The Hydrolysis of Trichloromethanesulphenyl Chloride: the Preparation of Dichloromethylene Sulphoxide

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Summary Dichloromethylene sulphoxide (thiophosgene *S*-oxide), has been isolated and identified as a product of the aqueous hydrolysis of trichloromethanesulphenyl chloride.

RATHKE'S EQUATION (1)[1] is generally accepted for the overall result of the hydrolysis of trichloromethanesulphenyl chloride, but further details of the mechanism are not established.

$$Cl_3C{\cdot}S{\cdot}Cl + 2H_2O \rightarrow 4HCl + CO_2 + S \qquad (1)$$

We report the isolation and identification of a new intermediate product of the reaction. The hydrolysis was carried out in a vigorously stirred heterogeneous system of trichloromethanesulphenyl chloride and water. On g.l.c. analysis of the organic layer, the presence of a new and relatively unstable compound was observed. This compound of a hitherto undetermined structure was isolated by repeated distillation of the organic layer using an effective column under reduced pressure. It is a pale yellowish liquid, b.p. 43—45°/30 torr, n_D^{20} 1·5588, and is a very strong lachrymator, far stronger than trichloromethanesulphenyl chloride.

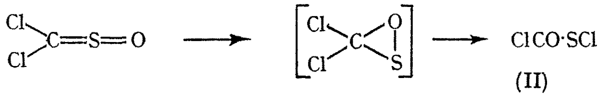
The i.r. spectrum of this compound is extremely simple and the absorption bands (1052 and 1156 cm.$^{-1}$) are in a very close agreement with those described[2] for the C=S=O group.

From its analysis and i.r. spectra, and the absence of any ^{1}H n.m.r. signal the compound was assigned the structure (I), dichloromethylene sulphoxide. Assuming that the unstable trichloromethanesulphenic acid is produced first, we can describe this reaction by equation (2):

$$Cl_3C{\cdot}S{\cdot}Cl \xrightarrow[-HCl]{H_2O} [Cl_3C{\cdot}S{\cdot}OH] \xrightarrow{-HCl} \underset{(I)}{Cl_2C{=}S{=}O} \qquad (2)$$

Dichloromethylene sulphoxide (thiophosgene *S*-oxide) was earlier invoked to explain some reactions of trichloromethylthio-compounds,[3] but it was neither identified nor isolated. It may be obtained by fractionation of the organic layer and also by extraction of the aqueous layer, *e.g.* with methylene chloride. The total yield of dichloromethylene sulphoxide is strongly dependent on experimental conditions because of its instability, particularly at higher temperatures; in our experiments it was approximately 30%.

The decomposition of (I) is a complicated reaction and can be monitored by g.l.c. analysis. We conclude that a rearrangement of (I) into chlorocarbonylsulphenyl chloride (II) is a most important reaction [equation (3)]:



(3)

(II)

This conclusion was supported by the presence of a strong carbonyl absorption band (1800 cm.$^{-1}$) in the i.r. spectrum after decomposition.

The rearrangement of (I) into (II) occurs very quickly in concentrated sulphuric acid, so dichloromethylene sulphoxide may well be an intermediate in the recently described preparation of chlorocarbonylsulphenyl chloride by hydrolysis of trichloromethanesulphenyl chloride in concentrated sulphuric acid.[4]

In aqueous media, chlorocarbonylsulphenyl chloride is readily decomposed into sulphur, carbon dioxide, and hydrogen chloride according to equation (4):

$$\mathrm{ClCO{\cdot}SCl + H_2O \rightarrow CO_2 + 2HCl + S} \qquad (4)$$

This result is also in agreement with Rathke's equation (1). But it should be noted that if the hydrolysis of trichloromethanesulphenyl chloride to dichloromethylene sulphoxide (step 1) is relatively simple and unambiguous as shown by g.l.c., the next steps will be more complicated. Dichloromethylene sulphoxide also reacts under hydrolysis conditions in a different way, and does not produce simple inorganic compounds (S,CO_2,HCl) but a mixture of complicated organic sulphur compounds.

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