1263. *The Preparation, Properties, and Kinetics and Mechanism of Hydrolysis of Some Chloropentakis(alkylamine)chromium(III) Salts*

By A. Rogers and P. J. Staples

A series of complexes corresponding to the formula $[Cr(RNH_2)_5Cl]Cl_2$ (R = H, Me, Et, allyl, Bu^n, or Bu^i) has been prepared. Their hydrolyses have been studied over a wide range of acid concentrations at constant ionic strength. Experiments using buffer solutions suggest that these reactions are base-catalysed. The mechanism of these hydrolyses is discussed.

In neutral aqueous solutions the complexes $[Cr(RNH_2)_5Cl]Cl_2$ decompose completely to yield the green chromium(III) salts. If, however, these complexes are dissolved in dilute perchloric acid, the chloro-group is slowly replaced by water. The main product is presumably the aquopentakisalkylaminechromium(III) ion. Attempts to prepare salts of this ion have so far proved unsuccessful.

The hydrolyses of the compounds of this series have been studied at 60° at constant ionic strength over a wide range of acid concentration (0·005—1·00M). For all the compounds studied, the plot of first-order rate constant against acid concentration is a rectangular hyperbola. At higher acid concentrations the rate of hydrolysis reaches a limiting value. These results suggest that the hydrolyses are base-catalysed. Buffer-ratio experiments support this view. Experiments performed in the presence of bases, *e.g.*, dichloroacetate ions, sulphate ion–hydrogen sulphate ion buffers, all gave considerably increased rate constants.

Preparation of Compounds.—Mandal prepared the salts of $[Cr(RNH_2)_5Cl]^{2+}$ where R = Me,[1] Et,[2] Pr^n,[3] and Bu^n.[4] In our hands, however, Mandal's methods for the ethylamine and n-propylamine derivatives did not give the required product but yielded chromic hydroxide. The methylamine and n-butylamine analogues were prepared by other methods (see Experimental section). The preparations of the allylamine and isobutylamine derivatives are reported for the first time. The equivalent conductivities (Table 1) were measured as rapidly as possible to avoid any errors due to hydrolysis. The values obtained support the assigned formulæ.

TABLE 1

Equivalent conductivities (mho cm.$^{-2}$ mole^{-1}) of some cobalt(III)* and chromium(III) complexes at 20° in aqueous solution

Complex	Equiv. cond.	Complex	Equiv. cond.
trans-[Co en$_2$(NO$_2$)$_2$]NO$_3$	153	[Cr(EtNH$_2$)$_5$Cl]Cl$_2$	237
cis-[Co en$_2$(NH$_3$)SCN](SCN)$_2$	272	[Cr(Pr^{n}NH$_2$)$_5$Cl]Cl$_2$	272
[Co(NH$_3$)$_5$H$_2$O]Br$_3$	453	[Cr(Bu^{i}NH$_2$)$_5$Cl]Cl$_2$	258
[Cr(MeNH$_2$)$_5$Cl]Cl$_2$	242	[Cr(CH$_2$:CH·CH$_2$·NH$_2$)$_5$Cl]Cl$_2$	249

* Included for comparison.

RESULTS

The replacement of the chloro-group from chloropentakisalkylaminechromium(III) salts. The reaction,

$$[Cr(RNH_2)_5Cl]^{2+} + H_2O \longrightarrow [Cr(RNH_2)_5H_2O]_3^+ + Cl^-$$
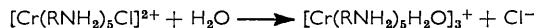
has been studied over a range of perchloric acid concentrations at constant ionic strength ($\mu = 1·0$ g.-ions l.$^{-1}$ using sodium perchlorate). In the case of the ammine and ethylamine analogues the runs were studied spectrophotometrically, the results were very similar to those obtained using the argentometric technique.

[1] H. Mandal, *Ber.*, 1919, **52**, 1489.
[2] H. Mandal, *Ber.*, 1915, **48**, 2055.
[3] H. Mandal, *Ber.*, 1916, **49**, 1307.
[4] H. Mandal, *Ber.*, 1919, **52**, 330.

At a given pH and ionic strength the rates of release of chloride ions from these complexes are pseudo-first-order, *i.e.*, rate = k_f[complex]. Table 2 shows the first-order dependence of the rate on the concentration of complex. Table 3 shows the variation of rate constant with acid concentration.

TABLE 2

Mean rate constants for the replacement of the chloro-group from some chloropenta-kisalkylaminechromium(III) salts at varying complex concentrations $\mu = 1\cdot00$; $[HClO_4] = 0\cdot100\text{M}$; $60\cdot0°$

R = H		R = Et		R = Allyl	
10^4[complex]	$10^5 k_t$	10^4[complex]	$10^5 k_t$	10^4[complex]	$10^5 k_t$
1·07	37·2	7·48	4·70	7·87	4·84
2·46	40·3	14·8	4·85	16·0	4·85
4·63	37·1	29·8	4·74	30·2	4·58
8·25	38·1	57·2	4·87	49·6	4·98

TABLE 3

The variation of the rate of replacement of the chloro-group from $[Cr(RNH_2)_5Cl]Cl_2$ with the stoicheiometric acid concentration, $\mu = 1\cdot00$; $60\cdot0°$ *

$[HClO_4]$ mole l.$^{-1}$ R =	$10^5 k_t$ (sec.$^{-1}$)				
	H	Me	Et	Allyl	Pr^n‡
1·000	32·9	3·47	2·76	2·84	
0·850			2·68	2·64	4·16
0·800	33·2				
0·650	35·0	3·58	2·69	3·02	4·08
0·500	33·0		3·14	2·90	
0·400	32·0	3·78	3·60	2·92	4·54
0·325			3·79	3·68	
0·275				3·86	
0·250	35·4	3·93			5·80
0·225			4·47	4·27	
0·175	37·2				5·85
0·150		4·07	4·59	4·62	
0·100	40·3	4·27	4·68	4·98	7·48
0·075	41·7		5·19	5·76	
0·050	43·6	4·80	5·42	7·63	9·08
0·0375			6·26	8·11	
0·0250		5·54	6·95	9·15	11·9
0·0100	46·5	7·21	8·08	12·1	16·4
0·0050	48·0		11·9	18·6	
0·0010	51·5 †		16·9 †	25·6 †	

* The sodium perchlorate used contained small, but not negligible amounts, of sodium chloride; in all experiments corrections were applied for this.   † Complex completely destroyed to yield green chromium(III) salts.   ‡ In this case the reaction did not go to completion, " infinity " readings corresponded to *ca.* 60% reaction.

The hydrolysis of chloropentakisalkylaminechromium(III) salts in buffer solutions. The results reported above suggest that these reactions are base-catalysed. In order to test this hypothesis, experiments were carried out in buffer solutions at constant ionic strength ($\mu = 1\cdot0$ g.-ion l.$^{-1}$) using sodium perchlorate as the non-catalytic salt. The buffer solutions used were (*a*) sodium dichloroacetate–dichloroacetic acid and (*b*) sodium sulphate–sodium hydrogen sulphate. In both cases the rate of hydrolysis was increased. The increase in rate over the rate in perchloric acid (*i.e.*, in the absence of buffer) at the same pH was directly proportional to the concentration of added base, *i.e.*, if k_0 = rate constant for hydrolysis at a given pH in perchloric acid solution, k = rate constant for hydrolysis at the given pH in the presence of a buffer, and [B] = concentration of buffer, then $k_B/[B]$ = constant, where $k_B = k - k_0$.

In each buffer experiment the pH of the buffer at $60\cdot0°$ was measured to check that it remained constant throughout a series of experiments. The results are summarised in Tables 4 and 6, which also include the measured pH values.

Tables 5 and 7 give the values of k_0 (*i.e.*, the rate constant for hydrolysis in perchloric acid solutions) for the complexes at the appropriate pH for the dichloroacetate and sulphate buffers, respectively.

It must be pointed out that, in the case of the chloropentamminechromium(III) compound, the rate of hydrolysis was also studied spectrophotometricallv. After seven half-lives the spectrum of the solution corresponded to that of the aquopentamminechromium(III) ion. However, if the solution was examined after twenty half-lives the colour had changed from orange to purple which suggests that sulphate or hydrogen sulphate ions attack the aquopentamminechromium(III) ion initially formed. Further studies of this subsequent reaction were carried out. Attempts to isolate a sulphatopentamminechromium(III) salt from the product solutions have so far proved unsuccessful.

TABLE 4

Mean rate constants for the hydrolysis of chloropentakisalkylaminechromium(III) salts in the presence of sodium dichloroacetate–dichloroacetic acid buffers $\mu = 1 \cdot 0$; 60·0°

$[OAcCl_2^-] =$ $[HOAcCl_2]$ (mole l.$^{-1}$)	pH	R = H			R = Et			R = Allyl		
		10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[OAcCl_2^-]$ (l. mole^{-1} sec.$^{-1}$)	10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[OAcCl_2^-]$ (l. mole^{-1} sec.$^{-1}$)	10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[OAcCl_2^-]$ (l. mole^{-1} sec.$^{-1}$)
0·075	1·41	44·2	1·7	22·7				8·82	1·22	16·3
0·100	1·36	44·6	2·1	21·0	7·46	2·06	20·6	9·25	1·65	16·5
0·125	1·35				7·93	2·53	20·2	9·90	2·30	18·4
0·150	1·34	45·8	3·3	22·0	8·63	3·23	21·5	10·25	2·65	17·7
0·175	1·34	46·6	4·1	23·4	8·68	3·28	18·7	10·50	2·90	16·6
0·200	1·33	47·5	5·0	25·0	9·67	4·27	21·4	10·78	3·08	15·4

TABLE 5

Rate constants (k_0 values) for the hydrolysis of chloropentakisalkylamine-chromium(III) salts in perchloric acid; pH = 1·35; $\mu = 1 \cdot 0$, 60·0°

R	H	Me	Et	Allyl
10^5k_t (sec.$^{-1}$)	42·5	4·80	5·40	7·60

TABLE 6

Mean rate constants for the hydrolysis of chloropentakisalkylaminechromium(III) salts in the presence of sodium sulphate–sodium bisulphate buffers: $\mu = 1 \cdot 0$; 60·0°

$[Na_2SO_4] =$ $[NaHSO_4]$ (mole l.$^{-1}$)	pH	R = H			R = Et			R = allyl		
		10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[SO_4^{2-}]$ (l. mole^{-1} sec.$^{-1}$)	10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[SO_4^{2-}]$ (l. mole^{-1} sec.$^{-1}$)	10^5k (sec.$^{-1}$)	10^5k_B (sec.$^{-1}$)	$10^5k_B/$ $[SO_4^{2-}]$ (l. mole^{-1} sec.$^{-1}$)
0·100	1·19	57·3	14·9	149	10·82	5·52	55·2	12·5	5·9	59·0
0·150	1·17	67·3	24·9	166	12·61	7·31	48·7	14·8	8·2	54·7
0·200	1·14	77·8	35·4	177	14·78	9·48	47·3	16·7	10·1	50·5
0·250	1·14	87·9	45·5	182	17·87	12·6	50·2	20·0	13·4	53·7

TABLE 7

Rate constants (k_0 values) for the hydrolysis of chloropentakisalkylamine-chromium(III) salts in perchloric acid: pH = 1·16; $\mu = 1 \cdot 0$; 60·0°

R	H	Et	Allyl
10^5k_t (sec.$^{-1}$)	42·4	5·30	6·60

The effect of ionic strength on the rates of the hydrolyses of chloropentakisalkylaminechromium(III) salt. The hydrolyses of the ethylamine and allylamine derivatives were studied at 60·0° keeping the perchloric acid concentration constant and varying the ionic strength with sodium perchlorate. The marked dependence of the rate of hydrolysis on the ionic strength is shown in Table 8.

Arrhenius parameters. The rates of hydrolysis have been studied at ionic strength 1·0 g.-ion l.$^{-1}$ (sodium perchlorate) and with 0·400M-perchloric acid at various temperatures. The results are summarised in Table 9. At this perchloric acid concentration the rates of hydrolysis have reached their asymptotic minimum values. The Arrhenius parameters calculated from

these results are given in Table 10. The variation of the rates of hydrolysis at $[HClO_4] = 0.0100$M with temperature has also been measured. No Arrhenius parameters have been calculated from these results as the plots were curved. This suggested that at lower acid concentrations there are at least two reactions occurring simultaneously (see Discussion section).

TABLE 8

The variation of the rate of replacement of the chloro-group from chloropentakisalkyl-aminechromium(III) salts with ionic strength at constant pH = 1·00; 60·0°

Ionic strength (g.-ion l.⁻¹)	$\mu^{\frac{1}{2}}$	R = Et		R = allyl	
		$10^5 k_f$ (sec.⁻¹)	$5 + \log_{10} k$	$10^5 k_f$ (sec.⁻¹)	$5 + \log_{10} k_f$
0·100	0·316	8·20	0·914	10·49	1·021
0·300	0·547	7·32	0·864	8·20	0·914
0·500	0·706	4·80	0·682	6·81	0·834
0·800	0·894	4·32	0·636		
1·00	1·00	4·56	0·659	5·41	0·734
1·30	1·14	3·92	0·593		
1·50	1·22₅	3·25	0·512	4·09	0·612
2·00	1·41	2·49	0·396	3·09	0·490

TABLE 9

Mean rate constants for the replacement of the chloro-group from some chloropenta-kisalkylaminechromium(III) salts at different temperatures; $\mu = 1.0$; $[HClO_4] = 0.400$M ($[HClO_4] = 1.00$M in case of R = Me)

Temp.	R = Allyl $10^5 k_f$ (sec.⁻¹)	R = Et $10^5 k_f$ (sec.⁻¹)	Temp.	R = H $10^5 k_f$ (sec.⁻¹)	Temp.	R = Me $10^5 k_f$ (sec.⁻¹)
50·1°	0·926	1·08	45·5°	7·78	50·1°	1·38
55·3	1·63	2·06	52·3	15·5	60·0	3·47
60·0	2·92	3·60	60·0	33·0	67·8	8·62
65·0	5·96	6·75	66·7	68·3		

TABLE 10

Arrhenius parameters for the replacement of the chloro-group from chloro-pentakisalkylaminechromium(III) salts at $\mu = 1.0$; $[HClO_4] = 0.400$M

Complex	E (kcal. mole⁻¹)	$\log_{10} A$
$[Cr(NH_3)_5Cl]$	22·9	17·2
$[Cr(EtNH_2)_5Cl]$	26·6	13·0
$[Cr(CH_2{:}CH{\cdot}CH_2NH_2)_5Cl]$	26·6	12·9

DISCUSSION

There are several reports of the hydrolyses of halogenopentamminechromium(III) salts.[7-10] Although the results of the separate investigations appear to conflict with one another, all the results, save one, can be reconciled on the basis of this investigation. Ogard and Taube [7] measured the rates of hydrolysis of the halogenopentammine-chromium(III) ions over the temperature range 25·2—40·8° at ionic strength 1·1. The results of this earlier investigation agree with ours (Figure 1). Freundlich and Bartels [8] also measured the rates of hydrolysis of halogenopentamminechromium(III) salts at various temperatures but they did not record any ionic-strength data. This omission means that the agreement between our results and theirs must be regarded as fortuitous. Ogard and Taube [7] stated that the rate constant for hydrolysis is independent of pH over the acid range $[H_3O^+] = 1.0—0.2$. Our results agree with this statement. In this investigation, however, a much wider range of acid concentration was used and a plot of acid concentration against rate constant is a rectangular hyperbola. Nazarenko and

[7] R. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 1084.
[8] H. Freundlich and R. Bartels, *Z. phys. Chem.*, 1922, **101**, 177.
[9] Y. P. Nazarenko and Y. I. Bratushko, *Ukrain. khim. Zhur.*, 1962, **28**, 17.
[10] M. Parris and W. J. Wallace, *Inorg. Chem.*, 1964, **3**, 138; M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Amer. Chem. Soc.*, 1961, **83**, 2453.

Bratushko [9] report much higher rate constants for the hydrolysis of chloropentammine-chromium(III) salts than the other workers. This may be explained by the fact that they appear to have worked in neutral, aqueous solution. The results reported here show that at these lower acid concentrations the rate of hydrolysis is greatly increased (if Nazarenko and Bratushko's results are extrapolated to 60° a rate constant of $10^5 k_f = 68$ sec.$^{-1}$ is obtained. This would be in line with our results in weakly acidic solutions). Thus, all the aforementioned results can be fitted into one scheme.

Wallace and his co-workers [10] measured the rates of hydrolysis of halogenopentammine-chromium(III) salts by polarography. Their results do not agree with others reported in the literature and it has been shown recently [11] that the polarographic technique gives erroneous results for this type of system.

From the form of the dependence of the rate constant on acid concentration it is clear that the reaction cannot be explained entirely in terms of a direct aquation, *i.e.*, the mechanism is neither pure S_N1 nor pure S_N2, since either of these mechanisms would give rise to first-order kinetics which are independent of the pH. The limiting rate at
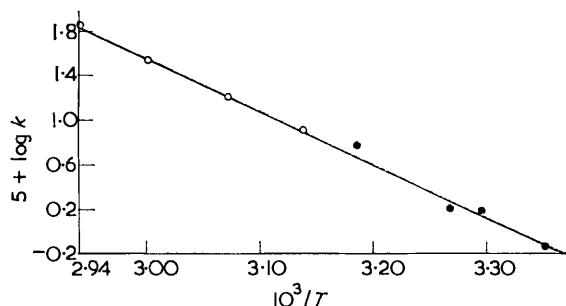

FIGURE 1. Variation of rate constant of hydrolysis of $[Cr(NH_3)_5Cl]^{2+}$ ion with temperature: ●, ref. 7; ○, this work

high acid concentrations corresponds to straightforward aquation. This view is supported by the fact that the rate constants are of the same order of magnitude as those for the analogous cobalt(III) systems, suggesting that the mechanisms are similar. Various other possibilities have, therefore, been considered to account for the remainder of the reaction.

One possible explanation of our results was that the reaction proceeded by a chromous-ion catalysed path. This could be ruled out, however, as Ogard and Taube [7] have shown that when chromous ions are present halogenopentamminechromium(III) salts are completely decomposed to yield ammonium ions and chromic salts. In this investigation, except at the very lowest acid concentrations, the "infinity" spectra correspond to aquopentamminechromium(III) salts.

In a recent Paper Balzani *et al.*[12] showed that the rates of hydrolysis of dicyanobis-2,2'-bipyridyl)iron(II) and of dicyanobis-(*o*-phenanthroline)iron(II) are independent of acid concentration between pH 4 and 1, but that, when the acid concentration is increased further, the rate of hydrolysis decreases. This was said to be due to the fact that protonated species react slower than unprotonated ones. Such an explanation is hardly feasible in our case for the following reasons.

(i) There are no very obvious likely sites for protonation.

(ii) These complexes would be reasonably strong bases to protonate in the acid range required by this theory.

(iii) In our case the rate constant for hydrolysis falls to a limiting value asymptotically at higher acid concentrations whereas for the iron(II) system the rate of hydrolysis is constant and then begins to fall sharply at the highest acid concentrations. This rapid decrease in rate constant is observed in the pH region where a high degree of protonation occurs. No corresponding region is found for the chromium system.
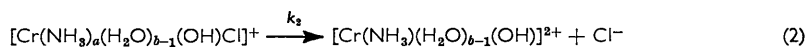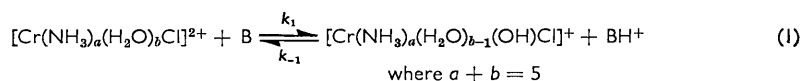
[11] C. W. Merideth, W. D. Mathews, and E. F. Orlemann, *Inorg. Chem.*, 1964, **3**, 320.

[12] V. Balzani, V. Carassiti, and L. Moggi, *Inorg. Chem.*, 1964, **3**, 1252.

The results quoted in this Paper resemble those reported [13] for the aquation of *cis*- and *trans*-dichlorobisethylenediaminechromium(III) salts. The rate of hydrolysis increases somewhat as the acid concentration decreases and the reactions are catalysed by sulphate ions. MacDonald and Garner [13] attribute this increase in rate in the presence of sulphate ions to a mechanism involving ion-pairs. Whilst this has not been disproved here, it would seem to be unlikely as the results given in Table 2 were all obtained using perchlorate ion concentration 1·0M. Furthermore, these workers observed that the ethylenediamine ligands were replaced to some extent. In this investigation it was found that the ammine groups were also replaced to some extent as green chromic salts were formed at pH 4. It is not easy to reconcile this result with the observation that in 0·1M-sodium hydroxide solution only the chloro-groups appear to be replaced. Presumably it is possible to study the basic hydrolysis at pH 13 because the chlorohydroxoammine species is not formed as fast as the hydroxopentammine ion under those conditions.

It is therefore postulated that, at lower acid concentrations, a conjugate-base reaction of either the substrate or a chloroaquoammine species occurs along with direct aquation. For various reasons the chloroaquoammine seems to be the more likely reactant. Merideth *et al.*[11] report analogous pH dependence for the hydrolysis of dichlorotetra-aquochromium(III) ion in acid solution. Replacement of ammine- by aquo-groups would enhance the contribution of the conjugate base path by increasing the acidity of the complex. *cis*- and *trans*-[Cr en$_2$Cl$_2$] are hydrolysed much slower than the cobalt(III) analogues at pH 13 and one would expect the pentammine species to behave in a similar way. If the increases in rate noted here were due to a conjugate-base mechanism involving the chloropentamminechromium(III) ion the rate of basic hydrolysis at pH 13 would be fast. It is much more probable, therefore, that the mechanism involves a conjugate base of an aquated species, *e.g.*, [Cr(NH$_3$)$_4$(H$_2$O)Cl]$^{2+}$.

Consider the mechanism

$$[Cr(NH_3)_a(H_2O)_bCl]^{2+} + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr(NH_3)_a(H_2O)_{b-1}(OH)Cl]^+ + BH^+ \qquad (1)$$

$$\text{where } a + b = 5$$

$$[Cr(NH_3)_a(H_2O)_{b-1}(OH)Cl]^+ \overset{k_2}{\longrightarrow} [Cr(NH_3)(H_2O)_{b-1}(OH)]^{2+} + Cl^- \qquad (2)$$

The complex ion produced by step (2) then reacts further with water and is protonated to give the aquo-complex. This step could equally well be a bimolecular attack by water followed by protonation but as the possibilities are kinetically indistinguishable the simpler form is used for convenience.

Since both ammine and aquoammine complexes of chromium are very weak acids (ref. 14*a*, p. 386 *et seq.*) then the restriction $k_1 \ll k_{-1}$ holds. General base catalysis requires $k_2 \sim k_{-1}$ and if the intermediate is a chloroaquoammine complex this is quite feasible {for the analogous complexes [Cr(NH$_3$)$_6$]$^{3+}$ and [Cr(NH$_3$)$_5$H$_2$O]$^{3+}$ pK_a changes from 14 to 5·2}. Some qualitative experiments were performed on the chloroaquotetramminechromium(III) salt reported by Pfeiffer.[15] The complex is stable in 1·0M-perchloric acid but is hydrolysed faster at pH 2 and 3. The increase in rate is not, however, large enough to account for the increase in rate noted in this investigation when the pH is altered from 0 to 2 or 3. Only one isomer of the chloroaquotetrammine complex was available, however, so no positive conclusions can be drawn from these results. From a steady-state analysis the mechanism gives [16]

$$\text{Rate} = k_2[Cr(NH_3)_a(H_2O)_{b-1}(OH)Cl]^+ = \frac{k_2[Cr(NH_3)_a(H_2O)_bCl]^{2+}\Sigma_i k^i_1[B^i]}{\Sigma_i k^i_{-1}[BH^+] + k_2}$$

[13] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, 1961, **83**, 4152.
[14] (*a*) " Mechanism of Inorganic Reactions," F. Basolo and R. G. Pearson, Wiley, 1958; (*b*) F. Basolo, J. G. Bergman, R. E. Meeker, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676.
[15] P. Pfeiffer, *Ber.*, 1905, **38**, 3592.
[16] R. P. Bell, " Acid–Base Catalysis," Oxford University Press, 1941, pp. 114 et seq.

If a small amount of the aquo-species is present in equilibrium with the substrate then the reaction will appear to be first-order in substrate.

In moderate acid B = H_2O and BH^+ = H_3O^+ so that

$$k_{obs} \propto (k_1 k_2 [H_2O]/(k_{-1}[H_3C^+] + k_2)$$

At very high acid concentration this expression nears zero but, for intermediate values, $k_{obs} \propto 1/[H_3O^+]$. The rate of aquation in the acid-independent range must be due to a direct reaction with water and not to base catalysis by water molecules since the rate constant for the latter reaction tends to zero in this region. If the observed rate constants in the intermediate region are corrected for the competing direct reaction, a graph of $1/(k_{obs} - k_L)$ against $[H_3O^+]$ gives a straight line, in agreement with the hypothesis (Figure 2). Further evidence of the mixed nature of the reaction comes from the Arrhenius plot. If the acid concentration is kept above 0·4M good straight lines are obtained but at lower acid concentrations the plots are curved.
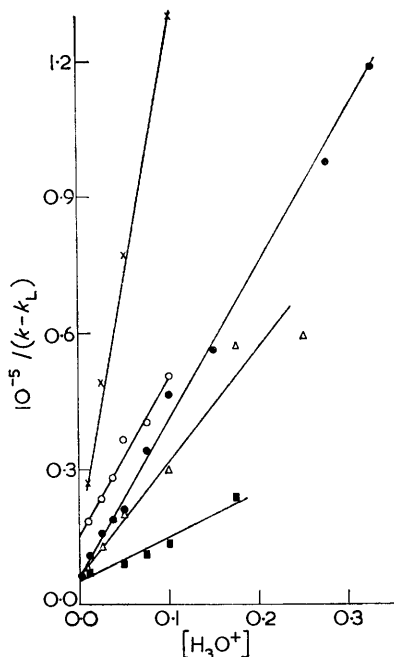

FIGURE 2. Variation of reciprocal of corrected rate constant of hydrolysis of $[Cr(RNH_2)_5Cl]^{2+}$ ions with acid concentration. ×, R = Me; ○, R = Et; ●, R = allyl; △, R = Pr^n; ■, R = H

So far, the discussion has been confined to the chloropentamminechromium(III) ion but it seems clear from the results that all the amine complexes react by similar mechanisms.

It has been noticed that as the bulkiness or chain length of the alkyl group increases the rate of bimolecular hydrolysis of alkyl halides decreases, whilst the rate of unimolecular hydrolysis increases. Although the results for the alkylamine complexes in this study are similar, the variation in limiting rate of hydrolysis at high acid concentration with alkyl group is similar to that noted for alkyl halides. Although the base strengths of the alkyl-amines present in the complexes studied here are all of the same order, a correlation between limiting rate of hydrolysis and base strength can be suggested tentatively (Table 11).

TABLE 11

The variation of limiting rate of hydrolysis of $[Cr(RNH_2)_5Cl]Cl_2$ with base strength of the alkylamine

R =	Me	Et	Pr^n
Base strength of amine $10''K_a$	2·29	2·14	2·63
$10^5 k_L$ (sec.$^{-1}$)	3·57	2·68	4·58

These results are very much in line with those of Basolo *et al.*[14] for the hydrolysis of substituted pyridinechlorobisethylenediaminecobalt(III) and dichlorotetra(substituted pyridine)cobalt(III) complexes.

The rate of hydrolysis of the chloropentamminechromium(III) ion is considerably faster than the rates for the alkylamine analogues which are all relatively similar to each other. This would indicate that the presence of a hydrocarbon shell is the important factor rather than the nature of the alkyl group present.

EXPERIMENTAL

Preparations.—Chloropentakismethylaminechromium(III) *chloride.* Methylamine was generated from methylamine hydrochloride and soda-lime and condensed on a cold-finger. The amine was then allowed to drop on to anhydrous chromic chloride (2·0 g.). The product was dissolved in dilute hydrochloric acid, filtered, and gently evaporated to smaller volume. The red crystals which separated were filtered off and dried (0·5 g.) [Found: C, 19·0; H, 7·8; Cl(total), 34·3; Cl(ionic), 23·0. Calc. for $C_5H_{25}Cl_3CrN_5$: C, 19·1; H, 8·0; Cl(total), 34·0; Cl(ionic), 22·7%].

Chloropentakisethylaminechromium(III) *chloride.* Anhydrous chromic chloride (11·0 g.) was added in small amounts to pure anhydrous ethylamine (25 ml.). The mixture was cooled between each addition since the reaction was exothermic. The resulting product was shaken with ether to remove the excess of amine and then dried. The complex was purified by dissolving in methanol and reprecipitating it with ether. Yield 5·5 g. [Found: C, 31·4; H, 9·0; Cl(total), 27·9; Cl(ionic), 18·8; Cr, 13·4. Calc. for $C_{10}H_{35}Cl_3CrN_5$: C, 31·3; H, 9·1; Cl(total), 27·8; Cl(ionic), 18·6; Cr, 13·6%].

Chloropentakisethylaminechromium(III) *perchlorate.* Chloropentakisethylaminechromium(III) chloride (1·0 g.) was dissolved in water (10 ml.) and perchloric acid (2 ml.; 5M) was added. Red crystals separated out and were recrystallised from hot water. Yield 1·0 g. (Found: C, 23·5; H, 6·9; Cl, 6·85. Calc. for $C_{10}H_{35}Cl_4CrN_5O_8$: C, 23·5; H, 6·8; Cl, 6·95%).

Chloropentakis-n-propylaminechromium(III) *chloride.* Anhydrous chromic chloride (8·6 g.) was added in small portions to pure anhydrous n-propylamine (25 ml.). When the reaction appeared to be complete the mixture was heated gently, cooled, and washed with ether. The crude product was purified by dissolving it in methanol and adding ether. On standing, red crystals (2·3 g.) were formed and filtered off [Found: C, 39·7; H, 9·8; Cl(total), 23·7; Cl(ionic), 16·1; Cr, 11·7. Calc. for $C_{15}H_{45}Cl_3CrN_5$: C, 39·8; H, 9·9; Cl(total), 23·7; Cl(ionic), 15·8; Cr, 11·5%].

Chloropentakis-n-butylaminechromium(III) *chloride.* Anhydrous chromic chloride (6·5 g.) was added to pure anhydrous n-butylamine (25 ml.) and the mixture gently heated under reflux until the reaction started. The flask was then cooled because the reaction became violent. When the reaction was apparently complete the mixture was heated for a further 15 min. The resulting tar was left under ether overnight. The product was dissolved in methanol, filtered, ether was added, and the mixture was allowed to evaporate at room temperature. The crude product was purified by dissolving in methanol and reprecipitating with ether. Yield, 1·2 g. [Found: C, 45·6; H, 10·3; Cl(total), 20·4; Cl(ionic), 13·6; Cr, 10·1. Calc. for $C_{20}H_{55}Cl_3CrN_5$: C, 45·8; H, 10·5; Cl(total), 20·4; Cl(ionic), 13·6; Cr, 9·9%].

Chloropentakisisobutylaminechromium(III) *chloride.* Anhydrous chromic chloride (6·5 g.) was added to pure anhydrous isobutylamine (25 ml.) and the mixture heated under reflux for 30 min. to start the reaction. The flask was then cooled in an ice-bath because the reaction became very vigorous. The *product* was filtered off, washed with ether, and recrystallised from hot methanol. Yield, 2·7 g. [Found: C, 45·6; H, 10·4; Cl(total), 20·4; Cl(ionic), 13·4; Cr, 10·1%].

Chloropentakisallylaminechromium(III) *chloride.* Anhydrous chromic chloride (8·8 g.) was added in small quantities to pure allylamine (25 ml.). The reaction was very vigorous and the flask had to be cooled. The resulting solid was left under ether overnight to remove the excess of amine. The tarry solid was dissolved in the minimum quantity of methanol, filtered, and the red compound precipitated by the addition of ether. The *complex* was recrystallised from hot methanol. Yield, 3·6 g. [Found: C, 40·4; H, 7·7; Cl(total), 24·2; Cl(ionic), 16·2; Cr, 11·7. $C_{15}H_{35}Cl_3CrN_5$ requires C, 40·6; H, 7·9; Cl(total), 24·0; Cl(ionic), 16·0; Cr, 11·7%].

Chloropentakisallylaminechromium(III) *chloride perchlorate.* Chloropentakisallylamine-chromium(III) chloride (1·0 g.) was dissolved in water (5 ml.) and perchloric acid (2 ml.; 5M) was added. Red *crystals* were filtered off and recrystallised from warm water. Yield, 1·0 g. [Found: C, 35·4; H, 6·7; Cl(total), 13·4; Cl(ionic), 6·6. $C_{15}H_{35}Cl_3CrN_5O_4$ requires C, 35·4; H, 6·9; Cl(total), 13·7; Cl(ionic), 6·85%].

Analyses of Compounds.—Chromium. The complex (*ca.* 0·03 g.) was decomposed by boiling with aqueous sodium hydroxide solution. The solution was neutralised with dilute sulphuric acid and then oxidised by boiling with potassium persulphate (10 ml.; 10% solution) for 2 hr. The resulting potassium dichromate solution was diluted to 100 ml. in a graduated flask. Aliquot portions (25 ml.) of this dichromate solution were added to ferrous ammonium sulphate solution (50 ml.; 0·05N) and the excess of ferrous ammonium sulphate was estimated by back-titration with standard potassium dichromate solution (0·1N) using *N*-phenanthranilic acid indicator.

Total chloride. The complex (*ca.* 0·03 g.) was decomposed by boiling with sodium hydroxide solution. The solution was rendered slightly acid with 1 : 1 concentrated nitric acid and the free chloride ions present were estimated potentiometrically with silver nitrate solution (0·025N) using a calomel half cell and a silver electrode with an ammonium nitrate–agar bridge.

Ionic chloride. The complex (0·03 g.) was dissolved in cold methanol or water and the chloride ions present were estimated as rapidly as possible by potentiometric titration with silver nitrate solution (0·025N).

Argentometric runs. The method used for all complexes was as follows. Aliquot portions of the reaction mixture were withdrawn at timed intervals, cooled, diluted, and the ionic chloride present estimated potentiometrically with silver nitrate. In a separate series of experiments the aliquot portions were quenched by pasing them through an ion-exchange column (Amberlite IR-120 sodium form) and the free ions were estimated argentometrically. The two sets of experiments gave the same results within experimental error. Another set of experiments was performed in blackened vessels. The results were the same as those obtained using clear vessels.

DEPARTMENT OF CHEMICAL TECHNOLOGY, BRADFORD INSTITUTE OF TECHNOLOGY,
BRADFORD 7, YORKS. [*Received, November 25th*, 1964.]