311. *Substitution Reactions in the Trisethylenediaminecobalt*(III) *Ion.*

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The hydrolysis of the trisethylenediaminecobalt(III) ion is studied at relatively high alkali concentrations and high temperatures. The ion is stable at low temperatures and low alkali concentrations in the absence of catalysts. The rate is followed spectrophotometrically at temperatures from 70° to 90° C.

Although each run gives a first-order plot, the overall reaction has second-order kinetics. The effect of increasing the ionic strength of the reaction mixture with sodium nitrate is investigated; no appreciable salt effect is observed, probably owing to the high ionic strength of the mixtures.

The activation energy for $[\mathrm{Co\ en_3}]^{3+} \longrightarrow [\mathrm{Co\ en_2(OH)_2}]^{+}$, which involves the rupture of two bonds, is 38 kcal. mole^{-1} for concentrations of hydroxyl ion greater than 0·1N. Below this the dependence of rate on concentration of hydroxyl-ion changes and the activation energy appears to become smaller. Possible mechanisms for the reaction are discussed.

RECENT studies of substitution reactions in octahedral complexes of tervalent cobalt have been due mainly to Bailar,[1] Ingold and Nyholm,[2] and Basolo [3] and their collaborators. Much has appeared more recently, dealing mostly with reactions of ions of the general formula $[\mathrm{Co\ en_2X_2}]^{+}$.[4, 5] We have begun to investigate the more stable trisethylenediamine ion. The first experiments used the trisethylenediaminechromium(III) ion, but even at as low as 50° the complex ion decomposed in solution too rapidly to allow the study of any reaction with other ions (such as chloride). At 35° no reaction could be observed, although Schläfer and Kling [6] found a slow transformation of $[\mathrm{Cr\ en_3}]^{3+}$ into $[\mathrm{Cr\ en_2(H_2O)_2}]^{3+}$ in solution at room temperature during some weeks.

Attention was therefore directed to the trisethylenediaminecobalt(III) ion, which is more stable. We tried to study the substitution of ethylenediamine by chloride ion, but this did not occur even in aqueous solution at 100°. Reaction with hydroxyl ion did, however, occur at measurable rates in aqueous solution above 70°. Taube [7] has stated (apparently on Jørgensen's authority) that $[\mathrm{Co\ en_3}]^{3+}$ is unaffected by boiling alkali, but this does not appear to be so, although it does not completely decompose to the oxide.[8] Bjerrum and Rasmussen [9] studied the reaction

$$[\mathrm{Co\ en_3}]^{3+} + 2\mathrm{OH}^- \rightleftharpoons [\mathrm{Co\ en_2(OH)_2}]^{+} + \mathrm{en}$$

in aqueous solution, in the presence of charcoal as a catalyst, at 25°. The product contained approximately equal amounts of the *cis*- and the *trans*-isomer. We used a large excess of alkali, but no charcoal, so as to lead to hydroxylation rather than to aquation.

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[1] (*a*) Bailar and Auten, *J. Amer. Chem. Soc.*, 1934, **56**, 774; (*b*) Bailar, Haslam, and Jones, *ibid.*, 1936, **58**, 2226.

[2] (*a*) Brown, Ingold, and Nyholm, *J.*, 1953, 2674; (*b*) Brown and Ingold, *ibid.*, p. 2680; (*c*) Brown and Nyholm, *ibid.*, p. 2696.

[3] (*a*) Basolo, Bergmann, and Pearson, *J. Phys. Chem.*, 1952, **56**, 22; (*b*) Pearson, Boston, and Basolo, *J. Amer. Chem. Soc.*, 1952, **74**, 2943.

[4] Basolo, *Chem. Rev.*, 1953, **52**, 459.

[5] Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.

[6] Schläfer and Kling, *Z. anorg. Chem.*, 1956, **287**, 296.

[7] Taube, *Chem. Rev.*, 1952, **50**, 69.

[8] Brigando, *Compt. rend.*, 1953, **236**, 708.

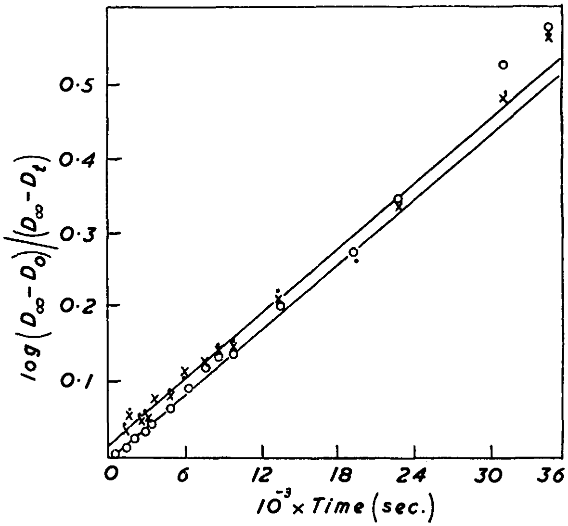
[9] Bjerrum, J., and Rasmussen, *Acta Chem. Scand.*, 1952, **6**, 1265.

EXPERIMENTAL

Trisethylenediaminecobalt(III) chloride was prepared according to the method of "Inorganic Syntheses."[10] It was analysed for cobalt by the pyridine–thiocyanate method after being evaporated with concentrated sulphuric acid, and for chloride by titration with silver nitrate [Found: Co, 15·9, 15·1; Cl, 28·3, 28·5, 28·5. Calc. for $Co(C_2H_8N_2)_3Cl_3,1{\cdot}5H_2O$: Co, 15·8; Cl, 28·6%]. The standardised sodium hydroxide solutions used were carbonate-free.

Absorption spectra were measured on a Unicam S.P. 500 spectrophotometer. The reaction was followed by reading optical density at 560 mμ, where the absorption of $[Co\,en_3]^{3+}$ is negligible; at 510 mμ, where the absorption is still low, and *cis*- and *trans*-$[Co\,en_2(OH)_2]^+$ both have maxima; and at 460 mμ, where $[Co\,en_3]^{3+}$ has a maximum and the curves for the two dihydroxo-compounds cross. One set of readings was taken at 494 mμ, where $[Co\,en_3]^{3+}$ and $[Co\,en_2(OH)_2]^+$ have the same extinction coefficient. This showed that the total cobalt concentration in the solution was not changing through evaporation.

Experiments were carried out in stoppered 250 ml. "Pyrex" flasks. The solutions used were approximately 2·8mM in $[Co\,en_3]^{3+}$. Weighed amounts of the salt were placed in 250 ml. volumetric flasks and sodium hydroxide solution was added to make 250 ml. The standard solutions were then transferred to the reaction flasks in the thermostat, and about 3 min. allowed for the mixture to reach equilibrium before readings were taken. Samples were withdrawn at intervals and chilled in an ice-bath before the optical density was measured.



Reaction of $[Co\,en_3]Cl_3$ *with* 0·5N-*sodium hydroxide at* 70°.

○ Readings at 560 mμ.
× Readings at 510 mμ.
$k = 3{\cdot}32 \times 10^{-5}$ sec.$^{-1}$.

Results.—The reactions followed a first-order course with respect to alkali concentration. A typical run is shown in Fig. 1, which also shows that the slopes derived from readings at 510 mμ and 560 mμ agree well. There is some deviation from linearity in the later stages. In Table 1 the variation of rate constant with temperature is shown; the activation energy is about 38 kcal. mole^{-1}.

TABLE 1. *Values of rate constant for constant sodium hydroxide concentration* (0·5N) *at different temperatures.*

Temp. (° c)	70·0	75·2	80·0	91·0
10^5k (sec.$^{-1}$)	3·32	8·53	20·0	85·0

TABLE 2. *Variation of rate constants with sodium hydroxide concentration at* 80°.

[NaOH] (N)	0·05	0·10	0·20	0·50	0·664	1·0
10^4k (sec.$^{-1}$)	1·28	1·54	1·65	2·00	2·17	2·65

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[10] Work, "Inorganic Syntheses," McGraw-Hill Book Company, Inc., New York, 1946, Vol. II, p. 221.

In Table 2 are listed the values of *k* found at constant temperature (80°) and ammine concentration, for different concentrations of sodium hydroxide. A plot of these data shows that the dependence of the rate constant on sodium hydroxide concentration is linear down to 0·1N, although the point corresponding to 0·05N-NaOH is much lower than the straight line which joins the values of *k* found at higher concentrations. In 0·01N-NaOH there was little or no reaction after about a week.

It was not possible to detect a change in the rate of reaction on increasing the concentration of ammine, no doubt owing to the large excess of alkali present.

The effect of ionic strength on the reaction rate was studied by adding sodium nitrate to the reaction mixture: results for 80° are in Table 3.

TABLE 3. *Variation of rate constant with ionic strength at* 80° C.

$[NaNO_3]$ (M)	0	0·1	0·2	0·3	0·4
10^5k (0·1N-NaOH)	15·4	10·7	8·68	—	5·57
10^5k (0·5N-NaOH)	20·0	19·2	22·2	17·3	—

TABLE 4. *Variation of rate constant with concentration of sodium hydroxide at constant ionic strength at* 80° C.

$[NaNO_3]$(M)	0	0·2	0·4
[NaOH](N)	0·5	0·3	0·1
10^5k (sec.$^{-1}$)	20·0	14·75	5·57

The graph of log *k* as a function of (ionic strength)$^{\frac{1}{2}}$ is, for 0·1N-NaOH, linear with a slope of −1·14, about one-third of the theoretical value for a reaction between a univalent and a tervalent ion. In 0·5N-NaOH, there is no appreciable salt effect.

These results agree with those of Ašperger and Ingold,[11] who found no salt effect in their experiments on the reaction of sodium hydroxide with the *trans*-(chloronitrobisethylenediamine)-cobalt(III) ion, no doubt owing to their working at the high ionic strength necessary to secure a measurable rate of reaction. When the ionic strength was kept constant at 0·5 and the ratio of sodium hydroxide to sodium nitrate varied, rate constants proportional to the concentration of sodium hydroxide were obtained, thus confirming the overall second-order kinetics of the reaction.

DISCUSSION

The experimental data at a concentration of sodium hydroxide of 0·5N satisfy an equation of the form $k_2 = 6{\cdot}5 \times 10^{19} \exp(-38{,}000/\boldsymbol{RT})$. This means that the energy of activation has the unusually high value of about 38 kcal. mole^{-1}, in contrast with the much lower values of 20—30 kcal. found by Ingold, Nyholm, and their collaborators[11,12,13] for most substitution reactions in $[Co\ en_2Cl_2]^+$, $[Co\ en_2(NCS)X]^+$, and $[Co\ en_2NH_3X]^{2+}$, including the bimolecular reaction with hydroxyl ion. At lower concentrations of sodium hydroxide, the reaction mechanism changes, and an activation energy of 32 kcal. mole^{-1} was found for a solution 0·05N in sodium hydroxide. These high activation energies seem to be an expression of the great stability of the $[Co\ en_3]^{3+}$ ion, even as compared with the $[Co(NH_3)_6]^{3+}$ ion. This stability has often been noticed, and is possibly due to steric effects.

Substitution of $[Co\ en_3]^{3+}$ by hydroxyl ion necessarily involves the introduction of two substituents, and takes place apparently in two stages, one of which is bimolecular and rate-controlling. The kinetic expression for the variation of rate constant with temperature in 0·5N-sodium hydroxide indicates that the frequency factor is approximately 10^{20}, even higher than the value of 10^{17} found by Brønsted and Livingstone[14] for the reaction of hydroxyl ion with the chloropentamminocobalt(III) ion. Ašperger and Ingold found a " normal " frequency factor of 10^{11}—10^{12} in the bimolecular substitution of $[Co\ en_2Cl_2]^+$

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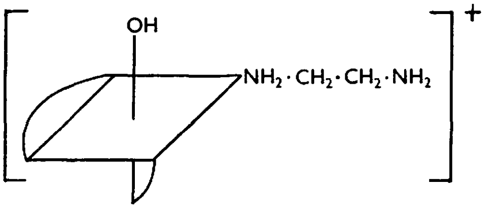
[11] Ašperger and Ingold, *J.*, 1956, 2862.
[12] Ingold, Nyholm, and Tobe, *J.*, 1956, 1691.
[13] Nyholm and Tobe, *J.*, 1956, 1707.
[14] Brønsted and Livingstone, *J. Amer. Chem. Soc.*, 1927, **49**, 435.

by OH^-. In the language of the transition-state theory, the present results can be said to imply an entropy of activation of approximately 30 cal. (mole deg.)$^{-1}$ in accordance with the value to be expected for a reaction involving ions of charges $+3$ and -1. This result is obtained by writing the Eyring equation in the form

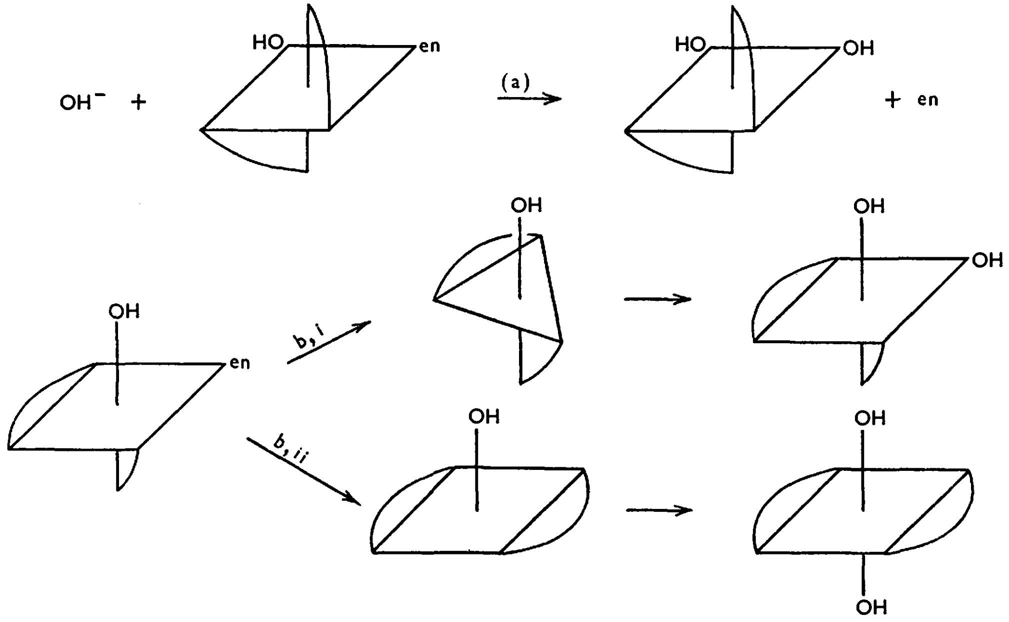
$$k_2 = \mathrm{e}\ (\boldsymbol{R}T/\boldsymbol{N}h)\ \exp\ (\Delta S^*/\boldsymbol{R})\ .\ \exp\ (-E_A/\boldsymbol{R}T)$$

and inserting the appropriate experimental data (E_A is the Arrhenius activation energy).

The reaction appears to take place by way of an intermediate ion in which the ethylenediamine molecule which is being replaced is attached at one end only, as in (I). This first stage must be the rate-determining one, as no trace of an intermediate was detected by spectrophotometry. The spectra of pentammines are quite different from those of tetrammines, so that if the course of the reaction had involved a rapid formation of an intermediate which then decomposed rapidly, this should have been detectable. It seems reasonable to postulate an intermediate ion of the structure suggested; there are in fact stable co-ordination compounds in which ethylenediamine functions as a unidentate group (see, for example, Drew,[15] Job,[16] and Bjerrum [17]). In the present instance, the adjacent OH group is no doubt responsible for the instability of the second Co–N bond. It has been suggested, particularly by Pearson, Meeker, and Basolo,[18] that the



(I)



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[15] Drew, *J.*, 1932, 2328.

[16] Job, *Ann. Chim.* (*France*), 1928, **9**, 166.

[17] Bjerrum, J., " Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941, p. 92.

[18] Pearson, Meeker, and Basolo, *J. Inorg. Nuclear Chem.*, 1955, **1**, 342.

substitutions involving the hydroxyl ion proceed *via* the conjugate base of the cobalt-ammine (mechanism S_N1CB rather than S_N2). This point has been discussed by Ašperger and Ingold,[11] who adhere to the S_N2 mechanism. A firm decision on the question in respect of the ion under discussion would require further work which it has not so far been possible to carry out. Evidence that analogous reactions are in fact S_N2, however, seems adequate. The intermediate could then, either by an edge-displacement giving, with another OH^- ion, $[Co\ en_2(OH)_2]^+$ [path (a)], or by a first-order heterolysis [path (b)], yield the final equilibrium mixture of isomers. The equilibrium between the *cis*- and the *trans*-form is attained so rapidly at the experimental temperatures that the two mechanisms could not be distinguished on this basis. Possibly the former is the more likely mechanism, although the change in configuration in path (b), second stage, could be facilitated by the "*trans*-effect."[19, 20]

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[19] Quagliano and Schubert, *Chem. Rev.*, 1952, **50**, 201.
[20] Chatt, Duncan, and Venanzi, *Rec. Trav. chim.*, 1956, **75**, 681.