212. *Mechanisms of Octahedral Substitution Reactions in Non-aqueous Solutions. Part III.* The Replacement of Co-ordinated Water in* trans-*Aquonitrobis(ethylenediamine)cobalt*(III) *Ions.*

By M. N. Hughes and M. L. Tobe.

The anation of *trans*-[Co en$_2$ NO$_2$ H$_2$O]$^{2+}$ by Cl$^-$, Br$^-$, SCN$^-$, and NO$_3^-$ has been studied spectrophotometrically in acetone, dimethylformamide, and sulpholan (tetrahydrothiophen 1,1-dioxide). Thiocyanate enters at a rate that is independent of its concentration but which depends upon the nature of the solvent. In acetone, nitrate behaves similarly and is some 20% more reactive. Chloride and bromide enter at rates that depend upon their concentration and which, at lower concentrations, can be represented by Rate = $(k_1 + k_2[Y^-])$,[complex], where Y = Cl or Br, and at higher concentrations become independent of anion concentration. This limiting rate is virtually independent of the nature of the solvent. Furthermore, the rates of reaction with bromide in acetone and sulpholan are almost identical over the whole range of concentration.

The behaviour of this and other systems is discussed in terms of ion-association between the cationic and anionic reagents. Conductimetric evidence is presented for very strong association between two anions and one cation and, in the case of Cl$^-$ and Br$^-$ in acetone, a third anion adds to the aggregate. Once the ion-association pre-equilibria are taken into account the observations can be unified in terms of " rearrangement " of the ion aggregates at rates that are not greatly dependent upon the nature of the entering group or the nature of the solvent. The application of the concept of molecularity to such aggregates is discussed.

The study of the aquation of complexes of the type [Co en$_2$ A X]$^{n+}$ has led to the conclusion that there is a duality of mechanism that depends upon the electron displacing properties of ligand A.[1] When A possesses a pair of electrons that can conjugate with the orbital on the cobalt that is being vacated by the leaving group, the mechanism is unimolecular, and when it cannot do this the mechanism is bimolecular. Conjugative electron-withdrawing properties in A promote this bimolecular reaction. Based as it is upon a rather arbitrary assignment of electron displacement properties, this mechanistic assignment needs further confirmation under conditions where the kinetics ought to indicate the mechanism. Therefore studies were made in non-aqueous and non-interfering solvents. The *cis*- and *trans*-[Co en$_2$ Cl$_2$]$^+$ cations have been used as models for the unimolecular reaction and there is now considerable evidence from their reactions in non-aqueous solvents to confirm this assignment of mechanism.[2] Complexes of the type [Co en$_2$ NO$_2$ X]$^+$, where X = *cis*- or *trans*-Cl or -Br, have been used as models for the bimolecular mechanism but the results were equivocal. Ašperger *et al.*[3] studied the replacement of Cl by SCN$^-$ in methanol solution and found the rate to be independent of [SCN$^-$] in the *cis*-complex and to have a partial first-order dependence on [SCN$^-$] in the *trans*-complex. Langford and Tobe [4] showed that, when X = *trans*-Br, the rate of its replacement by thiocyanate was first order with respect to [SCN$^-$] in sulpholan over the whole range of concentration studied, but that the rate of entry of chloride ions, although possessing the same kinetic

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* Part II, Tobe and Watts, *J.*, 1964, 2991.

[1] Ašperger and Ingold, *J.*, 1956, 2862; Basolo and Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 4878; Ingold, Nyholm, and Tobe, *Nature*, 1960, **187**, 477.

[2] (*a*) Brown and Ingold, *J.*, 1953, 2674; Brown and Nyholm, *J.*, 1953, 2696; Pearson, Henry, and Basolo, *J. Amer. Chem. Soc.*, 1957, **79**, 5379, 5382; Bosnich, unpublished results; (*b*) Tobe and Watts, *J.*, 1962, 4614; (*c*) Tobe and Watts, *J.*, 1964, 2991.

[3] Ašperger, Pavlović, and Orhanović, *J.*, 1961, 2142.

[4] Langford and Tobe, *J.*, 1963, 506.

form at low concentrations, is much faster and becomes independent of chloride concentration at higher concentrations. Recently, Langford and Langford[5] have shown that, in dimethylformamide, when X = *trans*-Cl, the rate of entry of thiocyanate is independent of its concentration over the whole range studied.

We now report the replacement of X = *trans*-H_2O in the hope of finding a consistent explanation of these widely differing observations. The aquo-complex was chosen for a number of reasons. First, the possibility of a base-catalysed reaction[6] is eliminated since the most acidic protons are those attached to the aquo-oxygen and, if one is removed, the resultant hydroxo-ligand is far more difficult to replace. Secondly, the higher positive charge on the complex might further favour the bimolecular mechanism; thirdly, the anation, being the reverse of aquation, should throw some light on the mechanism of the latter process.

Kinetics.—All these anation reactions result in considerable change in the visible and ultraviolet spectrum and so could conveniently be studied spectrophotometrically. The complex was provided as the soluble *trans*-$[Co\,en_2\,NO_2\,H_2O](ClO_4)_2,5H_2O$ and the anion as a soluble and well-dissociated salt. The change of optical density was followed at 370 mμ and since the anionic reagent was always in considerable excess the reactions were carried out under pseudo first-order conditions. The pseudo first-order rate constants were obtained graphically from the slope of the semilogarithmic plot of $\log_{10}[D_\infty - D_t]$ against time, where D_t and D_∞ are the optical densities measured at time "t" seconds and after ten half-lives respectively. In all cases D_∞ corresponds closely to that expected for the *trans*-isomer of the product (Table 1) and an independent study of the spectrum of the final solution indicated that the reaction went to completion and produced only the *trans*-isomer. There was, at first, certain difficulty in achieving reproducibility for, although the perchlorate of the aquo-complex was reasonably soluble in all of the solvents, the other salts and those of the products were not, so that all data were obtained under conditions of supersaturation. On many occasions precipitation occurred and the experiment was spoiled but this could be detected instantly. Another source of irreproducibility arose from catalysis by trace impurities in the reagents and the solvents and it was necessary to use carefully purified materials. Lithium salts could be unreliable, especially anhydrous lithium bromide, but no difficulty was encountered in purifying the quaternary ammonium, phosphonium, and arsonium salts. The semilogarithmic plot was linear for 3 half lives in the absence of these disturbances. The pseudo first-order rate constants are plotted as a function of anion concentration in Figs. 1, 2, and 3, where each point represents the average of at least three separately determined rate constants covering a ten-fold range of initial complex concentration (10^{-4}—10^{-5}M).

TABLE 1.

Comparison of the molar extinction coefficients of the reaction products of substitution into *trans*-$[Co\,en_2NO_2H_2O]^{2+}$ with those of the authentic *trans* isomers of the products in dimethylformamide at 370 mμ (mole^{-1} cm.$^{-1}$).

	Reaction product	Pure *trans*-isomer
trans-$[Co\,en_2\,NO_2\,Cl]^+$	1340	1410
trans-$[Co\,en_2\,NO_2\,Br]^+$	2320	2380
trans-$[Co\,en_2\,NO_2\,NCS]^+$	1180	1170
trans-$[Co\,en_2\,NO_2\,NO_3]^+$	1150	—

The wavelength of the peak in the visible region also corresponds with that of the trans isomer (in parentheses): Bromonitro-complex, 500 (500), chloronitro-complex, 489 (489), isothiocyanatonitro-complex 465 (464) * (all values in mμ).

* Langford and Langford's value ($\varepsilon_{max.}$ at 460 mμ = 247 l. mole^{-1} cm.$^{-1}$)[5] does not agree with our results ($\varepsilon_{max.}$ at 464 mμ = 305 mole^{-1} cm.$^{-1}$) nor with Ašperger, Pavlović, and Orhanović's value (300 l. mole^{-1} cm.$^{-1}$).[3]

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[5] Langford and Langford, *Inorg. Chem.*, 1963, **2**, 300.

[6] Pearson, Schmidtke, and Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 4434.

The effect of varying the ionic strength, of adding small quantities of water or $CoBr_2$ and of varying the temperature are shown in Table 2; the limiting rates are independent of ionic strength, the small quantities of water introduced by using the hydrated complex did not have a significant effect upon the kinetics, and the presence of cobalt(II) impurities does not lead to catalysis. The activation energy (21 kcal./mole) is quite usual for this type of complex.

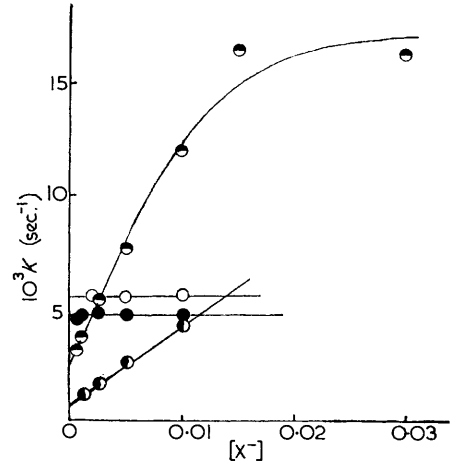

FIG. 1. First-order rate constants for the displacement of H_2O in *trans*-[Co en_2 NO_2 H_2O]$^{2+}$ by anions in acetone at 25·0°.

○ X = NO_3^-.
● X = SCN^-.
◐ X = Cl^-.
◓ X = Br^-.

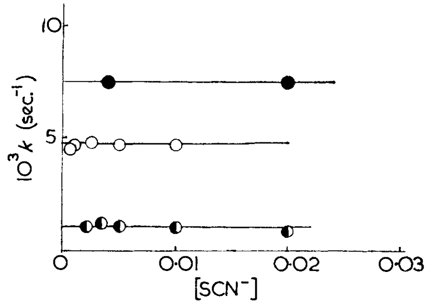

FIG. 2. First-order rate constants for displacement of H_2O in *trans*-[Co $en_2NO_2H_2O$]$^{2+}$ by SCN^- at 25·0°. ○ in acetone; ● in dimethylformamide; ◐ in sulpholan.

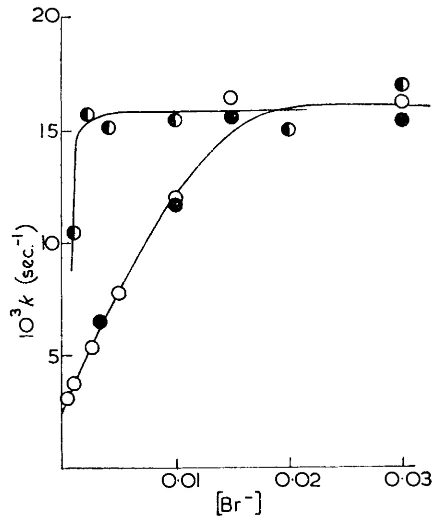

FIG. 3. First-order rate constants for the displacement of H_2O from *trans*-[Co $en_2NO_2H_2O$]$^{2+}$ by Br^- at 25·0°. ○ in acetone; ● in sulpholan; ◐ in dimethylformamide.

Conductivity Studies of Ion Association.—In these solvents of moderately low dielectric constant [$(CH_3)_2CO$ = 20·4, $(CH_3)_2NCHO$ = 37·6, and sulpholan = 44 at 25·0°] extensive ion association should be expected, especially with a dipositive cation. In view of the conclusions to be drawn from the kinetics it was thought desirable to obtain non-kinetic evidence for the extent, and if possible, the nature of this association. Previous studies of

TABLE 2.

Effect of added salts, water and cobaltous ions on the rate constants for the replacement of co-ordinated water at 25·0°.

[Anion]	Supplied as	In presence of	k_1 (sec.$^{-1}$)
	(a) *In dimethylformamide solution*		
0·01M-Br$^-$	$[Ph_3MeP]Br$	—	0·0153
,,	,,	0·10M-$NaClO_4$	0·0142
0·00125M-SCN$^-$	$[PhMe_3N]SCN$	—	0·0078
,,	,,	0·01M-$NaClO_4$	0·0078
0·020M-SCN$^-$	,,	—	0·0074
,,	,,	½% H_2O	0·0080
	(b) *In acetone solution*		
0·0025M-Br$^-$	LiBr	—	0·0054
,,	,,	0·5% H_2O	0·0054
,,	,,	2·5% H_2O	0·0052
0·0050M-Br$^-$	,,	—	0·0077
,,	,,	0·0005M-$CoBr_2$	0·0083
0·020M-Br$^-$	,,	—	0·0022 *
0·030M-Br$^-$	,,	—	0·0022 *

* Rates measured at 10·0°.

the unipositive cations, *cis*- and *trans*-$[Co\,en_2\,Cl_2]^+$ indicated that, in the case of the *cis*-complex, ion-association was considerable in solvents such as methanol,[2a] dimethylformamide,[2b] and dimethyl sulphoxide (DMSO).[2c] In addition, the dipositive cation *cis*-$[Co\,en_2\,DMSO\,Cl]^{2+}$ formed an ion triplet with two chloride ions at high chloride concentration in dimethyl sulphoxide.[2c]

Solutions were prepared containing varying ratios of complex perchlorate to quaternary salt while maintaining a constant total concentration and their conductivities were measured as soon after mixing as possible and at intervals of 15 seconds afterwards. Even though, at high bromide-ion concentration, the reaction was more than 15% complete before the first measurement could be made, no difficulty was encountered in extrapolating to the time of mixing because very little change was observed throughout the reaction. This constancy of conductivity is further evidence for the formulation of these reactions as inner-sphere–outer-sphere rearrangements of the type

$$trans\text{-}[Co\,en_2\,NO_2\,H_2O]^{2+}\ldots.nX^- \longrightarrow trans\text{-}[Co\,en_2\,NO_2\,X]^+..(n-1)X^-\ldots.H_2O$$

The conductivities of solutions of the *trans*-nitroaquo-perchlorate and the quaternary salt were measured in acetone and dimethylformamide over a range of concentration in order to provide calibration curves, and using these we could calculate what the conductivity of the mixture would have been if the individual species were not interacting. In every case the measured conductivity was less than that calculated by this method and the decrease, expressed as a percentage of the calculated conductivity, has been plotted against the composition of the mixture, expressed as [anion]/([anion] + [complex]) in Figs. 4 and 5.

This presentation of data closely resembles a continuous variation technique but the interpretation of the form is fraught with pitfalls. First, because the complex cation is dipositive and the quaternary cation only unipositive it is not possible to maintain a constant ionic strength and this changes by a factor of three during the variation. Any attempt to hold the ionic strength constant would require the addition of a non-interacting electrolyte whose conductivity would then swamp the effect we were seeking. Secondly, the quaternary salts and the complex perchlorate are not fully dissociated in solution so that an exact calculation of the conductivity expected for no interaction is not possible. This is not a serious objection in the studies made at the lowest concentrations. Finally, the continuous variation treatment can break down if there is a sequence of equilibria unless the successive *overall* association constants are sufficiently different.[7] The results in Fig. 5 lead us to conclude that, in spite of all these possible sources of error, the main conclusions regarding the stoicheiometry of the ion-aggregate are correct. The fact that the position of the maximum percentage loss of conductivity is independent of total concentration and remains at the composition, $\mathrm{Br^-}$: *trans*-$[\mathrm{Co\,en_2NO_2H_2O}]^{2+} = 3 : 1$ indicates quite clearly that the species *trans*-$[\mathrm{Co\,en_2NO_2H_2O}]^{2+}$.... $3\mathrm{Br^-}$ is actually

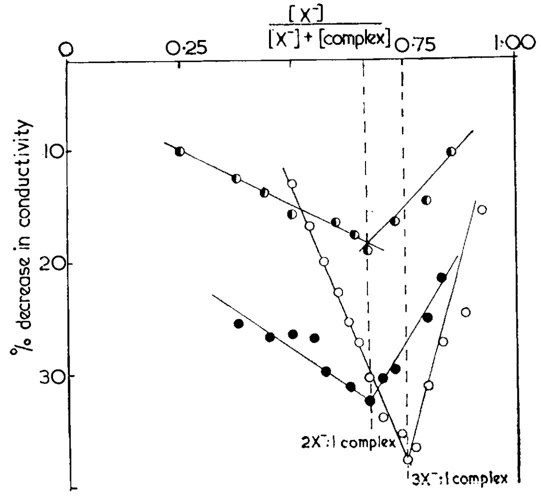

FIG. 4. Conductivity defects arising from ion-association at 25·0°.

○ Complex + $\mathrm{Br^-}$ in acetone.
● Complex + $\mathrm{SCN^-}$ in acetone;
◐ Complex + $\mathrm{Br^-}$ in dimethylformamide.

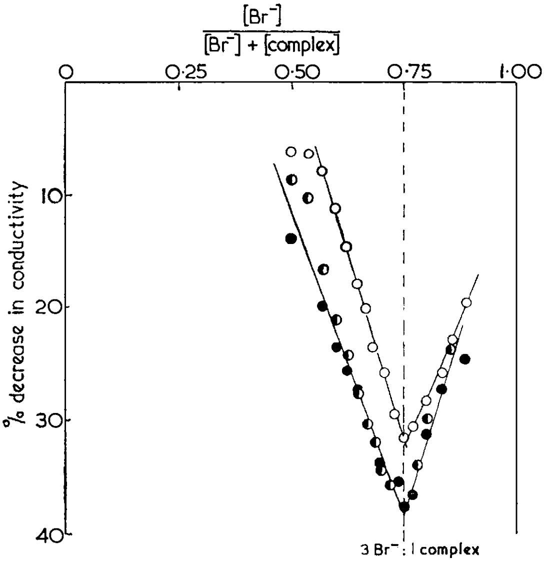

FIG. 5. Conductivity defects arising from ion-association between *trans*-$[\mathrm{Co\,en_2NO_2H_2O}]^{2+}$ and $\mathrm{Br^-}$ in acetone at 25·0°.

○ $[\mathrm{Br^-}] + [\mathrm{complex}] = 5{\cdot}0 \times 10^{-4}$M.
● $[\mathrm{Br^-}] + [\mathrm{complex}] = 1{\cdot}0 \times 10^{-3}$M.
◐ $[\mathrm{Br^-}] + [\mathrm{complex}] = 2{\cdot}0 \times 10^{-3}$M.

present in the acetone solutions containing sufficient bromide ions. The similarity of the behaviour of the complex with chloride ions suggests a limiting aggregate of the form *trans*-$[\mathrm{Co\,en_2NO_2H_2O}]^{2+}$.... $3\mathrm{Cl^-}$. Thiocyanate, on the other hand, reaches its limit at the *trans*-$[\mathrm{Co\,en_2NO_2H_2O}]^{2+}$.... $2\mathrm{SCN^-}$ in both acetone and dimethylformamide, and bromide, in dimethylformamide, forms a 2 : 1 limiting aggregate and there is no indication of the addition of a third bromide ion at high concentrations. Although these results give

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[7] Woldbye, *Acta Chem. Scand.*, 1955, **9**, 299.

no indication of the ion-association constants, it is clear that, apart from the system in dimethylformamide, the dissociation of the 2 : 1 aggregates is very slight.

DISCUSSION

The common feature present in all the types of kinetic form demonstrated for the substitution reactions of complexes of the type $[\mathrm{Co\,en_2\,NO_2\,X}]^{n+}$ in non-aqueous solution is the attainment of a limiting anion-independent rate of reaction at sufficiently high anion concentrations. There are examples where this limit is reached at concentrations lower than those used here in which case the rate appears to be independent of anion concentration, *e.g.*,

$$trans\text{-}[\mathrm{Co\,en_2\,NO_2\,H_2O}]^{2+} + \mathrm{SCN}^- \longrightarrow trans\text{-}[\mathrm{Co\,en_2\,NO_2\,NCS}]^+ + \mathrm{H_2O}$$

In other cases the limiting rate is reached within the limits of the concentration studied, *e.g.*,

$$trans\text{-}[\mathrm{Co\,en_2\,NO_2\,H_2O}]^{2+} + \mathrm{Br}^- \longrightarrow trans\text{-}[\mathrm{Co\,en_2\,NO_2\,Br}]^+ + \mathrm{H_2O}$$

In the cases where the anion-independent rate was not observed there is ample evidence to suggest that, had it been possible to study a sufficiently high concentration of anion, the limiting rate would have been observed. Ašperger, Pavlović, and Orhanović's data for the *trans*-chloronitro-complex [3] lie on a curve whose shape is consistent with the eventual attainment of a limiting rate (at anion concentrations of 5—10M).

Limiting rates are also observed in the reactions of *cis*- and *trans*-$[\mathrm{Co\,en_2\,Cl_2}]^+$ cations in non-aqueous solvents [2] and so it is necessary to decide whether this similarity of behaviour at higher anion concentration indicates an identity of mechanism or whether it arises from a cause that is not the slow (as distinct from the rate-determining) step in the substitution reaction.

The limiting rate can be interpreted as the result of a pre-equilibrium association between the cationic and anionic components of the solution. The complex cation can be pictured as being surrounded by a solvation shell that is more resistant to the passage of anions than is the bulk solvent and the ion-aggregates can be looked upon as species in which one or more anions are occupying positions in the inner solvation shell. In the nomenclature of Winstein and Robinson [8] these would be called *intimate* ion aggregates.

Since the attraction between the complex cation and the anions is counterbalanced by the repulsion between the individual associated anions and by the solvation of the anions, there must be a maximum number of anions that can be accommodated in the aggregate. A situation may, therefore, be reached when nearly all of the substrate is in the form of the maximum ion-aggregate. Any further increase in the concentration of the anion in the bulk solvent will not change the immediate environment of the complex ion and, since the complex can only react with this immediate environment, such a concentration change will not be felt by the complex and therefore will not affect the rate of reaction. In this way it is possible to obtain a limiting rate that is independent of the concentration of added anionic reagent, *irrespective of the actual mechanism of the act of substitution.* This situation has been discussed for the mechanisms of " ionic " substitution reactions of organic compounds in non-polar solvents such as benzene and sulphur dioxide.[9] The permanent charge distribution on the inorganic complex makes the ion association extremely important in dipolar solvents that have moderate dielectric constants (20—40), and so it is not necessary to work in non-polar solvents to observe the same effect. Limiting rates can be observed in aqueous solution if the charges on the reagents are large enough, as for example in the reaction [10]

$$[\mathrm{Co(NH_3)_5H_2O}]^{3+} + \mathrm{SO_4}^{2-} \longrightarrow [\mathrm{Co(NH_3)_5SO_4}]^+ + \mathrm{H_2O}$$

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[8] Winstein and Robinson, *J. Amer. Chem. Soc.*, 1958, **80**, 169.
[9] Ingold, Pedler Lecture, *Proc. Chem. Soc.*, 1957, 279.
[10] Taube and Posey, *J. Amer. Chem. Soc.*, 1953, **75**, 1463.

The stoicheiometry of the limiting ion-aggregate will depend upon the nature of the complex, its charge, the nature of the anion and the nature of the solvent. The limit is not necessarily determined by the saturation of the charge on the complex cation and such a restriction would have made our kinetic observations inconsistent with the known solvatabilities of the anions in the various solvents. For example, sulpholan solvates bromide much less effectively than it does thiocyanate[11] so that one would expect the bromide aggregate to saturate at a lower concentration of anion but it is observed that the thiocyanate gives the limiting rate first. Furthermore, bromide ions are more solvated in dimethylformamide than they are in acetone and yet, in spite of the twofold difference in dielectric constant, the limiting rate is reached in dimethylformamide at a much lower concentration.

The existence of the 3 : 1 bromide (or chloride)–complex aggregate, that is indicated by the conductivity experiments in acetone (and presumably sulpholan), removes these anomalies since the dependence of the rate upon bromide concentration is a reflection of the conversion of more and more of the substrate from the 2 : 1 into the 3 : 1 aggregate. Similarly, the behaviour of the complex with bromide ions in dimethylformamide represents the conversion of the 1 : 1 into the 2 : 1 aggregate. In the solutions containing the complex and thiocyanate ions, the substrate remains as the 2 : 1 aggregate throughout. If, on the basis of this reasoning, one compares the rates of rearrangement of the 2 : 1 aggregate, which are collected in Table 3, it will be seen that the rate depends upon the nature of the anion and the nature of the solvent. In acetone, where all four reagents are compared, the rate constant has a significant dependence upon the nature of the anion although it is difficult to decide which are the properties that correlate with the reactivity.

TABLE 3.

First-order rate constants for the rearrangement of the 2 : 1 anion : cation aggregates at 25·0 (sec.$^{-1}$).

Solvent	Anion			
	Cl	Br	NO_3	NCS
Acetone	0·0007 *	0·0028 *	0·0056	0·0047
Dimethylformamide	—	0·0155	—	0·0075
Sulpholan	—	0·0025 *	—	0·0010

* These rate constants are obtained by extrapolating the experimental curves back to [Cl$^-$] or [Br$^-$] = 0.

The similarity of the limiting rates of entry of bromide ions into the complex in all three solvents at high bromide concentration is of great interest. This is observed in spite of the difference in the number of bromide ions present in the solvation shell and it is not yet clear whether the effect is purely coincidental or has some, as yet unrecognised, significance.

Is it possible to apply the concept of molecularity to these processes that involve the rearrangement of a previously assembled aggregate of reagents, and, if so, is it possible to distinguish experimentally between the different modes of reaction? The conceptual distinction can be made through a consideration of the timing of the bond-making and bond-breaking aspects of the substitution. If bond-making and -breaking are synchronous the process is clearly bimolecular, if bond-breaking precedes bond-making the process is unimolecular with a five-co-ordinate intermediate and if bond-making precedes bond-breaking the process is associative with a seven-co-ordinate intermediate. At first sight it might be thought that the dependence of the limiting rate upon the nature of the entering anion was conclusive evidence for assigning a bimolecular mechanism to the rearrangement, but, since these anions are initially present in the inner solvation shell of the complex, these rate differences, which are not very large, may be due to " solvation effects " of a

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[11] Langford, Thesis, Northwestern University, Evanston, Illinois, 1960.

unimolecular reaction. It is to be noted that the rate of rearrangement of the thiocyanate ion-triplet is dependent upon the nature of the solvent, to much the same extent. An experimental distinction might be made between the mechanisms were it possible to study the reaction in a region of anion concentration where the bulk of the substrate is in the form of the free ion. Here, a first-order dependence of rate upon the concentration of the anionic reagent would be observed if the reaction were bimolecular even though the act of substitution involves the rearrangement of the ion-aggregate and the first-order dependence arises from the pre-equilibrium that determines the concentration of the ion pair.

$$\mathrm{R{-}X}^{n+} + \mathrm{Y}^- \overset{K}{\rightleftharpoons} \mathrm{R{-}X}^{n+}\ldots\mathrm{Y}^- \text{ ion-pair}$$

$$\mathrm{R{-}X}^{n+}\ldots\mathrm{Y}^- \xrightarrow{k} \mathrm{R{-}Y}^{n+}\ldots\mathrm{X}^- \text{ bimolecular}$$

$$\text{Rate} = k[\mathrm{R{-}X}^{n+}\ldots\mathrm{Y}^-]$$

and $$[\mathrm{R{-}X}^{n+}\ldots\mathrm{Y}^-] = K[\mathrm{R{-}X}^{n+}][\mathrm{Y}^-]$$

If only a small part of the complex is associated,

$$[\mathrm{R{-}X}^{n+}] = [\text{complex}]$$

and so Rate $= kK[\text{complex}][\mathrm{Y}^-]$.

The unimolecular mechanism will also have a component of its rate law of exactly the same form as that deduced above, but, in addition, it is possible to observe dissociative reactions involving the free ion which will provide a zero-order component to the dependence upon anion concentration. The unimolecular reaction, at these low anion concentrations, will obey a rate law of the form

$$\text{Rate} = (k' + kK[\mathrm{Y}^-])[\text{complex}]$$

where k' and k are the rate constants for the unimolecular rearrangement of the free ion and the ion-pair, respectively. All of these remarks will be true only if the solvent does not participate directly in the act of substitution.

The very high first ion-association constants of the dipositive aquonitro-complex in these solvents made it impossible to observe the free ion under the conditions used to obtain pseudo-first-order kinetics and so the above test cannot be applied to these reactions and the apparent zero-order component k_1 that is observed refers to the rearrangement of a lower ion aggregate and not to the reaction of the free ion (Table 3). In this case the kinetic form should not be taken as conclusive evidence for a unimolecular reaction. On the other hand, the reaction between *trans*-$[\mathrm{Co\,en_2NO_2Br}]^+$ and SCN^- in sulpholan does show this limiting behaviour in the region of low anion concentration[4] and this could be interpreted in terms of a bimolecular mechanism.

TABLE 4.

First-order rate constants for reactions of the type: $[\mathrm{Co\,en_2\,AX}] + \mathrm{Y} \longrightarrow [\mathrm{Co\,en_2\,AY}] + \mathrm{X}$.

A	X	Y	Solvent	k (sec.$^{-1}$)	Ref.
trans-OH	Cl	H_2O	H_2O	$1{\cdot}6 \times 10^{-3}$	12
,,	H_2O	,,	,,	$1{\cdot}25 \times 10^{-3}$	13
trans-NO_2	Cl	SCN^-	DMF	$1{\cdot}8 \times 10^{-5}$	5
,,	H_2O	,,	,,	$7{\cdot}5 \times 10^{-3}$	This work

Further indication of a change in mechanism on changing ligand A (the non-participating ligand) from a potential π donor, *e.g.*, $\mathrm{H\ddot{O}}$—, to a potential π acceptor, *e.g.*, O_2N–, can be found in Table 4; whereas the rates of displacement of chloride from the

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[12] Baldwin, Chan, and Tobe, *J.*, 1961, 4637.

[13] Kruse and Taube, *J. Amer. Chem. Soc.*, 1963, **83**, 2642.

trans-chlorohydroxo-complex, and water from the *trans*-aquohydroxo-complex are similar, the rates of displacement of chloride and water from their *trans* nitro-complexes differ by a factor of 400. Under the influence of the *trans*-hydroxo-ligand, which is thought to promote a unimolecular reaction, the greater inherent weakness of the Co–OH_2 bond is countered by the greater attraction of the dipositive complex so that the net rate of bond-breaking is close to that of the chloro-complex where the Co–Cl bond is inherently stronger but the unipositive charge does not exert so great an attraction. If the *trans*-nitro-group causes the mechanism to change to bimolecular, bond-breaking will be less important and the higher charge on the dipositive aquo-complex will assist bond-making better than the single charge on the unipositive nitrochloro-complex.

EXPERIMENTAL

trans-*Aquonitrobis*(*ethylenediamine*)*cobalt*(III) *Perchlorate Pentahydrate*.—The compound *trans*-[Co en_2 NO_2 Cl]NO_3 (3 g.) was dissolved in the minimum of water (200 ml.) and the solution kept for 72 hr. at room temperature (so that aquation was complete) and then passed slowly down a column of anion exchange resin (Amberlite IRA 400) in the hydroxide form. The effluent, which contained *trans*-[Co en_2 NO_2 OH]OH, was acidified to pH = 3 with perchloric acid and then freeze-dried. Light was excluded from the solutions at all stages. A yellow crystalline *solid* was obtained [Found: Co, 11·1, water of crystallisation, 16·9%; Equiv., 257. $C_4H_{18}CoN_5O_3(ClO_4)_2,5H_2O$ requires Co, 11·1; water of crystallisation, 16·6%; Equiv., 271].

It is not possible to remove the water of crystallisation by warming the material at low pressures over phosphoric oxide and if more drastic heating is employed (>100°) the water is displaced but the aquonitro-complex is transformed into a red material which is now being studied. The heating often results in an explosion and can only be safely carried out on a small scale. It was possible to remove some of the water of crystallisation by dissolving the complex in anhydrous acetone and then removing the solvent at low pressure. This material has the same kinetic, spectroscopic, and conductimetric properties as the pentahydrate and so the latter was used for the kinetic and conductimetric studies. The significant quantities of water thereby introduced into the solution do not appear to affect the kinetics.

The absorption spectrum agrees with the formulation as a pentahydrate ($\varepsilon_{\text{max.}}$ at 335 mμ = 952 l. mole^{-1} cm.$^{-1}$; lit.,[1] 965 l. mole^{-1} cm.$^{-1}$. The visible and near ultraviolet spectrum is identical with that of a solution of *trans*-[Co en_2 NO_2 Cl]ClO_4 that has been allowed to aquate in the presence of excess of mercuric perchlorate.

Phenyltrimethylammonium thiocyanate was prepared by neutralising an aqueous solution of trimethylanilinium hydroxide (prepared by passing a solution of the quaternary ammonium iodide down a column of anion exchange resin in the hydroxide form) with a solution of thiocyanic acid (prepared by passing a solution of potassium thiocyanate down a column of a cation exchange resin in the acid form). The resulting solution was freeze-dried and the quaternary ammonium thiocyanate recrystallised three times from ethanol (Found: SCN, 29·1. $C_{10}H_{14}N_2S$ requires SCN, 29·9%).

Tetraphenylarsonium chloride, $[Ph_4As]Cl,H_2O$, was prepared from a commercial sample of $[Ph_4As]Cl,HCl$ by neutralising the acid with sodium hydroxide in ethanol.[14] The precipitated sodium chloride was filtered off and the quaternary arsonium chloride precipitated by adding ether. It was recrystallised by dissolving it in the minimum of water and adding concentrated aqueous sodium chloride solution. The precipitated arsonium chloride was dissolved in chloroform and ether was added. After 15 min. the crystals were collected, washed with ether, and dried (P_2O_5) (Found: Cl, 7·9. $C_{21}H_{22}AsClO$ requires Cl, 8·1%).

All other salts used (LiCl, LiBr, $LiNO_3$, phenyltrimethylphosphonium bromide) were commercial samples, dried thoroughly and recrystallised repeatedly from acetone.

Acetone was purified by refluxing it with sufficient potassium permanganate to maintain the purple colour and the distillate was dried ($CaSO_4$). Fresh batches of the solvent were distilled each day, the fraction of b. p. 56·0—56·5° being collected.

Dimethylformamide was purified by the method of Thomas and Rochow.[15] The water was removed azeotropically with dried benzene and the solvent was further dried by shaking it with successive batches of anhydrous magnesium sulphate and then fractionally distilled.

[14] Bosnich, Thesis, Australian National University, Canberra, 1962.

[15] Thomas and Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.

Sulpholan was purified by the method of Burwell and Langford [11] whereby it was distilled, at 2 mm. pressure, from powdered NaOH.

Kinetics.—Reactions were carried out at 25·0° in thermostatted silica cells of the Unicam S.P. 500 spectrophotometer. The solutions were brought to the reaction temperature before mixing although in some cases the reaction was started by adding a small quantity of the solid complex to a solution of the quaternary salt previously brought to the reaction temperature. The total concentration of complex was determined from the value of the optical density extrapolated back to the time of mixing. When sulpholan was used it was necessary to add an excess of sodium perchlorate to keep the solution liquid at 25°. The reactions were therefore studied at a constant ionic strength, = 0·5M, in this solvent.

Conductivities.—These were measured in glass cells fitted with shiny platinum electrodes using a Wayne–Kerr bridge. Solutions were kept at 25·0° in an oil thermostat.

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