Decomposition of Methanesulphenyl Chloride in the Presence of Amines

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Summary Methanesulphenyl chloride reacts in the presence of secondary amines by heterolytic cleavage of the sulphur–chlorine bond yielding sulphenamides, and by an elimination of hydrogen chloride giving thioformaldehyde, and thence further products.

THE reactions of arenesulphenyl chlorides indicate routes involving both heterolysis[1] and homolysis[2] of the sulphur–chlorine bond. This work indicates that alkanesulphenyl chlorides react in two distinct ways with secondary amines.

Four major volatile components are formed from the reaction of methanesulphenyl chloride[3] with an excess of dialkylamine at -60°. Only one, the sulphenamide (30—40%), results from direct heterolysis of the sulphur–chlorine bond.

$$\mathrm{MeSCl} + 2\mathrm{R_2NH} \xrightarrow[\mathrm{Et_2O}]{-60^\circ} \mathrm{MeSNR_2} + \mathrm{R_2NH_2Cl}$$

$$(\mathrm{R} = \mathrm{Me, Et, and\ Pr^n}).$$

The others, bis(dialkylamino)methane $(\mathrm{R_2N})_2\mathrm{CH_2}$ (15—20%), dimethyl disulphide (20—25%), and dimethyl trisulphide (15—20%) result through a reaction sequence involving an intermediate $[\mathrm{CH_2S}]$.

This intermediate may result by two elimination pathways. One involves the homolytic cleavage of the S–Cl bond followed by H abstraction from the methylthio-radical so generated. The other pathway considered is the base-catalysed 1,2 elimination of hydrogen chloride.

$$\mathrm{MeSCl} \rightarrow \mathrm{MeS\cdot} + \mathrm{Cl\cdot}$$
$$\mathrm{MeS\cdot} + \mathrm{Cl\cdot} \rightarrow [\mathrm{CH_2S}] + \mathrm{HCl}$$
$$\mathrm{R_2NH} + \mathrm{MeSCl} \rightarrow \mathrm{R_2NH_2^+} + [\mathrm{CH_2S}] + \mathrm{Cl^-}$$

The *gem*-diamine and polysulphides result from the sequence formulated below. Support for the first step is found in the standard procedure for synthesising *gem*-diamines using formaldehyde and secondary amines.[4]

$$[\mathrm{CH_2S}] + 2\mathrm{R_2NH} \rightarrow (\mathrm{R_2N})_2\mathrm{CH_2} + \mathrm{H_2S}$$
$$\mathrm{H_2S} + \mathrm{MeSCl} \rightarrow \mathrm{MeSSH}$$
$$2\mathrm{MeSSH} \rightarrow \mathrm{Me_2S_3} + \mathrm{H_2S}$$
$$\mathrm{Me_2S_3} \xrightarrow{\mathrm{R_2NH}} \mathrm{Me_2S_2} + \mathrm{S}$$

The condensation of methanesulphenyl chloride and hydrogen sulphide, in a manner similar to the synthesis of trisulphides from sulphur dichloride and a thiol,[5] would give thermally unstable methyl hydrodisulphide.[6] This dissociates into hydrogen sulphide and dimethyl trisulphide, originally characterised from the reaction of ammonia with methanesulphenyl chloride.[7] Like other alkyl and aryl trisulphides, dimethyl trisulphide is desulphurised into the disulphide in the presence of dimethylamine.[8]

Further support for this thioaldehyde intermediate comes from the isolation of diethyl disulphide and trisulphide using ethanesulphenyl chloride and dimethylamine.

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