124. *The Infrared Spectrum of Thiocyanogen and Thiocyanogen Halides.*

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Spectra of solutions of thiocyanogen in, mostly, carbon disulphide and pentachloroethane are consistent with the usual formulation N:C·S·S·C:N. Spectra of thiocyanogen with chlorine indicate complete reaction to give thiocyanogen monochloride, followed by very rapid reactions to give consecutively two products, the first showing absorption bands characteristic of both C=N and C≡N groups and the second those of C=N. 1 : 1 Mixtures of thiocyanogen and bromine in the above solvents showed new bands together with those of thiocyanogen much reduced. Mixtures of thiocyanogen and iodine gave spectra indicating only partial reaction. Spectra obtained of thiocyanogen in diethyl ether differed from those in carbon disulphide, carbon tetrachloride, and pentachloroethane in having a broad band in the 2100 cm.$^{-1}$ region similar to those in organic isothiocyanates.

In a preliminary examination of the infrared spectra of thiocyanogen chloride in various organic solvents, bands were observed at ~1600 and ~900 cm.$^{-1}$: these were difficult to reconcile with the structure Cl·S·C:N expected from its reactions, so a more extended study was made, beginning with thiocyanogen itself.

Spectra of Thiocyanogen.—Spectra were obtained of solutions of thiocyanogen in pentachloroethane and in carbon disulphide. Some difficulty was met in obtaining solutions free from impurities, but when they were obtained bands were observed only at 2171, 673, 667, 490, and 359 cm.$^{-1}$ in the range examined (4000—350 cm.$^{-1}$) (Fig. 1). All these bands were weak (see below), the 670 doublet being the strongest and the 491 cm.$^{-1}$ band the weakest. This spectrum is fully consistent with the accepted structure N:C·S·S·C:N for thiocyanogen. The band at 2171 cm.$^{-1}$ is close in frequency to bands in all organic thiocyanates which show [1] a sharp and fairly weak band in the region 2130—2170 cm.$^{-1}$, whereas organic isothiocyanates are characterised by a broad strong band in the range 2040—2140 cm.$^{-1}$ which was not observed except when ether was used as a solvent (see below). Presumably the splitting of the triple-bond frequency by interaction of the two C≡N groups is too small to be detected under the experimental conditions used. The two bands at 673 and 667 cm.$^{-1}$ are in the region for C–S vibrations [2,3,4] and very close to frequencies observed [5] with sulphur cyanide at 684 and 665 cm.$^{-1}$. The weak band at

[1] Luskin, Gantert, and Craig, *J. Amer. Chem. Soc.*, 1956, **78**, 4965; Irwin, Ph.D. Thesis, Queen's University, Belfast, 1958; Caldow and Thompson, *Spectrochim. Acta*, 1958, **13**, 212; Lieber, Rao, and Ramachandran, *ibid.*, 1959, **13**, 296.

[2] Trotter and Thompson, *J.*, 1946, 481; Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429; Scott and McCullough, *J. Amer. Chem. Soc.*, 1958, **80**, 3554.

[3] Cymerman and Willis, *J.*, 1951, 1332.

[4] Bak, Hansen-Nygaard, and Pedersen, *Acta Chem. Scand.*, 1958, **12**, 1451.

[5] Pollock and Pullin, unpublished results.

491 cm.$^{-1}$ may be attributed to the S–S stretching vibration if it is assumed that the molecule is not centrosymmetric. This frequency is within the ranges (450—520 cm.$^{-1}$) found for aliphatic disulphides [2] and aromatic disulphides [3] (430—490 cm.$^{-1}$). There is some doubt about the frequency to be attributed to the vibration approximating to S–S stretching in S_2Cl_2: [6,7] the most likely possibilities [6,7] are 448 and 538 cm.$^{-1}$. The band at 359 cm.$^{-1}$ at the extreme wavelength limit of the potassium bromide optics must be assigned to a bending mode, probably of the ·S·C:N group because a band close to this frequency is found in compounds in which the S–S bond is believed to be broken. The spectrum of the thiocyanate ion [8] with which the spectrum of thiocyanogen might be compared shows, apart from small modifications due to crystal forces, bands at 2066, 470 (bending), and 743 cm.$^{-1}$. These and other results indicate a considerable multiple-bond character in the C–S link in the thiocyanate ion which would be expected to raise the bending frequency and the C–S stretching frequency and lower the C≡N frequency relative to those of thiocyanogen. Because of this it is not likely that the band at 491 cm.$^{-1}$ for thiocyanogen could be due to S–C≡N bending: on the other hand the 359 cm.$^{-1}$ band might be due to mainly this type of motion. It is worth noting that an isothiocyanate-type structure for thiocyanogen would be expected [9,10] to give an unresolved pair of bands in the region 850—1000 cm.$^{-1}$.

Spectra of Thiocyanogen—Chlorine Mixtures.—Although in preliminary experiments bands at $\sim$1600 and $\sim$900 cm.$^{-1}$ had always been observed when solutions of chlorine and thiocyanogen were mixed, scanning over the region of each band separately as soon as possible after mixing distinguished the original thiocyanogen monochloride bands from those of secondary products. For example, spectra taken immediately in the 1650—1550 cm.$^{-1}$ region showed no band, and the 900 cm.$^{-1}$ band is absent in spectra taken immediately in the 1000—850 cm.$^{-1}$ region. In this way it was established that the compound formed immediately on mixing equimolecular quantities of chlorine and thiocyanogen in solution gave peaks at 2162, 678, 520, and 353 cm.$^{-1}$ (Fig. 1). The secondary reactions of this compound and the products formed are discussed below. The spectrum of mixtures of chlorine and thiocyanogen in these solvents is thus consistent with the equilibrium $(N:C·S·)_2 + X_2 \rightleftharpoons 2X·S·C:N$ (X = Cl, Br, or I) lying right over to the right. In particular the C–S stretching band is now single, and the 520 cm.$^{-1}$ band (S–Cl stretching) is actually a doublet with frequencies approximately 523 and 516 cm.$^{-1}$ of which the lower frequency is the weaker. The ratio of these frequencies is exactly that for vibrations of the diatomic species S–^{35}Cl and S–^{37}Cl. Re-examination of the spectra showed the same type of doubling to be present in the 524 cm.$^{-1}$ band of thiocyanogen trichloride.[11] The reaction of thiocyanogen with chlorine to form thiocyanogen monochloride is very rapid, since the bands characteristic of the compound have grown to full intensity in the time (about 30 seconds) necessary to fill the cell and insert it in the spectrometer. The reaction is also quantitative or very nearly so. [The shoulder on the high-frequency side of the 2162 cm.$^{-1}$ band is due mainly, if not entirely, to further products (see below), and the shoulders on the low frequency side of the 678 cm.$^{-1}$ band of thiocyanogen monochloride, of which the more definite were at 673 and 657 cm.$^{-1}$, were not diminished in intensity by up to a ten-fold excess of chlorine. They appeared immediately and changed relatively slowly with time, so that they do not appear to be due to the main decomposition product of thiocyanogen monochloride or to residual thiocyanogen.] Thiocyanogen monochloride is thus comparable with iodine monochloride in its ready formation and small tendency to dissociation. The spectrum of three mols. of chlorine with one of thiocyanogen was observed for several hours, but no bands characteristic of thiocyanogen trichloride [11] were observed.

[6] Bernstein and Powling, *J. Chem. Phys.*, 1950, **18**, 1018.
[7] Hooge and Ketelaar, *Rec. Trav. chim.*, 1958, **77**, 902.
[8] Jones, *J. Chem. Phys.*, 1956, **25**, 1069.
[9] Thomas, *J.*, 1952, 2383.
[10] Goubeau and Reyhing, *Z. anorg. Chem.*, 1958, **294**, 96.
[11] Bacon, Irwin, Pollock, and Pullin, *J.*, 1958, 764.

This agrees with previous observations on the cryoscopic behaviour of 3 : 1 chlorine thio-cyanogen mixtures (ref. 12, pp. 765, 772).

  Spectra of Thiocyanogen—Bromine Mixtures.—Seel and Muller [12] obtained at —50° a compound whose analyses approximate to those for BrSCN. Addition of an equi-molecular amount of bromine to thiocyanogen in pentachlorethane, carbon tetrachloride, or carbon disulphide produced an immediate change in the spectrum. Absorption bands appeared at 2157, 676, 451, and 369 cm.$^{-1}$ (Fig. 1). The thiocyanogen bands remained, though much diminished in intensity. The spectrum of the mixture did not alter further for several hours. These results showed that there had been an immediate, but not

FIG. 1. *Spectra of solutions of thiocyanogen (continuous curves) and of thiocyanogen halides (broken curves). 1·0 mm. cells. Thiocyanogen halide spectra have been displaced downwards by 15% on the transmission scale.*
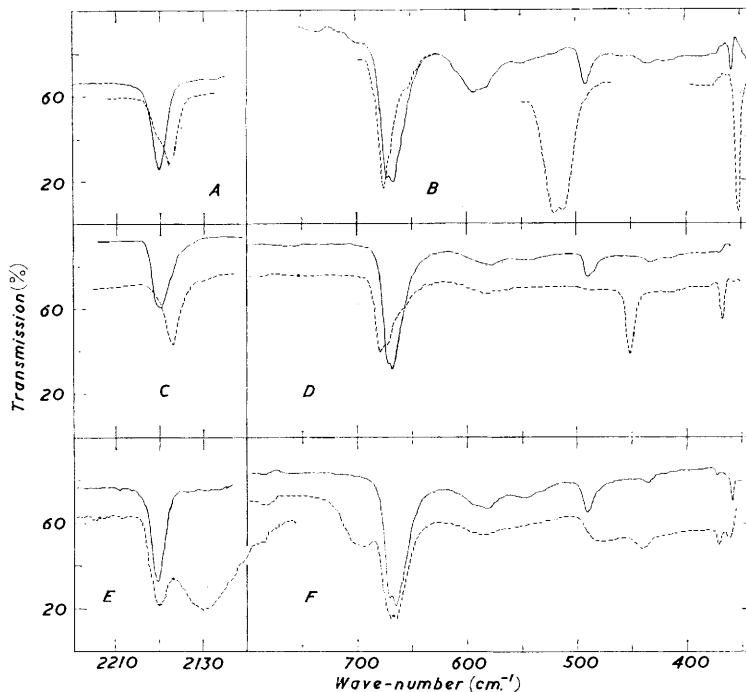
Top panel, $(SCN)_2$ and ClSCN: *A, in* C_2HCl_5, ~0·3M-$(SCN)_2$, ~0·4M-ClSCN; *B, in* CS_2, ~0·5M-$(SCN)_2$, ClSCN ~0·4M *for 670 and 520 cm.$^{-1}$ bands and* ~0·5M *for 360 cm.$^{-1}$ band.*
Middle panel, $(SCN)_2$ and BrSCN: *C, in* CCl_4, ~0·3₅M; *D, in* CS_2, ~0·3M.
Bottom panel, $(SCN)_2$ and equimolecular $(SCN)_2$-I_2 mixture: *E, in* C_2HCl_5, ~0·3M; *F, in* CS_2, ~0·4M.

quantitative, reaction. Attribution of the bands at 2157 and 676 cm.$^{-1}$ remains as for thio-cyanogen and thiocyanogen monochloride. Whilst it is natural by analogy with the latter to attribute the 451 cm.$^{-1}$ band to an S–Br stretching vibration, this is surprisingly high for this type of motion (cf. 354 cm.$^{-1}$ for the S–Br stretching modes in S_2Br_2 [7]).

  The spectra of mixtures of thiocyanogen and bromine in solution at room temperature can be interpreted in terms of the equilibrium given above. Spectra were taken of solutions containing various excesses, an insufficiency, and an equivalent quantity of bromine. For addition of equivalent quantities and without appreciable change of the total volume of the solution the intensity of the thiocyanogen band at 491 cm.$^{-1}$ was reduced to approximately 18% of its value in thiocyanogen solution: this corresponds

[12] Seel and Muller, *Chem. Ber.*, 1955, **88**, 1754.

to an equilibrium constant of ~85 for these conditions (dilute solution in carbon disulphide at room temperature). Addition of excess of bromine reduced the intensity of this band as expected, it being discernible for two- and three-fold, but not for ten-fold, excess of bromine. Thiocyanogen monobromide thus resembles iodine monobromide which is also formed by direct combination of the elements where the degree of dissociation in carbon tetrachloride solution at 25° is ~9%. Thiocyanogen monobromide does not, unlike the monochloride, show the rapid growth of strong bands due to decomposition products, although in a day-old solution bands had grown at 896 and 960 cm.$^{-1}$, indicating that thiocyanogen bromide slowly polymerises.

Spectra of Thiocyanogen–Iodine Mixtures.—Mixing solutions of iodine and thiocyanogen in the same solvents (carbon disulphide, pentachloroethane) caused immediate but small changes in the spectrum (Fig. 1). The thiocyanogen bands were diminished in intensity by about one-quarter and relatively broad new bands appeared with maxima at 2130, 700,

FIG. 2. *Spectra of solutions of thiocyanogen–iodine mixtures in ether, 0·25 mm. cells.*
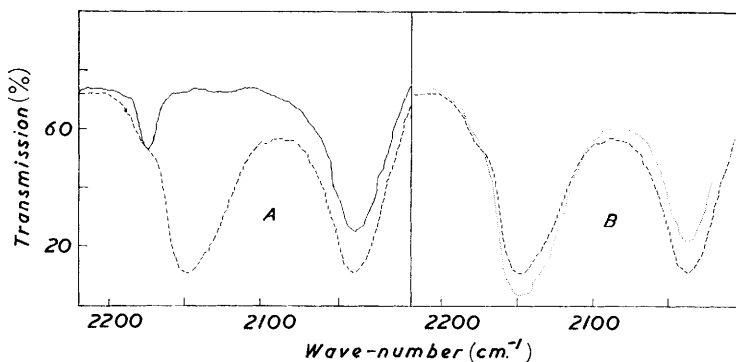
A : ———, 0·44M-*thiocyanogen in ether*; – – – –, *with one equiv. of iodine.* B, – – – –, *as in* A; . . . ., *solution saturated with iodine (nearly 3-fold excess). Note reduction in intensity of shoulder at* 2177 cm.$^{-1}$.

372, and 362 cm.$^{-1}$, possibly due to the equilibrium as above lying mainly on the side of the starting materials. Although the frequencies found are comparable to those for thiocyanogen monochloride and thiocyanogen bromide the intensity of the 2130 cm.$^{-1}$ band is much greater and is reminiscent of the broad intense band found for isothio-cyanates and attributed [9] to the unsymmetrical stretching motion of the ·N:C:S group.

Solutions of Thiocyanogen in Ether.—In the solutions discussed above it was not possible to check the effect of a large excess of iodine on the band intensities because iodine was not sufficiently soluble. Diethyl ether was accordingly chosen as a solvent. It was necessary to use 0·25 mm. cells which very much restricted the frequency ranges that could be studied. There were major changes for the spectrum of thiocyanogen itself in ether from those in the other solvents in the 2000—2200 cm.$^{-1}$ region and less reliable indications of major changes at lower frequencies. A strong broad band was consistently observed at ~2030 cm.$^{-1}$ which persisted with undiminished intensity, however carefully the reagents and solvents were dried. In very strong solutions (*e.g.*, 0·5M) a weaker band was observed also at ~2177 cm.$^{-1}$, and a reduction in the intensity of the ~2030 cm.$^{-1}$ band (Fig. 2). Addition of iodine caused changes, in particular formation of a band at ~2150 cm.$^{-1}$. The spectra both with and without iodine appeared markedly dependent on concentration and the solutions were not very stable. There appears to be some form of association between thiocyanogen and ether, possibly analogous to that between iodine and ether. The 2177 cm.$^{-1}$ band could then be due to thiocyanogen not associated with the ether. The spectra would then indicate that the concentration of this unbound

thiocyanogen is reduced on addition of iodine, presumably by formation of thiocyanogen iodide.

Band Intensities.—The bands were weak for thiocyanogen and the thiocyanogen compounds described above (except for solutions of thiocyanogen in ether). Decomposition products tended to have much stronger bands, so that a small amount of decomposition caused a big change in the spectrum. Rough measurements were made of the integrated intensities

$$A = \frac{2 \cdot 303}{cl} \int \log_{10} \left(\frac{I_0}{I}\right)_\nu d\nu$$

where c is the solute concentration in moles/l., l the cell thickness in cm., and ν are in cm.$^{-1}$ Values of $10^{-3}A$ for the C–S bands at $\sim$670 cm.$^{-1}$ of $(SCN)_2$, ClSCN, and BrSCN in CS_2 ranged between 0·4 and 0·6. $10^{-3}A$ values for the C$\equiv$N bands in $(SCN)_2$ and ClSCN were $\sim$0·3, and the value for BrSCN was similar. These values are of the same order as those for aliphatic cyanides.[13]

Secondary Reactions of Thiocyanogen Monochloride.—Spectra showing the decomposition of thiocyanogen monochloride and further reactions of the decomposition product were obtained in a number of solvents (*e.g.*, carbon tetrachloride, pentachloroethane, and carbon

Fig. 3. *Spectra showing the initial decomposition of CS$_2$ solutions of ClSCN and growth of bands due to the first decomposition product.*
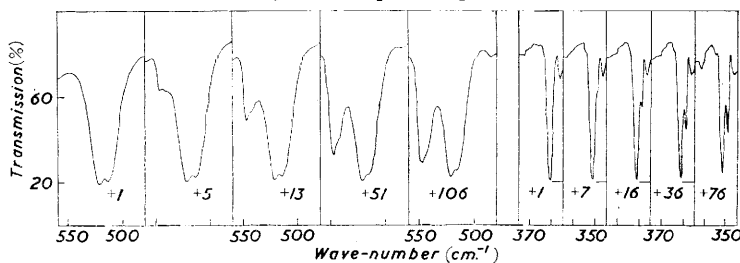
The figures marked + *are the time in minutes after mixing the* (SCN)$_2$ *and* Cl$_2$ *solutions. Initial* [ClSCN] *for the 500 cm.$^{-1}$ region, 0·4$_M$; for the 350 cm.$^{-1}$ region, 0·5$_M$. 1·0 mm. cells.*

disulphide). The solvents principally used were pentachloroethane for the 2100—2200 cm.$^{-1}$ and the 1500—1700 cm.$^{-1}$ region, and carbon disulphide for the remainder of the spectral range. Concentrations used were around 0·4$_M$. A series of spectra of thiocyanogen monochloride after various times was taken and a well-marked pattern of changes was observed. This pattern was reproducible but the rates of the reaction of

First decomp. product	Second decomp. product	SCNCl$_3$ and assignment [11]		First decomp. product	Second decomp. product	SCNCl$_3$ and assignment [11]
2174 w	—	—	—	750 m	766 m	762 w
1589 s	1590?	1603 } s 1589 }	C=N stretch	—	723 w 614 ms	—
910 vs	920 vs	923 } vs 905 }	C<antisym. stretch	548 m	—	542 } ms 524 }	S–Cl stretch
			in Cl·S·C(Cl)= or Cl$_2$C=	—	—	473 vs	bending
				—	440 w	430 w	bending
—	—	834 m		348 m	373 m 360 w	—

thiocyanogen monochloride prepared from different thiocyanogen solutions differed quite widely. Details of the initial changes were also followed by cycling rapidly over small spectral regions (Fig. 3). It was found that the original peaks at 2162, 678, 520, and 353 cm.$^{-1}$

[13] Skinner and Thompson, *J.*, 1955, 487.

due to the thiocyanogen monochloride molecule decreased steadily in intensity and new bands at 2174, 910, 750, 548, and 348 cm.$^{-1}$ appeared and grew rapidly (Figs. 4 and 5 and Table, " first decomposition product "). The intensities which these new bands would have had if conversion into the product had been complete were estimated from a comparison of their rates of increase with the rates of decrease of the thiocyanogen monochloride bands. Thus, it was found, for example, that the 910 cm.$^{-1}$ band was 10—15 times more intense than the 678 cm.$^{-1}$ band of chlorine thiocyanate. If these new bands are assumed to be due to a dimer the integrated molar intensity of this 910 cm.$^{-1}$ band in carbon disulphide becomes 20—30 times that of the 678 cm.$^{-1}$ band of the monomer also in this solvent. On the same basis the integrated molar intensity of the new band at 2174 cm.$^{-1}$ in pentachloro-ethane solution is 3—4 times greater than that of the band it replaces at 2162 cm.$^{-1}$. The 1600 cm.$^{-1}$ band appeared slightly less intense than the 910 cm.$^{-1}$ band: quantitative comparison was difficult owing to the overlapping of the decaying and the growing bands at $\sim$2170 cm.$^{-1}$. All these bands appear to belong to the same product since, within the

FIG. 4. *Spectra of ClSCN and decomposition product. Initial concn. 0·42M in CS₂. 1·0 mm. cell. Unshaded, hatched, and cross-hatched bands are those of ClSCN, the first decomposition product, and the second decomposition product respectively.*
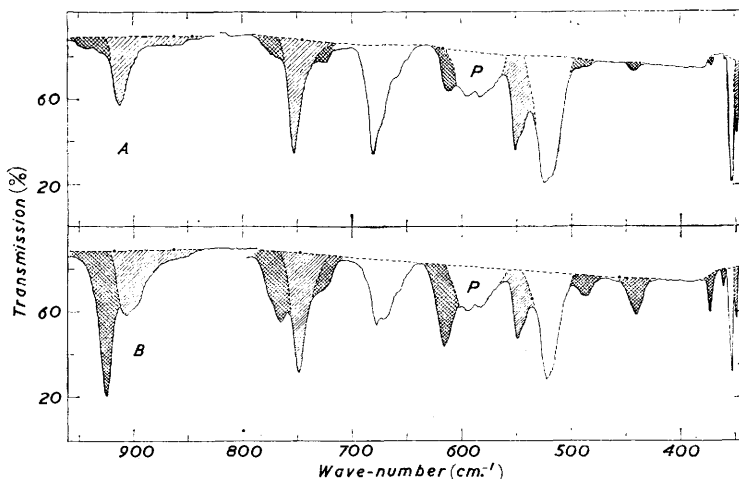
A, after 50—63 min.; B, after 570—583 min. The unshaded band marked P is probably due to a polymeric deposit on the cell windows. – – – – are the base lines used in determining the optical densities of the bands for Figs. 5 and 6.

experimental error, they grow and decay proportionately to one another (Fig. 5). The 520 cm.$^{-1}$ band of thiocyanogen monochloride appears exceptional since the optical density of its band maximum decreases more slowly than that of the 678 cm.$^{-1}$ band, and its shape changes, the lower-frequency component of the doublet at 516 cm.$^{-1}$ becoming less prominent as the overall intensity decreases (compare this band in Figs. 1 and 4). Spectra in this spectral region taken immediately and thereafter at four-minute intervals showed that the doublet structure was present from the beginning and that the lower-frequency component of the doublet at 516 cm.$^{-1}$ was decreasing relative to the higher frequency component from the first spectrum taken (Fig. 3). The most likely explanation seems to be that, as well as the band at 548 cm.$^{-1}$, the first decomposition product possesses a band underlying the 523 cm.$^{-1}$ component of the thiocyanogen monochloride band, so that the 520 cm.$^{-1}$ band appears to decay too slowly and to change shape.

After a further interval another set of bands appears (Figs. 4 and 6, Table 1, " second decomposition product "). These grow more slowly than the first set which are now

observed to pass through a maximum and decrease (Figs. 5 and 6). It appears that the first product is unstable and undergoes further reaction. The 1589 cm.$^{-1}$ band, however, does not decrease but becomes broader and continues to increase. This suggests that the second product also contains a band at or very near this frequency. For a solution stored for a month at 0° the peaks of all three products could be observed but no new peaks had appeared. Thus it appears that an equilibrium between thiocyanogen monochloride and the first and further decomposition products is set up. A plot of the optical density of the various bands against time is shown in Figs. 5 and 6. The optical densities for some of
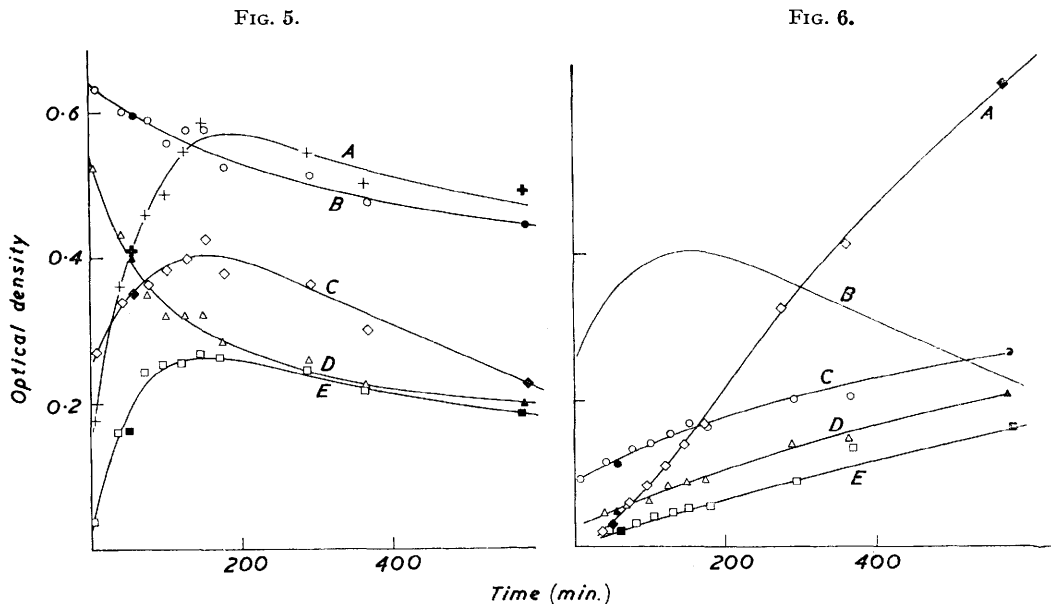
FIG. 5.   FIG. 6.

FIG. 5. *Plot of the optical density against time of the more intense bands of* ClSCN *and of the first decomposition product.*

The solution is the same as for Fig. 4; filled points show the optical densities of the bands in Fig. 4.
A, 750 cm.$^{-1}$; B, 520 cm.$^{-1}$; C, 548 cm.$^{-1}$; D, 678 cm.$^{-1}$; E, 910 cm.$^{-1}$.

FIG. 6. *As for Fig. 5, but for the second decomposition product with the plot of the 548 cm.$^{-1}$ band o the first decomposition product.*

A, 930 cm.$^{-1}$; B, 548 cm.$^{-1}$; C, 614 cm.$^{-1}$; D, 766 cm.$^{-1}$; E, 440 cm.$^{-1}$.

the bands were uncertain because the spectrum of the reaction mixture becomes complex with time and there is much overlapping.

The general pattern is reproduced in carbon disulphide, carbon tetrachloride, chloroform, and pentachloroethane. Because the rate is not reproducible in any particular solvent it is difficult to estimate the effect of solvent on the rate of the reactions. It is obvious, however, that the rate of decomposition of the chloride is faster in pentachloroethane than in carbon disulphide since it is possible to obtain spectra in carbon disulphide showing only ClSCN peaks but this is not possible in pentachloroethane. This effect of solvent on reaction rate has made it impossible to correlate fully the 2174 and the 1589 cm.$^{-1}$ band with the other bands of the first decomposition product. There is no solvent of sufficient transparency in both the 2100 cm.$^{-1}$ and the 900—400 cm.$^{-1}$ region and so it is not possible to say, for instance, that the 2174 cm.$^{-1}$ band reaches its maximum at the same time as the 910 cm.$^{-1}$ band. It is, however, reasonable to assume

that the bands at 2174 and 1589 cm.$^{-1}$ are caused by the same molecular species as the others noted above and in the Table for the first decomposition product.

Irradiation (mercury-vapour lamp) of solutions of thiocyanogen monochloride in carbon disulphide in Pyrex vessels did not accelerate the decomposition or alter the course of the reaction.

The rate of decomposition of thiocyanogen monochloride in carbon disulphide at different temperatures was studied. Samples prepared from the same sample of thiocyanogen were stored at 0°, 18°, and 32°; the rates both of the decomposition to the first product (as indicated, for instance, by the decrease of the 678 cm.$^{-1}$ band) and the decomposition of this product (as indicated, for instance, by the time to reach maximum optical density of the 750 cm.$^{-1}$ band) was greatest for the solution stored at 0° and least for that stored at 32°. These observations were repeated several times with fresh samples prepared from the same thiocyanogen solution as before. It is possible that this anomalous change of rate with temperature may be connected with the more ready precipitation of polymer material at the lower temperatures.

Nature of the Decomposition Products.—The main bands attributed to the first and second decomposition products of thiocyanogen monochloride are listed in the Table and are compared with those of SCNCl$_3$. The spectra of the first and the second decomposition products are similar to that of SCNCl$_3$. All three compounds possess very strong bands at ~1600 and ~900 cm.$^{-1}$ which in SCNCl$_3$ were attributed [11] to a C=N stretching vibration and to an asymmetric-type stretching vibration of the group Cl·S·C(Cl)= or of the group Cl$_2$C=. In addition the first, but not the second, product resembles SCNCl$_3$ in possessing bands in the 540 cm.$^{-1}$ region. It may be noted that the spectra do not provide evidence for disproportionation to SCNCl$_3$ and (SCN)$_2$ since the 473 and 834 cm.$^{-1}$ bands of SCNCl$_3$ are missing and this disproportionation would not explain the 614 and 440 cm.$^{-1}$ bands of the second product. The first product may be a dimer: 2N⋮C·S·Cl ⟶ N⋮C·S·N⋮C(Cl)·SCl, containing C≡N, C=N, and S–Cl bonds as required, and the grouping Cl·S·C(Cl)=. It will be expected to react further by addition at the triple bond, giving a product or products with more than one −C=N− grouping. There are numerous further modes of reaction of this dimer that could be suggested. One, based on the evidence that the second product does not appear to react further, and that the second product has no absorption in the range that could be attributed to an S–Cl stretching vibration, is cyclisation, for example to give a six-membered ring, Cl·C$\underset{N-S}{\overset{S-N}{\lessgtr}}$C·Cl, although cyclisation to larger rings is also possible. The broadness of the ~1600 cm.$^{-1}$ band in the second product suggests that more than one structure may be present. Baroni [14] determined the molecular weight of thiocyanogen monochloride in solution in bromoform cryoscopically. The values increased with time. For " freshly prepared " solutions the molecular weight was a little less than that of the dimer. Kaufmann *et al.*,[15] using the ebullioscopic method, several times obtained a value for the molecular weight corresponding to the monomer. This is interesting in view of the observation that thiocyanogen monochloride solutions appear to be more stable at 32° than at 0°.

Reaction of S(CN)$_2$ *with* SCl$_2$.—This was studied in the hope that it might provide a product identical with, or closely similar to, the first reaction product of thiocyanogen monochloride. Sulphur dicyanide was prepared as described by Schneider [16] and purified by sublimation. To this was added the equivalent amount of freshly distilled SCl$_2$. A violent reaction resulted in a liquid product. This was not further purified, but was diluted with solvent and its spectrum was measured. This product, although not identical with the first decomposition product, showed the same general features, most marked of which were a strong band around 1600 cm.$^{-1}$, and a very strong band just above

[14] Baroni, *Atti R. Accad. Lincei*, 1936, **23**, 871.
[15] Kaufmann and Liepe, *Ber.*, 1924, **57**, 923; Kaufmann, *Ber.*, 1927, **60**, 58.
[16] Schneider, *J. prakt. Chem.*, 1885, **32**, 187.

900 cm.$^{-1}$; there was also a weak peak at 2170 cm.$^{-1}$ and a medium-intensity peak at 745 cm.$^{-1}$.

EXPERIMENTAL

Apparatus.—Spectra were taken with a Perkin–Elmer model 21 double beam spectrophotometer fitted with sodium chloride and potassium bromide prisms. For work below 400 cm.$^{-1}$ slits were fixed at 1000 μ; otherwise the standard slit schedules of the instrument were used. The cell used was of the conventional demountable type, made with a suitable spacer between potassium bromide plates, modified to obviate contact of the experimental solution with metal. Teflon spacers were used, and Teflon inlet and outlet tubes which were closed, after filling, with Teflon stoppers. An all-glass syringe was used for filling the cell. Spacers were of thickness 1·0—0·1 mm. Potassium bromide plates were used throughout the range 4000—350 cm.$^{-1}$. The bromide plates of the cell had to be cleaned and repolished frequently because of a solid yellow-orange deposit on the plates. A Hilger variable-path cell with potassium bromide windows was used as a solvent cell, adjusted to give no bands with both cells full of solvent.

Solvents.—Because most of the compounds studied had weak absorption and were unstable in concentrated solution, thick cells had to be used and the solvents were chosen primarily for their transparency. Pentachloroethane was the most useful solvent at 4000—1300 cm.$^{-1}$. Carbon tetrachloride was sometimes used in this region, but $>0\cdot3$M-solutions were unstable because of the limited solubility of thiocyanogen in this solvent. Chloroform was not much used as a solvent (although sufficiently transparent in the region 4000—1600 cm.$^{-1}$) because of the growth of spurious bands possibly due to the uneven production of chloroform decomposition products in the solution and in the solvent cells. In the range 1300—350 cm.$^{-1}$, carbon disulphide was the most transparent solvent and was used except in special cases. " AnalaR " solvents were used where available. They were stored over phosphoric oxide.

Chemical Preparations.—The action of bromine on lead thiocyanate was used to prepare thiocyanogen solutions. Small-scale methods were used as 50 ml. of solution was sufficient for most experiments. Glassware, reagents, and solvents were carefully dried. Lead thiocyanate was prepared from " AnalaR " lead nitrate and ammonium thiocyanate by the method of Lambert and Dollear [17] and dried in a vacuum over phosphoric oxide for at least two days. A solution of the required strength, usually about 0·3M, of " AnalaR " bromine in a suitable solvent was prepared in a 250 ml. flask with a ground-glass stopper. Excess of lead thiocyanate was added, and the flask shaken until the bromine colour disappeared (the time varying with solvent—2 min. for carbon disulphide, $\leqslant$15 min. for ether). The thiocyanogen solution was decanted, and its concentration was determined by iodometric titration.[18] Fresh solutions of thiocyanogen were always used. Thiocyanogen chloride solutions were prepared by mixing solutions of dry chlorine and thiocyanogen in equimolecular proportions, concentrations being determined iodometrically before and after mixing. There was no noticeable change of colour when thiocyanogen and bromine solutions were mixed (as there was with thiocyanogen and chlorine solutions [18]), but there was a change of odour. Red crystals were slowly formed, particularly from solutions containing a large excess of bromine. These sublimed easily to form colourless crystals round the neck of the flask, but these colourless crystals readily decomposed, giving off bromine vapour. This substance might be the red solid isolated by Seel and Muller [12] by the action of excess of bromine on potassium thiocyanate at $-50°$, but could not be examined spectroscopically because of its instability. There was no detectable change of colour or odour on mixing of thiocyanogen and iodine.

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[17] Lambert and Dollear, *Oil and Soap*, 1946, **23**, 97.
[18] Angus and Bacon, *J.*, 1958, 774.