Reaction of Sulphur Dicyanide with Thiocyanate Ion

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Rates and products of the reaction of $S(CN)_2$ with the ion SCN^- are reported. They are consistent with formation of $(SCN)_2$ as an intermediate.

PREVIOUS work[1,2] has provided several examples of nucleophilic substitution reactions [equation (1)] at the carbon atoms in sulphur dicyanide, $S(CN)_2$. With the ion SCN^- such a step provides a path for isotopic exchange. Alternative reactions, *e.g.* (2), are accessible to study. The reverse of (2) was proposed[1] in order to interpret the formation of $S(CN)_2$ during hydrolysis of thiocyanogen, $(SCN)_2$. There is evidence that the products of decomposition of $(SCN)_2$ in aqueous solution are not simple; they include[3] yellow solids of poorly defined composition. It is also probable that $(SCN)_2$ is an intermediate in oxidations of SCN^- (with Cl_2, Br_2, HNO_3, H_2O_2, and $S_2O_8^{2-}$)[4] which produce similar yellow solids. However with H_2O_2 and HSO_5^- no traces of such products have been found,[5,6] and this may reflect the nature of the intermediates involved.

$$S(CN)_2 + B^- \longrightarrow BCN + SCN^- \qquad (1)$$

$$S(CN)_2 + SCN^- + H_3O^+ \longrightarrow (SCN)_2 + HCN + H_2O \qquad (2)$$

In the present study, the rates and products of reaction of sulphur dicyanide with the thiocyanate ion [equation (2)] have been investigated.

RESULTS AND DISCUSSION

Reaction Rates.—Over a range of conditions, rates of reaction were found to be first order in $S(CN)_2$ (rate constant, k_{obs}) within any one experiment. Values of k_{obs} (Table 1) obey equation (3) at constant $[H^+]$ and $[HCN]$. The value deduced for k_2 is in fair agreement with that found previously[1] in the absence of the ion SCN^-. Values of k_1 are strongly dependent on the acid and cyanide-ion concentrations. At least qualitatively, such observations are consistent with equation (2), if the reverse reaction is not negligible.

$$k_{obs} = k_1[SCN^-] + k_2 \qquad (3)$$

The variation of k_1 with temperature corresponded to an activation energy of 74 kJ mol^{-1}. In previous work[1] on the decomposition of sulphur dicyanide, at acidities comparable to those employed in the present study, upward curvature in first-order plots was observed towards increasing values of the rate. Using the appropriate values of k_1, such curvature may be predicted due to the increasing $[SCN^-]$ throughout the decomposition reaction.

Reaction Products.—Under the conditions of this study, the products of reaction included yellow materials $S(CN)_2,mH_2O$, having low solubilities in water. Such compounds were never detected in reactions at low concentrations of thiocyanate and cyanide ions. Concentrations of the other products (SCN^-, HCN, H^+, SO_4^{2-}, and HOCN) were all determined (typical results are shown in Table 2) and are in good agreement with

TABLE 1

Rates of decomposition of $S(CN)_2$ in aqueous acidic solutions containing SCN^- at 30 °C and I = 0·80M

$10^3[S(CN)_2]$ M	$[H^+]$ M	$[SCN^-]$ M	$[HCN]$ M	$10^5 k_{obs}$ s^{-1}	$10^4 k_1$ l mol^{-1} s^{-1}
2·35	0·200	0·200	0·200	3·84	1·76
3·64	0·200	0·200	0·200	3·94	1·81
4·70	0·200	0·200	0·200	3·85	1·76
5·15	0·200	0·200	0·200	4·02	1·85
9·66	0·200	0·200	0·200	4·06	1·87
4·55	0·075	0·200	0·200	3·52	1·60
4·68	0·130	0·200	0·200	3·65	1·66
4·61	0·360	0·200	0·200	4·29	1·98
4·49	0·200	0·120	0·200	2·47	1·78
4·51	0·200	0·160	0·200	3·20	1·79
4·62	0·200	0·240	0·200	4·72	1·83
4·26	0·200	0·320	0·200	6·32	1·87
4·26	0·200	0·400	0·200	7·98	1·91
4·76	0·200	0·200	0·080	4·41	2·04
4·61	0·200	0·200	0·120	4·20	1·94
4·86	0·200	0·200	0·240	3·71	1·69
4·62 [a]	0·075	0·200	0·200	3·68	1·68
4·61 [b]	0·075	0·200	0·200	3·68	1·68
4·59 [c]	0·075	0·200	0·200	8·83	3·95
4·35 [d]	0·075	0·200	0·200	0·685	0·316
4·45 [e]	0·075	0·200	0·200	0·134	0·065

[a] Ionic strength = 0·675M. [b] Ionic strength = 0·475M. [c] Temp. = 40·0 °C. [d] Temp. = 15·0 °C. [e] Temp. = 0 °C.

TABLE 2

Stoicheiometry of the decomposition of $S(CN)_2$ in aqueous acidic solutions at 30 °C

	Concentration/mol dm^{-3}			
Experiment	(i)	(ii)	(iii)	(iv)
Reactants				
$S(CN)_2$	0·0095	0·0340	0·0095	0·0095
SCN^-	0·2030	0·2030	0·1015	0·2030
HCN	0·000	0·000	0·1015	0·1015
H^+	0·2032	0·2032	0·1017	0·1017
Products				
HOCN	0·00064	0·00202	0·00077	0·00038
HCN	0·0080	0·0314	0·0041	0·0037
H^+	0·0076	0·0329	0·0048	0·0040
SCN^-	0·0052	0·0179	0·0032	0·0024
SO_4^{2-}	0·00198	0·0078	0·00095	0·00081
Step	Fraction of reaction			
(1)	0·07	0·06	0·08	0·04
(4)	0·63	0·69	0·30	0·26
(5)	0·30	0·25	0·62	0·70

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[2] M. Kuhn and R. Mecke, *Chem. Ber.*, 1960, **93**, 618.

[3] Beilstein, Springer, Berlin, 1921, series I, vol. III, p. 170.

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[5] G. M. Harris and I. R. Wilson, *J. Amer. Chem. Soc.*, 1960, **82**, 4515.

[6] R. H. Smith and I. R. Wilson, *Austral. J. Chem.*, 1966, **19**, 1357, 1365.

equation (1) ($B^- = H_2O$) together with the two additional steps (4) and (5). This Table also gives the fractional contribution from each of these three steps.

$$3S(CN)_2 + 4H_2O \longrightarrow 4HCN + 4H^+ + 2SCN^- + SO_4^{2-} \quad (4)$$

$$S(CN)_2 + mH_2O \longrightarrow S(CN)_2,mH_2O \quad (X) \quad (5)$$

It appears that step (1) is independent of those of (4) and (5). Thus the rate constants proposed[1] for this step predict a 6% contribution to the reaction of sulphur dicyanide and thiocyanate ion, in good agreement with our results. Also comparison of experiments (iii) and (iv) (Table 2) strongly suggests that steps (4) and (5) depend on the thiocyanate-ion concentration but (1) does not. Step (4) is not adequately interpreted using previous arguments,[1] which predict approximately equal yields of sulphate and cyanate ions.

If cyanate ions are formed in a different reaction path from those of (4) and (5), then the formation of sulphate ions and $S(CN)_2,mH_2O$ is directly dependent on the thiocyanate-ion concentration and both these products are equally dependent on the $S(CN)_2$ concentration. Addition of HCN depresses the formation of sulphate ions relative to that of $S(CN)_2,mH_2O$, with little change in the total rate of steps (4) and (5). Thus it is improbable that these steps are independent.

Solvent Dependence of Rates.—Measurements of the reaction rate were also made in dioxan (10 or 20% v/v)–water and methanol (water content *ca.* 4×10^{-3} mol dm^{-3}) solvents (Table 3). First-order dependences on $[S(CN)_2]$ and on $[SCN^-]$ were observed. In the methanol solutions, rates increased after about 1 half-life. Values of k_2 in the dioxan solutions were estimated by assuming a proportionality to the water concentration. In the methanol solutions, k_2 was measured independently. The rate of reaction increased somewhat with increase in the dioxan concentration. Similar changes were reported[7] for alkaline hydrolysis of ethyl acetate in solutions of low dioxan concentration. The rates observed in methanol solution are not greatly different from those in aqueous solution. Thus the rate-determining step does not appear to involve water molecules.

TABLE 3

Solvent dependence of rates of decomposition of sulphur dicyanide at 30 °C

Solvent	$10^3[S(CN)_2]$ M	$[H^+]$ M	$[SCN^-]$ M	$[HCN]$ M	$10^5\,k_{obs}$ s^{-1}	$10^4 k_1$ l mol^{-1} s^{-1}
Dioxan (10%)	2·60	0·203	0·203	0·203	4·74	2·18
Dioxan (20%)	5·20	0·203	0·203	0·203	5·64	2·62
Methanol	7·66	0·10	0·00	0·00	0·077	
Methanol	7·24	0·10	0·0354	0·00	0·627	1·55
Methanol	7·20	0·10	0·0642	0·00	$1{\cdot}06_2$	1·53

Since in these reactions, as in aqueous solution, a yellow material was precipitated, its composition cannot be that given in equation (5). The yellow materials may be related but, as previous experiments[4] showed, they are not of constant composition. We suggest that their formation in thiocyanate-ion oxidation reactions is due to the formation of substantial amounts of thiocyanogen as a reaction intermediate. The composition of such products appears to vary and further work is needed to establish their structures.

EXPERIMENTAL

Reagents.—Sulphur dicyanide was prepared by a published method[8] from freshly prepared[9] sulphur dichloride. The product (m.p. 64—65 °C) was resublimed immediately before use. Dioxane was purified according to the method in ref. 10. Other reagents were of analytical reagent quality and were used as received, apart from removal of water.

Analytical Methods.—The sum ($SCN^- + CN^-$) was determined by titration in acidic solution either (i) with 0·04M mercury(II) nitrate solution [potentiometric end-point or iron(III) alum indicator], or (ii) with 0·075M silver(I) nitrate solution (potentiometric end-point). Thiocyanate ions were determined similarly after removal of cyanide in a stream of nitrogen gas. Sulphate ions were determined gravimetrically with barium(II) chloride solution or by precipitation with lead(II) nitrate solution and EDTA titration.[11] Duplicate determinations were generally in agreement to within 0·5%. Cyanate and ammonium ion analyses were carried out by a semi-micro Kjeldahl distillation procedure.[5] Total acid was determined with carbonate-free sodium hydroxide solution.

Sulphur dicyanide was determined either (i) iodometrically,[1] or (ii) by addition of an excess of standard sodium thiosulphate solution and back titration with standard aqueous iodine solution. In both methods, 20 min were allowed before the final titration was carried out; HCN and SCN^- were shown not to interfere. Results of the two methods agreed to within 0·4%. Method (ii), developed for use in studies of thiocyanogen hydrolysis (Kerr and Wilson, unpublished work), depends upon reaction (6). This was shown by analysis for the ions SCN^- and CN^-,

$$S(CN)_2 + 2S_2O_3^{2-} + H^+ \longrightarrow HCN + SCN^- + S_4O_6^{2-} \quad (6)$$

formed from known quantities of $S(CN)_2$ and thiosulphate ions. When these analyses involved mercury(II), they required allowance for the subsequent reaction with the tetrathionate ions produced. Reaction (6) appears to be a further example of step (1).

The products of the reaction of sulphur dicyanide with the thiocyanate ion were analysed after completion of the

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[8] Ref. 3, p. 180.

[9] G. Bauer, 'Handbook of Preparative Inorganic Chemistry, 2nd edn., Academic Press, New York, 1963, vol. I, p. 370.

[10] A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., Longmans, London, 1956, p. 177.

[11] G. Schwarzenbach, 'Complexometric Titrations,' Methuen, London, 1957, p. 92.

reaction in sealed ampoules (used to avoid errors due to loss of HCN).

Determinations of the Reaction Rate.—Reaction rates were measured by periodic sampling of solutions in stoppered flasks and subsequent iodometric analysis. Reactions were initiated by addition of solid $S(CN)_2$ to aqueous acidic solutions containing sodium thiocyanate, cyanide, and perchlorate ions (to adjust the ionic strength). The temperature was thermostatically controlled to $\pm 0{\cdot}1$ K.

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