**486.** *The Acid-catalysed Reactions of Transition-metal Complexes. Part II.*[1] *The Acid-catalysed Aquations of* cis- *and* trans-*Dinitrobisethylenediaminecobalt*(III) *Salts.*

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The acid-catalysed aquations of *cis-* and *trans-*[Co en$_2$(NO$_2$)$_2$]NO$_3$ at 25, 35, and 45°, and at ionic strength 3·5, have been studied over a wide range of acid concentration. The rate of aquation is directly proportional to the stoicheiometric concentration of acid for both perchloric and nitric acids. The steric courses have been studied at 35° in 3·50M-perchloric acid, and the results show that these aquations proceed with virtually complete retention of configuration. In 3·50M-perchloric acid the rearrangement between *cis-* and *trans-*[Co en$_2$(NO$_2$)H$_2$O]SO$_4$ at 35° is shown to be very slow. Under similar conditions the replacement of the nitro-group from *cis-* and *trans-*[Co en$_2$(NO$_2$)H$_2$O]SO$_4$ is very slow also. The Arrhenius parameters for the acid-catalysed aquations of *cis-* and *trans-*[Co en$_2$(NO$_2$)$_2$]NO$_3$ and *cis-*[Co en$_2$(N$_3$)$_2$]ClO$_4$ are reported. The mechanisms of these reactions are discussed.

IN strongly acidic solutions of *cis-* and *trans-*dinitrobisethylenediaminecobalt(III) salts one of the nitro-groups is replaced by water, whereas in neutral or faintly acidic solutions no hydrolysis occurs. It was shown during this investigation that the replacement of the nitro-group in *cis-* or *trans-*nitroaquobisethylenediaminecobalt(III) sulphates is very slow (at 35·0° in 3·50M-perchloric acid the half-lives were estimated to be of the order of 1 to 2 days). Under similar conditions the rearrangement between the *cis-* and *trans-*nitro-aquo-ions was too slow to be measured before the hydrolysis reaction occurred.

The reactions studied can therefore be summarised:

cis- or trans-[Co en$_2$(NO$_2$)$_2$]$^+$ + H$_3$O$^+$ $\longrightarrow$ cis- or trans-[Co en$_2$(NO$_2$)H$_2$O]$^{2+}$ + H$_2$O + HNO$_2$
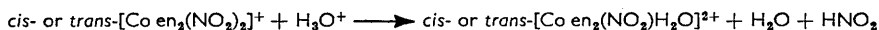
The reactions were not photocatalysed; separate experiments in clear and darkened vessels gave the same results within the limits of experimental error.

RESULTS

Acid-catalysed Aquation of cis- *and* trans-*Dinitrobisethylenediaminecobalt*(III) *Nitrates.—* (a) *Kinetics.* These reactions have been studied spectrophotometrically at 4000 Å. At this wavelength the extinction coefficients of *cis-* and *trans-*nitroaquobisethylenediaminecobalt(III) sulphates are the same. The main investigation was carried out at 35·0°, the ionic strength

[1] Part I, Staples, *J.*, 1964, 745.

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being constant at 3·5. Under these conditions the reactions are of second order—of first order in complex-ion concentration and first order in acid concentration, *viz.*,

$$\text{Rate} = k_{\text{s}}[\text{Complex}][\text{H}_3\text{O}^+].$$

However, as the acid was present in such a large excess, the reactions actually studied were of pseudo-first order, *i.e.*,

$$\text{Rate} = k_{\text{f}}[\text{Complex}], \text{ where } k_{\text{f}} = k_{\text{s}}[\text{H}_3\text{O}^+].$$

The results are summarised in Table 1.

In the majority of experiments perchloric acid was used together with sodium perchlorate to keep the ionic strength constant. Some experiments were performed with nitric acid and sodium nitrate, but the results were the same within experimental error (see Table 1).

The results obtained by studying the kinetics nitritometrically agree roughly with those obtained spectrophotometrically, but exact agreement was not possible because of the decomposition of nitrous acid. These experiments were carried out over the higher range of acid

TABLE 1.

Mean rate-constants (determined spectrophotometrically) for the acid-catalysed aquation of *cis*- and *trans*-dinitrobisethylenediaminecobalt(III) nitrate at ionic strength 3·5, at various acid concentrations and temperatures.

$$10^3[\text{Complex}] = 2\cdot00 \text{ or } 1\cdot00.$$

Confign.	Temp.	[Acid] (moles l.$^{-1}$)	$10^5 k_{\text{f}}$ (sec.$^{-1}$)	$10^5 k_{\text{s}}$ (l. mole^{-1} sec.$^{-1}$)	Confign.	Temp.	[Acid] (moles l.$^{-1}$)	$10^5 k_{\text{f}}$ (sec.$^{-1}$)	$10^5 k_{\text{s}}$ (l. mole^{-1} sec.$^{-1}$)
cis	25·0°	3·50	4·35	1·24	*trans*	25·0°	2·80	6·9	2·46
,,	,,	3·30	4·50	1·36	,,	,,	2·50	8·2	3·28
,,	,,	3·00	4·55	1·52	,,	35·0	3·50	34·7	9·9
,,	,,	2·80	3·96	1·39	,,	,,	3·30	32·5	9·8
,,	35·0	3·50	19·2	5·5	,,	,,	3·00	33·6	11·2
,,	,,	3·30	13·5	4·0$_5$	,,	,,	2·80	28·4	10·2
,,	,,	3·00	17·1	5·7	,,	,,	2·50	27·6	11·0
,,	,,	2·80	14·7	5·2$_5$	,,	,,	2·00	21·5	10·8
,,	,,	2·50	14·4	5·8	,,	,,	1·60	16·5	10·3
,,	,,	2·00	10·7	5·3$_5$	,,	,,	1·02$_5$	12·4	12·0
,,	,,	1·60	5·3	3·3	,,	,,	0·50	5·47	10·9
,,	,,	1·00	5·05	5·0$_5$	,,	,,	0·200	1·87	9·4
,,	,,	0·50	3·1	6·2	,,	,,	0·100	0·72	7·2
,,	,,	0·200	1·19	5·9$_5$	,,	,,	0·050	0·22	4·4
,,	,,	0·100	0·43	4·3	,,	44·65	3·50	144	41·1
,,	,,	0·050	0·31	6·2	,,	,,	3·30	105	35·1
,,	44·35	3·50	65·7	18·8	,,	,,	3·00	102	40·8
,,	,,	3·00	56·3	18·8	*cis*	35·0	3·50 *	17·6	5·5
,,	,,	2·50	52·3	20·9	,,	,,	3·00 *	18·5	6·2
trans	25·0	3·50	10·9	3·12	*trans*	,,	3·50 *	34·0	9·7
,,	,,	3·30	9·5	2·88	,,	,,	3·00 *	32·3	10·8
,,	,,	3·00	9·1$_5$	3·05					

* Runs in which nitric acid and sodium nitrate were used instead of perchloric acid and sodium perchlorate, respectively.

concentrations at 35·0°. The mean values obtained were $10^5 k_{\text{s}}(cis) = 4\cdot0 \pm 0\cdot6$ l. mole^{-1} sec.$^{-1}$ and $10^5 k_{\text{s}}(trans) = 10\cdot7 \pm 2\cdot6$ l. mole^{-1} sec.$^{-1}$.

These aquations were studied spectrophotometrically at three temperatures, and the Arrhenius parameters evaluated (see Table 2).

(b) *Steric Course.* The steric courses of these reactions were studied spectrophotometrically at 3200—3350 Å at 35·0°. In this region the spectra of the *cis*- and *trans*-nitroaquobisethylene-diaminecobalt(III) ions in 3·50M-perchloric acid are different. In spite of the difference in concentration (3·50M-instead of *ca.* 0·01M-perchloric acid), the spectra are similar to those

Arrhenius parameters for the acid-catalysed aquations of diacidobisethylenediamine-cobalt(III) salts at constant ionic strength. Values calculated from the equation $k = A \exp(-E/\mathbf{R}T)$.

Complex	Ionic strength (g.-ion l.$^{-1}$)	Activation energy (kcal. mole^{-1})	$\log_{10} A$
cis-[Co en$_2$(NO$_2$)$_2$]NO$_3$	3·5	25·6	13·9
trans-[Co en$_2$(NO$_2$)$_2$]NO$_3$	3·5	24·9	13·7
cis-[Co en$_2$(N$_3$)$_2$]ClO$_4$	2·0	26·7	15·9

reported by Asperger and Ingold.[2] As the possible second steps, *i.e.*, the acid-catalysed aquations of *cis*- and *trans*-nitroaquo-ions and the rearrangement between them, are very slow, the steric courses could be deduced by an examination of the spectra of the solutions after seven to ten half-lives. The results show that the *cis*-dinitrobisethylenediaminecobalt(III) ion aquates with complete retention of configuration, whilst the *trans*-dinitro-ion yields 90% *trans*-nitroaquobisethylenediaminecobalt(III) ion.

Acid-catalysed Aquation of cis-*Diazidobisethylenediaminecobalt*(III) *Perchlorate.*—This reaction was studied spectrophotometrically at 35·0 and 44·5°, the ionic strength being kept constant (2·0). The wavelength (5330 Å) was that at which the *cis*- and *trans*-azidoaquobisethylene-diaminecobalt(III) ions have the same extinction coefficient. These results, together with those obtained previously,[1] were used to evaluate the Arrhenius parameters (Table 2). The results are summarised in Table 3.
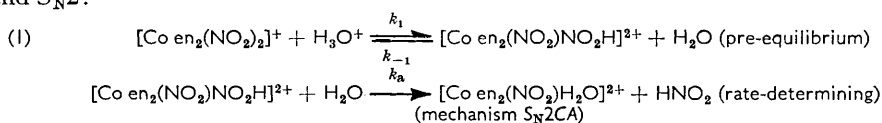
Table 3.

Mean rate-constants for the acid-catalysed aquation of *cis*-diazidobisethylenediamine-cobalt(III) perchlorate at ionic strength 2·0.
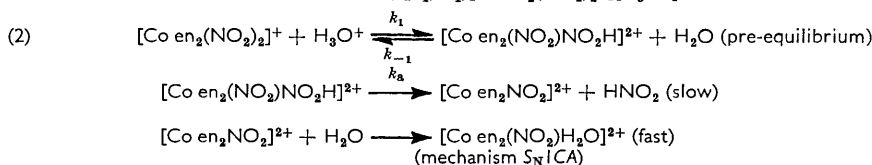
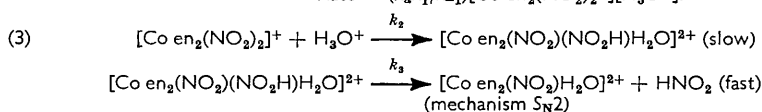| Temp.	25·0°	35·0°	35·1°	44·4°	44·5°
Mean $10^5 k_s$ l. mole^{-1} sec.$^{-1}$ ...	23·9 1	83·5	85·5	413	417

DISCUSSION

The results obtained in this investigation follow very closely those obtained for the acid-catalysed aquations of the *cis*- and *trans*-diazidobisethylenediaminecobalt(III) salts.[1] The same three mechanisms can be envisaged for both sets of systems, *viz.*, S_N1CA, S_N2CA, and S_N2:

(1) $\quad$ [Co en$_2$(NO$_2$)$_2$]$^+$ + H$_3$O$^+$ $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ [Co en$_2$(NO$_2$)NO$_2$H]$^{2+}$ + H$_2$O (pre-equilibrium)

$\quad$ [Co en$_2$(NO$_2$)NO$_2$H]$^{2+}$ + H$_2$O $\overset{k_a}{\longrightarrow}$ [Co en$_2$(NO$_2$)H$_2$O]$^{2+}$ + HNO$_2$ (rate-determining)
(mechanism S_N2CA)

Rate = $(k_a k_1/k_{-1})$[Co en$_2$(NO$_2$)$_2$$^+$][H$_3O^+$].

(2) $\quad$ [Co en$_2$(NO$_2$)$_2$]$^+$ + H$_3$O$^+$ $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ [Co en$_2$(NO$_2$)NO$_2$H]$^{2+}$ + H$_2$O (pre-equilibrium)

$\quad$ [Co en$_2$(NO$_2$)NO$_2$H]$^{2+}$ $\overset{k_a}{\longrightarrow}$ [Co en$_2$NO$_2$]$^{2+}$ + HNO$_2$ (slow)

$\quad$ [Co en$_2$NO$_2$]$^{2+}$ + H$_2$O $\longrightarrow$ [Co en$_2$(NO$_2$)H$_2$O]$^{2+}$ (fast)
(mechanism S_N1CA)

Rate = $(k_a k_1/k_{-1})$[Co en$_2$(NO$_2$)$_2$$^+$][H$_3O^+$].

(3) $\quad$ [Co en$_2$(NO$_2$)$_2$]$^+$ + H$_3$O$^+$ $\overset{k_2}{\longrightarrow}$ [Co en$_2$(NO$_2$)(NO$_2$H)H$_2$O]$^{2+}$ (slow)

$\quad$ [Co en$_2$(NO$_2$)(NO$_2$H)H$_2$O]$^{2+}$ $\overset{k_3}{\longrightarrow}$ [Co en$_2$(NO$_2$)H$_2$O]$^{2+}$ + HNO$_2$ (fast)
(mechanism S_N2)

Rate = k_2[Co en$_2$(NO$_2$)$_2$$^+$][H$_3O^+$].

[2] Asperger and Ingold, *J.*, 1956, 2862.

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All these mechanisms give rise to second-order kinetics. Mechanism (3) can be ruled out because it would have a very unfavourable entropy factor which should lead to slow reactions, whereas in fact the values of $\log_{10}A$ are rather high for reactions between two similarly charged species. Hammett has shown that a graph of $\log_{10}k_f$ against acidity function should give a straight line of unit slope. These conditions are not satisfied. However, a plot of $\log_{10}k_f$ against $\log_{10}$ (stoicheiometric acid concentration) gives a straight line of unit slope. This suggests that mechanism (1) operates in this system. It must be pointed out, however, that the values of acidity function used were those obtained by using organic bases, whereas in these investigations we should have used acidity functions determined by using indicators more similar to the actual substrates. Although H_0 was used instead of H_+ it has been shown that these two functions have a parallel relationship. Further evidence against mechanism (2) can be obtained from the steric course measurements. An S_N1CA mechanism would probably lead to appreciable amounts of stereo-change yet these aquations proceed mainly with retention of configuration.

EXPERIMENTAL

Preparations.—*cis*- and *trans*-Nitroaquobisethylenediaminecobalt(III) sulphates [3] and *cis*- and *trans* [4]-dinitrobisethylenediaminecobalt(III) nitrates were prepared by methods described in the literature.

Compound	Found (%)			(Calc. (%)		
	C	H	N	C	H	N
cis-[Co en$_2$(NO$_2$)H$_2$O]SO$_4$	14·3	5·4	—	14·15	5·3	—
trans-[Co en$_2$(NO$_2$)H$_2$O]SO$_4$	14·0	5·1	—	14·15	5·3	—
cis-[Co en$_2$(NO$_2$)$_2$]NO$_3$	14·6	4·9	29·3	14·4	4·85	29·4
trans-[Co en$_2$(NO$_2$)$_2$]NO$_3$	14·65	4·9	29·4	14·4	4·85	29·4

The more recent preparation [5] of *cis*-[Co en$_2$(NO$_2$)$_2$]NO$_3$ was also adopted, and the product was used for some of the steric-course experiments. The two preparations gave concordant results.

Spectrophotometric Runs.—Aliquot portions of the reaction mixture were withdrawn at timed intervals and run into test-tubes in an ice–salt bath. The optical density at 4000 Å was measured as quickly as possible in silica cells with a Unicam S.P. 500 spectrophotometer.

Nitritometric Runs.—Aliquot portions (5 ml.) of the reaction mixture were withdrawn at timed intervals and run into graduated flasks containing water (40 ml.) and a solution (5 ml.) of sulphanilic acid and sodium bromide (solution A of Ridd's method [6]). After 10 min. a solution (10 ml.) of 1-naphthylamine and borax (solution B) was added to each and the solutions were made up to the mark. The optical density at 4750 Å was measured with a Unicam S.P. 500 spectrophotometer.

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[3] Meyer and Rampoldt, *Z. anorg. Chem.*, 1933, **214**, 1.
[4] Hortzclaw, Sheety, and McCarty, *Inorg. Synth.*, **4**, 176.
[5] Harbulak and Albinak, *J. Inorg. Nuclear Chem.*, 1963, **25**, 232.
[6] Ridd, Thesis, London, 1951.