

149. *Chemical and Infrared Spectral Evidence for the Structure of Thiocyanogen Trichloride.*

By R. G. R. BACON, R. S. IRWIN, J. MCC. POLLOCK, and A. D. E. PULLIN.

Thiocyanogen trichloride is prepared in good yield from solutions of thiocyanogen and excess of chlorine or, less satisfactorily, from sulphur dichloride and cyanogen chloride. When it decomposes, sulphur dichloride and cyanuric chloride are formed. It behaves as a sulphenyl chloride, $\text{CNCl}_2 \cdot \text{SCl}$, and is related to compounds with the probable structures $(\text{CNCl}_2)_2\text{S}$ and $(\text{CNCl}_2 \cdot \text{S})_2$, preparations of which are described. Its behaviour towards salts (alkali-metal iodides, silver perchlorate, sodium *OO*-di-*n*-butyl thiophosphate) suggests that the group CNCl_2 is more likely to have the structure $\text{NCl} \cdot \text{CCl} \cdot$ than $\text{CCl}_2 \cdot \text{N} \cdot$. Thiocyanogen trichloride adds to *cyclohexene* to give 2-chloro*cyclohexyl* dichlorothiocyante, $\text{C}_6\text{H}_{10}\text{Cl} \cdot \text{S} \cdot \text{CNCl}_2$, reduction and oxidation of which are described.

The infrared spectrum has been obtained for the pure liquid, vapour, and solution from 4000 cm.^{-1} down to 400 cm.^{-1} . The spectrum is noteworthy in that the band characteristic of $\text{C} \equiv \text{N}$ is absent, whereas a strong band at 1600 cm.^{-1} is present which is assigned to a $\text{C} = \text{N}$ group. The interpretation of the spectrum is based on a comparison with those of the chloroethylenes, to which spectra it is remarkably similar. This provides strong evidence for the two structures $\text{Cl} \cdot \text{S} \cdot \text{CCl} \cdot \text{NCl}$ or $\text{CCl}_2 \cdot \text{N} \cdot \text{S} \cdot \text{Cl}$ although a distinction between these forms cannot be made.

FROM the interaction of thiocyanogen and chlorine in organic solvents Kaufmann and Liepe¹ obtained a solid, presumed to be monomeric thiocyanogen monochloride, but which Lecher and Joseph² and Baroni³ showed to be polymeric $(\text{SCNCl})_n$ ($n = \text{e.g.}, 2-6$). We have shown⁴ that the monomeric monochloride can in fact exist in organic solvents. With excess of chlorine Kaufmann and Liepe¹ obtained a relatively stable liquid, thiocyanogen trichloride, SCNCl_3 , and this was confirmed by Baroni.³ We now describe some chemical properties and the infrared absorption spectrum of the trichloride and discuss its structure in the light of the data now available.

Chemical Reactivity (by R. G. R. BACON and R. S. IRWIN).—Kaufmann and Liepe formulated the trichloride as $\text{SCl}_3 \cdot \text{C} \equiv \text{N}$ (I), *i.e.*, as cyanosulphur trichloride. If this structure were correct the relatively stable nature of the compound would present a striking contrast with the instability of known quadrivalent sulphur derivatives containing chlorine atoms. Sulphur tetrachloride, SCl_4 , is stated to be completely dissociated into SCl_2 , S_2Cl_2 , and Cl_2 in the liquid state.⁵ Alkyl- and phenyl-sulphur trichlorides, $\text{R} \cdot \text{SCl}_3$, decompose

¹ Kaufmann and Liepe, *Ber.*, 1924, **57**, 923.

² Lecher and Joseph, *Ber.*, 1926, **59**, 2603.

³ Baroni, *Atti R. Accad. Lincei*, 1936, **23**, 871.

⁴ (a) Angus and Bacon, following paper; (b) Bacon and Irwin, *J.*, 1958, 778.

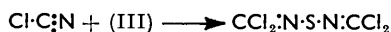
⁵ Lowry, McHatton, and Jones, *J.*, 1927, 746; Lowry and Jessop, *J.*, 1929, 1421; 1930, 782.

bromide. This was followed spectroscopically (see below). To take account of the observed mode of decomposition of thiocyanogen trichloride, the relation of (II) or (III) to cyanogen chloride and sulphur dichloride is represented as an equilibrium, which is disturbed by polymerisation of cyanogen chloride to cyanuric chloride, a process subject to catalysis.

A yellow liquid by-product, $C_2N_2Cl_4S$, appeared in yields of up to 20% in the preparation of thiocyanogen trichloride from thiocyanogen and chlorine. We regard this as sulphur bisdichlorocyanide (IV) and suggest its formation by an additional step:

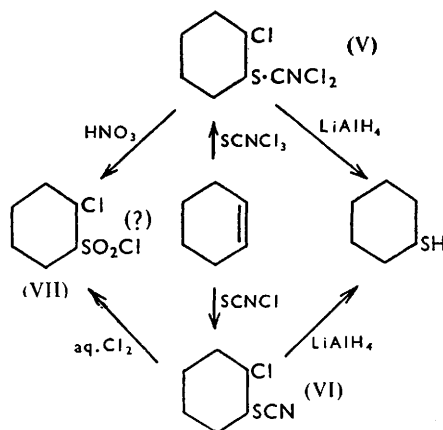


or



The $CNCl_2$ groups are linked by sulphide bonds in the postulated structure (IV), just as they are linked by a disulphide group in the compound (VIII) (see below).

Both structures (II) and (III) can be summarised in the formula $CNCl_2\cdot SCl$. The compound might therefore be expected to show typical reactions of sulphenyl chlorides, such as addition to olefins:¹⁰ $>C=C< + R\cdot SCl \longrightarrow >CCl-C(SR)<$. We found that thiocyanogen trichloride reacts vigorously with *cyclohexene* to give the expected addition compound (V) containing the dichlorothiocyano-group, a novel kind of substituent. To prove that this group is attached to the *cyclohexane* ring through sulphur, the addition compound (V) was reduced by lithium aluminium hydride to *cyclohexanethiol*. This thiol similarly resulted from reduction of 2-chloro*cyclohexyl* thiocyanate (VI), the addition product^{4a} of *cyclohexene* and thiocyanogen monochloride. The removal of chlorine from the *cyclohexane* ring in these reactions is interesting in view of the reported failure of *cyclohexyl* chloride to be reduced by lithium aluminium hydride.¹¹ The cyclic sulphide of *cyclohexene* may be an intermediate in the reduction of (V) and (VI),¹² and this sulphide is known to respond to lithium aluminium hydride.¹³ A further indication of a linkage through sulphur in (V) was the isolation of what was almost certainly 2-chloro*cyclohexane*-sulphonyl chloride (VII) when it was oxidised with nitric acid. The sulphonyl chloride (VII) was also obtained from the thiocyanate (VI) with aqueous chlorine, a known reagent for the conversion of thiocyanates into sulphonyl chlorides:¹⁴



¹⁰ N. Kharasch and co-workers, *J. Amer. Chem. Soc.*, 1947, **69**, 1612 and later papers; reviews by N. Kharasch, *J. Chem. Educ.*, 1956, **33**, 585, and N. Kharasch, Potempa, and Wehrmeister, *Chem. Reviews*, 1946, **30**, 269.

¹¹ J. E. Johnson, Blizzard, and Carhart, *J. Amer. Chem. Soc.*, 1948, **70**, 3664; cf. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publ., New York, 1956, p. 890.

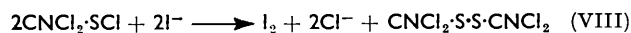
¹² Cf. van Tamelen, *J. Amer. Chem. Soc.*, 1951, **73**, 3444.

¹³ Mousseron, Jacquier, Mousseron-Canet, and Zagdoun, *Bull. Soc. chim. France*, 1952, **19**, 1042.

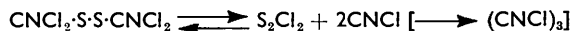
¹⁴ T. B. Johnson and Douglass, *J. Amer. Chem. Soc.*, 1939, **61**, 2548; T. B. Johnson, *Proc. Nat. Acad. Sci.*, 1939, **25**, 448.

Pure samples of (V) were relatively stable, but cyanuric chloride and other polymers were gradually formed in impure samples and appeared immediately when the hot liquid was exposed to air. The thiocyanate (VI) could not be converted into the addition compound (V) by reaction with chlorine, or the reverse by reaction with zinc or potassium iodide.

The reactivity of halogen in thiocyanogen trichloride was examined in other ways. When aqueous potassium iodide was briefly shaken with a carbon tetrachloride solution of the trichloride, reaction was confined to the sulphur-linked chlorine atom, producing one equiv. of iodine and a moderately stable liquid, believed to be the disulphide, bisdichlorothiocyanogen (VIII):



This transformation is analogous to the known reaction of sulphenyl chlorides and iodide.¹⁵ When the disulphide (VIII) decomposed, reaction appeared to take the course:



The reverse reaction was attempted by mixing sulphur monochloride and cyanogen chloride and this gave a small amount of a substance which, judged by the identity of infrared absorption spectra, was the disulphide (VIII). With iodide in acetic acid, the rapid liberation of 1 equiv. of iodine per mole of thiocyanogen trichloride was followed by slow liberation of a second equiv. With excess of silver perchlorate in benzene, not more than 2 equiv. of silver chloride were precipitated per mole of thiocyanogen trichloride. As a precipitation reagent we also used a benzene-soluble salt, sodium *OO*-di-*n*-butyl thiophosphate, $(\text{Bu}^n\text{O})_2\text{PO}\cdot\text{SNa}$,¹⁶ which we had studied in reactions with thiocyanogen monochloride.^{4b} With thiocyanogen trichloride in benzene solution, excess of the salt produced a precipitate of not more than 2 equiv. of sodium chloride, reaction of the first chlorine atom being much more rapid than that of the second. The results of these experiments suggest high reactivity in a sulphur-bound chlorine atom of the trichloride, less reactivity in a second chlorine atom, and low reactivity in the third. This is in harmony with structure (II) rather than (III).

A general conclusion to be drawn from the chemical investigations is that a cyanide group can accommodate two chlorine atoms to form a reasonably stable CNCl_2 group when this is linked to a sulphur atom. The CNCl_2 group is present in thiocyanogen trichloride (a sulphenyl chloride), in its olefin adduct (V) (a sulphide), in (IV) (a sulphide), and in (VIII) (a disulphide). The infrared absorption spectra of all four compounds contain numerous common features (see below).

Infrared Absorption Spectrum of Thiocyanogen Trichloride (By J. McC. POLLOCK and A. D. E. PULLIN).—The Raman spectrum of thiocyanogen trichloride⁹ shows the Raman shifts listed in the first column of Table 1. For easy comparison the absorption bands found in our infrared study of the compound are given in the second column.

The most important feature of the infrared spectrum is the virtual absence of a band characteristic of the $\text{C}\equiv\text{N}$ stretching vibration. This occurs around 2100 cm^{-1} and is found in the spectra of all organic thiocyanates,¹⁷ cyanogen halides,¹⁸ and the thiocyanate ion.¹⁹ In liquid layers 0.1 mm. thick we have observed a very weak narrow band at 2145 cm^{-1} in all four preparations so far examined, but this is so weak (optical density ~ 0.08), being about 500 times weaker than the 1594 cm^{-1} band, that we do not consider it to be a fundamental of SCNCl_3 . Although the intensity of the $\text{C}\equiv\text{N}$ stretching band is known

¹⁵ Orr and N. Kharasch, *J. Amer. Chem. Soc.*, 1953, **75**, 6030.

¹⁶ Foss, *Acta Chem. Scand.*, 1947, **1**, 8; cf. Ref. 4b.

¹⁷ Luskin, Gantert, and Craig, *J. Amer. Chem. Soc.*, 1956, **78**, 4965; Bacon and Guy, unpublished data.

¹⁸ West and Farnsworth, *J. Chem. Phys.*, 1933, **1**, 402.

¹⁹ Jones, *ibid.*, 1956, **25**, 1069.

to be variable, its absence from the infrared, together with Fehér and Weber's failure to observe it in their Raman work,⁹ makes it very unlikely that thiocyanogen trichloride

TABLE I.*

SCNCl ₃			CCl ₂ : CHCl †		SCNCl ₃		CCl ₂ : CHCl †	
Raman	Infrared		Raman	Infrared	Raman	Infrared	Raman	Infrared
1604 (10)	1603 (s)	} 1594 ‡	1586 (6)	1585 (s)	471 (7d)	473 (vs)	452 (3)	452 (s)
1587 (10)	1589 (s)				430 (1d)	430 (w)		
N.O.	923 (vs)	} 913 ‡	933 (1)	933 (s)	385 (3)	N.E.	380 (5)	N.E.
	905 (vs)				311 (2)	"		"
832 (1d)	834 (m)		845 (~1)	842 (s)	275 (2)	"	274 (5)	"
757 (2)	762 (w)				204 (7)	"	211 (4)	"
609 (2d)	N.O.		628 (5)	630 (s)		"	172 (5)	"
N.O.	542 (ms)	} 529 ‡						
	524 (vs)							

* N.O. = not observed; N.E. = not examined.

† Less C-H frequencies.

‡ These bands are doublets. The figures so marked are the weighted mean frequencies of the pairs, the weighting being based on the relative infrared intensities of the two components in each case.

has the triple-bond structure (I). Our infrared spectra for the pure liquid, vapour, and solution in carbon tetrachloride from 4000 cm.⁻¹ to 400 cm.⁻¹ are reproduced in Fig. 1.

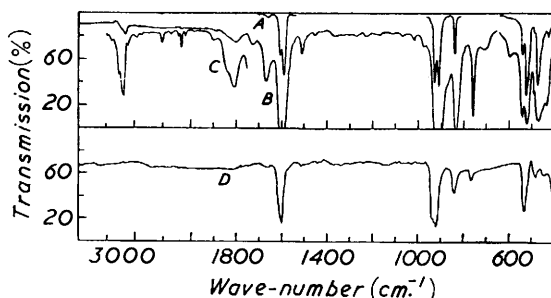


FIG. 1. Spectra of SCNCl₃. Upper panel: (A) 10% solution in CCl₄, 0.017 mm. cell in the rock-salt region, 0.027 mm. cell in the KBr region; (B) liquid SCNCl₃ in the same cells; (C) liquid SCNCl₃ in a 0.1 mm. cell. Lower panel: (D) vapour spectrum, 18 cm. cell, equilibrium vapour pressure at room temperature (~3.5 mm.).

From our interpretation of these spectra, it is possible to suggest two alternative structures (II) and (III); (II) is somewhat favoured on chemical grounds but our present spectroscopic evidence does not permit a distinction to be made between them. The strong band at 1600 cm.⁻¹ can only be explained by the presence of a C=N link, since SCNCl₃ is definitely monomeric under the experimental conditions. The C=S link is known to absorb at much lower frequencies, usually between 1100 and 1350 cm.⁻¹,²⁰ and the system ·N:C:S, like O:C:S, gives absorption bands above 2000 cm.⁻¹. A compound R·S·CCl:NR' [R = 2 : 4-C₆H₃(NO₂)₂, R' = *p*-C₆H₄Me], having a similar skeleton to that suggested for SCNCl₃, has a strong absorption band at 6μ, attributed to a C=N bond.²¹

For comparison of the spectrum of SCNCl₃ with those of related compounds, there do not appear to be any data on chlorine-substituted C=N systems. However, the spectra of NH₂Cl, NHCl₂, and NCl₃ are known,²² and in these compounds the N-Cl stretching frequencies are very similar to those of the related carbon compounds. On this basis, the structures suggested for thiocyanogen trichloride may be compared with the chlorine-substituted ethylenes.

It is clear from Table I that there is a close similarity between the spectra of thiocyanogen trichloride and of trichloroethylene²³ with respect to both frequencies and

²⁰ Mecke and Lüttringhaus, *Z. Naturforsch.*, 1955, **10b**, 367.

²¹ Havlik and Walk, *J. Amer. Chem. Soc.*, 1955, **77**, 5171.

²² Moore and Badger, *ibid.*, 1952, **74**, 6076.

²³ Allen and Bernstein, *Canad. J. Chem.*, 1954, **32**, 1044.

intensities. In view of the similarities of the disposition of atomic masses and force constants between the structures (II) and (III) and trichloroethylene, this affords strong evidence for these structures.* Distinction between the structures (II) and (III) on spectroscopic grounds does not yet seem possible. The spectral data for CF_2CCl_2 ,²⁴ CHCl:CCl_2 ,²³ and *cis*- and *trans*- CHCl:CHCl ^{25,26} suggest that a C-Cl stretching motion only gives rise to bands above 900 cm^{-1} in the antisymmetric stretching mode of a $=\text{CCl}_2$ group. This fact, however, does not necessitate assigning structure (III) to thiocyanogen trichloride in order to account for the 913 cm^{-1} band. Organic sulphides $\text{R}\cdot\text{S}\cdot\text{R}$ give frequencies very close to those of the corresponding halides RCl ,²⁷ so that interaction between the C-Cl and C-S stretching motions should occur in structure (II), making it, like structure (III), dynamically similar to trichloroethylene.

Because of the low symmetry of structure (II) or (III), and the strong interaction expected between the individual bond-stretching motions, it is not profitable to try to assign completely the bands to definite vibrational modes. It is probable that the 913 cm^{-1} band corresponds approximately to an antisymmetric stretching mode of the carbon single bonds. The band at 529 cm^{-1} may arise largely from S-Cl stretching motion (in CCl_3SCl a Raman shift of 536 cm^{-1} is assigned to the S-Cl stretching mode,²⁸ while in SCl_2 the S-Cl stretching vibrations occur²⁹ at 436 and 516 cm^{-1}), although, structure (III) being assumed, an alternative assignment to an N-S stretching mode is possible, as the N-S link gives bands in the 550 cm^{-1} region.³⁰

The spectra afford strong evidence for the presence of more than one structure in the samples of thiocyanogen trichloride. It is evident, *e.g.*, from Table I, that, the splitting of the major bands being disregarded, thiocyanogen trichloride shows one or possibly two bands more, in the bond-stretching region, than can be attributed to fundamental bands of a single structure, and since it does not seem possible to account for any of these bands as combination tones, the presence of more than one structure must be assumed. We have demonstrated the formation of thiocyanogen trichloride from sulphur dichloride and cyanogen chloride in ethyl bromide solution spectroscopically, by observing the increase in intensity with time of the two doublet bands at 1603 , 1589 , and 923 , 905 cm^{-1} . Spectra taken at different time intervals for a reaction mixture at 0° are shown in Fig. 2. This demonstrates the production of thiocyanogen trichloride, in agreement with the reversible reaction scheme on p. 765. The additional absorption band or bands in the spectrum of thiocyanogen trichloride may be due to other species in equilibrium with SCNCl_3 .

The infrared spectra of the related compounds (IV), (V), and (VIII) have been obtained in the rock-salt region (Figs. 3 and 4). The spectra of the sulphide (IV) and the disulphide (VIII) are very similar to that of thiocyanogen trichloride, and in each case there is no absorption in the 2100 — 2200 cm^{-1} region. As might be expected, the spectrum of the disulphide (VIII), in which the two CNCl_2 groups are linked by a disulphide unit is more similar to that of thiocyanogen trichloride than that of the sulphide (IV). In (VIII) the bands corresponding to the 1594 and the 757 cm^{-1} band of thiocyanogen trichloride are both displaced to lower frequencies (1588 and 735 cm^{-1}). In (IV) the corresponding lower-frequency band is at 777 cm^{-1} . Neither the sulphide (IV) nor the disulphide (VIII) shows a band of comparable intensity to the moderately strong band in thiocyanogen

* In CDCl:CCl_2 the 933 cm^{-1} band is replaced by a band at 876 cm^{-1} ; here, as in the other chlorine-substituted ethylenes, the interaction between the C-D bending and C-Cl stretching motions has lowered the frequency of the C-Cl stretching mode, so that the comparison with the spectra of CHCl:CCl_2 , as in Table I, rather than with CDCl:CCl_2 , is more appropriate.

²⁴ Nielsen and Claassen, *J. Chem. Phys.*, 1950, **18**, 485.

²⁵ Bernstein and Ramsay, *ibid.*, 1949, **17**, 556.

²⁶ Bernstein and Pullin, *Canad. J. Chem.*, 1952, **30**, 963.

²⁷ Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.

²⁸ Fehér and Berthold, *Z. anorg. Chem.*, 1956, **234**, 60.

²⁹ Clara Otero and José R. Barceló Matutano, *Anal. Fis. Quím.*, 1956, **52**, B, 291.

³⁰ Hofmann and Andress, *Z. anorg. Chem.*, 1956, **234**, 234.

trichloride at 834 cm^{-1} . The similarity of the spectra of thiocyanogen trichloride, (IV), (V), and (VIII) extends to the combination tones and overtones. Table 2 shows the probable attribution of the stronger infrared combination tones. For thiocyanogen trichloride the uncertainty with regard to resonance splitting of the combination levels which involve the 913 cm^{-1} fundamental makes the attributions less sure.

FIG. 2. Formation of SCNCl_3 from SCl_2 and ClCN in ethyl bromide solution at 0° : equivalent quantities of SCl_2 and ClCN , solution 50% by volume in ethyl bromide, 0.1 mm. cell.

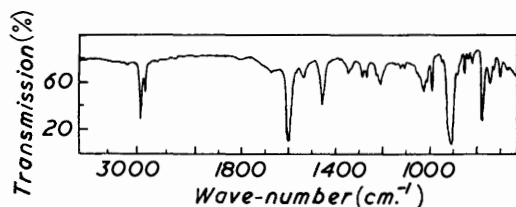
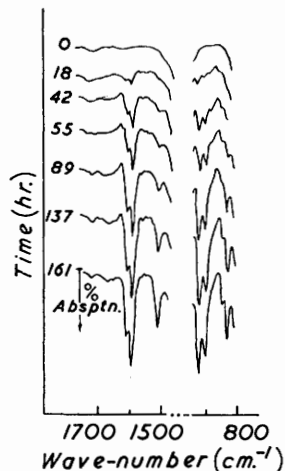


FIG. 3. Upper panel: spectrum of liquid film of (IV), i.e., $(\text{CNCl}_2)_2\text{S}$. Lower panel: spectrum of liquid film of (VIII), i.e., $(\text{CNCl}_2)_2\text{S}_2$.

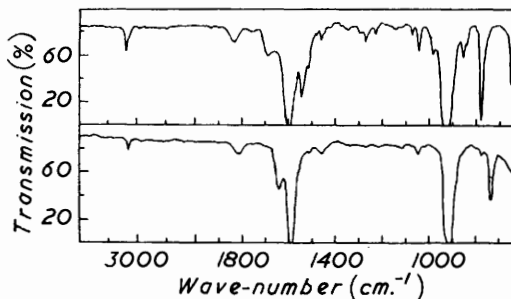


FIG. 4. Spectrum of liquid film of (V), i.e., adduct of cyclohexene and SCNCl_3 .

The spectrum of the addition compound (V) is more complex than those of thiocyanogen trichloride or structures (IV) and (VIII). The strongest bands in the rock-salt region are at 2935 , 1597 , 908 , and 775 cm^{-1} .

Slight further support for the presence of more than one structure in the samples of

TABLE 2.

Thiocyanogen trichloride	(IV)	(VIII)	(V)
3270			
1594 + 1665 = 3259			
3180	$2 \times 1594 = 3188$	3185	$2 \times 1597 = 3194$
1840 (sh)	$2 \times 923 = 1846$	1833	$2 \times 923 = 1846$
1805	$2 \times 905 = 1810$	1813	$2 \times 914 = 1828$
1665	$913 + 757 = 1670$	1687	$914 + 735 = 1649$
	$2 \times 832 = 1664$	$923 + 777 = 1700$	1675
1506	$2 \times 757 = 1514$	1543	$908 + 775 = 1683$
	$2 \times 777 = 1554$	1460	$2 \times 775 = 1550$
		1400	$2 \times 735 = 1470$
		1533	

thiocyanogen trichloride investigated is afforded by the splitting of the fundamental band at 1594 cm^{-1} . The combination tone $757 + 832 = 1589$ is a little lower than is required to give rise to the two components at 1589 and 1604 cm^{-1} by Fermi resonance,

which suggests that the two components of the 1594 cm.^{-1} band are due to the presence of two distinct structures. The splitting of the 913 cm.^{-1} band can be accounted for by interaction with the combination tone $609 + 311 = 920$. It seems likely that several low-lying fundamentals have not been observed. In particular there should be a fundamental corresponding to the C-S-Cl (or N-S-Cl) in plane bending. In $\text{CCl}_3\text{-SCl}$ a frequency of 131 cm.^{-1} was attributed²⁸ to the C-S-Cl deformation mode. A fundamental at about this frequency could provide an explanation of the splitting of the 529 cm.^{-1} band (*e.g.*, $385 + 144 = 529$). There is, however, the possibility of rotational isomerism due to different orientations of the S-Cl group.

EXPERIMENTAL

Thiocyanogen Trichloride.—(a) Bromine (0.1 mole) was rapidly decolorised when stirred at room temperature with lead thiocyanate (0.105 mole) in ethyl bromide (~250 ml.). The resulting thiocyanogen solution was separated from lead salts and treated with a stream of dry chlorine until saturated (periods of up to 1 hr.) at room temp. or at 0° . An orange colour developed. After removal of solvent and excess of chlorine at $\sim 10^\circ/20\text{ mm.}$, thiocyanogen trichloride was collected in yields of 11–13 g. (70–80%) as a pungent orange liquid, b. p. $40\text{--}41^\circ/9\text{ mm.}$, which distilled at $154\text{--}155^\circ/1\text{ atm.}$ with very little decomposition; Kaufmann and Liepe¹ give b. p. $54\text{--}56^\circ/20\text{ mm.}$, $152\text{--}153^\circ/1\text{ atm.}$ (Found: C, 7.8; N, 8.1; S, 19.1; Cl, 64.4. Calc. for CNCl_3S : C, 7.3; N, 8.5; S, 19.4; Cl, 64.7%). A pungent yellow liquid, regarded as *sulphur bisdichlorocyanide* (IV), b. p. $50^\circ/0.2\text{ mm.}$, was also obtained in these preparations as a clean-cut fraction (1–3 g.) (Found: C, 10.9; N, 12.3; S, 13.6; Cl, 63.4. $\text{C}_2\text{N}_2\text{Cl}_4\text{S}$ requires C, 10.6; N, 12.4; S, 14.1; Cl, 62.8%). (b) Sulphur dichloride, b. p. 59° , was prepared as described by Bothamley.³¹ Cyanogen chloride (12 g.) from a cylinder (Imperial Chemical Industries Limited) was condensed into ethyl bromide (40 ml.) containing sulphur dichloride (3 g.) and the solution was kept at 0° for 5 days. Thiocyanogen trichloride (1.3 g., 27%), b. p. $50\text{--}51^\circ/18\text{ mm.}$, was isolated as in method (a) and was converted into 2-chlorocyclohexyl dichlorothiocyane (V), identical in infrared absorption spectrum with the product obtained (see below) by using the thiocyanogen trichloride obtained by method (a).

Decomposition Products.—Carefully redistilled thiocyanogen trichloride remained unchanged for many weeks in sealed vessels. Decomposition, particularly marked in impure samples, was shown by deposition of cyanuric chloride, m. p. 145° (Found: C, 20.0; N, 22.7; Cl, 57.7. Calc. for $\text{C}_3\text{N}_3\text{Cl}_3$: C, 19.5; N, 22.7; Cl, 57.75%). A reasonably pure sample of the trichloride, which had been stored in the dark in a stoppered bottle for about one year, had deposited 61% of the theoretical amount of cyanuric chloride; the liquid residue yielded sulphur dichloride, b. p. $59^\circ/1\text{ atm.}$, as a dark red fuming liquid (70%), and a little unchanged thiocyanogen trichloride.

Hydrolysis Products.—Thiocyanogen trichloride was completely hydrolysed, exothermically, by shaking with about ten times its weight of cold water for about 1 hr. Sulphur was deposited. The pale yellow, acidic, aqueous solution responded strongly to qualitative tests for cyanogen chloride, hydrogen sulphide, and sulphate and chloride ions, responded weakly to tests for cyanide, thiocyanate, and sulphite ions, and gave weak indications of ammonia when warmed with alkali.

Reaction with Silver Perchlorate.—When 25 ml. portions of a benzene solution of silver perchlorate (0.10M) were treated with suitable proportions (see below) of a benzene solution of thiocyanogen trichloride (0.17M), during about 3 min. at room temp., the weight of precipitate deviated from the expected figure for silver chloride by $\pm 10\%$. Use of restricted amounts of thiocyanogen trichloride showed that not more than two-thirds of its chlorine could be thus utilised; 1 mol. of $\text{SCNCl}_3 + 1.0, 2.0, \text{ or } 3.0$ mol. of AgClO_4 gave 1.0, 2.0, and 2.0 mol. of AgCl , respectively. In the experiment at a 1 : 2 molar ratio the filtrate from the silver chloride gave no response with a fresh portion of silver perchlorate.

Reaction with Sodium OO-Di-n-butyl Thiophosphate.—This salt was prepared as previously described.^{4b} Solutions in carbon tetrachloride ($\sim 0.1\text{M}$), when mixed with solutions of thiocyanogen trichloride in carbon tetrachloride ($\sim 0.1\text{M}$), yielded precipitates of sodium chloride

³¹ Bothamley, *Trans. Faraday Soc.*, 1928, **24**, 47.

which sometimes contained a little organic matter but were free from thiocyanate; they were 97—100% pure by titration; 1.0 mol. of SCNCl_3 + 1.0 mol. of $(\text{BuO})_2\text{POSNa}$ gave 0.97 mol. of NaCl in a few minutes. The filtrate, treated with a further 1.0 mol. of $(\text{BuO})_2\text{POSNa}$, reacted slowly to give a fine precipitate and required several hours before yielding a further 1.07 mol. of NaCl in coagulated form. A similar result was obtained by mixing 1.0 mol. of SCNCl_3 + 2.0 mol. of $(\text{BuO})_2\text{POSNa}$ (yield, 1.96 mol. of NaCl). With 1.0 mol. of SCNCl_3 + 3 or more mol. of $(\text{BuO})_2\text{POSNa}$ the fine precipitate remained in suspension, coagulation presumably being prevented by the unchanged sodium dibutyl thiophosphate.

Reaction with Sodium or Potassium Iodide.—(i) 0.1M-Solutions of thiocyanogen trichloride in carbon tetrachloride were shaken for 3 min. with excess of 10% aqueous potassium iodide and the liberated iodine was estimated with thiosulphate. An average of 0.975 equiv. of iodine was found per mole of thiocyanogen trichloride. (ii) 0.1M-Solutions of thiocyanogen trichloride in dry acetic acid (5% of acetic anhydride present) liberated iodine when treated at room temperature with excess of 5% potassium iodide solution in the same solvent. The titre after 3 min. corresponded with 1.03 equiv. of iodine per mole of thiocyanogen trichloride and thereafter rose very slowly towards 2 equiv. per mole. Under similar conditions, but using sodium iodide, which Orr and Kharasch¹⁵ found to react more rapidly than potassium iodide with sulphenyl chlorides, 2.03 equiv. of iodine per mole were liberated after 3 minutes' reaction. Sulphur and cyanogen chloride were detected in this reaction.

Bisdichlorothiocyangen (VIII).—(a) Thiocyanogen trichloride (6.0 g.) in carbon tetrachloride (50 ml.) was vigorously shaken for 3 min. with a large excess of aqueous potassium iodide (30 g. in 50 ml. of water). The liberated iodine was immediately removed with aqueous thiosulphate and the decolorised organic layer was separated, filtered from deposited sulphur, dried, and distilled; the reaction product, now a red oil, yielded *bisdichlorothiocyangen* (VIII) as a pale yellow liquid with no fume and little odour (2.1 g., 45%), b. p. 64—68°/0.15 mm. (Found: C, 9.3; N, 10.6; S, 24.4; Cl, 54.6. $\text{C}_2\text{N}_2\text{Cl}_4\text{S}_2$ requires C, 9.3; N, 10.8; S, 24.8; Cl, 55.1%). One rather impure sample of this product decomposed during 4 days at room temp., depositing cyanuric chloride, m. p. and mixed m. p. 146°, and leaving a yellow oil, b. p. 136°, with the characteristic odour of sulphur monochloride.

(b) Sulphur monochloride (3.0 g.) and excess of cyanogen chloride (12 g.) in dry ethyl bromide (40 ml.) were kept for 6 days in the dark at 0°. After removal of solvent and unchanged reagents at 20 mm. pressure, there remained a small amount of yellow oil which yielded a fraction (0.54 g., 10%), b. p. 76—78°/0.4 mm.; this showed an infrared absorption spectrum identical with that shown by the product of method (a).

2-Chlorocyclohexyl Dichlorothiocyante (V).—Thiocyanogen trichloride (10 g.) in carbon tetrachloride (40 ml.) was treated during ~20 min. with excess of cyclohexene (15 g., 3 mol.) in carbon tetrachloride (10 ml.). The temperature rose to ~60° and the colour of the reagent disappeared. Distillation yielded *2-chlorocyclohexyl dichlorothiocyante* (V) (12.0 g., 80%), as a colourless oil, b. p. 80—82°/0.1 mm., n_D^{25} 1.5620, with a sweetish but disagreeable odour (Found: C, 34.35; H, 3.8; N, 5.8; S, 12.8; Cl, 43.15. $\text{C}_7\text{H}_{10}\text{NCl}_3\text{S}$ requires C, 34.1; H, 4.1; N, 5.7; S, 13.0; Cl, 43.15%). It was not obtained when *2-chlorocyclohexyl thiocyanate* (VI)^{4a} was treated with excess of chlorine in ethyl bromide. It was characterised by its infrared absorption spectrum (p. 770) and by its reduction and oxidation products (see below). Pure samples underwent no change during storage for several weeks, but impurities promoted decomposition to cyanuric chloride, amorphous white solid, and oils of higher b. p. (e.g., 80—130°/0.1 mm.). It appeared to be largely unchanged after 2 hours' heating with powdered zinc at 100°. It liberated iodine when shaken (3 min.) with sodium iodide in acetic acid, but no organic reaction product was isolated.

cycloHexanethiol.—(a) *2-Chlorocyclohexyl dichlorothiocyante* (V) (4.9 g., 0.02 mole) was slowly treated in ether with lithium aluminium hydride (0.04 mole). Reaction was completed by refluxing (2 hr.), the product decomposed with water, and the dried ethereal solution distilled, to yield *cyclohexanethiol* (0.55 g., 24%), b. p. 158—160°/1 atm. (lit. 158—160°). It was characterised as 1-cyclohexylthio-2:4-dinitrobenzene, m. p. 148°, as quoted by Bost, Turner, and Conn³² (Found: C, 51.15; H, 5.0; N, 10.15; S, 11.0. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{N}_2\text{S}$: C, 51.1; H, 5.0; N, 9.9; S, 11.3%).

(b) Reduction was carried out similarly, by use of *2-chlorocyclohexyl thiocyanate* (VI)^{4a} (0.02 mole) and lithium aluminium hydride (0.03 mole). An ammoniacal odour was noted.

³² Bost, Turner, and Conn, *J. Amer. Chem. Soc.*, 1933, **55**, 4956.

cycloHexanethiol was obtained in 30% yield and characterised as 1-*cyclohexylthio*-2 : 4-dinitrobenzene, m. p. and mixed m. p. with the sample from method (a) 148°. A liquid fraction, b. p. 56—57°/15 mm., obtained in one experiment, may have contained *cyclohexene thioepoxide*; it reacted with methyl iodide, as described for the thioepoxide by van Tamelen.¹²

cycloHexanesulphonyl Chloride (VII).—2-Chloro*cyclohexyl* dichlorothiocyante (V) (4.9 g., 0.02 mole) reacted very vigorously when added dropwise to fuming nitric acid (7.5 ml.), cooled by an ice-salt bath. After 2 days at room temperature the product was added to ice, and the oil which separated was ether-extracted and distilled, yielding a well-defined fraction (0.64 g., 15%), b. p. 72°/0.1 mm., n_D^{25} 1.5180, probably 2-chloro*cyclohexanesulphonyl chloride* (VII) (Found: C, 33.4; H, 4.3; S, 14.6; Cl, 32.6. $C_6H_{10}O_2Cl_2S$ requires C, 33.2; H, 4.6; S, 14.8; Cl, 32.7%). It resisted hydrolysis, but after boiling with water for 23 hr. the solution of sulphonic acid yielded a *S*-benzylthiuronium salt, m. p. 150—151°, which was not analytically pure. Preparation of (VII) was attempted by treating 2-chloro*cyclohexyl* thiocyanate (VI) in water with a stream of chlorine, following the general procedure of Johnson and Douglass.¹⁴ The product (42% yield) closely resembled that described above, but was not analytically pure. The infrared absorption spectrum of a liquid film showed very strong bands at 1165 and 1378 cm^{-1} , attributed to SO_2Cl , medium bands at 740 and 754 cm^{-1} , attributed to CCl , and other main bands at 2948 (s), 2869 (m), 2164 (w), 1458 (s), 1287 (m), 1266 (w), 1206 (m), 1125 (w), 911 (w), and 817 cm^{-1} (w).

Cryoscopic Data.—These were obtained as described for thiocyanogen monochloride.^{4b} (i) In benzene solution (1—2%) the average f. p. depression indicated a molecular weight of 159 ($CNCl_3S$ requires M , 164.5). (ii) Benzene solutions of chlorine and thiocyanogen (~0.1M) were mixed in a 3 : 1 molar ratio. Found f. p. depression, 0.538°; calc. for $3Cl_2 + (SCN)_2$ or $2Cl_2 + 2SCNCl$, 0.547°; calc. for $2SCNCl_3$, 0.274°. (iii) Benzene solutions of thiocyanogen and thiocyanogen trichloride (~0.1M) were mixed in a 1 : 1 molar ratio. Found f. p. depression, 0.745°; calc. for no reaction, 0.777°; calc. for $SCNCl_3 + (SCN)_2 \rightarrow 3SCNCl$, 1.166°.

Ebullioscopic Data.—In carbon tetrachloride, on use of a modified Cottrell apparatus,³³ the average elevation of b. p. indicated a molecular weight of 171.

Vapour Density.—In a conventional type of Victor Meyer apparatus, heated by boiling ethylene glycol, vapour density measurements indicated a molecular weight of 160.

Ultraviolet Absorption Spectra.—A Unicam S.P. 500 instrument was used. Absorption in the visible and the near-ultraviolet regions, by carbon tetrachloride solutions, was limited to the region above ~280 $m\mu$. With thiocyanogen trichloride, absorption began at 480 $m\mu$ and reached a maximum at 345 $m\mu$ ($\log \epsilon$ 1.93). With sulphur dichloride, absorption began at 450 $m\mu$ and reached no maximum but showed an inflection at 310 $m\mu$ ($\log \epsilon$ 2.40). With sulphur monochloride, absorption began at 410 $m\mu$ and reached a maximum at 304 $m\mu$ ($\log \epsilon$ 3.06).

Infrared Absorption Spectra.—Thiocyanogen trichloride was fractionated with a 12" jacketed column filled with glass helices; $SCNCl_3$ was collected at 50—51°/18 mm. A number of separate preparations were examined. The spectra were taken with a Perkin-Elmer Model 21 double-beam spectrophotometer, NaCl and KBr prisms being used. Water vapour, carbon dioxide, and ammonia bands were used for calibration. Spectra were taken as soon as possible after the liquid was fractionated (usually within about 10 min.) in order to avoid decomposition, although pure samples kept in a dry atmosphere for a month showed only very slight traces of decomposition. The vapour spectra were taken with 18 cm. cells, at room temperature (estimated vapour pressure 3.5 mm.). The vapour readily attacked several cements used for fixing the windows to the cells, giving spurious peaks after a few minutes. Eventually Bakelite cement No. J 11185 was found to be satisfactory at least for reasonable periods.

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³³ Linstead, Elvidge, and Whalley, "Modern Techniques in Organic Chemistry," Butterworths, London, 1955, p. 148.