) and (**4**) indicate a slow rate for (**1**) → (**X**) (k_2), but a fast reverse step (k_{-2}). The data from (**5**) and (**7**) indicate that the interconversions of (**1**) and (**2**) are fast (k_1 and k_{-1}). Route (**2**) → (**X**) → (**1**) must be faster than route (**1**) → (**X**) → (**2**), otherwise a more significant loss of deuterium would have been expected from (**6**) and (**7**).

TABLE

Kinetic energy releases (T) in meV and relative abundances of first field-free region metastable peaks[a] for hydrogen–deuterium loss from $(C_2H_{4-x}D_xS)^{+\cdot}$ ($x = 1$—3) ions.

Generated ion	$T_{0\cdot5}$ (H)[b]	$T_{0\cdot5}$ (D)[b]
CH_3CDS[c] (**3**)	159 ± 4 (1·0)	151 ± 3[d] (4·3)[e]
CD_3CHS[f] (**4**)	133 ± 3 (25)	145 ± 8 (1·0)
$CH_2{=}CHSD$[g] (**5**)	125 ± 2 (60)	149 ± 4 (1·0)
$CH_2{=}CDSH$[g] (**6**)	132 ± 7 (1·0)	147 ± 7 (1·0)
$CH_2{=}CDSD$[g] (**7**)	— (1·0)	— (1·2)

[a] Measurements were performed on an AEI MS 902S mass spectrometer as described in ref. 2. [b] Relative peak heights were measured. For D loss the peak heights were multiplied by $\sqrt{2}$ to correct for the relative broadening of the D loss peak. All metastable peaks had the same shape, being steep-sided with flat tops; the D loss peak from (**3**) had a dished summit. There is therefore a reverse activation energy associated with these fragmentations (ref. 7). [c] Generated from *trans*-2,4,6-trideuterio-2,4,6-trimethyl-1,3,5-trithian. [d] $T_{0\cdot5}$ for deuterium loss from $(CD_3CDS)^{+\cdot}$, generated from perdeuterio-2,4,6-trimethyl-1,3,5-trithian, 154 ± 4 meV. [e] $T_{0\cdot5}$ values and metastable peak abundances for this ion, generated from 2,4-dideuterio-2,4-dimethylthietan (**8**), were 163 ± 11 (1·0) and 148 ± 5 ($\leqslant 6$) for H and D loss respectively. [f] Generated from *trans*-2,4,6-trideuteriomethyl-1,3,5-trithian. [g] Generated from appropriately $[^2H_1]$-labelled cyclobutane thiols.

It remains briefly to comment on the significantly larger $T_{0\cdot5}$ values for H atom loss (Table) and for ethylene sulphide. One possible explanation is that there is a kinetic delay effect associated with these ions. MeCHS molecular ions which decompose in the first field-free region but which were generated *via* rearrangement of other $(C_2H_4S)^{+\cdot}$ structures, must have larger internal energies than those ions which already possess the MeCHS structure. For example, such a hypothesis explains the large $T_{0\cdot5}$ (H) values for compounds (**3**) and (**8**). However, the possibility of a small contribution from H (or D) loss from the methyl group cannot entirely be ruled out.

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