1343. *The Acid-catalysed Reactions of Transition-metal Complexes. Part III.*[1] *The Acid-catalysed Aquations of* trans-*Azidochlorobisethylenediaminecobalt*(III) *and* cis-*Nitrochlorobisethylenediaminecobalt*(III) *Salts*

By P. J. Staples

The acid-catalysed aquation of *trans*-[Co en$_2$(N$_3$)Cl]ClO$_4$ has been studied in a series of aqueous solutions of strong acids. The results can be interpreted in terms of a unimolecular dissociation of the protonated complex ion. The aquation of *cis*-[Co en$_2$(NO$_2$)Cl]Cl has been studied in sulphuric acid and the results are similar to those obtained for *trans*-[Co en$_2$(N$_3$)Cl]ClO$_4$.

If *cis*-[Co en$_2$(NO$_2$)Cl]ClO$_4$ or *trans*-[Co en$_2$(N$_3$)Cl]ClO$_4$ is dissolved in weakly or moderately acidic solutions, the chloro-groups are replaced by water to yield a mixture of the *cis*- and the *trans*-isomer of the corresponding aquo-complexes, *i.e.*,

$$[\text{Co en}_2(\text{X})\text{Cl}]^+ + \text{H}_2\text{O} \longrightarrow [\text{Co en}_2(\text{X})\text{H}_2\text{O}]^{2+} + \text{Cl}^- \text{ (where X} = \textit{cis}\text{-NO}_2 \text{ or } \textit{trans}\text{-N}_3)$$

Scheme A

However, when these compounds are dissolved in strongly acidic media (*e.g.*, 5—13·5M-sulphuric acid) it is immediately obvious that a different reaction occurs as the colour changes are markedly different. More detailed study shows that the hydrolyses in concentrated acids may be expressed:

$$[\text{Co en}_2(\text{X})\text{Cl}]^+ + \text{H}_3\text{O}^+ \longrightarrow [\text{Co en}_2(\text{Cl})\text{H}_2\text{O}]^{2+} + \text{HX} + \text{H}_2\text{O}$$

Scheme B

When solutions of *cis*-[Co en$_2$(NO$_2$)Cl]ClO$_4$ or *trans*-[Co en$_2$(N$_3$)Cl]ClO$_4$ in 75% sulphuric acid or 70% perchloric acid are kept at room temperature for 30—60 min. hardly any free chloride ion is liberated: as shown by the slight precipitation of silver chloride on the addition of silver nitrate solution. The visible absorption spectra of these solutions correspond to a mixture of *cis*- and *trans*-aquochlorobisethylenediaminecobalt(III) salts. If, however, these solutions are then warmed for 2 or 3 min. silver chloride is precipitated owing to hydrolysis of the aquochloro-species present in the solution.

As the sulphate ion is a nucleophile the possibility of sulphato-complex formation was considered. However, since the spectra of (a) an equilibrium mixture of *cis*- and *trans*-[Co en$_2$(Cl)H$_2$O]$^{2+}$ salts and (b) [Co en$_2$SO$_4$]$^+$ or [Co en$_2$(SO$_4$)H$_2$O]$^+$ salts are markedly different it is evident that sulphate attack does not occur except at late times, *i.e.*, after some hours.

Results

The Acid-catalysed Replacement of the Azido-group from trans-*Azidochlorobisethylenediaminecobalt*(III) *Salts*.—The reaction was studied spectrophotometrically at wavelengths 408 and 584 mμ. At these wavelengths the extinction coefficients of *cis*- and *trans*-chloroaquobisethylenediaminecobalt(III) salts are the same. The reaction was studied in sulphuric, perchloric, hydrochloric, and hydrobromic acids at 15·0° and sulphuric acid at 25·0°. The mean rate constants determined by this method are given in Table 1. For any given run, the rate is of first order in complex, *i.e.*, rate = k_f[complex]. The dependence of k_f on the acid concentration is more complicated (see Discussion section and Figure 1).

The Acid-catalysed Replacement of the Nitro-group from cis-*Nitrochlorobisethylenediaminecobalt*(III) *Salts*.—This reaction was studied spectrophotometrically at the wavelengths where *cis*- and *trans*-chloroaquobisethylenediaminecobalt(III) salts have the same extinction coefficient, *viz.*, 408, 455, and 584 mμ. Results for sulphuric acid at 15° are given in Table 2.

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[1] Part II, P. J. Staples, *J.*, 1964, 2534.

TABLE 1

Mean pseudo-first-order rate constants † for the replacement of the azido-group from *trans*-azidochlorobisethylenediaminecobalt(III) perchlorate in aqueous acids at 15·0°

* $[H_2SO_4]$ (mole $l.^{-1}$)	5·18	5·90	6·11	6·20	6·43	6·60	6·82	6·99	7·16			
* 10^3k_f (sec.$^{-1}$)	0·258	0·541	0·718	0·722	0·91	1·11	1·25	1·36	1·78			
* $[H_2SO_4]$ (mole $l.^{-1}$)	7·32	7·64	8·25	8·45	8·79	9·63	9·78	12·22	13·02			
* 10^3k_f (sec.$^{-1}$)	2·02	2·81	3·04	3·14	3·28	3·75	3·48	3·50	3·42			
$[HClO_4]$ (mole. $l.^{-1}$)	6·48	7·15	7·98	8·34	8·74	9·36	10·27	10·93	11·81	11·83	12·52	12·73
10^3k_f (sec.$^{-1}$)	0·35	1·12	2·20	2·48	2·69	3·23	4·30	4·58	4·78	5·01	4·83	5·10
$[H_2SO_4]$ (mole $l.^{-1}$)...	6·54	6·90	7·08	7·50	7·72	7·84	7·94					
10^3k_f (sec.$^{-1}$)	0·277	0·355	0·390	0·518	0·593	0·647	0·670					
$[H_2SO_4]$ (mole $l.^{-1}$)...	8·18	8·52	8·96	9·64	10·69	11·43	11·66					
10^3k_f (sec.$^{-1}$)	0·754	0·875	0·905	0·939	0·935	0·990	0·988					
[HCl] (mole. $l.^{-1}$) ...	6·37	6·63	6·85	8·12	9·24	10·16	10·48	10·92	11·29			
10^3k_f (sec.$^{-1}$)	0·206	0·217	0·284	0·70	1·70	2·26	2·38	2·43	2·62			

* At 25·0°. † All runs followed spectrophotometrically.

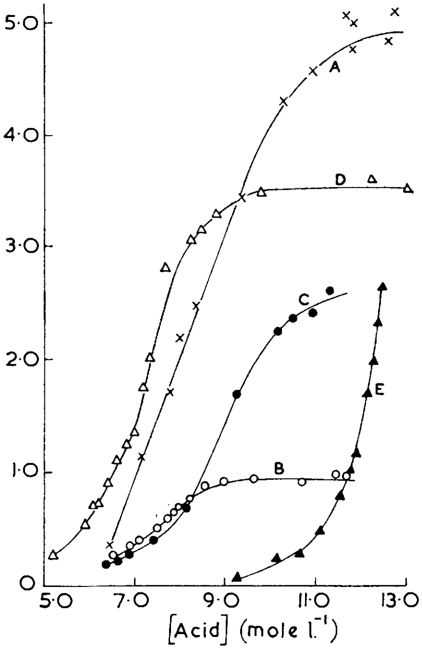

FIGURE 1. Variation of pseudo-first-order rate constant with acid concentration

(A) *trans*-[Co $en_2(Cl)N_3]ClO_4$ in $HClO_4$ at 15·0°
(B) ,, ,, in H_2SO_4 at 15·0°
(C) ,, ,, in HCl at 15·0°
(D) ,, ,, in H_2SO_4 at 25·0°
(E) *cis*-[Co $en_2(Cl)NO_2]Cl$ in H_2SO_4 at 15·0°

TABLE 2

Mean pseudo-first-order rate constants for the acid-catalysed replacement of the nitro-group from *cis*-nitrochlorobisethylenediaminecobalt(III) salts in aqueous sulphuric acid at 15·0°

$[H_2SO_4]$ (mole $l.^{-1}$)...	10·72	11·06	11·52	11·77	11·86	12·08	12·25	12·34	12·42
10^3k_f (sec.$^{-1}$)	0·329	0·488	0·80	1·01	1·19	1·70	2·00	2·34	2·66

It has been noted that this compound behaves in a similar way in hydrochloric acid. Owing to the very high acidities required for this hydrolysis it was not suitable for an extended study such as that carried out for *trans*-[Co $en_2(Cl)N_3]ClO_4$. However, in solutions up to the highest concentrations of hydrochloric acid available the behaviour was similar to that observed with sulphuric acid.

DISCUSSION

There are examples of acid-catalysed reactions of octahedral complexes of transition metals in the literature. In most cases a plot of log rate constant against log [Acid] is a straight line of unit slope. This type of acid dependence applies to diazido-,[2] dinitro-,[1] and difluoro-bisethylenediamine cobalt(III) salts[3] and various acetato- and substituted acetatopentamine complexes of rhodium(III) and iridium(III).[4] The results have been explained in terms of an S_N2CA mechanism. The data quoted in this Paper, however, are inconsistent with such a mechanism. A plot of rate constant against acid concentration is a very steep sigmoid curve (see Figure 1) and a plot of log k against log$[H_3O^+]$ has slope *ca.* 6. In the stronger acids, an acid concentration is reached at which the rate constant for the hydrolysis does not increase with further rise in acid concentration (*i.e.*, above this acid concentration the rate of hydrolysis is of zero order in acid concentration). It was noted during the experiments that at these higher acid concentrations the blue colour of the *trans*-$[Co\ en_2(Cl)N_3]^+$ ion changed immediately on solution to a very pale green. On rapidly cooling and diluting the solution the blue colour was regenerated. It was difficult to study this empirical observation on a quantitative spectrophotometric basis owing to the rapid hydrolysis of the complex. This observation, together with the kinetics would suggest that the green colour was due to a protonated complex ion, *viz.*, *trans* $[Co\ en_2(Cl)N_3H]^{2+}$.

The colour change and the limiting maximum rate constant at high acid concentrations suggested that the effective reactant was the protonated complex which was present in appreciable concentrations in the solutions studied. Under these conditions the " acidity " of the acid would be a more relevant characteristic than its stoicheiometric concentration and so a graph of log k against H_0 (acidity function) was drawn. Strictly speaking the acidity function H_+ was required but values for this function for a sufficiently wide range of acids and even over a wide enough range of concentrations for any given acid are not available at the present time. However, it has been shown that H_0 and H_+ are parallel[5] so that no gross error is introduced in the slope of the graph. It must also be pointed out that the acidity functions used here are those determined by using Hammett bases as indicators. It would be more satisfactory if a table of acidity functions determined with bases structurally similar to our substrates were available. A further point is that most of the H_0 values refer to 25·0° although some of these studies were done at 15·0°. The results gave, within experimental error, a plot of unit slope (see Figure 2) which deviated at high acid concentrations owing to the complete protonation of the complex. Such behaviour has been attributed to a mechanism in which the transition state does not involve the hydrolysing water molecule,[6] *i.e.*, the mechanism can be designated S_N1CA.

All the observed features are consistent with the following mechanism.

$$[SX]^+ + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [SXH]^{2+} + A^- \text{ (pre-equilibrium)}$$

$$[SXH]^{2+} \xrightarrow{k_2} [S]^{2+} + HX \text{ (rate determining)}$$

$$[S]^{2+} + H_2O \xrightarrow{k_3} [SH_2O]^{2+} \text{ (fast)}$$

where $[SX]^+ = [Co\ en_2(Cl)X]^+$, $[SXH]^{2+} = [Co\ en_2(Cl)XH]^{2+}$

$[S]^{2+} = [Co\ en_2Cl]^{2+}$, and $[SH_2O]^{2+} = [Co\ en_2(Cl)H_2O]^{2+}$

Rate $= k_2[SXH^{2+}]$, where $[SXH^{2+}]$ = concentration of $[SXH]^{2+}$, etc.

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[2] P. J. Staples, *J.*, 1964, 745.

[3] F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4883.

[4] F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1241.

[5] T. G. Bonner and J. C. Lockhart, *J.*, 1957, 364.

[6] L. P. Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940.

Consider the relationship between acidity function and indicator ratio

$$H_+ = \mathrm{p}K_a + \log(c_1/c_2)$$

where c_1 and c_2 are the concentrations of unprotonated and protonated base indicator, respectively.

Then
$$\begin{aligned}\log c_2 &= \mathrm{p}K_a - H_+ + \log c_1\\ &= -\log K_a + \log h_+ + \log c_1\\ c_2 &= (h_+/K_a)c_1 \qquad (1)\end{aligned}$$

If protonation of the substrate occurs to a large extent then the pre-equilibrium is analogous to an indicator equilibrium so that

$$[\mathrm{SXH}^{2+}] = (h_+/K_a)[\mathrm{SX}^+]$$

where XS^+ and SXH^{2+} represent the complex and its protonated form, respectively.

$$\text{Rate} = k_2(h_+/K_a)[\mathrm{SX}^+].$$

From equation (1)

$$c_2/c_1 = h_+/K_a$$

whence
$$c_1 = \frac{K_a}{h_+ + K_a}(c_1 + c_2)$$

i.e.,
$$[\mathrm{SX}^+] = \frac{K_a}{h_+ + K_a}([\mathrm{SX}^+] + [\mathrm{SXH}^{2+}]).$$

The quantity $([\mathrm{SX}^+] + [\mathrm{SXH}^{2+}])$ is the apparent stoicheiometric concentration of the substrate complex ion and can be designated c_a. Since the first-order rate constants for any run are calculated from the total amount of complex, protonated and unprotonated, present at any instant, c_a and not $[\mathrm{SX}^+]$, relates theory and experiment.

$$\text{Rate} = k_2 \cdot \frac{h_+}{h_+ + K_a} \cdot c_a \qquad (2)$$

As predicted by this equation, any given run is first-order in complex-ion concentration. Furthermore, at high concentrations of acid $h_+ \gg K_a$ and (2) reduces to

$$\text{Rate} = k_2 c_a,$$

i.e., the rate becomes independent of the acid concentration. At low acid concentrations $K_a \gg h_+$ and so

$$\text{Rate} = k_2 h_+ c_a/K_a$$

Therefore, $k_f = k_2 h_+/K_a$, where k_f = measured rate constant.

$$\log k_f = \log k_2 - H_+ + \mathrm{p}K_a$$

Thus, if $\log k_f$ is plotted against $-H_+$ a straight line of unit slope and intercept ($\log k_2 + \mathrm{p}K_a$) should be obtained. In practice, a plot of $\log k_f$ against $-H_0$ was made (the reasons for this have been given above) and a straight line of unit slope was obtained. The behaviour of the kinetics at both high and low concentrations of acid is, therefore, in agreement with prediction.

At intermediate concentrations of acid the dependence of the rate on acidity is more complicated since it is influenced by both h_+ and K_a

From (2),
$$\log k_f = \log k_2 - H_+ - \log(h_+ + K_a).$$

Or, for convenience,
$$\log k_f = \log k_2 - H_0 - \log(h_0 + K_a)$$

where the error in using H_0 and h_0 is compensated by a numerical error in K_a. This is relatively unimportant for the purpose of computing k_f. Since k_2 is known from the measurements at high acid concentration and pK_a is obtainable from the intercept on the logarithmic plot it is possible to construct curves for log k_f against $-H_0$ over the whole range of acid concentrations. The agreement between experiment and hypothesis is illustrated in Figure 2. The values of the parameters employed are given in Table 3.

TABLE 3

Values of parameters required in the calculation of the lines in Figure 2

Acid	Temp.	K_a	$4 + \log k_2$	Tables of $-H_0$
$HClO_4$	15·0°	20,000	1·67	Ref. 8
H_2SO_4	15·0	3500 *	0·995	7 and 9
H_2SO_4	25·0	3000	1·54	7 and 9

* This value was obtained by first taking the value of K_a at 25·0° and then readjusting slightly to give a better fit since the reaction was inconveniently slow at low acid concentrations and a good extrapolation could not be made directly.

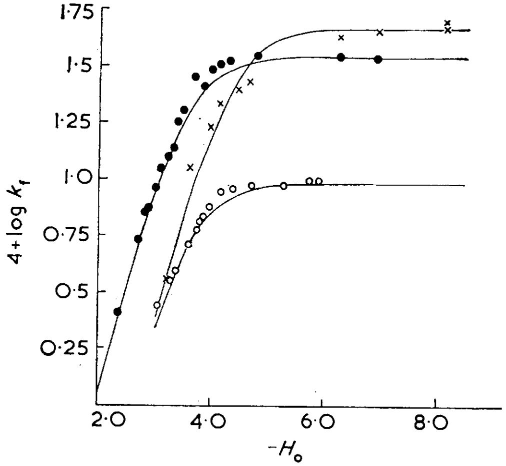

FIGURE 2. Experimental values of log k_f against $-H_0$ for
(○) *trans*-[Co en$_2$(Cl)N$_3$]ClO$_4$ in H_2SO_4 at 15·0°
(●) ,, ,, in H_2SO_4 at 25·0°
(×) ,, ,, in $HClO_4$ at 15·0°
The lines were calculated using the logarithmic form of equation 2 (see Table 3)

One very noticeable fact is that the actual value of the limiting maximum rate constant is not the same in all acids as would be expected from the foregoing mechanism but depends on the acid used. This fact may be explained in at least two ways: (i) on the basis of ion-pairing, and, (ii) as an effect of the different media, *e.g.*, 12M-perchloric acid and 12M-sulphuric acid. Therefore further investigation will be required to elucidate this problem.

EXPERIMENTAL

Preparation of Compounds.—*trans*-Chloroazido-[10] and *cis*-chloronitro-bisethylenediamine-cobalt(III) salts[11] were prepared by methods described in the literature. Samples were recrystallised to constant absorption spectrum. Criteria for purity were analyses and absorption spectra.

	Found				Calc.			
Analyses	C	H	Cl	N_3	C	H	Cl	N_3
trans-[Co en$_2$(Cl)N$_3$]ClO$_4$ ...	13·7	4·7	10·0	11·7	13·5	4·5	10·0	11·8
cis-[Co en$_2$(Cl)NO$_2$]Cl	16·5	5·7	24·0	—	16·2	5·4	23·8	—

Spectrophotometric Runs.—Aliquot portions (5 ml.) of the reaction mixture were withdrawn with a fast-delivery pipette and rapidly blown into Pyrex boiling-tubes placed in an acetone–solid carbon dioxide bath. After 2 or 3 min. when the temperature had been lowered sufficiently

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[7] F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 935.
[8] T. G. Bonner and J. C. Lockhart, *J.*, 1957, 2840.
[9] M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.
[10] P. J. Staples and M. L. Tobe, *J.*, 1960, 4812.
[11] A. Werner, *Annalen*, 1912, **386**, 1.

the solutions were carefully diluted with water while still in the cold-bath. Separate experiments showed that this dilution process did not lead to a rise in temperature which could have had a significant effect on the measured rate constants. The solutions were then made up to a standard volume and the optical density at the appropriate wavelengths was measured using a Unicam S.P. 600 Spectrophotometer with silica cells.

Standardisation of Acids.—Accurately weighed samples of the acid were titrated against standard borax solution with Methyl Red as indicator. The molarity of the acid at the appropriate temperature was then calculated from the percentage with the aid of density tables.[12]

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DEPARTMENT OF CHEMICAL TECHNOLOGY, BRADFORD INSTITUTE OF TECHNOLOGY,
BRADFORD 7, YORKS.
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[12] International Critical Tables, vol. 3.