

THE ACTION OF AQUEOUS CHLORINE ON *s*-TRITHIANE¹

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In a previous paper (1) reference was made to certain unknown substances which are formed along with chloromethanesulfonyl chloride when chlorine acts upon a cold aqueous suspension of *s*-trithiane. This paper describes an attempt to identify these unknown by-products and to discover the manner in which they are formed.

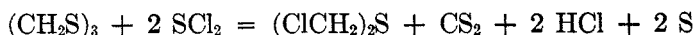
The system in which the aqueous chlorination of *s*-trithiane takes place is not ideal for the study of reaction mechanisms. Beginning with three phases, water, solid *s*-trithiane, and gaseous chlorine, it slowly undergoes change until the aqueous layer has become saturated with hydrogen chloride and the solid phase has disappeared, either by going into solution or by becoming dispersed by surface active transformation products. At one stage neither solid nor non-aqueous liquid phases are in evidence. Further chlorination causes the separation of a heavy oil, the distillation of which has led to the observations reported in this paper.

Previous workers (2) have recognized that formaldehyde and sulfur, the latter in the form of sulfur chloride or sulfate ion, are by-products of the formation of chloromethanesulfonyl chloride from *s*-trithiane by chlorination in the presence of water. The present study confirms the formation of formaldehyde, sulfate ion and sulfur dichloride and in addition establishes that methylene chloride, carbon tetrachloride, and 1,1'-dichlorodimethyl sulfide are also found in small amounts when the oily products from the complete or incomplete aqueous chlorination of *s*-trithiane are distilled. Careful fractionation has also revealed the presence of an unknown yellow liquid of high refractive index.

The unknown wax-like white solid previously reported (1) has been identified as trichloromethanesulfonyl chloride, $\text{Cl}_3\text{CSO}_2\text{Cl}$. This compound does not seem to be derived from chloromethanesulfonyl chloride, $\text{ClCH}_2\text{SO}_2\text{Cl}$, for exhaustive chlorination of a pure sample of the latter does not result in the introduction of additional chlorine atoms. The trichloromethanesulfonyl chloride may result from the oxidation of some intermediate such as trichloromethanesulfonyl chloride, Cl_3CSCl . Although this latter compound was never found among the products of distillation, a sample prepared by the method of Helfrich and Reid (3) readily yielded trichloromethanesulfonyl chloride on aqueous chlorination.

The presence of 1,1'-dichlorodimethyl sulfide among the distillation products suggests that a reaction reported elsewhere has occurred (4).

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There is uncertainty, however, as to whether the reaction shown takes place during the low-temperature chlorination or later during the distillation. The conditions under which 1,1'-dichlorodimethyl sulfide was isolated suggest the latter.

It was hoped that in this study the immediate precursor of chloromethanesulfonyl chloride might be found among the distilled products of partial chlorination but no such compound was found. The chlorination of trithiane was carried out in a non-aqueous medium, however, and from the resulting mixture a small yield of chloromethanesulfonyl chloride, ClCH_2SOCl , was obtained. This substance, when placed in water and further chlorinated, is readily transformed into chloromethanesulfonyl chloride and may well be a short lived intermediate along one path whereby chloromethanesulfonyl chloride is formed. If one accepts this postulate, the great reactivity of the chain hydrogens of aliphatic sulfonyl chlorides (5) offers a possible explanation for the origin of trichloromethanesulfonyl chloride and subsequently the corresponding sulfonyl chloride and carbon tetrachloride (6).

EXPERIMENTAL PART

Chlorination procedure. Finely ground trithiane was suspended in four to five times its weight of water in a three-neck flask fitted with mechanical stirrer. The flask was cooled by a mixture of ice and salt and chlorine was passed in at such a rate that the temperature did not rise above 10° . For complete chlorination the reaction was continued until a permanent color of excess chlorine appeared in the liquid. For partial chlorination the reaction was interrupted at various times, the flask weighed, and any liquid products siphoned off, dried and saved for distillation.

Table I indicates the course of a typical partial chlorination of 100 g. of s-trithiane in 400 g. water.

Distillation. In the analytical distillations to identify intermediate products a Todd Precise Fractionation Assembly was employed (7). In a typical run, 150 g. of the combined liquid products from the experiment described above was distilled using an 8 to 1 reflux ratio during the early part of the distillation but a more rapid rate toward the end. Weighed fractions of 1-2 g. were taken and the refractive index of each determined. Weight-refractive index and weight-boiling point graphs revealed the presence of the various components. The relative abundance of the principal fractions is shown in Table II.

Fractions A and B were treated with dilute sodium hydroxide solution to remove traces of sulfur dichloride and were then redistilled. Methylene chloride and carbon tetrachloride were identified by their boiling points and refractive indices.

Fraction C was collected as three portions of 1.0, 0.7, and 0.8 g. having refractive indices of n_D^{20} 1.5362, n_D^{20} 1.5509, and n_D^{20} 1.5368 respectively. The middle portion was analyzed.

Anal. Found: Cl, 64.34; S, 19.71

Atomic ratio: Cl:S = 2.92:1.0

Identification of 1,1'-dichlorodimethyl sulfide. The first 45 g. of liquid products to separate from another partial chlorination of 100 g. of s-trithiane was distilled at atmospheric pressure. There was much decomposition but 8 g. of colorless liquid boiling at $155-156^\circ$ (760 mm.) and $61-62^\circ$ (26 mm.) was obtained, n_D^{20} 1.5275. This liquid proved to be 1,1'-dichlorodimethyl sulfide, $\text{ClCH}_2\text{SCH}_2\text{Cl}$.

Anal. Calc'd for $\text{C}_2\text{H}_4\text{Cl}_2\text{S}$: Cl, 54.12; S, 24.47.

Found: Cl, 53.96; S, 24.42.

Sulfate ion formation during aqueous chlorination. In four trials in which the chlorina-

tion of 40 g. of *s*-trithiane suspended in 200 ml. of water was carried to completion, the aqueous layer was analyzed for sulfate ion. For each mole of *s*-trithiane the respective yields of sulfate ion were 0.699, 0.703, 0.699 and 0.656 mole.

Preparation of chloromethanesulfenyl chloride, ClCH₂SOCl. One hundred grams of dry *s*-trithiane suspended in 400 g. of anhydrous carbon tetrachloride was treated with chlorine by the same method previously described. The flask was weighed from time to time and the reaction was terminated when three moles of chlorine per mole of *s*-trithiane had been absorbed.

The carbon tetrachloride was removed at atmospheric pressure and the remaining yellowish-red liquid was distilled at reduced pressure. Small fractions were taken and

TABLE I
CHLORINATION OF *s*-TRITHIANE

ELAPSED TIME, HRS.	TEMP. °C	WT. GAINED, G.	OBSERVATION
2	6	86	No apparent change
3½	4	188	Still much white solid
4½	5	296	Tan colored solution or emulsion. No heavy liquid settled out
5½	0	380	43 g. liquid settled out and was removed.
6	0		21 g. liquid was removed
7	1		43 g. liquid was removed
overnight standing			48 g. liquid was removed

TABLE II
FRACTIONATION OF PRODUCTS

FRACTION	B.P./760 MM., °C	WT., G.	CHIEF COMPONENT
A	40-53	3.5	CH ₂ Cl ₂
Intermediate	53-66	1.0	
B	66-75	10.0	CCl ₄ and SCl ₂
Intermediate	75-117	3.0	
C	117-121	2.5	Unknown yellow compound
Intermediate	121-168	10.2	Probably ClCH ₂ SCH ₂ Cl and ClCH ₂ SO ₂ Cl
D	168-170	90.6	ClCH ₂ SO ₂ Cl
Residue and loss		26.4	

their refractive indices plotted against total weight of distillate. Five fractions had similar refractive indices but two of these comprising twenty grams were identical and furnished liquid for further study.

The bright yellow liquid was soluble in ether, alcohol, and carbon tetrachloride but insoluble in water and had the following properties: n_D^{20} 1.5434, d_4^{20} 1.5613, b.p. 64° (100 mm.), 30-32° (17 mm.). Molecular weight in benzene; 136, 137. Calc'd for ClCH₂SOCl; 117.

The measured value for the molecular refraction as determined by the Lorenz-Lorenz equation is 23.63. The calculated value for ClCH₂SOCl, using the atomic refractions for the Na_D line (8) (employing the mercaptan value for sulfur, 7.69, for want of a better value) is 24.24.

Anal. Calc'd for CH₂Cl₂S: Cl, 60.60; S, 27.40.

Found: Cl, 59.74, 61.18; S, 27.27, 27.87.

A portion of the liquid was chlorinated in cold water and was transformed into chloromethanesulfonyl chloride, the identity of which was established by formation of the *p*-toluidide and comparison with an authentic sample. The aqueous layer from the chlorination tested positive for sulfate ion but negative for formaldehyde.

On standing, chloromethanesulfonyl chloride slowly undergoes decomposition and evolves hydrogen chloride. The index of refraction of one specimen changed over several weeks from n_D^{20} 1.5458 to n_D^{20} 1.559.

Exhaustive chlorination of chloromethanesulfonyl chloride. Forty-four grams of pure chloromethanesulfonyl chloride was placed in 200 ml. of water and chlorinated at 0–1° for 5½ hours. After removal of excess chlorine, 28.5 g. of unchanged starting material was recovered. Distillation through an efficient column showed the complete absence of trichloromethanesulfonyl chloride.

Aqueous chlorination of trichloromethanesulfonyl chloride, Cl₃CSOCl. Chlorine was passed into a well-stirred, cold suspension of 5.9 g. of trichloromethanesulfonyl chloride in 100 ml. of water for four hours. The mixture was allowed to warm until the chlorine hydrate had decomposed, air was bubbled through until the color of excess chlorine had disappeared and the solid was separated by filtration. After standing on paper in a calcium chloride desiccator overnight 5.2 g. (75%) of slightly impure trichloromethanesulfonyl chloride was obtained.

Identification and reactions of trichloromethanesulfonyl chloride. *s*-Trithiane, suspended in cold water was chlorinated to completion. After removal of excess chlorine, washing, and drying, the oil was distilled at reduced pressure through an efficient column. A special still head permitted the collection of the white wax-like solid which first sublimed on a cold finger before turning the slightly higher boiling chloromethanesulfonyl chloride into the downward condenser. The solid always amounted to less than 10% of the final products.

In attempting to identify the unknown solid, hydrolysis experiments were carried out, the exact significance of which was not clear even after the compound was identified as trichloromethanesulfonyl chloride. Small samples were sealed in micro combustion tubes with 5 ml. water and heated at 100° for four hours. On opening the tubes the contents were analyzed for chloride and hydrogen ions, with the following results:

TUBE	WT. SAMPLE, G.	MOLAR RATIO		
		Cl ₃ CSO ₂ Cl	Cl ⁻	H ⁺
1	0.1002	1.0	2.1	4.6
2	0.1331	1.0	2.02	3.6

The solid melted at 140–141° and was found to have a molecular weight of 214 in benzene solution. Calculated for CCl₄O₂S, 218. The accepted melting point for trichloromethanesulfonyl chloride is 140–140.5°.

Anal. Calc'd for CCl₄O₂S: Cl, 65.09. Found: Cl, 65.37.

No anilide could be formed, and when a sample of the white solid was placed in sodium iodide solution, iodine was liberated. Both of these unexpected reactions are characteristic of trichloromethanesulfonyl chloride (9, 10).

An authentic sample of trichloromethanesulfonyl chloride was prepared and was found to melt unchanged when mixed with the unknown.

SUMMARY

1. The aqueous chlorination of trithiane has been studied and certain previously unrecognized products have been identified.
2. Chloromethanesulfonyl chloride has been prepared and characterized.

ORONO, MAINE

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