Reaction of Sulphite Ions with Cyanogen Chloride

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The reaction between cyanogen chloride and sulphite ions has been shown to involve the formation of a stable adduct. The formation and decomposition of this adduct have been studied by kinetic analyses, from which a reaction scheme is proposed. The activation energies of both reactions have been determined.

CHATTAWAY and WADMORE stated, in 1902,[1] that 'When solutions of cyanogen chloride and sulphurous acid or sulphites are heated to 100°, the latter are oxidised while the hydrogen cyanide (presumed to have been formed by the reduction of the cyanogen chloride) is destroyed probably hydrolysed.' A similar reaction was reported by Gutman,[2] in as much detail. No further communications have been published.

In the context of a general study of the reactions of cyanogen chloride, arising from the importance of this compound in effluent treatment, the kinetics of the reaction with sulphite ions, and related reactions, have been investigated and have led to a complete reappraisal of the reaction scheme. Within a certain range of hydrogen-ion concentration a stable adduct is formed, the formation and decomposition of which have been studied.

Preliminary Examination.—Tests were conducted to discover what were the reaction products; it was initially supposed that sulphate and cyanide ions would be among them. Tests were carried out in two non-aqueous solvents, carbon tetrachloride and formic acid, between 1 : 1 mixtures (0·3 mol l^{-1}) of cyanogen chloride and sulphur dioxide, but in neither case was there any evidence of reaction. Addition of solid cyanogen chloride to liquid sulphur dioxide likewise produced no reaction. Resort was perforce made to aqueous media; sulphur dioxide solution (1·0 mol l^{-1}, 5 ml) was added to an excess of cyanogen chloride and borax added to pH = 8. After 2 h all the cyanogen chloride had reacted, perhaps in part by hydrolysis. A silver(I) nitrate test identified chloride ions, and acidification of the product solution followed by making alkaline produced a little ammonia, indicating the formation of a trace of cyanate ions. The polysulphide,[3] Prussian blue, and Bark and Higson [4] tests for cyanide ions were all negative. Also negative were tests for formic acid and formaldehyde, and sulphide, thiosulphate, thiocyanate, and sulphamate ions. Repetition of the experiment with an excess of sulphur dioxide in the reaction mixture yielded negative tests again for those compounds not containing sulphur. The reaction mixture with an excess of cyanogen chloride was analysed quantitatively for sulphate ions by precipitation of barium sulphate. Two separate experiments showed that 2·3% of the sulphur dioxide had been converted to sulphate ions, a value easily accounted for by aerial oxidation of the initial solution.

Before addition of borax to the reaction mixture, sulphur dioxide and cyanogen chloride remained unreacted for several hours. After addition of borax to raise the pH to 8 or 9, the sulphur dioxide and sulphite ions rapidly disappeared and the concentration of the excess of cyanogen chloride decreased. However, if the same mixture was tested a day or two later, after all the cyanogen chloride had hydrolysed or otherwise reacted, sulphur dioxide was again detectable together with a trace of thiocyanate ions. Sulphur dioxide (or sulphite ions) was evidently being regenerated, but there was no trace of either cyanide ions or cyanogen chloride. Cyanate ions were identified so that the cyanide moiety was being converted to cyanate. The results were reproducible. At pH = 8—9, sulphite ions evidently react with cyanogen chloride to give a compound sufficiently stable to be chemically distinguishable from its components, and this compound slowly decomposes to give, finally, cyanate, chloride, and sulphite ions.

EXPERIMENTAL

The preparation and purification of cyanogen chloride solutions have been described.[5] Sulphur dioxide solutions were prepared from liquefied gas (B.D.H.), and partially stabilised by addition of a trace of disodium ethylenediaminetetra-acetate.[6] All other reagents were of AnalaR grade purity. The apparatus has been described previously.[5]

Procedure.—*Adduct formation*. The general procedure has been described previously.[5] Reaction mixtures were buffered, usually with borax adjusted to the required pH, and sampled at measured time intervals. The aliquot portions were analysed alternately for sulphite ions, using the coulometric method described elsewhere,[7] and for cyanogen chloride using a modification [8] of the spectrophotometric method of Bark and Higson.[4] The initial sulphite-ion concentration was determined before the addition of the aliquot portion of standardised cyanogen chloride solution to the buffer and a correction, usually less than 1%, was made for the dilution arising from addition of the cyanogen chloride solution. All runs were carried out at 26·5 °C, unless otherwise specified.

Adduct decomposition. The adduct is comparatively stable at pH = 9, but in more strongly alkaline media it decomposes to chloride, cyanate, and sulphite ions. The adduct was formed at pH *ca*. 8 in the same closed system as before [5] and, after a delay of at least 2 h to ensure that the system had reached a steady state, the sulphite-ion concentration was determined and the pH raised to a preselected

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[1] F. D. Chattaway and J. M. Wadmore, *J. Chem. Soc.*, 1902, **81**, 191.

[2] A. Gutman, *Ber.*, 1909, **42**, 3623.

[3] F. Feigl, 'Spot Tests in Inorganic Analysis,' 5th edn., Elsevier, Amsterdam, 1958, p. 277.

[4] L. S. Bark and H. G. Higson, *Talanta*, 1964, **11**, 621.

[5] P. L. Bailey and E. Bishop, preceding paper.

[6] R. E. Humphrey, M. H. Ward, and W. Hinze, *Analyt. Chem.*, 1970, **42**, 698.

[7] P. L. Bailey and E. Bishop, *Analyst.*, 1972, **97**, 311.

[8] P. L. Bailey and E. Bishop, *Analyst.*, 1972, **97**, 691.

value in the range pH = 10—12 by the addition of very strong sodium hydroxide solution. Timing was started as the pH was raised. Aliquot portions of the reaction mixture were analysed coulometrically for sulphite ions at measured time intervals. After sufficient readings, about eight, had been taken for a kinetic plot, the solution was made strongly alkaline by the addition of sodium hydroxide pellets (to minimise dilution of the solution). The residual adduct was allowed to decompose (2 min), and aliquot portions were analysed to obtain an infinity point for the run. Values of $\log_{10}([SO_3^{2-}]_\infty - [SO_3^{2-}]_t)$ were plotted against time, t, where $[SO_3^{2-}]_\infty$ is the coulometer reading in seconds for the infinity point samples and $[SO_3^{2-}]_t$ the reading for the sample at time t. The range covered was from pH = 10·1, below which regeneration of sulphur dioxide is so slow that aerial oxidation becomes important, to pH = 11·9, above which the reaction becomes too fast conveniently to be followed by this procedure.

RESULTS

Adduct Formation.—From the measurements, plots were constructed of the sulphite-ion concentration, $[SO_3^{2-}]$, the cyanogen chloride concentration, [CNCl], and $\log_{10} A$ (where A is the absorbance reading after correction for the blank) against time. These plots were analysed by the initial-rate method,[9] which is the only method permitted by the circumstances, and so interference in the analysis by intermediates was minimised. The analysis of the [CNCl] results proved more satisfactory by measuring the initial rate of decay from the $\log_{10} A$ against time plot on the assumption that equation (1) is applicable, where k_0' is the initial pseudo-

$$k_0' = 2{\cdot}303\, \mathrm{d} \log_{10} A/\mathrm{d}t = (1/[\mathrm{CNCl}]_0)\mathrm{d}[\mathrm{CNCl}]/\mathrm{d}t \quad (1)$$

first-order rate constant and $[\mathrm{CNCl}]_0$ is the initial cyanogen chloride concentration. The logarithmic plot was preferred because it was always more closely linear than the zero-order plot, so permitting more accurate graphical estimation of the initial decay rate. The range pH = 4·0—9·2 was covered: at pH < 4 the reaction was too slow; at pH > 9·2 the hydrolysis of cyanogen chloride competes too strongly with the reaction with sulphite ions when the reactants are at approximately equivalent concentrations.

From the results of preliminary reactions at pH = 9·17 in 0·018 mol l^{-1} borax, plots were made of $\log_{10}(-\mathrm{d}[\mathrm{CNCl}]/\mathrm{d}t)$ against $\log_{10}$ [CNCl] to discover the initial order of the reaction with respect to cyanogen chloride, because the normal first-order plots were curved, as expected, due to consumption of sulphite ions. In two consecutive runs with comparable initial concentrations of reactants, initial orders of 1·74 and 1·34 were obtained; both plots were almost linear. A complex mechanism is therefore indicated.

A series of runs was made at pH = 8·15, at which formation of the adduct is fairly rapid and its decomposition is negligibly slow; the formation of the adduct is also fast compared to hydrolysis of cyanogen chloride.[5] The concentrations of the reactants and the ratio between them were varied over a substantial range to probe the mechanisms. A typical set of results from a run, showing the variation of [CNCl], $[SO_3^{2-}]$, and $\log_{10} A$ with time, is depicted in Figure 1. Despite the large number of reactions conducted at pH = 8·15, the observed rates did not precisely correlate with concentrations. However, the second-order rate constant, k defined by equation (2), was calculated

$$-\mathrm{d}[\mathrm{CNCl}]/\mathrm{d}t = k[\mathrm{CNCl}][SO_3^{2-}] \quad (2)$$

from each run using the equation $k = k'/[SO_3^{2-}]$, and gave a value constant to ±10% after applying a small correction, usually less than 2%, for hydrolysis of cyanogen chloride. Results are collected in Table 1. A set of runs at diverse pH values (Table 2) showed the pH dependence of the second-order rate constant.

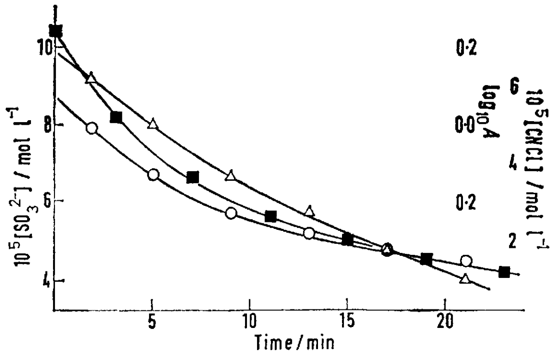

FIGURE 1 Variation of (○), [CNCl], (■), $[SO_2]$, and (△), $\log_{10} A$ with time during the formation of the adduct

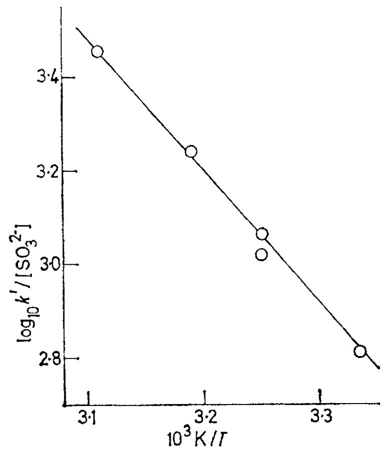

FIGURE 2 Arrhenius plot for the formation of the adduct

To determine the Arrhenius activation energy, reactions were performed at four temperatures from 26·5 to 47·2 °C. The Arrhenius plot is shown in Figure 2 and gave an activation energy of 54 kJ mol^{-1}. A wider temperature range, to secure a more accurate value, would not have been justified, because the assumption that the overall rate constant for the reaction, k, is equal to $k'/[SO_3^{2-}]$ has been shown to be an approximation. Tests in the absence of cyanogen chloride at the same temperatures showed that aerial oxidation of sulphite ion did not introduce any significant error.

Adduct Decomposition.—First-order plots were always satisfactorily linear over as much as five half-lives; an example is given in Figure 3. The pseudo-first-order rate constants, calculated from gradients of the first-order plots at diverse pH values, are plotted against pH in Figure 4. A least-squares treatment gave the gradient of this plot as 0·987, clearly showing that decomposition of the adduct is first order with respect to hydroxide as well as to sulphite ions. Hence the rate equation for the reaction is as in (3),

$$\mathrm{d}[SO_3^{2-}]/\mathrm{d}t = k[\mathrm{Adduct}][\mathrm{OH}^-] \quad (3)$$

[9] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, ch. 3.

TABLE 1

Kinetic data on the CNCl–SO_3^{2-} reaction at 26·5 °C and pH = 8·15

$10^5[SO_3^{2-}]_0$ / mol l^{-1}	10^5[CNCl]$_0$ / mol l^{-1}	$-10^6(d[SO_3^{2-}]/dt)_0$ / mol l^{-1} min^{-1}	-10^6(d[CNCl]/dt)$_0$ / mol l^{-1} min^{-1}	$10^2k'_{corr.}$ / min^{-1}	$10^{-2}k'/[SO_3^{2-}]$ / l mol^{-1} min^{-1}
7·00	1·51	2·17	1·14	7·20	10·29
6·90	2·22		1·87	6·24	9·04
14·17	2·04		2·92	13·70	9·67
23·19	2·64		5·87	21·07	9·09
10·14	2·39	3·55	2·13	9·44	9·31
13·06	1·54		1·47	11·97	9·17
7·97	3·63	5·68	2·28	6·17	7·74
6·84	4·85	5·55	2·43	5·35	7·82
8·43	6·20	5·06	4·22	6·63	7·86
10·37	7·61	9·29	5·78	8·08	7·79
7·18	7·80	8·26	4·62	5·80	8·08
7·03	2·59	2·02	1·30	6·15	8·75
8·07	5·68	5·55	2·61	5·13	6·36
10·36	5·73	8·66	4·57	8·76	8·46

TABLE 2

Kinetic data on the CNCl–SO_3^{2-} reaction at 26·5 °C and various pH

pH	$10^5[SO_3^{2-}]_0$ / mol l^{-1}	10^5[CNCl]$_0$ / mol l^{-1}	$-10^6(d[SO_3^{2-}]/dt)_0$ / mol l^{-1} min^{-1}	-10^6(d[CNCl]/dt)$_0$ / mol l^{-1} min^{-1}	$10^2k'_{corr.}$ / min^{-1}	$10^2k'/[SO_3^{2-}]$ / l mol^{-1} min^{-1}
7·43	9·98	2·46	6·16	1·79	7·04	7·05
7·43	8·66	1·58	2·82	1·12	6·31	6·97
7·43	9·51	5·47	5·08	2·18	3·80	4·00
7·43	12·56	3·26	4·82	2·05	6·60	5·25
7·43	6·56	7·75	5·18	2·83	4·21	5·43
7·43	13·02	4·48	6·54	3·54	8·61	6·61
7·43	10·28	4·30	3·88	—	6·88	6·69
9·17	11·93	5·70	8·99	5·73	10·71	8·98
9·17	13·01	3·65	6·79	4·21	12·50	9·61
7·72	7·76	3·72	2·98	1·67	4·55	5·86
7·21	8·99	3·24	2·70	1·36	4·12	4·58
6·98	7·89	5·10	2·61	1·61	3·12	3·95
6·66	8·25	5·18	2·13	1·12	2·24	2·72
6·30	7·14	4·79	0·775	0·436	1·19	1·71

on the assumption that the rate of sulphite ion production is proportional to the rate of adduct decomposition. From Figure 4 the value of k = 0·997 l mol^{-1} s^{-1}.

Several of the decomposition runs followed directly after formation runs, so a comparison could be made between the amount of sulphite ion regenerated during decomposition of the adduct with the amount of cyanogen chloride consumed during its formation. Some results for runs at 26·5 °C are presented in Table 3. The agreement

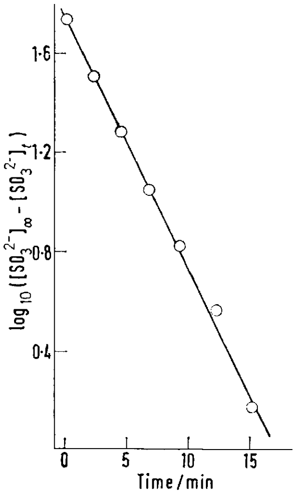

FIGURE 3 Plot of the logarithm of the amount of sulphite ion regenerated against time for the decomposition of the adduct

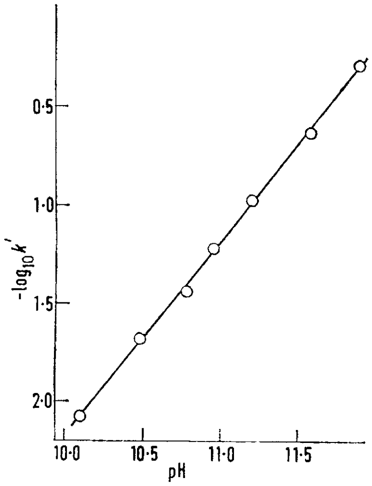

FIGURE 4 pH Dependence of the decomposition of the adduct

TABLE 3

Comparison of concentration changes

10^5[CNCl]$_0$ / mol l^{-1}	$10^5[SO_3^{2-}]_0$ / mol l^{-1}	$10^5\Delta[SO_3^{2-}]$ * / mol l^{-1}
5·73	10·36	5·06
5·10	7·92	5·26
5·18	8·25	5·47
3·24	8·99	3·74
4·67	6·35	4·26

* $\Delta[SO_3^{2-}]$ is the change in sulphite-ion concentration during the adduct decomposition.

is by no means perfect, but the ratio of cyanogen chloride to sulphite ion in the adduct is clearly 1 : 1. This has been confirmed by studying the concentration against time plots for the formation runs which show that the ratio of sulphite ion consumed to cyanogen chloride consumed tends towards 1 : 1 with time.

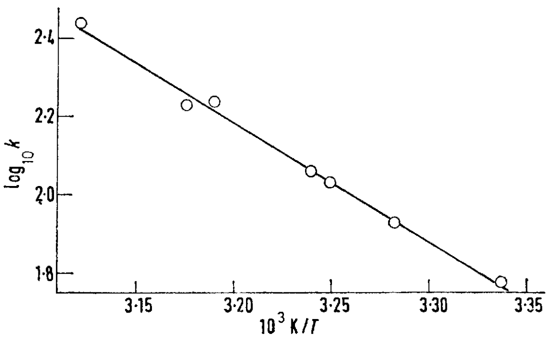

FIGURE 5 Arrhenius plot for the decomposition of the adduct

A series of decomposition reactions at temperatures from 26·5 to 47·2 °C was conducted. Values of the pseudo-first-order rate constant were measured and k calculated therefrom, assuming the rate equation (3) and using the appropriate value of pK_w at each temperature [10] to calculate the hydroxide-ion concentrations. The Arrhenius plot is shown in Figure 5 and a least-squares treatment gave an activation energy of 58·3 kJ mol^{-1}. This is remarkably close to the value, 59·1 kJ mol^{-1}, obtained for the hydrolysis of cyanogen chloride in the same medium.[5]

DISCUSSION

There are several strong pointers to the probable reaction mechanisms in the results described in the previous section.

(*a*) From the results in Tables 1 and 2, it frequently appears that the initial rate of decay of sulphite ion, in adduct formation, is just under twice that of the cyanogen chloride. At the beginning it appears that two sulphite ions are reacting with each cyanogen chloride molecule.

(*b*) Decomposition results in Table 3 suggest that the ratio of cyanogen chloride to sulphite ion in the adduct is 1 : 1; this conclusion is supported by the ratio of the amount of each reactant consumed in the formation experiment as the system approaches the steady state, which is also 1 : 1.

(*c*) The decrease of the second-order rate constant of the formation reaction with decrease in pH strongly indicates that the reacting sulphur(IV) species is sulphite ion. In Figure 6 the experimental points are superimposed on a calculated plot of Q against pH, where

$$Q = pq + r \qquad (4)$$

p = the fraction of the total species resulting from the added sulphur dioxide existing as sulphite ion at any given pH (assuming [11] $K = [HSO_3^-]/[H^+][SO_3^{2-}] = 10^{7.15}$ l mol^{-1}), $r = 70$ l mol^{-1} min^{-1} = $k = k'/[SO_3^{2-}]$ [taken as the first approximation to the overall rate constant from experiments at pH = 4 (ref. 12)], and $q = 880$ l mol^{-1} min^{-1} = (the apparent maximum value of $k'/[SO_3^{2-}]$ at high pH from a plot of $k'/[SO_3^{2-}]$ against pH) − r. The good agreement between experimental points and the theoretical curve strongly supports the validity of equation (4) and the deduction that sulphite ion is the reactive species.

(*d*) As in (*c*), when the pH is so low that the concentration of sulphite ions is negligible, *i.e.* at pH = 4, there yet remains a significant reaction. The rate equation must therefore contain terms independent of the sulphite-ion concentration.

(*e*) From (*a*), and also the non-integral reaction orders of the plots of ($\log_{10}$ d[CNCl]/dt)/$\log_{10}$ [CNCl] mentioned earlier, a sequential mechanism is implied. If all reaction intermediates in such a scheme were unstable, they would certainly be decomposed by the analytical reagents, bromine and pyridine in hydrochloric acid, or be caused to decompose by displacement of the equilibria consequent on removal of one or other reactant in the determination. This would result in reactant concentrations apparently decreasing in the ratio in which they combined in the final adduct, which is stable, and that ratio is 1 : 1. The ratio of the initial rates is not 1 : 1, so a semi-stable intermediate must be postulated which is not decomposed by the analytical reagents.

(*f*) The results discussed in (*a*) suggest that two sulphite ions and one cyanogen chloride molecule react fairly rapidly in successive steps which start the reaction sequence. Termolecular reactions being unlikely, it may be taken that a 1 : 1 intermediate is the first reaction product. That this must be unstable is evident from the points made in (*e*), and that it must react again

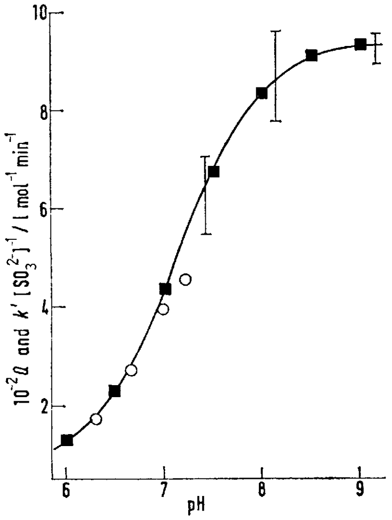

FIGURE 6 Comparison of the calculated (■) and experimental (o,I) values of Q and $k'[SO_3^{2-}]$ over the range pH 6—9

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[10] H. S. Harned and R. A. Robinson, quoted in R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1968, p. 544.

[11] L. G. Sillén, 'Stability Constants of Metal-ion Complexes,' Chem. Soc. Special Publ. No. 17, London, 1964, p. 229.

[12] P. L. Bailey, Ph.D. Thesis, University of Exeter, 1971.

quickly with a second sulphite ion is suggested by (*a*); consequently it may further be assumed that its concentration is low.

(*g*) The stability of the final adduct in solutions of pH = 8—9 compared to the instability of cyanogen chloride and sulphite-ion solutions in this range, together with the inertness of the adduct in the tests described in the Preliminary Examination section suggest that the adduct has adopted some particularly stable form. A further inference from (*a*) and (*f*) is that the stoicheiometry of the adduct may reasonably be 2 : 2.

(*h*) The production of some thiocyanate ion, indicated by a red colour with iron(III) ions in acid solution, as a secondary decomposition product suggests sulphur-carbon bonding in the adduct. The red colour is not formed by a freshly prepared solution of the adduct, but only after such a solution has been kept for 24 h at pH = 9.

(*i*) It is notable from the concentration against time plots of both reactants, mentioned in (*b*), that the ratio of reactants consumed approaches 1 : 1 more rapidly at lower pH values. This suggests a pH dependence in one of the final stages of the reaction, which results in more rapid reaction of a second cyanogen chloride molecule at lower pH values.

These considerations point to the following reaction sequence and rate equations. For the reasons stated in

$$SO_3^{2-} + CNCl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A \quad (5)$$

$$A + SO_3^{2-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B \quad (6)$$

$$B + CNCl \underset{k_6}{\overset{k_5}{\rightleftharpoons}} P \quad (7)$$

$$-d[CNCl]/dt = k_1[CNCl][SO_3^{2-}] + k_5[B][CNCl] - k_2[A] - k_6[P] \quad (8)$$

$$-d[SO_3^{2-}]/dt = k_1[CNCl][SO_3^{2-}] + k_3[A][SO_3^{2-}] - k_2[A] - k_4[B] \quad (9)$$

$$-d[A]/dt = k_3[A][SO_3^{2-}] + k_2[A] - k_1[CNCl][SO_3^{2-}] - k_4[B] \quad (10)$$

(*f*) the steady-state approximation may be applied to A, d[A]/d*t* = 0, so from equation (10), we obtain (11).

$$k_4[B] = k_3[A][SO_3^{2-}] + k_2[A] - k_1[CNCl][SO_3^{2-}] \quad (11)$$

Substituting this expression for k_4[B] in equation (9) gives (12). As long as the pH is kept low enough,

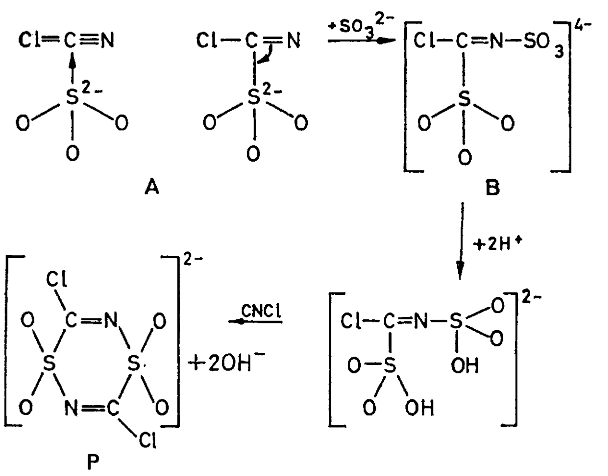
$$-d[SO_3^{2-}]/dt = 2k_1[CNCl][SO_3^{2-}] - 2k_2[A] \quad (12)$$

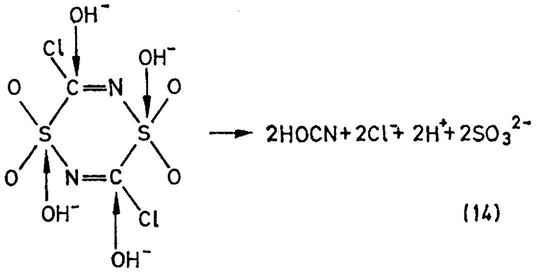
pH ⩽ 9, the product P is stable and k_6 may be assumed to be negligibly small. Hence, after substituting the value of [B] from equation (11), we obtain (13).

$$-d[CNCl]/dt = k_1[CNCl][SO_3^{2-}] + k_5[CNCl][SO_3^{2-}](k_3[A] - k_1[CNCl]) + k_2[A]\{(k_5/k_4)[CNCl] - 1\} \quad (13)$$

Whereas equations (12) and (13) satisfactorily describe the observed behaviour at least qualitatively, sufficiently consistent results have not yet been obtained to permit accurate evaluation of the rate constants other than that of k_1, which is shown to have a value of 880 l mol^{-1} min^{-1} at 26·5 °C. From (*i*) it seems probable that k_5 is a function of hydrogen-ion concentration.

Persistent attempts to isolate and characterise the product P have been unsuccessful, but it appears from the kinetic evidence that the adduct contains cyanogen chloride and sulphite ion in the ratio of 2 : 2. To account for the stability of the compound at pH ⩽ 9, a cyclic structure is likely, having a six-membered S–N–C ring; Graf[13] has postulated a S–N–O ring structure for one of the products of reaction of cyanogen chloride with sulphur trioxide, but this product was much less stable. A plausible reaction scheme is shown below. At higher pH values the adduct decomposes to regenerate sulphite ions. The close agreement between the activation energy for this reaction and that for the hydrolysis,[5] suggests that the same initial step is involved, replacement of a chloro-group attached to a carbon atom by a hydroxo-group as in (14). The first-order hydrogen-ion dependence suggests that attack by one hydroxide ion disrupts the molecule in the rate-determining step and the remaining break-up is fast.





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P. L. B. acknowledges support from Effluent Control International (now Oxy Effluent Control), Birmingham, and the S.R.C.

[2/2213 *Received, 22nd September*, 1972]

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[13] R. Graf, *Ber.*, 1956, **89**, 1077.