150. *Thiocyanogen Chloride. Part I. Chemical Evidence for the Existence of the Monomeric Compound in Solutions in Organic Solvents.*

By A. B. ANGUS and R. G. R. BACON.

Whereas previous descriptions of thiocyanogen chloride refer to relatively inert polymeric solids, the behaviour of fresh solutions made with equimolecular proportions of thiocyanogen and chlorine now suggests that they contain the reactive monomeric species Cl·S·CN. This adds immediately to olefins; in the case of ethylene and *cyclo*hexene the 2-chloroalkyl thiocyanate is thus obtained in high yield. With suitably reactive aromatic compounds it gives aryl thiocyanates, in good yield, and hydrogen chloride. Its reactivity towards dimethylaniline, phenol, and anisole is assessed in comparison with that of thiocyanogen and chlorine. Its observed properties suggest a compound polarised in the manner of $\overset{\delta-}{\text{Cl}}\text{–}\overset{\delta+}{\text{SCN}}$, with reactivity intermediate between that of chlorine and thiocyanogen and comparable with that of iodine chloride.

COMPOUNDS formed between halogens and pseudohalogens have been little investigated.[1] Thiocyanogen monochloride is such a compound. The parent pseudohalogen $(SCN)_2$, discovered by Söderbäck,[2] possesses many properties intermediate between those of bromine and iodine.[3] Thiocyanogen chloride might therefore be expected to show similar reactivity to iodine monochloride and bromine monochloride; such properties are now described.

A substance of the analysis SCNCl was isolated by Kaufmann and Liepe [4] after treating thiocyanogen with chlorine in halogenated hydrocarbons at about 0°. Since it was a crystalline solid, stable up to about 150°, and with very little chemical reactivity, it was evidently a polymer. This view was taken by Lecher and Joseph,[5] whose results suggested that the products made by Kaufmann's method were approximately hexameric, and by Baroni,[6] whose products were at least dimeric, even when made at —60°. Kaufmann's claim [7] that " thiocyanogen chloride " is monomeric when redissolved in boiling chloroform remains unconfirmed, though it is possible that the polymers can undergo some form of degeneration in hot organic solvents, for Lecher and Joseph used their polymer to convert dimethylaniline into *p*-thiocyanatodimethylaniline at 70—80°. The reaction of excess of chlorine with thiocyanogen produces a trichloride,[8] and decomposition reactions may produce sulphur chlorides and cyanuric chloride.

Seel and Müller [9] recently isolated thiocyanogen monobromide from sulphur dioxide solvent at —50° as a red, volatile, dissociable, and highly reactive crystalline solid. We have not tried to improve on the attempts of earlier workers to isolate the monomeric monochloride, but have examined the properties of the solutions obtained by mixing thiocyanogen and chlorine in organic solvents. These show the expected properties of solutions of Cl·SCN molecules. Their preparative applications have been indicated recently,[10] some of their physical properties are described in Part II (following paper), and

---

[1] Sharpe, *Quart. Rev.*, 1950, **4**, 115.
[2] Söderbäck, *Annalen*, 1919, **419**, 217.
[3] Reviewed by Wood, " Organic Reactions," Vol. 3, Wiley, New York, 1946, p. 240.
[4] Kaufmann and Liepe, *Ber.*, 1924, **57**, 923.
[5] Lecher and Joseph, *Ber.*, 1926, **59**, 2603.
[6] Baroni, *Atti R. Accad. Lincei*, 1936, **23**, 871.
[7] Kaufmann, *Ber.*, 1927, **60**, 58.
[8] Bacon, Irwin, Pollock, and Pullin, preceding paper.
[9] Seel and Müller, *Chem. Ber.*, 1955, **88**, 1747.
[10] Angus, Bacon, and Guy, *Chem. and Ind.*, 1955, 564.

various reactions will be reported later. We now describe two groups of experiments which first showed that Cl·SCN molecules add to olefinic bonds and cause thiocyanation of aromatic rings.*

We treated thiocyanogen solutions [2,3] with an equimolecular proportion of dissolved or gaseous chlorine. An immediate change in odour and colour occurs, the temperature rises slightly and the solution exhibits new physical and chemical properties. These changes we ascribe to the reaction: $(SCN)_2 + Cl_2 \longrightarrow 2Cl{\cdot}SCN$. The product is estimated iodometrically, like thiocyanogen or chlorine, through its instantaneous reaction with potassium iodide: $Cl{\cdot}SCN + 2I^- \longrightarrow SCN^- + Cl^- + I_2$. The titre of freshly prepared mixtures in dry purified solvents is typically 95—98% of the value to be expected from the titre of the components; lower figures are found if impure solvents are used. This deficiency could be due to side-reactions or to the consumption of some thiocyanogen chloride through reactions with contaminants or through polymerisation. The small loss in titre on mixing appears to be immediate, but there is a further and gradual deterioration, dependent on solvent, concentration, temperature, and illumination, which occurs when solutions are stored. Nevertheless, solutions can readily be prepared which show the reactions of thiocyanogen chloride during several days at 0—20°; they should be titrated just before use. In general, the preferred concentration range for reasonably stable solutions is 0·1—0·4N (0·05—0·2M)-Cl·SCN.

The choice of solvent is influenced by (*a*) its suitability as a medium for the reaction of thiocyanate and halogen,[2,3] (*b*) stability of the thiocyanogen solution thus produced, (*c*) the stability of the thiocyanogen chloride solution obtained by subsequent reaction with chlorine, and (*d*) the influence of the solvent on the reactions of the thiocyanogen chloride with organic compounds. Carbon tetrachloride was used in some experiments because it contains no replaceable hydrogen. It has limitations if, *e.g.*, 0·5—1N-thiocyanogen solutions are desired as a starting point, since the solution then obtained from lead thiocyanate and bromine is weaker than expected, rapidly declines in strength to $\sim$0·4N-$(SCN)_2$, and is often accompanied by highly unstable material, possibly undissolved thiocyanogen, in the residual lead salts. We also employed chloroform, preferably freed from ethanol. This was used by earlier workers for thiocyanogen chloride preparations; it is an excellent medium for the preparation of thiocyanogen and was found satisfactory for relatively concentrated reagent (2M-Cl·SCN) at low temperatures. Toluene was also used, because it remains liquid at low temperatures, but it is too reactive towards thiocyanogen chloride to be generally recommended.

Addition of an olefin to thiocyanogen chloride solution causes an immediate exothermic reaction in which an α-chloro-β-thiocyanato-compound is produced: $>C{:}C< + Cl{\cdot}SCN \longrightarrow >CCl{\cdot}C(SCN)<$. Ethylene and *cyclo*hexene thus gave, respectively, the known 2-chloroethyl thiocyanate and 2-chloro*cyclo*hexyl thiocyanate, in 80% yields. The latter compound had previously been prepared [11] by a reaction between *cyclo*hexene, phenyl iododichloride, and lead thiocyanate, in which thiocyanogen chloride may well have been an intermediate, but this preparation was incidental to other work and was not commented upon by the authors. Reaction of thiocyanogen chloride with styrene, *iso*butene, or butadiene yielded mixed products. This could be due to addition in both directions at the unsymmetrically substituted olefinic bonds, as occurs with iodine chloride.[12] There is also the possibility that secondary reactions had occurred or that the addition had given some *iso*thiocyanate, as is known for certain addition reactions between olefins and thiocyanic acid.[13] The rapidity with which thiocyanogen chloride combined with all the

* The addition reaction was observed during the War by one of us (R. G. R. B.) in the Research Laboratories of Imperial Chemical Industries Limited, Dyestuffs Division, whom we thank for permission to refer to the experiments.

[11] Farmer and Shipley, *J.*, 1947, 1519.
[12] Ingold and Smith, *J.*, 1931, 2742, 2752.
[13] Luskin, Gantert, and Craig, *J. Amer. Chem. Soc.*, 1956, **78**, 4965.

olefins shows it to be a more reactive compound than thiocyanogen, which exhibits negligible reaction unless subjected to ultraviolet irradiation.[14]

By analogy with iodine chloride, thiocyanogen chloride should act as a thiocyanating agent for aromatic compounds:

$$\text{RH} + \text{Cl·SCN} \longrightarrow \text{R·SCN} + \text{HCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Such reactions would involve transfer of all the thiocyanate groups from the reagent to the aromatic molecule, whereas substitutions with thiocyanogen involve transfer of only half the thiocyanate groups:

$$\text{RH} + (\text{SCN})_2 \longrightarrow \text{R·SCN} + \text{HSCN} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

We examined the behaviour of *NN*-dimethylaniline, phenol, and anisole; the relative reactivity of these compounds in nuclear substitutions diminishes in the order here given.[15] The reactions were in carbon tetrachloride, which is a poor medium for nuclear substitution, but was chosen for the reason given above.

Whereas Lecher and Joseph's polymeric thiocyanogen chloride attacked dimethylaniline only under drastic conditions, the reaction with our 0·1M-solutions was instantaneous at 0°, and *p*-thiocyanatodimethylaniline was isolated in 75% yield, reckoned on the basis of reaction (1), together with amorphous material. Dimethylaniline is so reactive that even thiocyanogen reacted with it instantaneously under the same conditions, giving the same product in practically quantitative yield, reckoned on the basis of reaction (2). The relative reactivity of Cl·SCN and $(\text{SCN})_2$ towards phenol could be readily distinguished; the former reaction was almost too fast for measurement at 0°, whereas the rate of the latter reaction exhibited the very poor reproducibility which is common for nuclear aromatic halogenations in carbon tetrachloride,[16] but the time required for 50% reaction was of the order of 100—1000 times greater than in the case of thiocyanogen chloride. The same product, *p*-thiocyanatophenol, was obtained, yields of isolated compound being of the order of 75%, reckoned on the basis of reactions (1) and (2) respectively. The gaseous product formed in the reaction with thiocyanogen chloride was hydrogen chloride, and the amount measured was in good agreement with the quantity of *p*-thiocyanatophenol isolated. In the case of anisole, neither thiocyanogen nor thiocyanogen chloride reacted over long periods, while chlorine, under similar conditions, reacted slowly. In none of our experiments with thiocyanogen chloride did we obtain evidence for nuclear chlorination.

From the experiments here reported the conclusions to be drawn are: (*a*) that monomeric thiocyanogen chloride appears to exist in organic solvents and to be polarised in the manner $\overset{\delta-}{\text{Cl}}\text{-}\overset{\delta+}{\text{SCN}}$; (*b*) that its chemical behaviour is broadly similar to that of the halogens and interhalogen compounds; (*c*) that its degree of reactivity is intermediate between that of thiocyanogen and chlorine and is somewhat comparable with that of iodine chloride; and (*d*) that it is probably not in equilibrium with thiocyanogen and chlorine, in which respect it appears to resemble iodine chloride rather than bromine chloride.

EXPERIMENTAL

Thiocyanogen Solutions.—Standard procedures [2,3] were used for the reaction of bromine with a small excess of lead thiocyanate, at 0°, to produce solutions varying from 0·1 to ~2N-thiocyanogen in chloroform, benzene, toluene, or ethylene dichloride. Thiocyanogen was estimated by adding an aliquot part to excess of 10% methanolic potassium iodide and titrating the liberated iodine with thiosulphate. With dry and purified materials the yields were usually 95—100% (on "AnalaR" bromine). Attempts to prepare ~N-solutions in carbon tetrachloride gave abnormally low conversions and abnormally unstable solutions; the residual

---

[14] Söderbäck, *Annalen*, 1925, **443**, 142.
[15] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.
[16] Robertson, de la Mare, and Johnston, *J.*, 1943, 276.

lead salts contained an unstable product (? thiocyanogen) which frequently showed sudden and exothermic decomposition as solvent evaporated. Preparations with light petroleum as solvent showed similar characteristics. 0·1—0·2N-Thiocyanogen in carbon tetrachloride showed very little change in titre over several days at 0°. Typical data for carbon tetrachloride solutions at 20° are:

Period of storage (hr.):	0·5	1	2	5	20	50
Concentration (N) (i) *	0·662	0·608	0·543	0·465	0·395	0·378
(ii)	0·240	0·240	0·239	0·235	0·220	0·200
(iii)	0·0977	—	—	—	0·0970	0·0936

* Initial strength, 0·74N; theoretical value from bromine consumed, 1·05N.

The hygroscopic ammonium, sodium, or potassium thiocyanates (an unconventional choice) could be used, in conjunction with bromine or chlorine, for the preparation of thiocyanogen in hydrocarbons or halogenated hydrocarbons (yields, up to 95% on halogen), provided the salt was thoroughly dried, finely ground, and used in considerable excess.

Thiocyanogen Chloride Solutions.—Chlorine was dried with sulphuric acid. For the larger-scale preparations the gas was passed into thiocyanogen solution through a flowmeter until the requisite gain in weight had occurred. For smaller quantities, separate solutions of thiocyanogen and chlorine were mixed in the requisite proportions, iodometric titrations being carried out on the components immediately before mixing and on the product immediately after mixing. Fresh solutions were clear, golden-yellow, and rather pungent. On keeping, their iodometric titre diminished and they slowly became turbid through deposition of amorphous yellow solid.

2-*Chloroethyl Thiocyanate.*—A solution of thiocyanogen (300 ml., 0·67M) in chloroform or toluene was cooled to −60° and 14 g. (0·2 mole) of chlorine were passed in, followed immediately at the same temperature by a stream of ethylene (~0·6 mole). The resulting yellow solution was allowed to attain room temperature and 2 g. of solid were filtered off. Distillation gave 2-chloroethyl thiocyanate (39 g., 80%) as a colourless oil, b. p. 99—100°/20 mm., 198—202°/766 mm. (lit.,[17] 202—203°), d_4^{23} 1·283, n_{D}^{23} 1·5100; it had an unpleasant, pungent odour and slightly vesicant properties (Found: C, 30·1; H, 3·4; N, 11·4; S, 26·7; Cl, 29·8. Calc. for C_3H_4NClS: C, 29·6; H, 3·3; N, 11·5; S, 26·4; Cl,29·2%). A sample obtained by refluxing ethylene dichloride with ammonium thiocyanate in ethanol (24% yield in 6 hr.) showed b. p. 99—100°/20 mm., d_4^{23} 1·281, n_{D}^{23} 1·5109.

2-*Chloro*cyclo*hexyl Thiocyanate.*—A solution of thiocyanogen in chloroform or toluene (200 ml., 1·00M) was treated at −60° with chlorine (14 g., 0·2 mole) and then with excess of *cyclo*hexene (0·5 mole), added dropwise. An immediate exothermic reaction occurred, giving a yellow solution, which when distilled yielded 2-chloro*cyclo*hexyl thiocyanate (56 g., 80%), b. p. 154—156°/21 mm., n_{D}^{14} 1·5308 (Farmer and Shipley [11] give b. p. 90—92°/0·1 mm., $n_{\mathrm{D}}^{18\cdot5}$ 1·5284) (Found: C, 48·1; H, 5·6; N, 7·9; S, 18·6; Cl, 19·9. Calc. for $C_7H_{10}NClS$: C, 47·8; H, 5·7; N, 8·0; S, 18·3; Cl, 20·2%).

Reaction with Other Olefins.—Under conditions similar to those described above *iso*butene gave a mixture of liquid fractions (60%), b. p. 60—130°/23 mm., some of which approximated in composition to C_5H_8NClS. Styrene gave oils (35%), b. p. 100—180°/30 mm., and much resin. Butadiene gave a mixture of liquid fractions and a viscous residue which decomposed.

Reactions with Dimethylaniline.—(*a*) Mixing at 0° of 0·1005M-thiocyanogen in carbon tetrachloride and 0·1044M-chlorine in carbon tetrachloride gave 0·0974M-thiocyanogen chloride (95% of theoretical strength). 720 ml. of this reagent (0·07 mole of Cl·SCN) were treated at 0° with dimethylaniline (8·5 g., 0·07 mole) dissolved in a little carbon tetrachloride; the temperature instantly rose by 10° and yellow solid separated. The precipitate and solution were extracted with excess of 5N-hydrochloric acid, which left some amorphous yellow solid (~1 g.) undissolved. Neutralisation of the acidic extract with ammonia yielded *p*-thiocyanatodimethylaniline (9·4 g., 75%), which crystallised from aqueous methanol in yellow needles, m. p. 72—73°, undepressed by a sample, m. p. 72—73°, prepared by use of ammonium thiocyanate and bromine.[18] (*b*) 0·0973M-Thiocyanogen was prepared in carbon tetrachloride from lead thiocyanate and bromine (97% yield). When dimethylaniline (0·05 mole) was added to 515 ml.

---

[17] James, *J. pr. Chem.*, 1879, **20**, 351; Josephson, *Biochem. Z.*, 1933, **265**, 448.

[18] "Organic Syntheses," Coll. Vol. 2, p. 574.

of the solution (0·05 mole of thiocyanogen) at 0°, reaction proceeded as in (*a*). *p*-Thiocyanatodimethylaniline, m. p. 72—73°, was isolated in 95% yield.

Reactions with Phenol.—(*a*) Solutions of phenol and of thiocyanogen chloride in carbon tetrachloride were rapidly mixed at 0° to give a solution initially 0·050M in phenol and 0·050M in Cl·SCN. Substitution occurred almost too rapidly for measurement, the temperature rising by 3°; iodometric titration showed reaction to be complete in ~10 min. *p*-Thiocyanatophenol was obtained, partly as a precipitate and partly by evaporation, in 84% yield and had m. p. 52—53° on recrystallisation from water; Söderbäck [2] gives m. p. 53—54°. Similar reactions were effected at 0° and at concentrations of 0·3M, the carbon tetrachloride solution (300 ml.) being swept with dry nitrogen which passed to a 2 ft. glass-packed scrubbing tower where it was in contact with aqueous N-sodium hydroxide. When reaction was over, the temperature was raised to the b. p. and the mixture kept under reflux for a few hours while the nitrogen stream was continued. The collected alkaline wash liquid was analysed volumetrically for chloride, which corresponded with 72—78% of the thiocyanogen chloride employed for the reaction. *p*-Thiocyanatophenol was isolated in an average yield of 73%, together with a little polymer and resin.

(*b*) The rate of reaction between phenol (0·050M) and thiocyanogen (0·050M) at 0° in carbon tetrachloride was followed by iodometric analysis. Rates were fairly slow but were non-reproducible, even in darkness; 2—24 hr. were required for 50% reaction.

(*c*) Under conditions similar to those described in (*a*) and (*b*) above, the reaction of phenol was even faster with chlorine than with thiocyanogen chloride.

Reactions with Anisole.—No significant reaction was observed at 0° in a carbon tetrachloride solution 0·1M in anisole and 0·1M in thiocyanogen chloride; the fall in titre of the solution was the same in the absence of anisole as in its presence. Under similar conditions, anisole and chlorine reacted slowly; ~20 hr. were required for 50% reaction.

QUEEN'S UNIVERSITY, BELFAST. [*Received, August 8th,* 1957.]