

59. *The Thermal Decomposition of 2 : 2'-Dichlorodiethyl Sulphide.*

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The thermal decomposition of 2 : 2'-dichlorodiethyl sulphide ("mustard gas") has been investigated at various temperatures. The main products isolated were hydrogen chloride, ethylene, ethylene dichloride, dithian, and 2 : 2'-dichlorodiethyl disulphide; at the highest temperatures hydrogen sulphide and vinyl chloride were found in addition. Decomposition appears to be complete at 450°.

IN spite of the military use of 2 : 2'-dichlorodiethyl sulphide and the large amount of work carried out on its preparation and properties, there is but little information on the products of its thermal decomposition. Bell, Bennett, and Hock (*J.*, 1927, 1805) note the formation of dithian and ethylene dichloride when the substance is heated in a sealed tube at 180° for 18 hours. Sartori ("The War Gases", p. 226) states that decomposition commences at about 150° and is complete at 500°, with evolution of hydrogen chloride and "toxic and lachrymatory gases", but gives no reference to the source of this information.

In the present investigation a qualitative and roughly quantitative determination has been made of the products, the nature and proportions of which vary with the temperature of heating. Decomposition in the liquid phase was followed by heating under reflux for two hours in a constant-temperature bath; the temperatures chosen were 180°, the lowest temperature at which decomposition proceeds at a reasonable rate, and the boiling point, which is about 220° at atmospheric pressure. The vapour-phase decomposition was investigated at 350° and 450°, the liquid being dropped into a heated packed column at the rate of about 1 ml./min.

The results are conveniently summarised in the following table; the yields of the various products are expressed as percentages of the initial weight of 2 : 2'-dichlorodiethyl sulphide used.

Temp.	180°.	B. p. ( <i>ca.</i> 220°).	350°.	450°.
Hydrogen chloride .....	8.0	21.2	25.8	31.5
Ethylene .....	4.2	11.2	7.9	10.4
Ethylene dichloride .....	6.9	11.1	—	—
Hydrogen sulphide .....	—	—	3.9	5.2
Vinyl chloride .....	—	—	14.6	19.4
Dithian .....	1.3	3.3	Trace	Trace
2 : 2'-Dichlorodiethyl disulphide .....	5.8	8.5	2.0	—
2 : 2'-Dichlorodiethyl sulphide recovered .....	56.0	14.2	13.0	—
Non-volatile residue .....	12.2	25.7	<i>ca.</i> 31	<i>ca.</i> 32 (by difference)
Carbon disulphide .....	—	—	<i>ca.</i> 1	<i>ca.</i> 1

The non-volatile residue from the 180° and the b. p. run, left after heating at 120°/4 mm., gave an average analysis of S, 43—44; Cl, 17—17.5%. The residue from the higher-temperature runs, being distributed over the interior of the column, was not available for analysis, but a survey of the products at 450° shows that it too must have a high sulphur and an even lower chlorine content since the characterised products leave only about 7% of the chlorine but 45% of the sulphur unaccounted for.

The principal decomposition product, hydrogen chloride, was to be expected in the thermal decomposition of an organic chloride. The exclusive formation of ethylene and complete absence of acetylene is interesting; possibly there is a reversal of the direct formation of 2 : 2'-dichlorodiethyl sulphide from ethylene and sulphur chlorides, for in the presence of excess of the chloro-sulphide at the high temperature any sulphur chlorides formed would be quickly destroyed with liberation of hydrogen chloride and formation of high-molecular-weight products such as occur in the non-volatile residue.



320 *Harley-Mason : Some Aliphatic Thiols and their Derivatives.*

A small amount of carbon disulphide was found in the cold trap after evaporation of the vinyl chloride from runs at 350° and 450° : the amount was too small for accurate determination.

2 : 2'-Dichlorodiethyl disulphide was found on fractionation of the residual material; b. p. 110°/4 mm. (slight decomp.); the analysis was poor (Found : S, 33·9; Cl, 36·3. Calc. for C<sub>4</sub>H<sub>8</sub>Cl<sub>2</sub>S<sub>2</sub> : S, 33·55; Cl, 37·1%). Bennett (*J.*, 1921, **119**, 424) records similarly poor analysis of his preparation, and further work by the author (unpublished) has confirmed the difficulty of obtaining good figures. Condensation with 2-hydroxyethanethiol gave a product, m. p. 81—82° *ex* alcohol, undepressed by admixture with a synthetic specimen, m. p. 81°.

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