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.

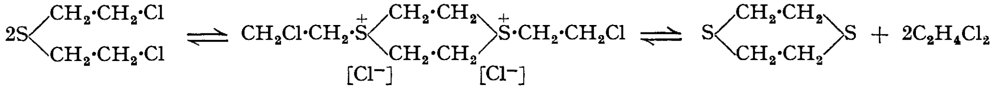
The results are conveniently summarised in the following table; the yields of the various products are expressed as percentages of the initial weight of 2 : 2′-dichlorodiethyl sulphide used.

Temp.	180°.	B. p. (*ca.* 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	*ca.* 31	*ca.* 32
			(by difference)	
Carbon disulphide	—	—	*ca.* 1	*ca.* 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.

Ethylene dichloride and dithian were found, as expected from the results of Bell, Bennett, and Hock (*loc. cit.*), whose theory of an intermediate sulphonium complex accounts satisfactorily for the formation of these products :



The yield of dithian was, however, smaller than expected and less than corresponds to the ethylene dichloride formed by the above reaction : the sulphonium complex, however, need not be only of the simple cyclic type shown but may equally well be of chain form, giving the non-volatile polymeric ethylene sulphide along with ethylene dichloride. The above workers carried out the decomposition in a sealed tube at 180° and obtained a 50% yield of dithian. Repetition of the experiment under their conditions gave yields of only 10% of dithian with considerable amounts of ethylene and hydrogen chloride : they did not record the formation of these gaseous products, whose presence is obvious on opening the sealed tube.

The formation of 2 : 2'-dichlorodiethyl disulphide is rather surprising, as it is less stable to heat than is the monosulphide.

A sharp division exists between the products at the two higher temperatures and the two lower. Hydrogen sulphide and vinyl chloride are formed at the higher temperatures, but no vinyl chloride and only a trace of hydrogen sulphide were found at the lower temperatures. Conversely, ethylene dichloride appears only at the lower temperatures, and the yield of ethylene relative to hydrogen chloride falls noticeably at the higher temperatures. These changes may be due in part to the change from glass to silica as the material of the reaction vessel; the introduction of silica rings into the decomposition at the b. p. did not produce any vinyl chloride but gave a small quantity of hydrogen sulphide and some acceleration of the normal reaction. Packing of the reaction vessel with glass-wool at this temperature gave no significant change, so the decomposition in glass at the b. p. is not a surface reaction : some surface reaction occurs on silica, though without appreciable change in the proportion of the products. These results are summarised in tabular form :

Effect of glass-wool and silica on decomposition at the boiling point : Products, %.

	Normal reaction.	With silica.	With glass-wool.
HCl	21·2	28·8	19·7
C_2H_4	11·2	14·4	10·8
H_2S	0	0·4	0

The reaction at 350° and 450° will take place largely in the vapour state, and this may well be the real cause of the difference in products. The persistence of some products from the lower-temperature liquid-phase reaction is to be expected as the material enters the column in liquid form.

It is noteworthy that the molecular ratio of hydrogen sulphide to vinyl chloride is almost exactly 1 : 2 at both temperatures; their formation would appear to be due to the simple reaction $S(CH_2\cdot CH_2Cl)_2 \longrightarrow H_2S + 2CH_2{:}CHCl$.

EXPERIMENTAL.

All decompositions were carried out in an atmosphere of nitrogen. For the runs at 180° and the b. p., the material was heated under a reflux air condenser in a flask immersed in an oil-bath; a slow stream of nitrogen was bubbled through to carry over volatile products. In the higher-temperature runs the nitrogen stream passed through the electrically heated quartz column packed with quartz rings down which the chloro-sulphide was dropped.

The volatile products were passed through a trap cooled in alcohol–solid carbon dioxide (— 78°), followed by bubblers containing water, alkali, and bromine-water successively to collect hydrogen chloride, hydrogen sulphide, and ethylene. At the end of a run, the apparatus was flushed out with nitrogen, then the bromine-water bubblers were replaced by fresh ones and the cold trap was allowed to warm to room temperature : vinyl chloride (b. p. — 14°) and dissolved hydrogen chloride and sulphide were then swept through and collected in the appropriate reagents.

Hydrogen chloride was collected in water and estimated by direct titration. Hydrogen sulphide was absorbed in sodium hydroxide solution and estimated as sulphide by iodine–thiosulphate titration. Ethylene was absorbed in bromine-water, and the ethylene dibromide collected and weighed after being washed with dilute alkali and water, and dried; its purity was checked by distillation. Ethylene dichloride was recovered from the cold trap and treated similarly. Vinyl chloride collected in the cold trap, and when this was allowed to warm, the chloride evaporated and was collected in bromine-water; the resulting 1-chloro-1 : 2-dibromoethane was separated, washed, dried, and weighed, and its purity checked by fractionation.

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 $C_4H_8Cl_2S_2$: 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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