984. *The Replacement of Chloride in* cis- *and* trans-*Aquochlorobisethylenediaminecobalt*(III) *Cations by Water.*

By S. C. Chan.

The rate constants of solvolytic replacement of chloride by water in *cis*- and *trans*-[Co $en_2H_2O,Cl]^{2+}$ cations (en = ethylenediamine) have been determined at 25° over the pH range 2—3. When allowances are made for isomerisation of the reactants, the rate constants are given by the expression $k = A + B/[H^+]$. This is consistent with reversible dissociation of the aquo-complex into the hydroxo-complex with retention of configuration. The term A is interpreted as the contribution from replacement of chloride in the aquo-complex, and the term B as that from reaction of the hydroxo-complex. The steric course of these reactions cannot be determined reliably, making conclusive assignment of mechanism impossible.

Aquo-complexes of the type [Co $en_2A,H_2O]^{n+}$ isomerise in aqueous solution at rates depending on the nature of the group A. When A = Cl, the rate of isomerisation[1] is such that it interferes with studies of the replacement of chloride by water in these complexes. Further complications are caused by their acidity, which is probably due to the withdrawal of electron density from the O–H bond as a result of the formation of the σ-bond with the metal by the oxygen lone-pair electrons. However, a knowledge of the rate and steric course of replacement of chloride by water in aquochloro-complexes is highly desirable, not only for further verification of the relation between mechanism and steric course advanced by Ingold, Nyholm, and Tobe,[2] but also for comparing[3] the water exchange in aquo-complexes of the type [Co $en_2A,H_2O]^{n+}$ with the reaction of the corresponding complexes [Co $en_2A,Cl]^{(n-1)+}$. Mathieu[4] obtained data for replacement of chloride in *cis*-[Co $en_2H_2O,Cl]^{2+}$ by water at 30° in various buffers, but appears not to have taken into account the isomerisation of the reactant. The present work shows that, when nitric acid alone is used to supply the hydrogen ions, both the *cis*- and the *trans*-aquochloro-complex react with water much more slowly than they isomerise. Attempted determinations of the steric course by the usual extrapolation techniques[1] indicate that reliable results cannot be obtained for these systems.

Results

Kinetics.—The rate of loss of chloride from the *cis*-aquochlorobisethylenediaminecobalt(III) cation in water at 30° has been determined by Mathieu[4] who observed an equilibrium whose constant depended on temperature, concentration of the cobalt complex, concentration of chloride ions, and pH. In this paper, the kinetics were followed for both isomers at 25° by titrating the chloride ion liberated; the anionic chloride was separated from the complex cation by means of a cation-exchange resin and was determined by the Volhard method. Titration after ten half-lives indicated that when the *cis*-complex was supplied as the sulphate, and under the conditions of the experiment, the reverse reaction did not observably affect the rate. The *trans*-[Co $en_2H_2O,Cl]^{2+}$ cation was prepared *in situ* by adding the calculated amount of nitric acid to *trans*-[Co en_2OH, Cl]Cl,H_2O and passing the resulting solution quantitatively through an ice-jacketed column of Amberlite resin IRA-400 in the nitrate form. Preliminary experiments also indicated that for the *trans*-complex in the nitrate form, the reverse reaction could be neglected if the initial solution was free from chloride ions. At first, the pH of the reaction mixture was kept constant by means of a sodium hydroxide–potassium hydrogen phthalate buffer and the reaction was studied over the pH range 4—5, in the hope of minimising the isomerisation by increasing the reaction rate. However, the results were inconsistent with the observations

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[1] Baldwin, Chan, and Tobe, *J.*, 1961, 4637.
[2] Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477.
[3] Martin and Tobe, *J.*, 1962, 1388.
[4] Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 2121.

of Baldwin, Chan, and Tobe [1] on the isomerisation of these complexes. After the contribution from the inverse-acid-dependent step was eliminated by extrapolation, the rate constants were higher than expected. From the work of Mathieu [4] and Bronsted [5] it is reasonable to attribute the increased rate of release of chloride ions to the interaction of buffers with the complex. So the use of buffers was abandoned and the reaction was studied at a lower pH (2—3), with only nitric acid to supply hydrogen ions. Appropriate pH values were obtained by adding known amounts of nitric acid to a solution of the complex in water. It was found that, except during the earliest stages in the reaction of the *trans*-complex, the plots of $\log_{10} (V_\infty - V_t)$ against time for each value of pH were straight lines having virtually identical slopes for the *cis*- and the *trans*-isomer at a particular pH. (V_t and V_∞ are the titres of silver nitrate consumed when the reaction is stopped at time t and after ten half-lives, respectively.) This was attributable to the rapid isomerisation of the reactants. In the case of the *trans*-cation, the greater initial slope, which corresponds to reaction of the pure *trans*-cation, was understandable on the grounds that (*a*) the isomer composition at equilibrium was much richer in the *cis*-isomer and (*b*) the *trans*-isomer reacts with water faster than does the *cis*-cation. The first-order rate constants for the aquation of the pure *trans*-complex and the equilibrium reactant mixture were determined from the initial and the final slope, respectively, of the semi-logarithmic plots; that for the reaction of the *cis*-cation was calculated by using the expression, $k_E = k_C f + (1 - f)k_T$, where k_C, k_T, and k_E are the first-order rate constants for reaction of the pure *cis*-cation, the pure *trans*-cation, and the equilibrium reactant mixture, respectively, with water, and f is the fraction of *cis*-aquochloro-isomer in an equilibrium mixture of *cis*- and *trans*-aquochloro-cations.[1] The resulting rate constants, which are collected in Table 1, have the following pH-dependence:

$$k_C = 1{\cdot}6 \times 10^{-6} + 2{\cdot}4 \times 10^{-9}/[H^+] \text{ (sec.}^{-1})$$
$$k_T = 2{\cdot}5 \times 10^{-6} + 3{\cdot}2 \times 10^{-9}/[H^+] \text{ (sec.}^{-1})$$

TABLE 1.

First-order rate constants for the reaction of *cis*- and *trans*-aquochlorobisethylenediamine cobalt(III) cations in aqueous solutions at 25°.

Concentrations in mmoles/l. Rate constants in sec.$^{-1}$.

cis-$[Co\ en_2H_2O,Cl]^{2+}$			*trans*-$[Co\ en_2H_2O,Cl]^{2+}$				
Initial [Complex]	$[H^+]$	10^6k_E	Initial [Complex]	$[H^+]$	10^6k_E	10^6k_T	10^6k_C
4·02	10·00	2·0	4·03	10·00	2·1	2·8	1·9
4·03	5·00	2·3	3·97	5·00	2·3	3·2	2·0
4·01	3·33	2·6	4·06	3·33	2·6	3·4	2·3
4·04	2·50	2·8	4·03	2·50	2·8	3·7	2·5
3·96	2·00	3·1	3·98	2·00	3·2	4·1	2·8
4·04	1·67	3·3	4·04	1·67	3·4	4·5	3·0
3·99	1·43	3·6	4·02	1·43	3·6	4·7	3·2
4·02	1·25	3·8	4·06	1·25	3·9	5·1	3·5
4·09	1·11	4·1	3·99	1·11	4·1	5·3	3·7
3·96	1·00	4·3	4·01	1·00	4·4	5·6	4·0

Attempted Determination of Steric Course.—Samples of the reaction mixture at various stages of the reaction were acidified before analysis. Each sample contained four light-absorbing species, namely, *cis*- and *trans*-$[Co\ en_2H_2O,Cl]^{2+}$ and *cis*- and *trans*-$[Co\ en_2(H_2O)_2]^{3+}$. Two samples of the reaction mixture were withdrawn almost simultaneously and frozen. In one, ionic chloride was titrated as described above, while the spectrum of the other was measured as soon as possible. The chloride titre afforded the total amount of products present. The isomer distribution was determined by a trial-and-error method whereby spectra were calculated on the basis of the known extinction coefficients of the pure components [6] for various isomer ratios within the limits of the known ratio of reactants to products. The combination giving a spectrum agreeing best over the whole visible wavelength range with that obtained experimentally for each sample was found. The composition of the product, expressed as % of *cis* product, was plotted against % of reaction completed, but the extrapolation to zero reaction proved unreliable. For the *cis*-isomer, values ranging from 90% to 100% of *cis*-product were

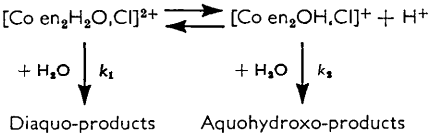
[5] Bronsted, *Z. phys. Chem.*, 1926, **122**, 383.

[6] Chan, Ph.D. Thesis, London, 1962.

obtained; for the *trans*-isomer, it was not possible to decide among the values within the range 0—50% of *cis*-product. Such results were due to the following factors: (*a*) The complicated nature of the system prevents mathematical analysis. (*b*) The overlapping spectra of the components limits the accuracy. (*c*) For the *trans*-isomer, the maximum variation in the amount of *cis*-product is in the region between 0% and 15% reaction, owing to the rapid isomerisation, but this is also the region most susceptible to experimental error (cf. Baldwin and Tobe [7]).

DISCUSSION

The expression for the variation of the rate constants with the hydrogen-ion concentration of the reaction medium, $k = A + B/[H^+]$, is consistent with the idea that the hydroxochloro-complex reacts with water very much faster than the corresponding aquochloro-complex in the system



i.e., $k_1 \ll k_2$. The dissociation of the aquo-complex into the hydroxo-complex has been proved as taking place with complete retention of configuration. This is reasonable since there is no cobalt–oxygen bond fission during protonation and de-protonation. The observed rate of reaction with water is given by

$$\text{Rate} = k_1[\text{Aquo-complex}] + k_2[\text{Hydroxo-complex}].$$

Since $K = [H^+][\text{Hydroxo-complex}]/[\text{Aquo-complex}]$, the rate expression becomes

$$\text{Rate} = k_1[\text{Aquo-complex}] + \frac{k_2K}{[H^+]}[\text{Aquo-complex}]$$

$$= (k_1 + k_2K/[H^+])[\text{Aquo-complex}],$$

so that

$$k = k_1 + k_2K/[H^+].$$

Thus the intercept for the straight-line plot of k against $1/[H^+]$ is identical with k_1, which is the true rate constant for the reaction of the aquo-complex after allowance for the dissociation. The slope is identical with k_2K, and k_2 is known from the work of Baldwin, Chan, and Tobe.[1] The constant K, obtained from the kinetic experiments, should be equal to the acid dissociation constant of the aquochloro-complex. The various constants are collected in Table 2.

TABLE 2.

Constants for the aquation of *cis*- and *trans*-aquochlorobisethylenediaminecobalt(III) complexes in aqueous solutions at 25°.

Initial complex	10^6k_1 (sec.$^{-1}$)	10^9k_2K (mole l.$^{-1}$ sec.$^{-1}$)	10^3k_2 * (sec.$^{-1}$)	10^6K (mole/l.)
cis	1·6	2·4	12	0·2
trans	2·5	3·2	1·6	2·0

* From ref. 1.

pK's for *cis*- and *trans*-aquochlorobisethylenediaminecobalt(III) cations have been given in the literature (7·6 for the *cis*-complex at 30°[8] and 7·2 for the *trans*-complex at 25°[9]). More recent unpublished determinations [10] under conditions that minimise displacement of co-ordinated chlorine gave values of 6·8 and 5·8 for the *cis*- and the *trans*-cation, respectively.

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[7] Baldwin and Tobe, *J.*, 1960, 4275.
[8] Pearson, Meeker, and Basolo, *J. Amer. Chem. Soc.*, 1956, **78**, 2673.
[9] Tobe, *Sci. Progr.*, 1960, **48**, 483.
[10] Chan and Tobe, unpublished observations.

In view of the sensitivity of these cations to water and the relatively high values of pK for the aquohydoxo-cations[9] (8·2 and 7·9 for the *cis*- and the *trans*-isomer, respectively), the smaller, more recent pK values for the aquochloro-cations are more reasonable. In view of the nature of the present determinations, our values (6·7 for the *cis*- and 5·7 for the *trans*-complex at 25°) are comparable.

There is no convenient natural zero of electropositivity or electronegativity within the range of orienting ligands so far studied. Since in these bisethylenediaminecobalt(III) complexes, most of the octahedral positions are occupied by en$_{\frac{1}{2}}$ groups, the en$_{\frac{1}{2}}$ group may be adopted as the working zero. On this scale, the OH_2 ligand is electronegative ($-I$) and therefore retards S_N1 and promotes S_N2 reactions, doing this more strongly in *trans*- than in *cis*-positions. However, the co-ordinated OH_2 ligand possesses a pair of unshared electrons which may be transferred to the metal by an electromeric ($+E$) effect. Although unshared electrons in the similar SMe_2 group are incapable of conjugation, it is not certain whether OH_2 is an effective electromeric ligand. If this $+E$ effect operates, it will leave untouched S_N2 reactions but will promote S_N1 reactions, chiefly of substrates having *cis*-related orienting and displaced groups. Table 2 shows that the rate of reaction of the *trans*-aquochloro-cation with water is greater than that of the *cis*-ion by a factor of 1·6, but a conclusion that these reactions took place by an S_N2 mechanism is hazardous as it is not certain whether this comparatively small difference can be mechanistically significant.

The steric course for the reaction of $[Co\ en_2A,Cl]^{n+}$ with water has been more useful for the assignment of mechanism, as *trans*-isomers undergoing bimolecular reaction do so with retention of configuration. Unimolecular reactions take place with extensive change of configuration. Unfortunately, for the system under investigation, the steric course cannot be determined owing chiefly to the fact that the complexes isomerise more rapidly than they react with water.

EXPERIMENTAL

Preparations.—*cis*-Aquochlorobisethylenediaminecobalt(III) sulphate was prepared from the *trans*-dichloro-chloride by Werner's method.[11] It was purified by dissolving it in the minimum amount of water at 40°, cooling the filtered solution in ice, and adding ethanol {Found: Co, 16·7; co-ord. Cl, 10·0; Cl^-, 0. Calc. for $[Co(C_2H_8N_2)_2,H_2O,Cl]SO_4,1\frac{1}{2}H_2O$: Co, 16·6; co-ord. Cl, 10·0%}.

trans-Hydroxochlorobisethylenediaminecobalt(III) chloride was made by the method of Meisenheimer and Kiderlen[12] by adding an aqueous solution of diethylamine to the *trans*-dichloro-chloride. The crude product was recrystallised twice by dissolution in the minimum amount of ice-cold water and addition of ethanol to the rapidly filtered solution {Found: Co, 20·7; Cl^-, 12·6; co-ord. Cl, 12·4. Calc. for $[Co(C_2H_8N_2)_2OH,Cl]Cl,H_2O$: Co, 20·7; Cl^-, 12·5; co-ord. Cl, 12·5%}.

Kinetics.—Weighed amounts of the complex were dissolved in the solvent previously brought to the required temperature. The buffers used in the earlier runs were Clark and Lub's formulation.[13] Light was excluded and samples were withdrawn from time to time. The ionic chloride was determined by passing the sample through a cation-exchange resin (Amberlite IR-120; H^+ form) and estimating the hydrochloric acid in the effluent by the Volhard method. The resin column was surrounded by ice–water to reduce reaction of the complex absorbed on the resin. The resin was flushed continually with water between separations.

Spectrophotometric measurements were made with a Unicam S.P. 500 quartz spectrophotometer and 4-cm. silica cells. pH measurements of the buffer solutions were made with a Pye Universal pH meter.

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DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF HONG KONG, HONG KONG.

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[11] Werner, *Annalen*, 1912, **386**, 122.

[12] Meisenheimer and Kiderlen, *Annalen*, 1924, **438**, 241.

[13] Lange, " Handbook of Chemistry," Handbook Publ., Inc., Sandusky, Ohio, 1956, 9th edn., p. 951.