

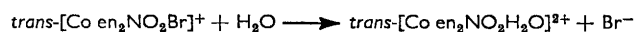
77. Mechanism and Steric Course of Octahedral Aquation. Part VI.*
The Non-solvolytic Aquation of trans-Bromonitrobis(ethylenediamine)-cobalt(III) Salts.

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The aquation of *trans*-[Co en₂NO₂Br]⁺ has been studied in water-tetrahydrothiophen dioxide mixtures over the full composition range. At low water content, the back-reaction becomes overwhelmingly important and it is necessary to study the aquation by an indirect method, whereby the aquo-complex is made to react with thiocyanate ions as fast as it is formed. At low water concentrations there is a linear dependence of the rate of aquation upon the concentration of water, and there is an almost linear relation between the rate of aquation and the volume fraction of water over the whole range of composition. In dry tetrahydrothiophen dioxide, the thiocyanate enters the complex by a different path and there is first-order dependence of the rate on the concentration of thiocyanate ions. Preliminary observations of the replacement of co-ordinated bromide by chloride ions indicate that the rate-dependence on anion concentration arises from the formation of ion-pairs, and so no deduction can be made at this stage about the molecularity of these reactions. It is suggested that the composition of that part of the solvent shell that is in direct contact with the complex ion has much more significance than the composition of the bulk solvent in determining the rate of reaction.

A SERIOUS difficulty in investigations of the mechanism of aquation under solvolytic conditions is that it is not possible to determine the order of the reaction with respect to the entering group. As a result, it has been necessary, in the past, to ascertain the mechanism by other, more equivocal approaches so that few clear-cut decisions could be made between the dissociative (S_N1) and bimolecular (S_N2) modes of nucleophilic substitution.¹ Aquation in non-aqueous solvents has received little attention, partly because of solubility difficulties, but mainly because of its reversibility.

The present work was designed to measure the kinetic dependence of the reaction



on the concentration of water in the mixed solvent system, tetrahydrothiophen 1,1-dioxide ("sulpholane"; referred to below as the sulphone) and water. Resorting to mixed solvents is no guarantee that the information concerning the kinetic role of water will be forthcoming, as the several effects of the solvent change on the reaction kinetics may operate simultaneously and obscure one another. Further, the solvent may assume the role of reagent so that a new solvolytic reaction is observed. The sulphone-water system is, however, favourable for such a study since, at low concentrations, the water activity

* Part V, *J.*, 1962, 1388.

¹ Tobe, *Sci. Progr.*, 1960, **48**, 483; Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 4736.

increases rapidly with increasing water content,² with a result that the variation of the bulk properties of the solvent is negligible over a substantial range of water activity.

(1) *Kinetics*.—In pure water the aquation goes sensibly to completion. It was followed conductometrically and spectrophotometrically and was found to follow a first-order rate law. The rate constants were determined from the plots of time against $\log_{10} (C_{\infty} - C_t)$ for the conductivity experiments, and $\log_{10} (D_{\infty} - D_t)$, for the spectrophotometric experiments, where C and D refer to the conductivities and optical densities, respectively, and the subscripts t and ∞ refer to measurements made at time t and after ten half-lives. The spectrum of the product corresponded very closely with that of a pure specimen of the *trans*-[Co en₂NO₂H₂O]²⁺ cation,³ indicating that aquation took place with complete retention of configuration.

As the content of sulphone in the solvent increased, the reverse reaction became significant and the aquation did not go to completion. Provided more than 90% of the complex was in the aquo-form at equilibrium, it was possible to obtain the first-order rate constant by inserting in the above expression values for D_{∞} calculated by assuming complete aquation. When the back-reaction became more important, this approximation could no longer be used and the data were treated on the basis of opposed first- and second-order reactions. In order to simplify the calculation and ensure that $[\text{Br}^-] = [\text{Aquo-complex}]$ throughout the reaction, the complex was supplied as the perchlorate, and the rate constant for the aquation was determined graphically, making use of the expression

$$\frac{k(2a - x_e)t}{x_e} = 2.303 \log_{10} \frac{ax_e + x(a - x_e)}{a(x_e - x)},$$

where a is the initial concentration of the bromo-complex and x and x_e are the concentrations of the aquo-complex at time t and at equilibrium, respectively. These concentrations were determined from the spectrophotometric measurements. The lower limit of applicability of this treatment was reached when equilibrium corresponded to less than 10% of aquation (<8 vol. % of water). Here, the change of optical density due to the reaction was small compared with the optical density itself and the derived rate constants were unreliable.

In order to study the important region where the concentration of water is low enough for the kinetic aspects to be separable from the solvent effects, it was necessary to devise a method to prevent the reverse reaction from taking place by removing one or other of the products as fast as it was formed. Removal of the bromide ion was not feasible since mercuric ions removed the co-ordinated bromide immediately and it was suspected that silver ions would behave similarly, although less effectively, and the reaction was too fast for it to be possible to remove any precipitate before making a measurement. The alternative approach was therefore tried, namely, removal of the aquonitro-cation. It has already been shown that the very similar *cis*-[Co en₂NO₂H₂O]²⁺ reacts irreversibly with azide and thiocyanate ions in aqueous solution,⁴ at rates increasing with increasing anion concentration, and the studies of the reverse of the aquation of the bromonitro-complex have shown that the rate of this "anation" increases as the sulphone content of the solvent increases. It was hoped that it would thus be possible to remove the aquo-complex fast enough for the original aquation to be studied, without introducing a new mode of reaction. The reaction between *trans*-[Co en₂NO₂Br]⁺ and SCN⁻ was studied in the solutions with the low water content, thiocyanate being chosen in preference to azide because of its low basicity. In the presence of sufficient thiocyanate, the reaction appeared to be a straightforward replacement of bromine by thiocyanate at a rate independent of the thiocyanate concentration but dependent on the concentration of

² Langford, Thesis, Northwestern University, Evanston, Illinois, 1960.

³ Asperger and Ingold, *J.*, 1956, 2862.

⁴ Basolo, Stone, and Pearson, *J. Amer. Chem. Soc.*, 1954, **76**, 3079.

water. The first-order rate constants were determined spectrophotometrically from the change of optical density at 4400 Å and 4650 Å, and are plotted, in Fig. 1, against the concentration of thiocyanate added as trimethylanilinium thiocyanate. It is clear that the rate is almost independent of the concentration of thiocyanate, but dependent on the concentration of water. For the two higher concentrations of water, 4% and 10% volume fraction, this behaviour is observed only at those concentrations of thiocyanate that are high enough to ensure that the aquo-complex is consumed as soon as it is formed. At lower thiocyanate concentrations, sufficient of the aquo-complex is present at the intermediate stages of the reaction to spoil the determination of the rate constants, since the aquo-complex absorbs less light than the thiocyanato-product and causes the rate of change of optical density to be less than the true rate of aquation. It was possible, in the solvent containing a 10% volume fraction of water, to compare the aquation rate constant that was determined directly with that obtained from the study of thiocyanate entry and, although the extrapolation in the second case is large, it appears that the two values are in reasonable agreement. The rate constants for all the aquations are collected in Table 1, where the water content is expressed in terms of volume fraction (%), mole

TABLE 1.

Rate constants for the aquation of *trans*-bromonitrobis(ethylenediamine)cobalt(III) salts in water-sulphone mixtures.

Temp.	Concn. of water			1st-order rate constants (10^{-4} sec. $^{-1}$)		
	Vol. fraction (%)	Mole fraction (%)	Relative activity	Direct	Indirect (SCN $^{-}$)	Conduct.
0.0°	100	100	1.00	—	—	1.4
25.0	„	„	„	43	—	42
36.0	„	„	„	—	—	190
25.0	81	96	0.98	38	—	—
0.0	51	85	0.93	—	—	0.67
25.0	„	„	„	21	—	21
„	41	79	0.91	19	—	—
„	22	60	0.84	13	—	—
„	10	37	0.72	4.6	4.6	—
„	4.0	25	0.57	—	2.7	—
„	2.0	9.8	0.24	—	0.92	—
„	1.0	5.1	0.12	—	0.45	—
„	0.40	2.1	0.060	—	0.29	—
„	<0.1	<0.5	<0.025	—	<0.10 *	—

* Extrapolated from results at 34.6° reported in Table 2.

fraction (%), and relative activity, the last from the measurements of Burwell and Langford.⁵ The final value of the aquation rate, that at approximately zero water content, was estimated from the studies of the replacement of bromide by thiocyanate at water concentrations less than 0.1% by volume (estimated cryoscopically) and at 34.6°, a reaction which is discussed in more detail in the next section.

(2) *Reaction between trans-Bromonitrobis(ethylenediamine)cobalt(III) Perchlorate and Anionic Reagents in the Anhydrous Sulphone.*—(a) *Replacement by thiocyanate.* Experiments to check whether there was a residual rate of replacement by thiocyanate in the absence of water showed that there was a residual rate and that it was proportional to the concentration of added thiocyanate. For convenience, this reaction was studied at a higher temperature than the aquation. The reaction was followed spectrophotometrically by studying the change in optical density at 4650 Å (corresponding to a maximum in the spectrum of the *trans*-[Co en₂(NCS)NO₂]⁺ cation in water) and at 4600 Å (where the *cis*- and the *trans*-product have equal absorption). The rate constants were the same for both sets of measurements, and the spectrum of the product indicated that

⁵ Burwell and Langford, *J. Amer. Chem. Soc.*, 1959, **81**, 3799.

it was almost entirely the *trans*-isomer. The rates were measured in the presence of a sufficient excess of thiocyanate, provided as trimethylanilinium thiocyanate, for the kinetics to be essentially first-order, and the rate constants were calculated from the slopes of the plots of $\log_{10} (D_{\infty} - D_t)$ against time. These plots were linear up to the first half-life, but then the slope decreased even though the reaction went to completion. The retardation is due to the bromide ions released during the reaction and can be explained in the light of the information gained from the study of substitution by chloride. The rate constants are collected in Table 2. Other measurements, carried out in solvents that

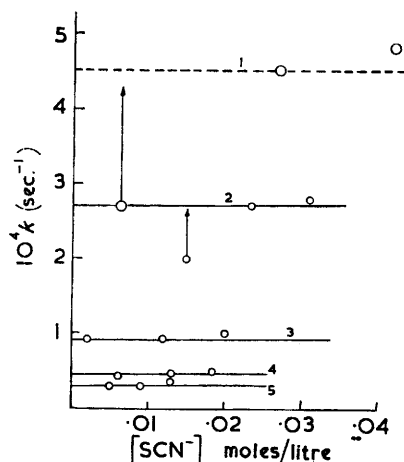


FIG. 1. Apparent first-order rate constants for the replacement of co-ordinated bromine by thiocyanate in the presence of the following volume fractions of water (%): (1) 10% (the broken line represents directly measured aquation rate constant); (2) 4%; (3) 2%; (4) 1%; (5) 0.4%.

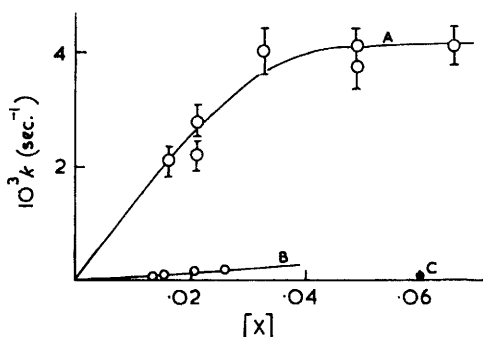


FIG. 2. Rate constants for the reaction, $\text{trans-}[\text{Co en}_2\text{NO}_2\text{Br}]^+ + \text{X}^- = [\text{Co en}_2\text{NO}_2\text{X}]^+ + \text{Br}^-$.

(A) $\text{X} = \text{Cl}^-$ (added as Ph_4AsCl). (B) $\text{X} = \text{SCN}^-$ [added as $\text{Me}_3\text{PhN}(\text{SCN})$]. (C) $\text{X} = \text{H}_2\text{O}$.

were less rigorously dried indicated, not only the expected small thiocyanate-independent component of rate, but also that k_2 had decreased markedly.

(b) *Replacement by chloride.* Because of the help they will give in the understanding of the mechanism of the reactions already described, some preliminary results for the

TABLE 2.

Rate constants for the replacement of bromine by thiocyanate in *trans*-bromonitro-bis(ethylenediamine)cobalt(III) perchlorate in the anhydrous sulphone at 34.6° .

Initial [Complex] (mmole/l.)	Initial [NCS ⁻] (mmole/l.)	$10^3 k_1$ (sec. ⁻¹)	$10^3 k_2$ (l. sec. ⁻¹ mole ⁻¹)
1.05	13.4	8.0	6.0
1.49	15.4	9.9	6.4
0.69	20.8	13	6.3
0.50	26.0	18	6.9

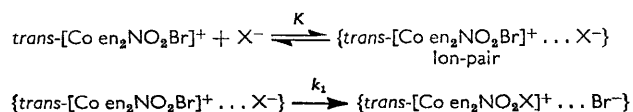
replacement of co-ordinated bromine by chloride are given in Fig. 2. The rates were measured spectrophotometrically, but the accuracy is less than in the studies of replacement by thiocyanate because of the smaller relative change in light absorption. These results will be published in more detail elsewhere, but it is of interest to note that (a) the

chloride ion is apparently a much more powerful reagent than thiocyanate, and (b) a limiting, chloride-independent rate is observed when $[Cl^-] > 0.04M$; also that the plot of $\log_{10} (D_\infty - D_t)$ against time remained sensibly linear over the whole of the reaction. This observation is used in support of the ion-pair hypothesis advanced below since the released bromide ions are able to displace thiocyanate ions from the ion-pairs but cannot compete with the excess of chloride ions present.

Discussion.—For the aquation of $trans-[Co en_2NO_2Br]^+$ in sulphone–water mixtures it is difficult to choose the correct way of expressing the dependence of the rate on the concentration of the changing solvent medium. There are at least three ways of expressing the concentration of the water in the reaction mixture, namely, volume fraction (or weight fraction), molar fraction, and relative activity. Our sulphone has a molecular weight of 120 and a density of 1.26 g./ml. at 25°, and hence the molar fraction of water in a particular sulphone–water mixture will be greater than the volume fraction. In addition, measurement of the water-vapour pressure above the liquid indicates a large positive deviation from Raoult's law,² and so the relative activity of water is considerably greater than the molar fraction at most compositions. In summary, on progressive addition of the sulphone to water, the volume fraction of water decreases most rapidly, its molar fraction more slowly, and the relative activity at first hardly changes at all.

It is possible to envisage two regions of changing water concentration, and the information to be gained from each can throw light on two different aspects of the reaction mechanism. The first region contains those mixtures where water must be considered as part of the solvent and the reaction is essentially solvolytic, although only one component of the solvent can act as reagent. A study of this region can increase our knowledge of the solvation aspects of the solvolysis. The second region is that where the water concentration is very low, where the solvent can be considered to be sulphone and the reagent (water) has the properties of an uncharged solute in ideal dilute solution. Unfortunately, because of the nature of water and its smallness when compared with the sulphone, this region is barely amenable to study and this investigation only just crosses its border.

In discussing the non-solvolytic reaction, it is convenient to consider the aquation results in conjunction with the information available about replacement by thiocyanate and chloride in the anhydrous solvent. In this region there is a linear dependence of rate on the concentration of water, irrespective of the units in which it is expressed since, in this low concentration region, the three scales are linearly related. It appears that, within the limits of experimental error, the line can be extrapolated through the origin and there is no water-independent rate. The results in Fig. 2 also show that, for a particular concentration of reagent, chloride is more effective than thiocyanate and both are considerably more effective than water. An interpretation of the second-order rate law observed for aquation and replacement by thiocyanate as indisputable evidence for a bimolecular process is not justified in the light of the limiting rate observed for substitution by chloride ions. On the other hand, a bimolecular mechanism for the aquation, as deduced from a study of the rates of the solvolytic aquation of complexes of the type $[Co en_2ACl]^{n+}$,³ is compatible with the observations. The results admit, for replacement by thiocyanate and chloride, an interpretation in terms of reaction only through the formation of an ion-pair, in accordance with the following sequence:



The general rate expression,

$$\text{Rate} = k_1 K [\text{Total bromo-complex}] [X^-] / (1 + K[X^-]),$$

reduces to a simple second-order form when $K[X^-] \ll 1$ and becomes independent of $[X^-]$ when $K[X^-] \gg 1$. Whereas there is no independent information about the magnitude of the ion-pair formation constants between this complex cation and the various anions, it is reasonable to expect that chloride forms an ion pair much more readily than thiocyanate does, solely on the basis of what is known about the ability of the sulphone to solvate the thiocyanate ion.² The kinetic form does not tell us anything about the mechanism with which the ion-pair reacts. It may be a dissociative process in which the ion-paired X^- is readily available to enter the five co-ordinated intermediate; or it may be a bimolecular process in which the increasing development of the Co-X bond as the reaction develops assists the rupture of the Co-Br bond. The inclusion of aquation in this scheme

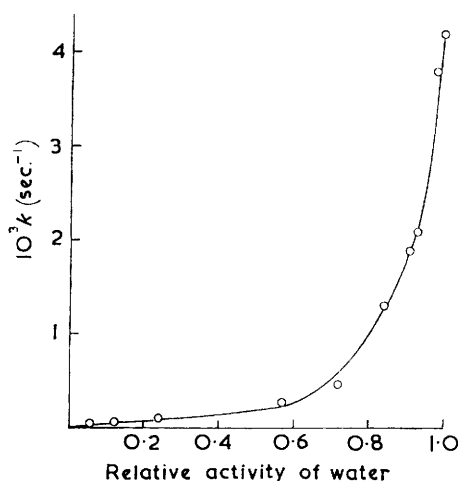


FIG. 3. Rate constants for aquation of *trans*-[Co en₂NO₂Br]⁺ in sulphone-water mixtures as a function of the relative activity of the water.

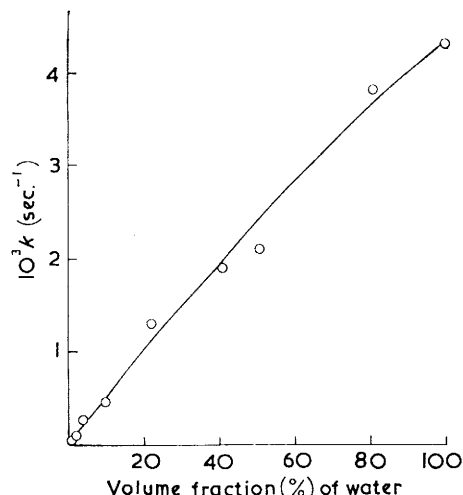


FIG. 4. Rate constants for the aquation of *trans*-[Co en₂NO₂Br]⁺ in sulphone-water mixtures as a function of the volume fraction (%) of water.

requires that ion-pairing, in this context, be regarded as a form of solvation whereby the anion occupies a place in the inner solvation shell. The electrostatic attractions, which serve to make the anion able to compete with the solvent when there is such a large difference in concentration, also prevent other anions from joining the first one. The neutral water molecule can also be considered as competing for a place in the inner solvation shell, but, in dilute solution, it does so far less efficiently than the anions. Water, however, possesses the advantage at higher concentrations since, whereas one anion in the solvent shell represents a limit, any number of water molecules can solvate the complex cation, limited only by size and competition with the sulphone.

The region of solvolysis may be understood by an extension of the above remarks. If the aquation rate constant is plotted against the relative water activity (Fig. 3), the dependence is linear up to a relative activity of 0.4; above this, the rate starts to increase rapidly and increases roughly as the seventh power of the activity. It is doubted that the form of this dependence has any significance. Although it is possible to explain this behaviour in terms of changes in the nature of the bulk solvent, it is of more value to realise that the volume fraction of the water corresponding to a relative activity of 0.4 is only 3% and, further, the "solvent effect" on the rate is almost completely lost if the rate is plotted against volume fraction (Fig. 4). In the latter case a smooth curve is obtained which does not depart greatly from linearity over the entire composition range from pure water to pure sulphone. There is little doubt that this has a significance greater

than coincidence. Adamson⁶ observed a similar relationship for the solvolysis of $[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]^-$ in mixed solvents in which only one of the components could act as substituting reagent. The volume-fraction dependence can be understood in terms of the idea that the complex reacts only with its immediate environment. It is necessary to accept that the solvent shell, unlike the co-ordination shell, does not have a fixed co-ordination number and that its occupation, other factors apart, is determined by size, so that one sulphone molecule may occupy space equivalent to four or five water molecules. This being so, in a mixed solvent the relative numbers of the two species in the solvation shell will be determined by the volume-fraction composition of the bulk solvent provided that they have equal solvating power. Any difference in this power will lead to a fractionation in the solvent shell and it is of interest that the slight convexity of the curve in Fig. 4 may indicate the slightly greater solvating power of water.

The problem of the mechanism of the actual act of replacement remains. The observations could easily be explained in terms of a dissociative mechanism in which there is a slow heterolysis of the Co-Br bond. The five-co-ordinated intermediate will have a life shorter than the relaxation time of the solvation shell of the complex and if, within this shell, there is not a suitably available and oriented reagent, the bromide ion will rejoin the cobalt atom and the event will be unobservable. A bimolecular mechanism of the type deduced for the solvolytic aquation of the chloronitro-complexes in aqueous solution is not ruled out if one makes the assumption that most of the activation energy required for the process is provided by the complex cation, which assembles this energy by interaction with the solvent environment. The cation remains activated for a time that is smaller than the relaxation time of the solvent shell, so that only a reagent, neutral or anionic, that is already present in the first solvation sphere can attack successfully.*

The effect of small amounts of water on the reactivity of the thiocyanate ion is considerable. In the experiments in which replacement by thiocyanate was used as a probe for the aquation, the complete lack of dependence of the rate of reaction on the concentration of thiocyanate was puzzling in the light of the known second-order rate constant for the direct attack. This, however, was consistent with the observation that, in the damp sulphone, although the kinetic form of replacement thiocyanate was essentially first-order with respect to the anion concentration, the rate constant was considerably smaller than was observed for the dry solvent. The most probable explanation is that the small amount of water solvates the thiocyanate ion even better than the sulphone does and reduces its tendency to form an ion-pair. This leads us to predict that replacement by chloride should be even more sensitive to the presence of traces of water, but this has not yet been tested.

EXPERIMENTAL

trans-Bromonitrobis(ethylenediamine)cobalt(III) Salts.—The salt, *trans*- $[\text{Co en}_2(\text{NO}_2)_2]\text{NO}_3$ (40 g.), prepared by the method of Holtzclaw *et al.*,⁷ was added, in small portions, to hot 60% hydrobromic acid (100 ml.), and the mixture was heated on a steam-bath. Any lumps formed were broken. Oxides of nitrogen were evolved and the mixture soon changed to an orange-brown paste. More hydrobromic acid (40 ml.) was added and on further heating the mixture became thicker and the colour became deeper chocolate-brown. After 1 hr. the mixture was set aside to cool and the solid filtered off, washed with water (50 ml.), ethanol (100 ml.), and ether (50 ml.) and air-dried. This salt was the perbromide, $[\text{Co en}_2\text{NO}_2\text{Br}](\text{Br}_3)$ (yield 67 g.), and was converted into the bromide by suspension in ethanol (300 ml.), addition of anisole (25 ml.), and refluxing for 1 hr. The crude bromide was filtered off, washed with hot alcohol and then ether, and air-dried (yield 45 g.). The bromide was recrystallised by grinding it with portions of bromine-free 45% hydrobromic acid (150 ml. in all) and adding an equal volume of alcohol

* We are indebted to Professor A. W. Adamson for this suggestion.

⁶ Adamson, *J. Amer. Chem. Soc.*, 1958, **80**, 3183.

⁷ Holtzclaw, Sheetz, and McCarty, *Inorg. Synth.*, 1953, **4**, 177.

to the filtrate. Well-formed needles (10 g.) of the bromide separated when the mixture was left overnight in the refrigerator {Found: Co, 14.9; co-ordinated Br, 20.7; Br⁻, 20.7. Calc. for [Co(C₂H₈N₂)₂NO₂Br]Br: Co, 15.3; co-ordinated Br, 20.7; Br⁻, 20.7%}. The success of the preparation depends upon stopping the initial heating at the correct moment. With too little heating, the product is contaminated with *trans*-[Co en₂(NO₂)₂]⁺ salts; with too much, *trans*-[Co en₂Br₂]Br is formed. The latter is insoluble in concentrated hydrobromic acid and is removed in the final recrystallisation.

trans-Bromonitrobis(ethylenediamine)cobalt(III) perchlorate was prepared by adding perchloric acid to a freshly prepared ice-cold aqueous solution of the bromide. The red-brown crystals were filtered off, washed with a little cold water, alcohol, and ether, and air-dried. The isomeric purity of the bromide and the perchlorate was established by measuring the spectra of their solutions when aquation was complete, both in the absence and in the presence of mercuric perchlorate. These spectra and that of *trans*-[Co en₂NO₂H₂O]⁺⁺ were identical. Under these conditions, the aquo-complex does not isomerise.

Other Materials.—Trimethylanilinium thiocyanate was prepared from the iodide by treatment with silver oxide and neutralisation of the resultant basic solution with thiocyanic acid, prepared by passing an aqueous solution of potassium thiocyanate through an Amberlite IR-120 resin column in the acid form. The neutralised solution was freeze-dried and the residue recrystallised three times from 19:1 ethanol-water. Gravimetric determination of thiocyanate (as AgSCN) indicated that the salt was 99.3% trimethylanilinium thiocyanate.

Tetrahydrothiophen 1,1-dioxide was obtained from L. Light Ltd., and distilled at 1–2 mm. from powdered sodium hydroxide according to the recommendation of Burwell and Langford.⁵

Kinetic Methods.—(a) *Conductometric.* Solvent samples, in a conductance cell fitted with bright platinum electrodes, were placed in a thermostat-bath, and pure nitrogen was bubbled through them until the conductivity reached a constant value. A small weighed sample of the complex was added and dissolved rapidly, aided by the agitation by the gas. The conductance was measured with a Phillips AC bridge.

(b) *Spectrophotometric.* In solutions of high water content (*t*₁ = 3–5 min.), samples of the complex were weighed into stoppered, silica, spectrophotometer cells and the solvent and cells were placed in the thermostat-bath separately at the reaction temperature. The cells were then placed in a Unicam S.P. 500 quartz spectrophotometer, and known volumes of solvent were pipetted into them. After rapid mixing, the changes in absorption were measured. Since room temperature was close to 25° and the reactions were fast, the cells were not placed in a thermostatically-controlled cell-holder. The reaction was followed by the change in optical density at 5000 Å. In pure water the molar extinction coefficient of the product at this wavelength was 56.8 in good agreement with that (56) found for an authentic sample of the *trans*-[Co en₂NO₂H₂O]²⁺ complex. When reactions were studied at other temperatures, or when the slower reactions in solvents of low water content were followed, the cell chamber was placed in a thermostatically-controlled bath. Experiments starting severally from the aquonitro- and the bromonitro-complexes were performed to evaluate the extinction coefficients of both complexes. The extinction coefficients at the wavelengths studied were not sensitive to solvent and varied by less than 5% over the whole range of solvent composition.

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