# 151. *Thiocyanogen Chloride. Part II.* Some Physical Properties of its Solutions.*

By R. G. R. BACON and R. S. IRWIN.

Cryoscopic measurements show that thiocyanogen monochloride is essentially monomeric in fresh solutions. In highly polar solvents it exhibits weak electrical conductivity, comparable with that of thiocyanogen, but less than that of iodine chloride. Precipitation reactions with the salt $(Bu^nO)_2PO{\cdot}SNa$ in carbon tetrachloride show that SCN is the more electropositive partner in Cl·SCN, like iodine in iodine monochloride; these reactions involve displacement of the pseudohalogen $[(Bu^nO)_2PO{\cdot}S]_2$, which is more electropositive than thiocyanogen. Compound formation between equimolecular amounts of thiocyanogen and chlorine is proved (as in the case of iodine monochloride) by examination of absorption spectra in the visible and near ultraviolet regions. The known properties of thiocyanogen chloride could be accounted for by a structure polarised $Cl-\overset{\delta-}{S}-\overset{\delta+}{C}\equiv N$, but the infrared absorption spectrum suggests that this does not accurately represent the nature of the bonds in the molecule. All measurements made on thiocyanogen chloride solutions are limited by their instability, which varies with the nature of the solvent and with other factors.

IT was shown in Part I that a rapid chemical change occurs when solutions of thiocyanogen and chlorine are mixed in equimolecular proportion. The mixture behaves as a solution of reactive molecules of formula Cl·SCN, in which the thiocyanate group is the more electropositive partner. As further evidence for the nature of these solutions we now report (*a*) cryoscopic measurements, (*b*) ionic precipitation reactions, (*c*) electrical conductivity measurements, and (*d*) spectroscopic characteristics. Some comparisons have been made

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* Part I, preceding paper.

both with thiocyanogen and with iodine chloride; thiocyanogen chloride somewhat resembles the latter compound in chemical properties.

All measurements on thiocyanogen chloride inevitably lack precision because it cannot be isolated for purification. It is generated in solution and the yield, as measured by iodometric titration, is not quantitative (see Part I); also it decomposes at a rate influenced by the nature and purity of the solvent, and by temperature and light. Suitable solvents are, for example, acetic acid or carbon tetrachloride, in which decomposition is usually not greater than 0·5%/hr. at 20° in 0·1N-solution. Measurements are therefore necessarily made in the presence of varying amounts of contaminants, among which polymers are probably important. When investigating the stability of solutions we paid attention to the effect of hydrogen chloride on decomposition rate, since this compound is produced when thiocyanogen chloride participates in substitution reactions (Part I). In 0·1—0·5N-Cl·SCN in acetic acid at 20°, the presence of an equimolecular quantity of hydrogen chloride had a negligible effect.

*Cryoscopic Measurements.*—Measurements in benzene, acetic acid, and bromoform all indicated that the substance in freshly prepared solutions is essentially monomeric, and not a polymer such as earlier workers described (see Part I). Decomposition rate was higher than usual in the solutions being examined, possibly because of the increase in concentration which accompanies freezing. Mean deviations from the theoretical molecular weight were ~+3%, which, if significant, could be due to a slight degree of polymerisation. The cryoscopic technique was checked with iodine chloride, measurements being made on solutions of the purified solid and also on solutions prepared, analogously to thiocyanogen chloride, by mixing iodine and chlorine.[1] The measurements in bromoform were similar in principle to those of Lecher and Goebel,[2] who showed that the freezing-point depression due to $Br_2$ molecules in this solvent was not changed when they were replaced by $(SCN)_2$ molecules through reaction with a suspension of lead thiocyanate: $Pb(SCN)_2 + Br_2 \longrightarrow PbBr_2 + (SCN)_2$. In the present case the depression due to chlorine was not altered by stirring with a 0·5 molar proportion of lead thiocyanate, the reaction occurring being:[3] $Pb(SCN)_2 + 2Cl_2 \longrightarrow PbCl_2 + 2Cl{\cdot}SCN$. Because of its reactivity this solvent is by no means an ideal choice.

*Ionic Precipitation Reactions.*—Reactions were examined for evidence of the polarisation $\overset{\delta+}{SCN}-\overset{\delta-}{Cl}$ which had been indicated by the mode of substitution in aromatic compounds (Part I). Like iodine chloride, thiocyanogen chloride gave an immediate precipitate with silver perchlorate in organic solvents, but more attention was given to reactions with sodium *OO*-dialkyl thiophosphates. These compounds[4] have the unusual property of very high solubility in water coupled with substantial solubility in organic solvents, including hydrocarbons and chlorinated hydrocarbons. We found that the di-*n*-butyl compound had particularly good solubility in organic solvents. It appeared to be completely dissociated in aqueous solution and to be associated about ten-fold in benzene.

Dissolved in carbon tetrachloride with an equimolecular proportion of thiocyanogen chloride, the salt gave a precipitate of sodium chloride, free from thiocyanate, in 90% yield. This is due to the reaction:

$$2(Bu^nO)_2PO{\cdot}SNa + 2Cl{\cdot}SCN \longrightarrow 2NaCl + (SCN)_2 + [(Bu^nO)_2PO{\cdot}S]_2 \quad . \quad (1)$$

which may be linked with:

$$(SCN)_2 + [(Bu^nO)_2PO{\cdot}S]_2 \rightleftharpoons 2(Bu^nO)_2PO{\cdot}S{\cdot}SCN \quad . \quad . \quad . \quad (2)$$

In the same solvent, with a 2 : 1 thiophosphate : Cl·SCN ratio, the precipitated salt

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[1] Gillam and Morton, *Proc. Roy. Soc.*, 1929, *A*, **124**, 604.

[2] Lecher and Goebel, *Ber.*, 1921, **54**, 2223.

[3] Bacon and Guy, unpublished data.

[4] Foss, *Acta Chem. Scand.*, 1947, **1**, 8.

consisted of equal proportions of sodium chloride and sodium thiocyanate. The latter can be attributed to a reaction (3) occurring in conjunction with (1):

$$2(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}SNa} + (\mathrm{SCN})_2 \longrightarrow 2\mathrm{NaSCN} + [(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}S}]_2 \quad . \quad . \quad (3)$$

We demonstrated reaction (3) by mixing the thiophosphate with thiocyanogen in carbon tetrachloride, whereupon sodium thiocyanate was precipitated quantitatively. We also carried out a reaction analogous to (1), but using iodine chloride, and a quantitative precipitation of sodium chloride occurred:

$$2(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}SNa} + 2\mathrm{ICl} \longrightarrow 2\mathrm{NaCl} + \mathrm{I}_2 + [(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}S}]_2 \quad . \quad . \quad (4)$$

The phosphorus compound produced in reactions (1), (3), and (4) is one of the group called by Foss [4] dialkylthiophosphatogens. He prepared the dimethyl and diethyl compounds with the aid of bromine in ether and we used his method to isolate a sample of the di-*n*-butyl compound:

$$2(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}SNa} + \mathrm{Br}_2 \longrightarrow 2\mathrm{NaBr} + [(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}S}]_2$$

This was an oil, unstable to heat, like its homologues. Reaction (3) has a formal similarity (involving disulphide-bond fission) with the double-decomposition process in aqueous solution which Foss [4] used to prepare the higher dialkylthiophosphatogens from the water-soluble dimethyl compound:

$$2(\mathrm{RO})_2\mathrm{PO{\cdot}S}^- + [(\mathrm{MeO})_2\mathrm{PO{\cdot}S}]_2 \longrightarrow 2(\mathrm{MeO})_2\mathrm{PO{\cdot}S}^- + [(\mathrm{RO})_2\mathrm{PO{\cdot}S}]_2 \text{ (precipitated)}$$

Reaction (1) demonstrates that the SCN group is the more electropositive partner in the compound Cl·SCN, just as iodine is in ICl [reaction(4)]. Also, the experiments provide new examples of displacement reactions between pseudohalogens, *i.e.*, displacement of $(\mathrm{RO})_2\mathrm{PO{\cdot}S}$ from its salts by the more electronegative SCN group. Foss [4] found the redox potential for the system $2(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}S}^- \longrightarrow [(\mathrm{Bu^nO})_2\mathrm{PO{\cdot}S}]_2 + 2e$ to be $-0{\cdot}51$, which is close to the value for $\mathrm{I^-I^-}$ ($-0{\cdot}54$), whereas the value for $\mathrm{SCN^-SCN^-}$ has been found [5] to be $-0{\cdot}77$. The suggested reaction (2) between the two pseudohalogens would be analogous to those which occur between pairs of halogens, or between a halogen and a pseudohalogen.

*Electrical Conductivity.*—Iodine chloride conducts in polar solvents and precise data have been obtained [6] for its conductivity in the molten state, which is probably due to the self-ionisation $2\mathrm{ICl} \longrightarrow \mathrm{I}^+ + \mathrm{ICl_2}^-$. Thiocyanogen has been found to be non-conducting in halogenated hydrocarbons, ether, and carbon disulphide and to display weak conductivity in mixtures of ethyl bromide and acetone.[7] We found thiocyanogen chloride to be non-conducting in carbon tetrachloride, chloroform, and benzene, and we compared it with iodine chloride and with thiocyanogen in solvents of higher dielectric constant. Typical data are shown in the Table. No great accuracy can be claimed since

*Molar conductance* (*ohm*$^{-1}$ *cm.*$^2$) *of solutions at* 25°.

| | $(\mathrm{SCN})_2$ | | Cl·SCN | | ICl | |
|---|---|---|---|---|---|---|
| Solvent | 0·08M | 0·008M | 0·08M | 0·008M | 0·08M | 0·008M |
| Acetic acid ($\varepsilon = 7$) ...... | slight | slight | slight | slight | $4 \times 10^{-4}$ | $3 \times 10^{-4}$ |
| Acetic anhydride ($\varepsilon = 20$) | $1{\cdot}4 \times 10^{-2}$ | $2{\cdot}1 \times 10^{-2}$ | $0{\cdot}9 \times 10^{-2}$ | $3{\cdot}1 \times 10^{-2}$ | $12 \times 10^{-2}$ | $35 \times 10^{-2}$ |
| Nitromethane ($\varepsilon = 39$) ... | $3{\cdot}7 \times 10^{-2}$ | $7 \times 10^{-2}$ | $0{\cdot}5 \times 10^{-2}$ | — | 1·5 | 2·5 |

chemical reactions occurred quite readily in the case of iodine chloride in acetic anhydride and thiocyanogen chloride in nitromethane; their effect was minimised by taking rapid readings on fresh solutions. The data show the molar conductance of thiocyanogen

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[5] Bjerrum and Kirschner, *Kgl. Danske Videnskab. Selsk.*, 1918, **5**, No. 1.

[6] Greenwood and Emeléus, *J.*, 1950, 987.

[7] Fialkov and Kleiner, *J. Gen. Chem., U.S.S.R.*, 1941, **11**, 671.

chloride to be of the same order as that of thiocyanogen and to be lower than that of iodine chloride by a factor of 10—100.

*Spectroscopic Characteristics.*—When solutions of thiocyanogen and chlorine are mixed, their colours, very pale yellow and green-yellow respectively, are replaced by the intenser golden-yellow of thiocyanogen chloride solution. Analogous interactions between chlorine, bromine, and iodine were investigated in carbon tetrachloride by Gillam and Morton,[1] with the aid of absorption spectra in the visible and near-ultraviolet regions. We used the same method in the present case and observed a similar result (Fig. 1) to that reported by Gillam and Morton for the formation of iodine chloride. The peaks characteristic of chlorine ($\lambda_{max.}$ 327 mμ, $\varepsilon_{max.}$ 90) and of thiocyanogen ($\lambda_{max.}$ 295 mμ, $\varepsilon_{max.}$ 140) were completely absent from the absorption spectrum of the mixture in carbon tetrachloride, which we regard as characteristic of thiocyanogen chloride ($\lambda_{max.}$ 372 mμ, $\varepsilon_{max.}$ ~15; $\lambda_{min.}$ 338 mμ, $\varepsilon_{min.}$ ~10). In acetic anhydride the curve was similar, but with a peak at slightly shorter wavelength ($\lambda_{max.}$ 366 mμ), while the curve in *n*-hexane was practically identical with that in carbon tetrachloride ($\lambda_{max.}$ 375 mμ); the rise in the curve continued down to 225 mμ.

FIG. 1. *Spectra in carbon tetrachloride at room temperature. A,* 0·0129M-Cl·SCN; *B, theoretical curve for a* 0·0129M-*solution containing a non-reacted equimolecular mixture of* $(SCN)_2$ *and* $Cl_2$; *C, due to* 0·00645M-$(SCN)_2$, *and D, due to* 0·00645M-$Cl_2$, *are added to give B.*

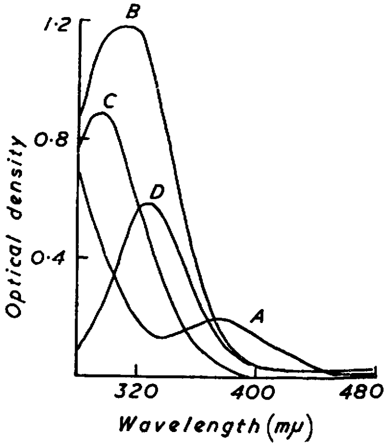
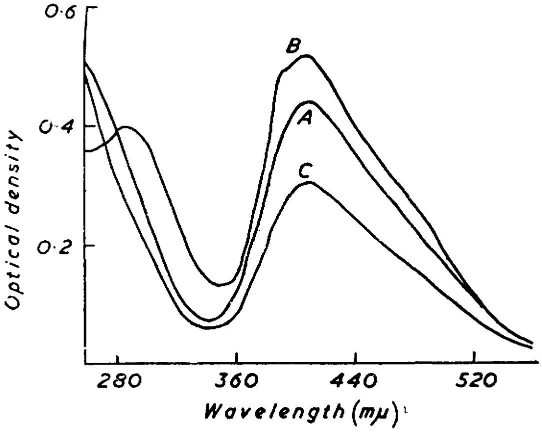


FIG. 2. *Spectra in carbon tetrachloride at room temperature. A, observed curve for a* 0·00517M-*solution, made from an equimolecular mixture of* $(SCN)_2$ *and* $Br_2$; *B, theoretical curve for solution A if no reaction has occurred,* i.e., *summation of curves for* 0·00259M-$(SCN)_2$ *and* 0·00259M-$Br_2$; *C, solution A after* 100 *hr. in the dark at room temperature.*



By contrast (Fig. 2) the absorption spectrum (*A*) for a mixture of bromine and thiocyanogen in carbon tetrachloride approached much more closely to the summation curve (*B*) for the two components. In the mixture (*A*) the bromine peak at 411 mμ was somewhat less intense than in (*B*) and there was a considerable fall from this initial intensity when the mixture was kept, indicating some kind of chemical change. The thiocyanogen peak was not present at 295 mμ in (*A*), but absorption was displaced to shorter wavelengths, beyond the range which could be examined in this solvent. Further investigation is needed to determine whether these effects can be attributed to an equilibrium such as $Br_2 + (SCN)_2 \rightleftharpoons 2BrSCN$. No chemical evidence has yet been reported for the existence of thiocyanogen bromide in solution, though a compound believed to be BrSCN has been isolated at −50° as a readily dissociating red solid.[8]

A preliminary investigation of infrared absorption spectra showed the need of great caution in interpreting results, since observed bands may be due to impurities, or to polymers and other decomposition products. Solutions of thiocyanogen of reasonable

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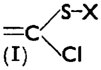
[8] Seel and Müller, *Chem. Ber.*, 1955, **88**, 1747.

concentration may be prepared in purified (ethanol-free) chloroform. A 0·48M-solution in this solvent showed bands at 3050 (m) and 2175 cm.$^{-1}$ (m) (in the range 800—4000 cm.$^{-1}$). Thiocyanogen chloride (initially 0·43M) showed the following characteristics in the same solvent (1200—1250 cm.$^{-1}$ region uncertain because of high absorption by chloroform):

| Frequency (cm.$^{-1}$) | 3050 | 2170 | 1595 | 1453 | 1345 | 930 * | 912 * |
|---|---|---|---|---|---|---|---|
| Freshly prepared solution | w | w | s | — | vw | — | ms |
| After 24 hr. (33% decomposition) | w | w | s | ms | ms | vs | m |
| After 296 hr. (100% decomposition) | vw | vw | — | vs | s | — | — |

* Complex group of bands; rate of replacement of the 912 cm.$^{-1}$ band was not reproducible.

Organic thiocyanates and *iso*thiocyanates are respectively characterised [9] by a strong peak at 2130—2160 cm.$^{-1}$ and a strong band at 2040—2180 cm.$^{-1}$. The frequency in this region is very weak in Cl·SCN and only moderate in $(SCN)_2$. Strong peaks observed at 1600 and ~930 cm.$^{-1}$ in the Cl·SCN spectrum are also found in the spectra of the trichloride $Cl{\cdot}S{\cdot}CNCl_2$ and its derivatives [10] and have been attributed, respectively, to a C : N link and to a chlorine atom linked, *e.g.*, as in (I). When the thiocyanogen chloride solutions are kept, these two bands diminish, while others appear (at 1527, 1482, 1453, 1345, 1317, and 1070 cm.$^{-1}$) and increase in intensity, though not synchronously; the 1070 cm.$^{-1}$ band is due to a solid deposit, probably polymeric, on the walls of the cell, while the others seem to indicate a series of decomposition reactions.


(I)

*General Conclusions.*—The properties examined support the postulate (Part I) that thiocyanogen chloride exists in solution as a monomer, polarised in the manner $\overset{\delta+}{SCN}-\overset{\delta-}{Cl}$. Its chemical behaviour is in harmony with a classical valence-bond structure $Cl-S-C{\equiv}N$, capable of undergoing heterolytic fission at the Cl–S link. On the other hand, its infrared absorption characteristics suggest that such a representation is inadequate. We propose to carry out further investigations of the infrared spectra of sulphur-containing pseudo-halogens and their derivatives. The formulation of their bonds may well prove a general problem and we have already met another example in the compound $Cl{\cdot}S{\cdot}CNCl_2$.[10] A less closely related case [11] is the unstable, polymerisable compound $S_2N_2$, which is isoelectronic with Cl·SCN.

## EXPERIMENTAL

*Thiocyanogen Chloride Solutions.*—The usual precautions were taken to dry reagents, solvents, and glassware thoroughly. Lead thiocyanate was prepared from " AnalaR " lead nitrate and ammonium thiocyanate by the procedure recommended by Lambou and Dollear [12] and was stirred in the solvent with " AnalaR " bromine. The resulting thiocyanogen solution was displaced from the reaction flask through a sintered-glass plate into a volumetric flask, and washings from the residual salts were displaced similarly. Thiocyanogen chloride was generated in a thiocyanogen solution by adding a calculated quantity of chlorine solution. The latter was made by passing the gas from a cylinder through scrubbing towers containing concentrated sulphuric acid and absorbing it in dry solvent. Solutions of chlorine, thiocyanogen and thiocyanogen chloride were stored in the dark and were estimated by reaction with excess of methanolic potassium iodide, followed by iodometric titration. Thiocyanogen chloride was commonly used in ~0·1N(~0·05M)-solution.

Solutions in acetic anhydride showed ~2% decomposition (by titration) in 20 hr. at 20°. Solutions in carbon tetrachloride or in acetic acid (the latter solvent having been previously refluxed with 5% acetic anhydride) showed ~10% decomposition in 20 hr. at 20°. Solutions in *n*-hexane or benzene were considerably less stable. Solutions in nitromethane had poor stability (~10% decomposition in 1 hr.). In all solvents except acetic anhydride the initial titre for the thiocyanogen chloride was less, by 2—7%, than the figure to be expected from the titre of its components.

The effect of dry hydrogen chloride on the stability of the reagent in solution in acetic acid

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

[10] Bacon, Irwin, Pollock, and Pullin, *J.*, 1958, 764.

[11] Goehring, *Quart. Reviews*, 1956, **10**, 437.

[12] Lambou and Dollear, *Oil and Soap*, 1946, **23**, 97.

(treated as above) was determined by iodometric titration. The following are typical decomposition rates (%/hr.) observed 1—20 hr. after mixing, at 20° in darkness: 0·1N-Cl·SCN, 0·4; 0·1N-Cl·SCN + 0·1N-HCl, 0·3; 0·3N-Cl·SCN, 0·2; 0·3N-Cl·SCN + 0·3N-HCl, 0·3; 0·5N-Cl·SCN, 0·5; 0·5N-Cl·SCN + 0·5N-HCl, 0·8.

*Cryoscopic Measurements.*—(a) *In benzene.* To avoid inconsistencies caused by absorption of water, f. p. determinations were carried out in presence of phosphoric oxide (~0·5%), as recommended by Roberts and Bury.[13] Titrations showed that the presence of this compound improved the stability of thiocyanogen chloride in benzene at 20°. In the time needed for freezing and melting operations (~30 min.) there was an average decline of 5% in the strength of 0·1N-solutions. A normal Beckmann-type apparatus was used with platinum stirrer, mechanically maintained in slow motion. Some precautions recommended by Thompson and Ubbelohde [14] were used in handling the thermometer. Light was excluded from the apparatus. The benzene was purified by refluxing with phosphoric oxide and distillation, and its f. p. determined on the same sample as that used for the reagent. Solutions of thiocyanogen and chlorine were prepared, titrated, and mixed, and the mixture titrated immediately before f. p. determinations. The initial titre of the mixture was used in the molecular-weight calculation. Molecular-weight values were mainly between 96 and 98 and averaged 96·7 (theory 93·5). To check the accuracy of the method, exactly the same procedure was used on mixtures of chlorine and iodine (Found: *M*, 163—165. Calc. for ICl: *M*, 162·4).

(b) *In acetic acid.* The procedure described for benzene was used, except that moisture was excluded by passage of a slow current of dry nitrogen through the apparatus. The average decline in titre during the freezing and melting operations was 6%. The molecular-weight values showed a wider scatter than in benzene but averaged 95. The average found with a purified commercial sample of iodine chloride was 167.

(c) *In bromoform.* A procedure similar to that of Lecher and Goebel [2] was used. Purified bromoform is unstable. Chlorine was passed into the solvent to give a solution showing f. p. depression of 0·532° under dry nitrogen. Lead thiocyanate was added in an amount calculated to give a $\mathrm{Pb(SCN)_2 : Cl_2}$ ratio of 1 : 2, and the mixture stirred to effect reaction. The f. p. depression was then 0·507° (5% below its initial value).

*Reactions involving* OO-*Di*-n-*butyl Thiophosphate.*—(i) The salt was prepared by Foss's general procedure [4] for the potassium salt. The sodium salt crystallised from light petroleum (b. p. 60—80°) in hygroscopic needles. It showed infrared absorption bands (5% chloroform solution) at 3337 (w), 2961 (w), 1466 (w), 1381 (w), 1220 (w), 1133 (vs), 1066 (s), 1024 (s), 1000 (s), 973 (s), 889 (s), and 818 cm.$^{-1}$ (s). Depression of f. p. in 3% aqueous solution indicated complete dissociation. Depression of f. p. in 3% benzene solution indicated ~ten-fold association (Found: *M*, 2370 ± 100).

(ii) A solution of the salt (0·02 mole) in anhydrous ether (100 ml.) was treated with bromine (0·01 mole) in anhydrous ether (100 ml.). The precipitated sodium bromide was filtered off and the colourless filtrate was washed with water and dried, and the solvent evaporated, leaving *bis*-(OO-*di*-n-*butylthiophosphatogen*) [*bisdi*-n-*butoxyphosphinyl disulphide*] as a very pale yellow oil which could not be distilled without decomposition (Found: C, 42·8; H, 7·7. $\mathrm{C_{16}H_{36}O_6S_2P_2}$ requires C, 42·7; H, 8·0%); ultraviolet absorption max. (0·007M-$\mathrm{CCl_4}$ solution) was 266 mμ (log ε 2·09). Reaction was also carried out with a mixture prepared in carbon tetrachloride, 0·022M in $\mathrm{(SCN)_2}$ and 0·044M in $\mathrm{(Bu^nO)_2PO{\cdot}SNa}$. Sodium thiocyanate was immediately precipitated (99% of theoretical amount) and the filtrate showed the same ultraviolet characteristics as the above sample ($\lambda_{\max.}$ 264 mμ, log ε 2·13).

(iii) A mixture was prepared in carbon tetrachloride, 0·0484M in Cl·SCN and 0·0968M in $\mathrm{(Bu^nO)_2PO{\cdot}SNa}$. The colour immediately faded. The finely divided salt which immediately separated was extracted into water and recovered by evaporation. Analysis by a standard procedure [15] showed NaCl, 50·4; NaSCN, 49·6%; the total weight of precipitate was 99% of the theoretical for a mixture of this composition.

(iv) A mixture was prepared in carbon tetrachloride, 0·0488M in Cl·SCN and 0·0488M in $\mathrm{(Bu^nO)_2PO{\cdot}SNa}$. The salt, which immediately appeared as a finely divided precipitate, was isolated by filtration and found to be exclusively sodium chloride (yield, 90% of the theoretical).

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[13] Roberts and Bury, *J.*, 1923, 2037.

[14] Thompson and Ubbelohde, *Trans. Faraday Soc.*, 1950, **46**, 349.

[15] Kolthoff and Stenger, " Volumetric Analysis," Vol. 2, Interscience, New York, 1947, pp. 266—268.

(v) A mixture was prepared in carbon tetrachloride, 0·0472M in ICl and 0·0472M in $(Bu^nO)_2PO{\cdot}SNa$. The colour changed from brown to the red-brown of iodine. Salt was immediately precipitated and when isolated by filtration was found to be exclusively sodium chloride (yield, 97% of the theoretical).

*Conductivity Measurements.*—A standard type of conductivity cell and bridge assembly was used (limit of measurement: specific conductance $\not< 1 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$). In " AnalaR " acetic anhydride, 0·05M-thiocyanogen showed excellent stability at 20° (no change during 3 hr., then decomposition at ~0·04%/hr.). The stability of 0·12M-thiocyanogen chloride was also good in this solvent at 20° (no change during 2 hr., then decomposition at ~0·15%/hr.). A fairly fast reaction occurred with iodine chloride and acetic anhydride, leading to a moderate increase in conductivity (max. after ~10 min. at 0·25M) followed by a fall to zero (~100 min.). In purified nitromethane the stability of 0·1M-thiocyanogen was good (0·25% decomposition/hr.), but the stability of thiocyanogen chloride was poor (decomposition ~10%/hr.); no reaction was noticed with iodine chloride. In the cases where reaction with solvent intruded, the effect was minimised by taking readings as quickly as possible after the preparation of solutions.

*Spectroscopic Data.*—Absorptions in the visible and near ultraviolet regions were recorded on a Unicam S.P. 500 spectrophotometer at room temperature, using a quartz cell of 1 cm. light path. Infrared spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer.

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QUEEN'S UNIVERSITY, BELFAST.

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