Hydrolysis of Cyanogen Chloride

By **Peter L. Bailey** and **Edmund Bishop**,* Department of Chemistry, The University of Exeter, Stocker Road, Exeter EX4 4QD

The hydrolysis of cyanogen chloride has been studied in buffered media. Rate equations have been derived, general base catalysis has been identified, and the activation energy of the reaction has been measured. The effects of several additives on the rate of hydrolysis have been examined. The chlorine-catalysed hydrolysis has been investigated and the catalytic species has been conclusively identified as dissolved molecular chlorine.

HYDROLYSIS of cyanogen chloride is the rate-determining step in the destruction of cyanide in industrial wastes by chlorination. With large volumes of waste and a hold-up time of 10—20 min, large expensive treatment tanks are required. An excess of chlorine is used in the process because (*a*) complete removal of cyanide is required, (*b*) the excess of chlorine catalyses the hydrolysis of cyanogen chloride, and (*c*) the electrometric sensing system, which controls the chlorine dosing, has an appreciable time lag. A fundamental study has been made of the controlling parameters of the uncatalysed hydrolysis, and also of the catalytic effect of an excess of chlorine. An important study, from the Water Pollution Research Laboratory over twenty years ago,[1,2] provided the design basis for treatment plants up to the present day. Neither this nor earlier work [3] provided a mechanism for chlorine catalysis, or identified the catalytic species.

As a basis for the present work, the rate constants, reaction orders, and activation energy of the uncatalysed reaction have been reinvestigated, as previously adumbrated.[4]

EXPERIMENTAL

Reagents.—Cyanogen chloride solutions were made by dilution of stock solutions prepared by a modification of Eden and Wheatland's method; [1] a silver(I) nitrate scrubber was added to the recirculation chain to ensure removal of hydrogen cyanide. In later experiments commercial liquid cyanogen chloride (Fluka) was used, which proved to contain up to 7% of hydrogen cyanide. The latter was removed from solutions of the gas by potentiometric titration with silver(I) nitrate and filtration; the filtrate was backtitrated with chloride ions to reduce the silver(I) ion concentration to a negligible level. Solutions of cyanogen chloride prepared by the two methods were shown to hydrolyse at identical rates. Solutions, both stock and dilutions, were made up in 0·01 mol l^{-1} perchloric acid at pH = 2·0, at which hydrolysis proceeds at the minimum rate.

Stock solutions of sodium hypochlorite were prepared by passing chlorine (I.C.I.) into 1·0 mol l^{-1} sodium hydroxide (AnalaR) until an excess was apparent. Chlorine dioxide solutions were prepared by treating sodium hypochlorite with sodium chlorite. The potassium cyanate used was of laboratory reagent grade purity; all other reagents were AnalaR.

Apparatus.—The reactions were conducted in a closed system because of the volatility of cyanogen chloride and chlorine. The reaction vessel (1000 ml) was suspended in a water tank thermostatted to ±0·1 °C. The clamped lid carried five standard sockets into which were inserted a mercury-sealed mechanically driven stirrer, a thermometer, a glass electrode, a salt bridge making external contact to a s.c.e. reference electrode, and a tube, extending below the surface of the solution, for the extraction of aliquot portions by pipette and which was stoppered when not in use. The assembly was tested and shown to be leak-proof. The glass electrode was calibrated before each run.

Procedure.—Since the reactions studied were pH dependent, they were, with exceptions to be mentioned, performed in 0·018 mol l^{-1} borax solution. The pH of the reaction mixture was continuously monitored by means of the glass and reference electrodes to confirm constancy. The pH of the borax medium (420 ml) was adjusted to the required value by additions of strong perchloric acid or sodium hydroxide solutions, and allowed to reach thermal equilibrium. A small aliquot portion of stock cyanogen chloride solution was added to give an initial concentration of *ca*. 5×10^{-5} mol l^{-1}, which is relevant to the industrial situation, within the range of the analytical method, and gives a convenient reaction rate. The reaction mixture was sampled at timed intervals by means of a pipette (5 ml), and the aliquot portions analysed for cyanogen chloride by

---

[1] G. E. Eden and A. B. Wheatland, *J. Soc. Chem. Ind.*, 1950, **69**, 166.

[2] G. E. Eden, B. L. Hampson, and A. B. Wheatland, *J. Soc. Chem. Ind.*, 1950, **69**, 244.

[3] C. C. Price, T. E. Larson, K. M. Beck, F. C. Harrington, L. C. Smith, and I. Stephanoff, *J. Amer. Chem. Soc.*, 1947, **69**, 1640.

[4] P. L. Bailey and E. Bishop, *Proc. Soc. Analyt. Chem.*, 1970, **7**, 150.

the method previously described.[5] For runs in the presence of an excess of 'chlorine,' an aliquot portion of freshly standardised sodium hypochlorite was added to the buffer medium before the cyanogen chloride. The chlorinated buffer medium was used to prepare the blank solution for the cyanogen chloride analyses, which were performed by a procedure modified for the presence of chlorine.[5] After complete hydrolysis of the cyanogen chloride, the residual chlorine was determined by addition of iodide ions, acidification, and titration with standard sodium thiosulphate solution.

RESULTS AND DISCUSSION

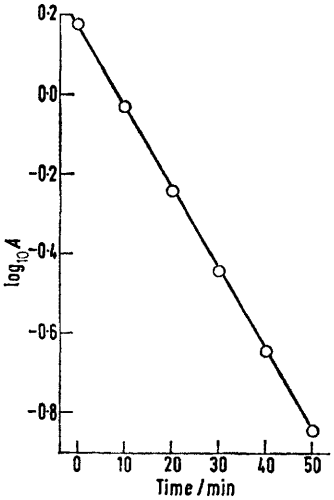


FIGURE 1 Typical uncatalysed hydrolysis plot of $\log_{10} A$ (A = absorbance) against time at pH = 10

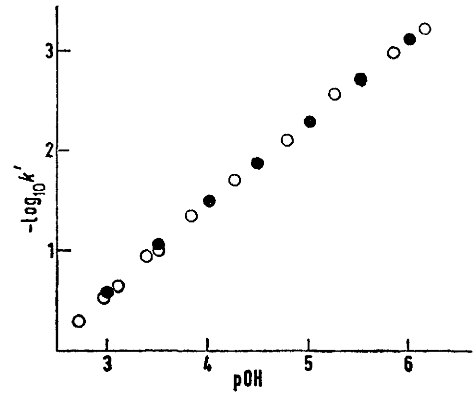


FIGURE 2 Plot of $-\log_{10} k'$ against pOH for the uncatalysed hydrolysis: (●), calculated points; (○) experimental points

Hydrolysis in the Absence of Chlorine.—(i) *Rate constants and reaction orders*. The hydrolysis was found to be first order in cyanogen chloride. Plots of the logarithm of the spectrophotometer absorbance readings against time regularly showed very close adherence to linearity over up to five half-lives (Figure 1). To examine the order with respect to hydroxide ion, a series of hydrolyses was carried out in the range pH = 7·5—11·2 and the results analysed by determination of the pseudo-first-order rate constants, k', from gradients of first-order plots. In Figure 2, values of log k' are plotted against pOH (= pK_w − pH). At high hydroxide-ion concentrations, pOH = 3—4, the order of reaction closely approaches unity; the gradient of the line is 0·96. As the hydroxide-ion concentration decreases, so does the apparent order of reaction until, at pOH = 6, it is 0·8. From these results, k' has been shown to obey the relation (1). Analysis of curves such as those in Figures 1 and 2 gave the following values for the rate constants

$$k' = k_1 + k_2[\mathrm{OH}^-] + \frac{k_3}{(1 + K[\mathrm{H}^+])} \cdot [\mathrm{Borax}] \quad (1)$$

at 26·5 °C: $k_1 = 1{\cdot}55 \times 10^{-4}$ min^{-1}; $k_2 = 272$ l mol^{-1} min^{-1}; and $k_3 = 0{\cdot}361$ l mol^{-1} min^{-1}. The formation constant of the acid involved in the borax buffer, K, is assigned the value $10^{9{\cdot}17}$ l mol^{-1}, corresponding to the pH at which the maximum buffer capacity is exhibited. Theoretical values of log k' calculated from the rate constants k_1, k_2, and k_3 are plotted in Figure 2 for comparison, and may be seen adequately to describe the observed behaviour.

TABLE 1

Analysis of pseudo-first-order rate constants

pH	k'	=	k_1	+	$k_2[\mathrm{OH}^-]$	+	$\frac{k_3}{(1 + K[\mathrm{H}^+])} \cdot [\mathrm{Borax}]$
7·95	$7{\cdot}96 \times 10^{-4}$	=	$1{\cdot}55 \times 10^{-4}$	+	$2{\cdot}72 \times 10^{-4}$	+	$3{\cdot}69 \times 10^{-4}$
8·45	$2{\cdot}05 \times 10^{-3}$	=	$1{\cdot}55 \times 10^{-4}$	+	$8{\cdot}60 \times 10^{-4}$	+	$1{\cdot}04 \times 10^{-3}$
8·95	$5{\cdot}32 \times 10^{-3}$	=	$1{\cdot}55 \times 10^{-4}$	+	$2{\cdot}72 \times 10^{-3}$	+	$2{\cdot}44 \times 10^{-3}$
9·45	$1{\cdot}30 \times 10^{-2}$	=	$1{\cdot}55 \times 10^{-4}$	+	$8{\cdot}60 \times 10^{-3}$	+	$4{\cdot}26 \times 10^{-3}$
9·95	$3{\cdot}29 \times 10^{-2}$	=	$1{\cdot}55 \times 10^{-4}$	+	$2{\cdot}72 \times 10^{-2}$	+	$5{\cdot}57 \times 10^{-3}$
10·45	$9{\cdot}23 \times 10^{-2}$	=	$1{\cdot}55 \times 10^{-4}$	+	$8{\cdot}60 \times 10^{-2}$	+	$6{\cdot}17 \times 10^{-3}$
10·95	$2{\cdot}79 \times 10^{-1}$	=	$1{\cdot}55 \times 10^{-4}$	+	$2{\cdot}72 \times 10^{-1}$	+	$6{\cdot}39 \times 10^{-3}$

Equation (1) indicates consumption of cyanogen chloride by reactions with water, hydroxide ion, and the basic borax species. The last term derives from a consideration of the proportion of borax present in the basic form at a given hydrogen-ion concentration, making the simplest assumption as to the nature of the acid–base equilibrium. The reaction of cyanogen chloride with borax is an example of general base catalysis. The relative magnitudes of the three terms in (1) are important and are shown in the breakdown in Table 1. To test the borax dependence of (1), the borax concentration was varied in a series of experiments and the results compared with those predicted by equation

---

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

(1) (Table 2). The small differences between experimental and calculated values may partly be attributed to the decrease in activity coefficient of the basic species as its concentration increases, and, probably less significantly, to the tendency of the species present to polymerise;[6] unfortunately these suggestions are difficult quantitatively to evaluate.

TABLE 2

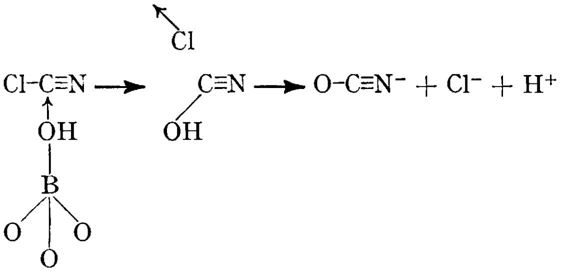
Variation of k' with borax concentration at 26·5 °C and pH = 9·17

[Borax]/mol l^{-1}	k'/min^{-1}	$k_{calc.}$/min^{-1}
$1{\cdot}80 \times 10^{-2}$	$7{\cdot}91 \times 10^{-3}$	
$3{\cdot}60 \times 10^{-2}$	$1{\cdot}061 \times 10^{-2}$, $1{\cdot}045 \times 10^{-2}$	$1{\cdot}117 \times 10^{-2}$
$0{\cdot}90 \times 10^{-2}$	$6{\cdot}95 \times 10^{-3}$, $6{\cdot}97 \times 10^{-3}$	$6{\cdot}30 \times 10^{-3}$

It seems probable that the borax species reacts as a hydroxo-group donor, analogous to the behaviour of $B(OH)_4^-$ ion in catalysing the hydrolysis of compounds such as ethyl malonate and acetaldehyde.[7] Structurally,[8] the borax ion has two tetrahedral O_3BOH^- groups, and it is not implausible that its hydroxo-groups should react in a similar way to those in $B(OH)_4^-$. Furthermore, Nies and Campbell[9] assert that, ' borax acts, as far as pH is concerned, much as though it were dissociated completely into free boric acid molecules and an equal concentration of monoborate ions, which are hydrated, $B(OH)_3$ and $B(OH)_4^-$.' Thus for borax, the hydrogen-ion concentration obeys equation (2),

$$[H^+] = [B(OH)_3]/K[B(OH)_4^-] \qquad (2)$$

where K is the formation constant of $B(OH)_3$, better than do other inorganic borate compounds, which obey the relation over only a very narrow range of pH because of polymerisation. This behaviour supports the analogy between the reactions of $B(OH)_4^-$ and the basic borax species, and the reaction mechanism (3) may be proposed.



$$\underset{\substack{\uparrow \\ OH-B(O)_3}}{Cl-C\equiv N} \longrightarrow \underset{OH}{\overset{\nwarrow Cl}{C\equiv N}} \longrightarrow O-C\equiv N^- + Cl^- + H^+ \qquad (3)$$

(ii) *The Arrhenius activation energy.* A series of hydrolyses at 5—45 °C, pH = 10·1, was carried out. The half-life of the reaction varied from about 10 h at 5 °C to 1 min at 45 °C. Second-order rate constants, k, were calculated from (4) which is a fair approximation

$$k = k'/[OH^-] \qquad (4)$$

at pH = 10·1; a treatment accounting for all three reactions) with water, hydroxide ion, and the basic borax species) would require a knowledge of the variations of K, k_1, k_2, and k_3 with temperature separately. The simple treatment seems adequate, bearing in mind the theoretical and experimental limitations on the accuracy of activation energies. The value of $[OH^-]$ in (4) is derived from $pOH = pK_w - pH$, using Harned and Robinson's values for pK_w at the various temperatures.[10] The Arrhenius plot of log k against T^{-1} is shown in Figure 3. A least-squares treatment of the results gives an Arrhenius activation energy of 59·1 ± 0·5 kJ mol^{-1}.

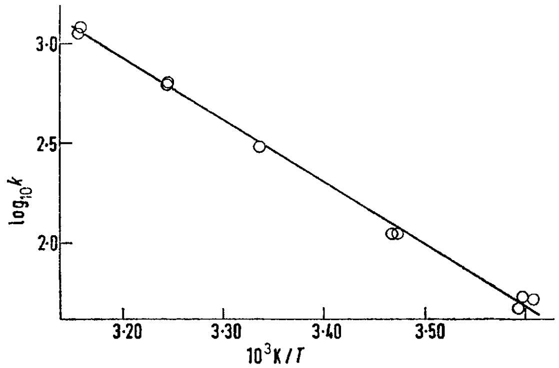


FIGURE 3 Arrhenius plot for the uncatalysed hydrolysis

Eden and Wheatland[1] obtained a value of 12·4 kcal mol^{-1} (51·9 kJ mol^{-1}), at pH=11 in a medium of $1{\cdot}58 \times 10^{-3}$ mol l^{-1} borax and $5{\cdot}09 \times 10^{-2}$ mol l^{-1} sodium carbonate, over a temperature range of 0—30 °C. Douglas and Winkler[11] and Lister[12] obtained values around 21 kcal mol^{-1} (88 kJ mol^{-1}), but the media were either unbuffered[12] or ' buffered ' to pH = 4—6 with carbon dioxide;[11] these results therefore apply to the reaction of cyanogen chloride with water and not that with hydroxide ion, as in the present work and that of Eden and Wheatland. The present result is a good approximation to the activation energy of the reaction, but must be treated as conditional until the separate effects of temperature on k_1, k_2, and k_3 can be evaluated and the appropriate corrections applied.

(iii) *Ionic strength.* A brief investigation of the effect of ionic strength on hydrolysis rate was made by addition of sodium perchlorate to increase the ionic strength by (*a*) *ca.* 35% ($1{\cdot}94 \times 10^{-2}$ mol l^{-1}) and (*b*) *ca.* 110% ($6{\cdot}22 \times 10^{-2}$ mol l^{-1}). Values of the pseudo-first-order

---

[6] R. G. Bates, ' Determination of pH,' Wiley, New York, 1964, ch. 4.

[7] R. P. Bell, J. O. Edwards, and R. B. Jones in ' The Chemistry of Boron and its Compounds,' ed. E. L. Muetterties, Wiley, New York, 1967, p. 219.

[8] A. F. Wells, ' Structural Inorganic Chemistry,' 3rd edn., Clarendon Press, Oxford, 1962, p. 836.

[9] N. P. Nies and G. W. Campbell in ' Boron, Metallo-Boron Compounds, and Boranes,' ed. R. M. Adams, Interscience, New York, 1964, p. 85.

[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] D. E. Douglas and C. A. Winkler, *Canad. J. Res. B.*, 1947, **25**, 381.

[12] M. W. Lister, *Canad. J. Chem.*, 1957, **35**, 736.

rate constant, k_1, at 26·5 °C and pH=10·12 were (*a*) $4{\cdot}38 \times 10^{-2}$ min^{-1} and (*b*) $4{\cdot}07 \times 10^{-2}$ min^{-1}, in contrast to $4{\cdot}56 \times 10^{-2}$ min^{-1} with no added sodium perchlorate.

An increase in the ionic strength therefore produces a small decrease in the rate of hydrolysis. Debye–Hückel theory would not predict a primary kinetic salt effect as cyanogen chloride is uncharged. The decrease corresponds to a secondary salt effect caused by a decrease in the activity coefficients of the reactants: that of hydroxide ion will decrease by about 10% [13] when the ionic strength is doubled from 6 to 12×10^{-2} mol l^{-1}; such calculations for borax must necessarily be approximate.

(iv) *Effect of additives.* The effects of certain additives on k' are shown in Table 3; other halogen species are treated later. The various metal ions have little effect; the slight increases found with nickel(II) and cobalt(II) are difficult to explain. The decrease with chloride ion is a secondary ionic strength effect as in (iii). Phosphate ion, which has been reported to catalyse the hydrolysis,[3] had no effect.

TABLE 3

Effect of various additives on k'

Additive	Initial concn. / mol l^{-1}	10^5[CNCl]$_0$ / mol l^{-1}	pH	$10^2k'$ / min^{-1}
			10·12	4·56 [a]
			9·17	0·79 [a]
(1) Fe^{II}	$1{\cdot}8 \times 10^{-3}$	5·01	10·10	4·35
(2) Hg^{II}	$1{\cdot}0 \times 10^{-3}$	3·85	10·10	4·11
(3) Ni^{II}	$5{\cdot}0 \times 10^{-5}$	4·19	10·10	4·81
(4) Ni^{II}	$1{\cdot}7 \times 10^{-4}$	4·48	10·10	4·81
(5) Cd^{II}	$3{\cdot}3 \times 10^{-5}$	1·49	10·12	4·63
(6) Co^{II}	$1{\cdot}7 \times 10^{-4}$	1·69	10·11	4·87
(7) Cl$^-$	$2{\cdot}0 \times 10^{-2}$	3·57	10·10	4·14
(8) Cl$^-$	$2{\cdot}0 \times 10^{-2}$	3·53	10·10	4·23
(9) NH_3	$2{\cdot}0 \times 10^{-2}$	3·34	10·11	11·62
(10) NH_3	$8{\cdot}0 \times 10^{-5}$	4·30	10·10	4·54
(11) CN$^-$	$2{\cdot}0 \times 10^{-2}$	3·20	10·13	9·59
(12) CN$^-$	$1{\cdot}0 \times 10^{-3}$	3·23	10·12	5·37
(13) CNO$^-$	$1{\cdot}0 \times 10^{-3}$	3·18	10·10	4·55
(14) SO_2	$1{\cdot}4 \times 10^{-4}$	3·53	10·16	17·9
(15) H_2O_2	$2{\cdot}0 \times 10^{-4}$	7	9·13	20
(16) Br_2	$8{\cdot}0 \times 10^{-5}$	4·71	9·19	0·76
(17) HPO_4^{2-}	$2{\cdot}0 \times 10^{-2}$	4·30	10·12	4·24
(18) HCO_3^-–CO_3^{2-}	$2{\cdot}0 \times 10^{-2}$ [b]	5·52	10·10	6·02
(19) HCO_3^-–CO_3^{2-}	$2{\cdot}0 \times 10^{-2}$ [b]	5·87	10·09	6·16
(20) HCO_3^-–CO_3^{2-}	$4{\cdot}0 \times 10^{-2}$ [b]	4·26	10·09	7·55

[a] Calculated value. [b] No borax buffer was used.

Ammonia. Experiment (9), and perhaps (10), reflects the direct reaction of cyanogen chloride with ammonia to produce cyanamide, first investigated by Cloez and Cannizzaro,[14] and cursorily examined by Price,[3] but a full study of this reaction has yet to be made.

Cyanide ion. Reaction between cyanogen chloride and cyanide ion is clearly shown. A similar effect, in different circumstances, was observed by Schulek and Pungor.[15,16] Using solutions of concentrations appropriate to titrimetry, they found that, when an excess of cyanide ion was added to cyanogen chloride, the ability of the latter to oxidise iodide ion vanished, and one cyanide ion was consumed for each cyanogen chloride molecule. They attributed this effect to the formation of an inactive complex of the type CNCl,CN; no more plausible explanation can be offered.

Hydrogen peroxide. This additive produced a startling increase in the rate of loss of cyanogen chloride, even at low concentration. This is attributed to the powerful hydroxo-group donor properties of hydrogen peroxide, promoting rapid substitution of a hydroxo-group for the chlorine atom at the carbon atom in cyanogen chloride.

Carbonate ion. The accelerating action of the carbonate species lends weight to the proposal of general base catalysis of cyanogen chloride hydrolysis. The catalytic effect is approximately linear in carbonate concentration and, assuming that carbonate ion is the catalytic species, the rate equation is as in (5), where k_1 and k_2 have the

$$k' = k_1 + k_2[\mathrm{OH}^-] + k_3^*[\mathrm{CO_3}^{2-}] \qquad (5)$$

values previously determined and $k_3^* = 2{\cdot}0 \pm 0{\cdot}2$ l mol^{-1} min^{-1}. As predicted by the Brønsted relation, the catalysis is greater for carbonate ion than for borax.

The reaction of cyanogen chloride with sulphur dioxide is discussed in the following paper.

Hydrolysis in the Presence of Chlorine.—Exploratory experiments to locate the approximate reaction rates gave surprising results. A stock solution of sodium hypochlorite many months old was used to give an initial concentration of available chlorine of 8×10^{-5} mol l^{-1} with a cyanogen chloride concentration of 3×10^{-5} mol l^{-1}. No increase in the rate of hydrolysis at pH = 9·2 and 10·2 was observed, and no significant decrease in the amount of available chlorine occurred over 75 min. When a freshly prepared sodium hypochlorite solution was used to give an initial available concentration of 8×10^{-4} mol l^{-1} at pH = 9·17, no trace of cyanogen chloride could be detected after 2 min. For an initial available chlorine concentration of 8×10^{-5} mol l^{-1} at pH = 9·17, the hydrolysis half-life was 1·9 min as opposed to 95 min in the absence of chlorine. These and other results are collected in Table 4. It is notable that successive runs with the same sodium hypochlorite solution showed decreasing rates, and that rates for one

TABLE 4

Results of chlorine-catalysed hydrolyses

Sodium hypochlorite	10^5[‘ Available chlorine ’] / mol l^{-1}	k' / min^{-1}	
		at pH = 9·17	at pH = 10·12
Nil	0	$7{\cdot}91 \times 10^{-3}$	$4{\cdot}56 \times 10^{-2}$
Old soln.	8·0	$7{\cdot}59 \times 10^{-3}$	$4{\cdot}90 \times 10^{-2}$
Soln. (1):			
(*a*) Fresh	8·0	$3{\cdot}83 \times 10^{-1}$	Fast
(*b*) 14 days old	8·0	$3{\cdot}21 \times 10^{-1}$	Fast
Soln. (2)			$1{\cdot}49 \times 10^{-1}$
			$1{\cdot}19 \times 10^{-1}$
Soln. (3)		$2{\cdot}61 \times 10^{-2}$	$9{\cdot}24 \times 10^{-2}$

---

[13] W. J. Moore, ‘ Physical Chemistry,’ 4th edn., Longmans, London, 1963, p. 351.

[14] Cloez and Cannizzaro, *Annalen*, 1851, **78**, 229.

[15] E. Schulek and E. Pungor, *Analyt. Chim. Acta*, 1951, **5**, 137.

[16] E. Pungor and E. Schulek, *Ann. Univ. Sci. Budapest, Sect. Chim.*, 1960, **2**, 99.

solution showed no relation to results for any other solution. To discover which of the many possible chlorine species is responsible for the catalysis, a series of experiments was performed with additions of each of the possible species in turn and the pseudo-first-order rate constants determined. The results are shown in Table 5 together with those for added bromine or iodine monochloride. Chloride and perchlorate ions have already been shown to be non-catalytic in the previous section (iv).

TABLE 5

Effect of various halogen additives on k'

	Additive	Concn. mol l^{-1}	k' min^{-1}
At pH = 9·17	None	0	$7{\cdot}91 \times 10^{-3}$
	ClO_2^-	8×10^{-5}	$9{\cdot}07 \times 10^{-3}$
	ClO_2(aq)	4×10^{-5}	$8{\cdot}0 \times 10^{-3}$
	Cl_2(aq)	8×10^{-5}	$4{\cdot}00 \times 10^{-2}$
		8×10^{-5}	$3{\cdot}08 \times 10^{-2}$
	Br_2(aq)	8×10^{-5}	$7{\cdot}6 \times 10^{-3}$
	$ClO^- + HgO$	8×10^{-5}	7×10^{-3}
	ICl	3×10^{-3}	$8{\cdot}0 \times 10^{-3}$
At pH = 10·12	None	0	$4{\cdot}56 \times 10^{-2}$
	ClO_3^-	8×10^{-5}	$4{\cdot}47 \times 10^{-2}$
	$ClO^- + HgO$	8×10^{-5}	$4{\cdot}64 \times 10^{-2}$

The purpose of adding yellow mercury(II) oxide (2 g) to fresh sodium hypochlorite (100 ml) was to remove dissolved molecular chlorine. The colour of the solution changed from strong yellow-green to very pale green, and the corrosion potential produced at a gold electrode disappeared. The reactions are (6) and (7) and the

$$HgO + Cl_2(aq) \longrightarrow Cl_2O + Hg \qquad (6)$$

$$Cl_2O + H_2O \longrightarrow 2HClO \qquad (7)$$

chlorine is converted to hypochlorous acid. The solution was standardised after addition of the mercury(II) oxide, immediately before use in each experiment, to determine the available chlorine concentration. Mercury(II) ion has already been shown to have no effect on the rate of hydrolysis of cyanogen chloride.

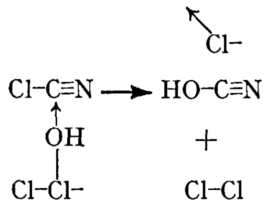
Chlorite ion caused a slight acceleration of hydrolysis, but nothing like enough to account for the catalysis usually observed. The only solutions that did produce catalysis were chlorine water and untreated sodium hypochlorite containing an evident excess of chlorine. Such a solution stored in a clear glass bottle slowly lost its colour, as did the gas above the solution, and at the same time its catalytic properties decreased and finally vanished.

Clearly, therefore, the catalytic species is dissolved molecular chlorine; a surprising result because chlorine could not be expected to have more than a transitory existence at pH = 9—10. This suggests that the rate of equilibration of the hydrolysis of chlorine is slow at such hydroxide-ion concentrations, or that the Cl_2(aq) species is stabilised by the buffer which is unlikely. Little seems to have been published on the subject except for studies on the hydrolysis of chlorine in unbuffered or relatively acidic media. Having identified the catalytic species, it would have been interesting to investigate the reaction mechanism. This would require a method of determination of traces of elemental chlorine in a large excess of hypochlorous acid and hypochlorite ions at total available chlorine levels of the order of 10^{-4} mol l^{-1}.

At pH <9, the reaction[17] between chlorine and cyanate ions produced by the hydrolysis of cyanogen chloride becomes significant and, at pH = 7, is very rapid so that catalysis of the hydrolysis ceases. At pH = 2, virtually no hydrolysis, catalysed or otherwise, was detected. At pH >10, the results become rather irreproducible because of the more rapid removal of free chlorine from the solution. Only in the very narrow range pH = 8·5—10·5 is the catalysis relatively free from interference.

Knowing the identity of the catalyst, it is possible to propose a plausible mechanism. Eigen and Kustin[18] have shown that in hydrochloric acid at pH = 1—3 the first step in the hydrolysis of chlorine is the formation of the ion Cl_2OH^- [equation (8)], and this has been corroborated.[19] There is no reason to suppose that the same mechanism does not apply at pH >9 and so the relative stability of Cl_2OH^- with respect to Cl_2 and OH^- must be quite large. However, Cl_2OH^- is unstable with respect to loss of chloride ion, and it is feasible that in the presence of cyanogen chloride or borax, which provide hosts for the hydroxide ion, the back reaction could be made energetically more favourable, so permitting transference of the hydroxo-group to the carbon atom of the cyanogen chloride with the liberation of a chlorine molecule ready to repeat the cycle [equation (9)].

$$Cl_2 + OH^- \rightleftharpoons Cl_2OH^-; \quad K = 10^5 \text{ l mol}^{-1} \qquad (8)$$



$$\mathrm{Cl{-}C{\equiv}N \longrightarrow HO{-}C{\equiv}N + Cl{-}Cl + Cl^-} \qquad (9)$$

In summary, the fact has emerged that dissolved molecular chlorine is present in greater concentration than equilibrium data would indicate, and is the catalytic species responsible for the increase in the rate of hydrolysis of cyanogen chloride when an excess of ' available chlorine ' is added to cyanide in solutions in the range pH = 8·5—10·5.

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

[2/2203 *Received*, 21*st September*, 1972]

---

[17] M. W. Lister, *Canad. J. Chem.*, 1956, **34**, 489.

[18] M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, 1962, **84**, 1355.

[19] A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, 1962, **66**, 701.