

XXIX.—*The Action of Chlorine on Organic Thiocyanates.*  
Part I. *Methyl Thiocyanate.*

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THE action of chlorine on methyl thiocyanate was first investigated by Cahours (*Annalen*, **61**, 96), who found that cyanuric chloride and a heavy oil were formed; some time later, in 1854, Riche studied the reaction more closely (*Annalen*, **92**, 357).

In continuation of my work with ethylene chlorothiocyanate, I was led to examine the action of chlorine on methyl and ethyl thiocyanates, in the hope originally, of obtaining chlorinated thiocyanates as substitution products; but as I have already shown in a short notice (*J. pr. Chem.* **30**, 316) the thiocyanate group is at once attacked by the chlorine, the whole of the cyanogen combining with it to form cyanuric chloride.

The result of Riche's work with methyl thiocyanate is the formation of cyanuric chloride, and a liquid boiling from  $70^{\circ}$  to  $200^{\circ}$ , from which he separated two main products; the one boiling below  $86^{\circ}$ , stated to be a mixture of sulphur dichloride with carbon tetrachloride, and the other boiling from  $140^{\circ}$  to  $170^{\circ}$ , which after shaking with potassium hydroxide, and drying over calcium chloride, boiled at  $150^{\circ}$  to  $160^{\circ}$ ; this had the composition  $C_2SCl_6$ .

100 grams of pure methyl thiocyanate was placed in a flask surrounded by cold water, and a slow stream of dry chlorine passed in, in diffused light. At first very little hydrogen chloride was given off, the chlorine being completely absorbed. The colourless liquid became yellow, and at last deep orange. In about two hours hydrogen chloride is evolved in large quantities, and this continues throughout the reaction, but there is very little rise of temperature. After chlorine had been passed in for five hours, the flask was allowed to stand in a cool place during the night, when a quantity of large, colourless, well-formed monoclinic crystals separated. The supernatant liquid was poured off, and again treated with chlorine to complete saturation, finally in sunlight, and until hydrogen chloride ceased to be evolved, this liquid on standing deposited a fresh quantity of the crystals.

*Examination of the Crystals.*—These were freed from adhering liquid by pressing them between filter-paper, and further purified by standing over sulphuric acid and lime. A melting point determination gave  $146^{\circ}$ , and their other properties showed them to be pure cyanuric chloride. Some of the crystals were so large and well formed that it was my intention to have them measured; but this has already been done by Hofmann in his recent work on cyanuric ethers (*Ber.*, **19**, 2063), while these experiments were in progress.

From 100 grams of methyl thiocyanate, I have obtained on an average 65 to 70 grams of pure cyanuric chloride, the calculated quantity being 84 grams, so that this is a most advantageous method for preparing this important substance.

*Examination of the Liquid.*—The orange-coloured liquid on fractional distillation yielded three fractions: one boiling from  $70^{\circ}$  to  $75^{\circ}$ , another distilling from  $148^{\circ}$  to  $150^{\circ}$ , and the third, in small quantity, above  $200^{\circ}$ . From the last fraction I have, in spite of several different

experiments, been unable to obtain any definite result. It contains varying quantities of cyanuric chloride, and this cannot be removed by distillation, as the substance is gradually decomposed into a liquid which begins to boil at 70°.

Fraction 70—75°. This is of a deep orange colour, with red vapour. An analysis showed it to consist of a mixture of thiocarbonyl chloride and carbon tetrachloride, very nearly in the proportion of 2 mols. of the former to one of the latter:  $2\text{CSCl}_2 + \text{CCl}_4$ . It is not immediately acted on by water; it may in fact be shaken with it without showing any sign of decomposition, and this proves sulphur dichloride to be absent. It fumes strongly in air, its vapour causes a copious flow of tears, and acts most violently upon the respiratory organs. I obtained as much as 50 grams of this liquid from 100 of methyl thiocyanate, and endeavoured to separate it into thiocarbonyl chloride and carbon tetrachloride by further fractional distillation, but this cannot be done to any extent by observing the thermometer. If, however, the first portion of the distillate be again and again distilled slowly, until about one-fourth has been collected, it will be found to consist almost entirely of thiocarbonyl chloride. One sample prepared in this way weighed 10 grams, and gave the following numbers on analysis:—

- I. 0.2856 gram substance, after oxidation with concentrated nitric acid at 200° in a sealed tube, produced 0.541 gram  $\text{BaSO}_4$  = 26.01 per cent. sulphur.  
 II. 0.2025 gram substance burnt with lime gave 0.531 gram  $\text{AgCl}$  = 64.85 per cent. chlorine.

	Calculated for $\text{CSCl}_2$ .		Found.	
	12	10.43	I.	I.
C.....	32	27.83	—	—
S.....	71	61.74	26.01	—
$\text{Cl}_2$ .....	—	—	—	64.85
	115	100.00		

The liquid was preserved in a small stoppered cylinder, and after standing a few days, large well-formed rhombic crystals had separated; these were pressed between filter-paper, dried over lime, and analysed. They melted at 115°.

0.2355 gram substance burnt with  $\text{CuO}$  and  $\text{PbCrO}_4$  gave 0.004 gram  $\text{H}_2\text{O}$  and 0.0905 gram  $\text{CO}_2$ .

0.2735 gram substance oxidised with concentrated nitric acid at 200° gave 0.5600 gram  $\text{BaSO}_4$ .

	Calculated for (CSCl <sub>2</sub> ) <sub>x</sub> .		Found.	
			I.	II.
C.....	12	10·43	10·48	—
S.....	32	27·83	—	28·12
Cl <sub>2</sub> .....	71	61·74	—	—
	<hr/>	<hr/>		
	115	100·00		

In the *Annalen*, 167, 180, B. Rathke describes a polymeric modification of thiocarbonyl chloride, which he obtained by the action of chlorine on carbon bisulphide, and with which these crystals are undoubtedly identical. The properties and reactions have been fully described by Rathke, and I will only add that they *sublime* slowly if kept in a stoppered cylinder, forming extremely well formed, strongly refractive crystals; if heated in a bulb-tube, they vaporise readily, condensing to a beautifully crystalline mass. They are insoluble in water, sparingly soluble in alcohol, and easily dissolved by ether. I have found their melting point to be 114—115°, at which temperature they sublime; Rathke gives 112·5°. He also states in his memoir that "the formation of these crystals seems to depend on the action of light." I have not found this to be the case. Several small cylinders containing thiocarbonyl chloride were exposed to light for several days, but no crystals formed. On opening each of them, crystals immediately made their appearance. A cylinder containing both crystals and liquid was exposed to sunlight, the crystals disappeared, and did not again form, even after an interval of three weeks. On opening and shaking, they immediately reappeared.

Fraction 148—150° (uncorr.). A pale-yellow liquid obtained in much larger quantity than that of low boiling point, which on analysis was found to have the formula CScCl<sub>4</sub>.

- I. 0·3690 gram substance on combustion with CuO and PbCrO<sub>4</sub> gave 0·0855 gram CO<sub>2</sub>.  
 II. 0·3185 gram substance gave 0·4375 gram BaSO<sub>4</sub> after oxidation by concentrated HNO<sub>3</sub> at 200°.  
 III. After rectifying again—  
 0·154 gram substance produced 0·2115 gram BaSO<sub>4</sub>.  
 IV. 0·2075 gram on ignition with lime gave 0·6350 gram AgCl.

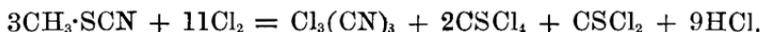
	Calculated for thiocarbonyl tetra- chloride, CScCl <sub>4</sub> .		Found.			
			I.	II.	III.	V.
C.....	12	6·45	6·31	—	—	—
S.....	32	17·20	—	18·86	18·83	—
Cl <sub>4</sub> .....	142	76·35	—	—	—	75·76
	<hr/>	<hr/>				
	186	100·00				

The substance probably contains very small quantities of sulphur monochloride, b. p. 138°, and this accounts for the sulphur estimations coming out too high.

This liquid proves to be identical with that which Rathke (*Annalen*, 167, 180) obtained by the action of chlorine on carbon bisulphide in presence of a small quantity of iodine, and named by him *perchloromethyl mercaptan* from its supposed analogy to methyl mercaptan, with its hydrogen substituted by chlorine,  $\text{CCl}_3\cdot\text{SCl}$ . This formula is unsupported experimentally, and the substance might, I think, be more conveniently termed *thiocarbonyl tetrachloride*, thus bringing out its analogy to thiocarbonyl chloride,  $\text{CSCl}_2$ ,\* the constitution of which is also an open question.

From 100 grams of methyl thiocyanate, 83 grams of thiocarbonyl tetrachloride were obtained, after acting on the liquid of low boiling point\* with chlorine in order to obtain a maximum yield.

The chief reaction which takes place with methyl thiocyanate and dry chlorine is consequently the following:—



No satisfactory results can be obtained on fractional distillation unless chlorine be passed in, in sunlight, towards the end of the reaction, so as to displace all the hydrogen; as the intermediate products  $\text{CH}_3\text{SCl}$ ,  $\text{CH}_2\text{SCl}_2$ , &c., cannot be separated in a sufficiently pure condition.

It seems to me not improbable that the cyanogen-group is attacked first of all, and that the residue  $(\text{CH}_3\text{S})$  acts just as methyl disulphide,  $(\text{CH}_3)_2\text{S}_2$ , would. I hope shortly to study the action of chlorine on this substance, and it may possibly prove to be a fruitful method for preparing thiocarbonyl chloride,  $\text{CSCl}_2$ , in quantity.

*Action of Chlorine on Thiocarbonyl Chloride,  $\text{CSCl}_2$ . Formation of Thiocarbonyl Tetrachloride,  $\text{CSCl}_4$ .*

The conversion of thiocarbonyl chloride into thiocarbonyl tetrachloride by assimilation of two atoms of chlorine takes place at ordinary temperatures with the greatest ease.

A slow stream of dry chlorine was passed into a cylinder surrounded by cold water and containing 5 grams of thiocarbonyl chloride. The chlorine is completely absorbed, and in a very short time the liquid changes colour from deep orange to light yellow. On distillation, it

\* See below "Action of Chlorine on Thiocarbonyl chloride."

was found to pass over almost entirely between 148° and 150° (uncorr.). An estimation of the chlorine gave the following numbers:—

0·2775 gram substance ignited with lime, finally produced 0·8520 gram AgCl.

	Calculated for $\text{CSCl}_4$ .	Found.
Cl .....	76·35 per cent.	75·95

A few drops of a dark red liquid distilled over first of all; this was not unaltered thiocarbonyl chloride but proved to be mainly sulphur dichloride. It was immediately decomposed by water, becoming coated with a film of sulphur; in odour too, it differed characteristically from thiocarbonyl chloride.

It will be clear from this reaction, that chlorine must be passed into that portion of the liquid of low boiling point obtained in the first rectification, if a maximum yield of thiocarbonyl tetrachloride be required.

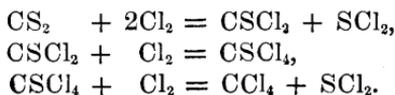
*Action of Chlorine on Thiocarbonyl Tetrachloride.*

The formation of sulphur dichloride in the previous reaction seemed to indicate a decomposition of thiocarbonyl tetrachloride, and this has been proved to be the case.

Chlorine was passed into a flask surrounded by warm water, containing 5 grams of pure thiocarbonyl tetrachloride, for one hour. At the end of this time, there was no perceptible difference in the colour of the liquid, but on distillation about one-third passed over between 60° and 120°, and this consisted mainly of sulphur dichloride and carbon tetrachloride. The presence of the former was easily established by its reaction with water, and after distilling with excess of sodium hydroxide in a current of steam, a liquid was obtained boiling at 78—80°, and having all the properties of carbon tetrachloride. It was evident, then, that the following reaction had taken place:—



The well-known fact that carbon bisulphide is decomposed by dry chlorine almost entirely into sulphur dichloride and carbon tetrachloride, seems in view of these experiments to be the final result of a series of reactions, viz. :—



Returning now to Riche's work on this subject—it is to a large extent inaccurate—his supposed compound,  $\text{C}_2\text{SCl}_6$ , was undoubtedly

a mixture of thiocarbonyl tetrachloride,  $\text{CSCl}_4$ , with cyanuric chloride, the latter being lost sight of in consequence of determining the percentage of sulphur by difference and not directly, and assuming carbon, sulphur, and chlorine only to be present. Neither was the liquid of low boiling point analysed; had this been done, it is probable that Kolbe's discovery of thiocarbonyl chloride would have been confirmed a few years after it was made.

*Action of Thiocarbonyl Tetrachloride on Alcohol.*

Rathke has assumed  $\text{CSCl}_4$  (perchloromethyl mercaptan) to have the constitution  $\text{CCl}_3\cdot\text{S}\cdot\text{Cl}$ , and this assumption is further borne out by its formation from methyl thiocyanate. I have endeavoured to obtain some confirmation of this formula by examining the action of alcohol on this compound. Those atoms of chlorine directly combined with carbon should not be attacked, whereas the group ( $\text{SCl}$ ) would possibly yield  $\text{S}(\text{OC}_2\text{H}_5)'$ , or, at any rate, be so acted on as to give some insight into its constitution.

The action of alcohol, which I have not yet been able to complete, has produced quite an unexpected result. On mixing thiocarbonyl tetrachloride with twice its volume of absolute alcohol it is dissolved, and in a short time the temperature of the mixture rises very considerably. After digestion on the water-bath, a heavy, yellow oil separates; this cannot be distilled. It is very sparingly soluble in alcohol, insoluble in water, but soluble in ether. Analyses point to the formula  $\text{CS}_3\text{Cl}_3$ ; probably  $\text{C}_2(\text{SCl})_6$ .

On fractioning the alcoholic liquid, a substance was isolated which is insoluble in water, and contains neither chlorine nor sulphur. After shaking with a saturated solution of calcium chloride to remove the last traces of alcohol, it boiled at  $126^\circ$ , and analyses indicated that its formula is  $\text{C}_3\text{H}_6\text{O}_2$ .

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