

LOSS OF SULPHUR BY ELECTRON IMPACT
ON ALIPHATIC COMPOUNDS

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Madsen and co-workers (1) recently reported skeletal rearrangements by electron impact on some sulphides, disulphides, sulphoxides and sulphones. They observed loss of S, SH, SH₂, S₂, SO and SO₂, and the appearance of rearrangement peaks with intensities from 2 to 30% of the base peak. Their compounds all contained aromatic or benzylic groups so that the rearrangement ions would be stabilized.

Our observations on saturated and unsaturated aliphatic sulphur compounds are collected in the table and may be compared with the relevant results of Levy and Stahl (2), and of Hebreck and Kiser (3). In all our spectra the rearrangement ion (M-S)⁺ is less than 1% of the base peak (the ion in the spectrum of methyl vinyl sulphide at m/e 42, 3.6%, is mainly isotopic). Of the 34 dialkyl sulphides reported by Levy and Stahl (2), only five had a peak greater than 1% at the mass number corresponding to (M-S)⁺; the most intense, from diethyl sulphide, was 9.2%. These peaks probably included a contribution from ions containing sulphur which would not be distinguished at low

resolution. This may also be the case with the (M-SH) ions of Levy and Stahl's compounds.

Relative Abundance of Rearrangement Ions
in the Mass Spectra of Some Aliphatic Sulphides,
Sulphoxides, Sulphones and Disulphides

Compound	(M-S) ⁺	(M-SO) ⁺	(M-SO ₂) ⁺	(M-SO ₂ H) ⁺
CD ₃ SCD ₃	x	x	3.0	17.4
	(M-S) ⁺	(M-SH) ⁺	(M-SH ₂) ⁺	(M-SH ₃) ⁺
CH ₃ SCH=CH ₂	3.6	95.1	x	10.7
CH ₃ SC≡CH	x	10.0	x	x
CH ₃ SCH ₂ CH=CH ₂	x	2.6	1.5	2.4
CH ₃ SCH=CHCH ₃	x	5.5	2.2	9.1
	(M-SO) ⁺	(M-SOH) ⁺	(M-SOCH ₂) ⁺	(M-SOCH ₃) ⁺
CH ₃ SOCH ₃	x	4.9	4.7	5.3
CH ₃ SOCH=CH ₂	10.6	17.0	x	8.1
	(M-SO ₂) ⁺	(M-SO ₂ H) ⁺	(M-SO ₂ H ₂) ⁺	(M-SO ₂ H ₃) ⁺
CH ₃ SO ₂ CH ₃	x	3.2	7.4	2.8
CH ₃ SO ₂ CH=CH ₃	4.7	4.2	x	1.8
	(M-S) ⁺	(M-2S) ⁺	(M-SH) ⁺	
CH ₃ SSCH ₃	1.5	x	13.5	
CH ₃ CH ₂ SSCH ₂ CH ₃	1.5	3.2	x	

Abundances shown as % of the base peak; x, less than 1%

The rearrangement ion (M-SH_n) becomes important only when it is stabilized, i.e., C₂H₃⁺ from dimethyl sulphide, C₃H₅⁺ and C₃H₃⁺ from methyl vinyl sulphide, and C₃H₃⁺ from methyl ethynyl sulphide. Our observations on dimethyl sulphide-d₆ confirm those of Levy and Stahl (2) on dimethyl sulphide.

Methyl vinyl sulphoxide shows the rearrangement ions $C_3H_5^+$ and $C_3H_3^+$. These also appear in the spectrum of methyl vinyl sulphone but are relatively less intense. Both compounds show an ion at m/e 42 which may be either $C_3H_6^+$ or $C_2H_2O^+$ or both. From the disulphides only the rearrangement ion $C_2H_5S^+$ is notable; it may have the structure $(CH_3-S-CH_2)^+$.

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References

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