124. *The Structure of the Dimer of Thiocarbonyl Chloride and its Hydrolysis Product. Infrared Absorption Data on Some Compounds containing the Thiocarbonyl Group.*

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The infrared absorption spectra of dimeric thiocarbonyl chloride and its hydrolysis product confirm the structures 2 : 2 : 4 : 4-tetrachloro-1 : 3-dithia*cyclo*butane and 4 : 4-dichloro-1 : 3-dithia*cyclo*butan-2-one, respectively, for these compounds. The assignment for the C=S stretching frequency is discussed and the spectra of some compounds containing this group are reported.

THE photochemical dimerisation of thiocarbonyl chloride was first observed by Rathke;[1] Carrara[2] confirmed the dimeric nature of the product. The trichloromethyl chlorodithioformate structure (I), originally assigned by Rathke, was questioned by Schönberg and Stephenson,[3] who proposed the cyclic 2 : 2 : 4 : 4-tetrachloro-1 : 3-dithia*cyclo*butane structure (II) which was supported by Delépine, Labro, and Lange.[4] Schönberg and

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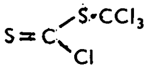
[1] Rathke, *Annalen*, 1873, **167**, 205; *Ber.*, 1888, **21**, 2539.

[2] Carrara, *Gazzetta*, 1893, **23**, 12.

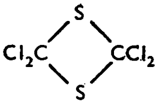
[3] Schönberg and Stephenson, *Ber.*, 1933, **66**, 567.

[4] Delépine, Labro, and Lange, *Bull. Soc. chim. France*, 1935, **2**, 1970.

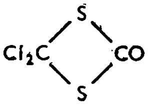
Stephenson found that the dimer is depolymerised both thermally and photochemically and, on controlled hydrolysis, furnishes a derivative, $C_2S_2OCl_2$, for which they advanced structure (III). To avoid structural implications the name " carbon sulphoxy chloride " has been suggested [5] for the hydrolysis product and will be used in this paper. Recently White [5] has shown that the compounds identified previously as thiocarbamoyl oxides (commonly known as " thiuram oxides ") (IV) are, instead, the isomeric thiocarbamoyl carbamoyl sulphides (V). White believes that the formation of the sulphides (V) from " carbon sulphoxy chloride " and secondary amines gives some credence to structure (VI), considered but rejected by Delépine, Labro, and Lange [4] for " carbon sulphoxy chloride " as not according with refractivity data.



(I)



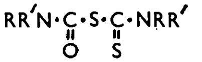
(II)



(III)

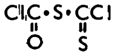
$\mathrm{RR'N{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}O{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}NRR'}$

(IV)



$\mathrm{RR'N{\cdot}\underset{\underset{O}{\|}}{C}{\cdot}S{\cdot}\underset{\underset{S}{\|}}{C}{\cdot}NRR'}$

(V)



$\mathrm{Cl\underset{\underset{O}{\|}}{C}{\cdot}S{\cdot}\underset{\underset{S}{\|}}{C}Cl}$

(VI)

In the hope of establishing the structure of dimeric thiocarbonyl chloride and " carbon sulphoxy chloride " their infrared absorption spectra have been examined. Demonstration of the presence or absence of a C=S group in the dimer should serve to distinguish between formulæ (I) and (II). Similarly, for " carbon sulphoxy chloride," the presence of a C=O and/or C=S group should permit, if not the complete establishment of its structure, the elimination of some formulæ previously advanced.

The spectrum of a carbon disulphide solution (~10%) of thiocarbonyl chloride has three very strong bands at 1120, 810, and 780 cm.$^{-1}$. These correspond to the 1138 cm.$^{-1}$ band and the doublet at 811 and 794 cm.$^{-1}$ recently reported by Haszeldine and Kidd,[6] the former being allocated to the C=S stretching mode, the others to the C–Cl stretching vibrations. In the spectrum of the dimer (Figure) as a solid film (thickness ~0·05 mm.), nowhere in the range 5000—850 cm.$^{-1}$ did the optical density exceed 0·15. A strong band of density 1·3 occurred at 810 cm.$^{-1}$ adjacent to a broad region of strong absorption (D >1·5) extending from 800 cm.$^{-1}$ to beyond 650 cm.$^{-1}$. The spectrum of a solid film (~0·05 mm.) of " carbon sulphoxy chloride " is much more complex than that of a solution in carbon disulphide (Figure). In the solid, complex absorption appears in the region 1800—1700 cm.$^{-1}$ with a weak band at 1837 cm.$^{-1}$, two strong bands at 1767 and 1717 cm.$^{-1}$, and a weak shoulder at 1656 cm.$^{-1}$. In solution only two strong bands appear, at 1780 and 1710 cm.$^{-1}$. Strong absorption also occurs in the region 880—700 cm.$^{-1}$. The location of the bands is given in the subjoined Table.

Infrared spectrum of " carbon sulphoxy chloride."

Solid	1837 w,	1767 s,	1717 s,	1656 w, sh,	1599 m,	1500 w,	1459 w,	1227 w,	1110 w,	968 m
CS_2 solution		1780 s,	1710 s,		CS_2			1221 w,	1092 w,	943 m

Solid	880 s,	837 m, sh,	829 s,	807 w, sh,	793 w,	769 w, sh,	752 s,	732 s,	697 m
CS_2 solution	859 s,	831 s					758 s,	715 m	

Herzberg,[7] Bailey and Cassie,[8] Robinson,[9] and McKean, Callomon and Thompson,[10] studied the spectra of carbon disulphide and carbonyl sulphide but assignments based on

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[5] White, *Canad. J. Chem.*, 1954, **32**, 867.

[6] Haszeldine and Kidd, *J.*, 1955, 3871.

[7] Herzberg, " Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, 1950, p. 285.

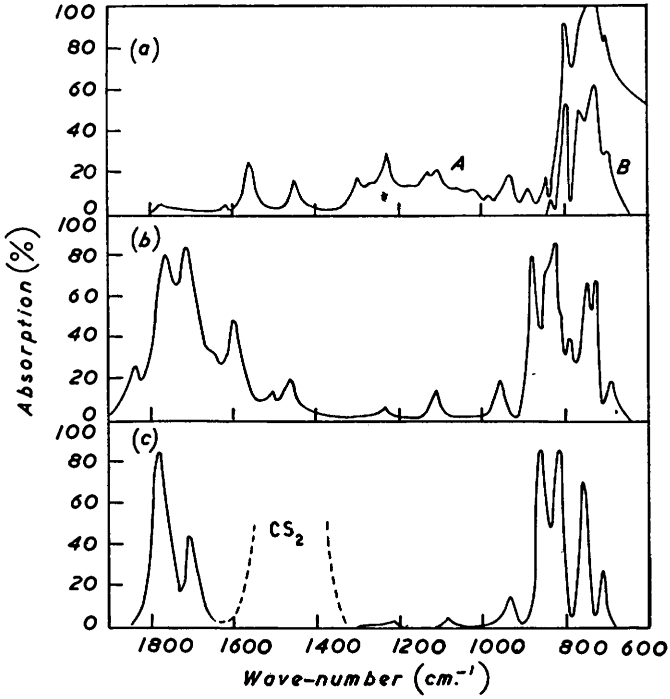
[8] Bailey and Cassie, *Proc. Roy. Soc.*, 1932, *A*, **135**, 375.

[9] Robinson, *J. Chem. Phys.*, 1951, **19**, 881.

[10] McKean, Callomon, and Thompson, *ibid.*, 1952, **20**, 520; *Proc. Roy. Soc.*, 1951, *A*, **200**, 341.

these simple, doubly-unsaturated molecules cannot be regarded as a reliable guide to the position of the C=S stretching vibration in other compounds. In view of the meagre and conflicting evidence on the assignment of the C=S band in various substances of this type [11-15] we examined the spectra of some representative compounds.

As already noted, the spectrum of thiocarbonyl chloride shows three intense bands; of these, the band at 1120 cm.$^{-1}$ is assigned to the C=S stretching vibration. Ethylene trithiocarbonate in carbon tetrachloride shows strong absorption at 1074 cm.$^{-1}$ (1060 cm.$^{-1}$ as thin solid film). This agrees with the value 9·27 μ (1078 cm.$^{-1}$) recently reported by Haszeldine and Kidd [6] for the same compound and is assigned to the C=S vibration. The spectrum of potassium ethyl xanthate (potassium chloride disc) shows three bands of comparable intensity at 1143 cm.$^{-1}$, a doublet at 1120 and 1105 cm.$^{-1}$ (main peak), and at 1055 cm.$^{-1}$; a weak band also appears at 820 cm.$^{-1}$. It is known that the C–O band appears in the region ~1100 cm.$^{-1}$ (cf. Jones, Kynaston, and Hales [16]), and the precise identity of the C=S band is not certain in this case. The 820 cm.$^{-1}$ band may be due to the C–S stretching vibration but this would appear to be somewhat outside the normal range (cf. Bellamy,[13] p. 291). Comparison of the spectra of urea and thiourea, and carbanilide and thiocarbanilide (potassium chloride discs) permits the definite assignment of the C=S vibration in thiourea and thiocarbanilide to 1408 and 1344 cm.$^{-1}$, respectively, by elimination of some bands common to both systems. Similarly, in the case of oxamide (ν for



(*a*) *Dimer of thiocarbonyl chloride: A, solid film, ~50 μ; B, capillary.*
(*b*) *" Carbon sulphoxy chloride," solid film, ~50 μ.*
(*c*) *" Carbon sulphoxy chloride," solution in* CS$_2$, *60 μ path length.*

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[11] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[12] Thompson, Nicholson, and Short, *Discuss. Faraday Soc.*, 1950, **9**, 222.
[13] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 293.
[14] Miller in Gilman's " Organic Chemistry," John Wiley and Sons Inc., 1953, Vol. III, ch. 2.
[15] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.
[16] Jones, Kynaston, and Hales, following paper.

C=O, 1660 cm.$^{-1}$) and dithio-oxamide, the C=S band in the latter appears at 1425 cm.$^{-1}$. Again comparison of the spectra of β-resorcylic acid (ν for C=O 1637 cm.$^{-1}$) and the corresponding dithio-acid (2 : 4-dihydroxydithiobenzoic acid) suggests that the band at 1125 cm.$^{-1}$ in the latter is due to the C=S vibration. No definite conclusions could be drawn from the spectra of phloroglucinolcarboxylic acid and its dithio-analogue (2 : 4 : 6-trihydroxydithiobenzoic acid) because of their greater complexity. It is thus evident that the frequency of the C=S stretching mode is subject to wide variations within the range 1400—1000 cm.$^{-1}$ depending upon the nature of the structural environment. Since this work was completed Mecke, Mecke, and Lüttringhaus[17] have published data on the position of the C=S and C=O bands in a number of corresponding compounds. They found the ratio of the two frequencies in any pair of compounds to be fairly constant and involving an overall C=S frequency range of 1234—1053 cm.$^{-1}$ for compounds other than those containing the thioureide function where the range was 1400—1130 cm.$^{-1}$. Moreover, the relative intensities of the two bands were approximately the same. Mecke and Mecke[18] have also published additional information on the spectra of some cyclic thiopeptides, the values for the C=S stretching frequency again falling in the same range (1209—1047 cm.$^{-1}$). On somewhat slender evidence, Marvel, Radzitzky, and Brader[19] tentatively assign the C=S frequency in dithio-esters to the 1195—1170 cm.$^{-1}$ region and in thioamides to 1265—1180 cm.$^{-1}$.

These considerations together with some intensity calculations indicate that a solid sample, 0·05 mm. thick, of material possessing structure (I) should have an absorption band with an optical density of the order of 5 somewhere in the range 1400—1000 cm.$^{-1}$ The absence of any band, even approaching this order of intensity, strongly supports the cyclic structure (II) for the dimer of thiocarbonyl chloride. The C–S stretching vibration, which should figure in the spectrum of this compound, normally appears as a weak absorption in the range 700—600 cm.$^{-1}$. This region also covers the strong C–Cl stretching absorption, and the identification of the C–S modes with any certainty in the spectrum of dithiocarbonyl chloride spectrum is not possible. Similar cyclic structures have been postulated for the related silicon oxyhalides, thiohalides, and selenohalides.[20-22] Thioaldehydes and thioketones also polymerise readily to give dimeric and trimeric cyclic compounds from which the C=S group is absent.[23]

The spectrum of " carbon sulphoxy chloride " displays marked absorption in the 1800—1700 cm.$^{-1}$ region and this may be taken as fairly conclusive evidence of the presence of a C=O group. The complex nature of the absorption, particularly of the solid, is not understood. In solution, two strong bands only appear in this range and these have shifted slightly from their position in the spectrum of the solid. In the range where C=S absorption should appear, two weak bands occur at 1227 and 1110 cm.$^{-1}$ but their low intensity suggests that they are not due to the C=S stretching vibration. The bands at 880—700 cm.$^{-1}$ arise from the C–Cl and C–S stretching vibrations and similar absorption is to be found in the spectrum of the dimer of thiocarbonyl chloride. These results strongly support the cyclic structure (III) for " carbon sulphoxy chloride."

EXPERIMENTAL

The Dimer of Thiocarbonyl Chloride and " Carbon Sulphoxy Chloride."—These compounds were prepared by Schönberg and Stephenson's method[3] and were crystallised from light petroleum (b. p. 60—80°) giving materials of m. p. 119° and 70°, respectively. " Carbon sulphoxy chloride " sublimes easily.

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[17] Mecke, Mecke, and Lüttringhaus, *Z. Naturforsch.*, 1955, **10**, *B*, 367.

[18] Mecke and Mecke, *Chem. Ber.*, 1956, **89**, 343.

[19] Marvel, Radzitzky, and Brader, *J. Amer. Chem. Soc.*, 1955, **77**, 5997.

[20] Etienne, *Bull. Soc. chim. France*, 1953, 791.

[21] Schumb and Holloway, *J. Amer. Chem. Soc.*, 1941, **63**, 2753.

[22] Weiss and Weiss, *Angew. Chem.*, 1954, **66**, 714.

[23] Rodd, " Chemistry of Carbon Compounds," Elsevier Publishing Co., Vol. IA, 1951, pp. 487, 521; Vol. IIIA, 1954, 516.

2 : 4-*Dihydroxy- and* 2 : 4 : 6-*Trihydroxydithiobenzoic Acids.*—With the exception of these two compounds all the other compounds containing the C=S group were commercial specimens suitably purified. 2 : 4-Dihydroxydithiobenzoic acid was prepared by Lippmann's method[24] from resorcinol and potassium ethyl xanthate. It was also obtained by shaking a solution of resorcinol (11 g.) in sodium hydroxide solution (4 g. in 50 ml. of water) with carbon disulphide (7·6 g.) for 3 days at room temperature, extracting the unchanged disulphide with ether and acidifying the dark red aqueous solution with dilute hydrochloric acid. The yield of dithio-acid was 7 g. An extension of this method to phloroglucinol (12·6 g.) gave 2 : 4 : 6-*trihydroxydithiobenzoic acid* (8·5 g.), m. p. 150° (decomp.), after crystallisation from benzene–alcohol (Found: C, 41·2; H, 3·2; S, 31·9. $C_7H_6O_3S_2$ requires C, 41·5; H, 3·0; S, 31·6%).

Infrared Absorption Spectra.—These were measured with a modified Hilger D209 double-beam instrument.[25] The compounds were examined in solution in carbon tetrachloride or carbon disulphide, and/or in potassium chloride discs,[26] or as thin solid films from a melt between rock-salt plates. Accuracy of wavenumber measurement is about ±3 cm.$^{-1}$ at 1700 cm.$^{-1}$ and about ±1 cm.$^{-1}$ at 1200 cm.$^{-1}$.

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[24] Lippmann, *Monatsh.*, 1889, **10**, 617.

[25] Hales, *J. Sci. Instr.*, 1949, **26**, 359; 1953, **30**, 52.

[26] Hales and Kynaston, *Analyst*, 1954, **79**, 702.