# Anation Reactions in Octahedral Cobalt(III) Complexes

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Abstract: We have undertaken the study of the rates of reaction and steric course for a number of reactions of the type *cis*-[CoX(SOL$_1$)(en)$_2$]$^{2+}$ + Y$^-$ = *cis*- and *trans*-[CoXY(en)$_2$]$^+$ + SOL$_1$, where X$^-$ and Y$^-$ are one of the ions chloride or bromide, in the solvent SOL$_1$ and in other solvents SOL$_2$ where SOL$_1$ and SOL$_2$ are N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), methanol, or tetramethylene sulfone (TMS). The kinetic results all show an S$_N$1IP[1a] character. The steric course of the anation reaction varied markedly with Y$^-$ concentration and with the degree of association of the reacting complex and the anion Y$^-$. In some cases SOL$_2$ for SOL$_1$ exchange is found to precede anation while in others direct anation of the reactant is observed. In general, isomerization of the products is observed and in some cases this isomerization is so fast that the products appear to form in the equilibrium ratio. That is, the initial product is in some cases the result of kinetic control, and in others is equilibrium controlled.

Not many reactions of the type

$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+} + \text{Y}^- =$$
$$cis\text{- and } trans\text{-[CoXY(en)}_2]^+ + \text{SOL}_1$$
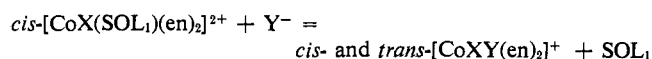
have been studied in aqueous solutions because of the general stability of aquo complexes in water. Taube, *et al.*,[2,3] have recently examined some anation reactions in complexes of the type [CoY(NH$_3$)$_5$]$^{n+}$ in competition with the predominant aquation reaction. Basolo and Pearson[1b] have also discussed the nature of the transition state in such reactions and agree that "bond breaking is much more important than bond making in the transition state."
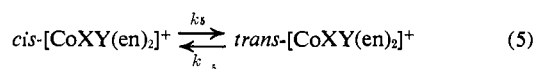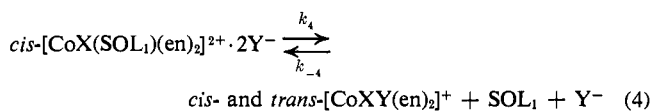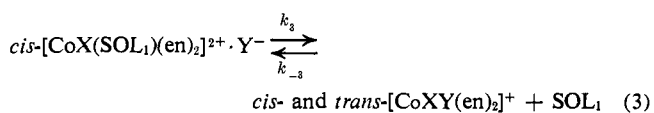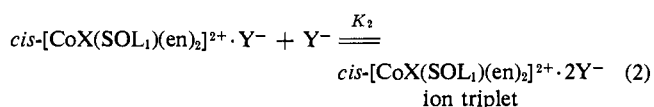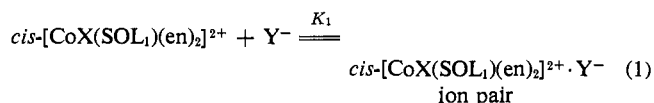
These results are compatible with the present study in that the primary mechanism is a dissociative one. However, here the similarity between the results ends since in the present work anation is the more significant reaction, in some cases the only observed reaction. The systems also differ in that in our solvents of lower dielectric constant many kinetic features are a result of ion association which is not as significant in aqueous solution.

Basolo, Stone, Bergmann, and Pearson[4] have studied the anation of *cis*-[CoNO$_2$(OH$_2$)(en)$_2$]$^{2+}$ in water, but the interpretation of their results as emphasized by Langford and Johnson[5] is complicated by the possibility of ion association. It is felt that in nonaqueous media the effects of ion association can be gauged more easily since, in general, ion association constants are larger, and thus easily determined, and because reactions can be followed in conditions varying from the reactions of the free ion to reactions under conditions of virtual complete ion association.

The present study develops on the ideas of Tobe, *et al.*,[6-10] and of this group.[11] Previously the main

concern has been with the kinetic form in relation to the dependence of the over-all rate of anion entry on anion concentration. Although this procedure has led to a good general description of the path of substitution, it has resulted in the loss of much detailed understanding which is available from the steric course of substitution.

It is constructive and economical of space to formulate two general reaction sequences to account for the observed results. In some systems it will be possible to neglect certain of the reactions. The first of the sequences is applicable to the systems in which the complex reactant contains the solvent as a coordinated ligand.

$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+} + \text{Y}^- \overset{K_1}{\rightleftharpoons}$$
$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+}\cdot\text{Y}^- \quad (1)$$
$$\text{ion pair}$$

$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+}\cdot\text{Y}^- + \text{Y}^- \overset{K_2}{\rightleftharpoons}$$
$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+}\cdot2\text{Y}^- \quad (2)$$
$$\text{ion triplet}$$

$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+}\cdot\text{Y}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}}$$
$$cis\text{- and } trans\text{-[CoXY(en)}_2]^+ + \text{SOL}_1 \quad (3)$$

$$cis\text{-[CoX(SOL}_1)(\text{en})_2]^{2+}\cdot2\text{Y}^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}}$$
$$cis\text{- and } trans\text{-[CoXY(en)}_2]^+ + \text{SOL}_1 + \text{Y}^- \quad (4)$$

$$cis\text{-[CoXY(en)}_2]^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} trans\text{-[CoXY(en)}_2]^+ \quad (5)$$

The ion association equilibria 1 and 2 are fast while the substitution steps 3, 4, and 5 are slow, and their rate constants are of the same order of magnitude. Both the *cis*- and *trans*-[CoXY(en)$_2$]$^+$ species will in general be involved in ion association equilibria which will affect the equilibrium ratio of these isomers.[6,11b-d,12-14] These effects have been well de-

(1) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967: (a) p 211; (b) p 166.

(2) A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

(3) G. E. Dolbear and H. Taube, *ibid.*, **6**, 60 (1967).

(4) F. Basolo, B. D. Stone, J. G. Bergmann, and R. G. Pearson, *J. Am. Chem. Soc.*, **76**, 3079 (1954).

(5) C. H. Langford and M. P. Johnson, *ibid.*, **86**, 229 (1964).

(6) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).

(7) M. N. Hughes and M. L. Tobe, *ibid.*, 1204 (1965).

(8) B. Bosnich, J. Ferguson, and M. L. Tobe, *ibid., A*, 1636 (1966).

(9) M. L. Tobe, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, Chapter 1.
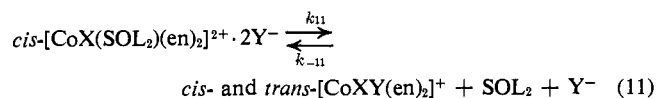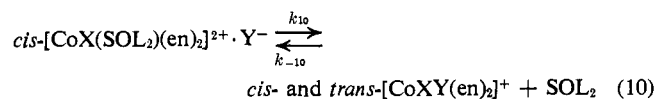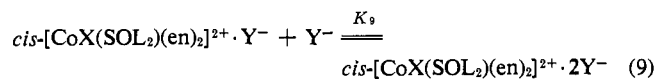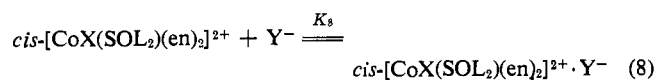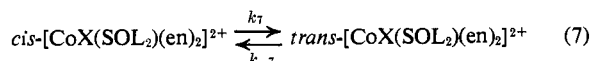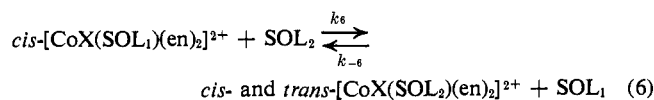
(10) M. L. Tobe, "Studies on Chemical Structure and Reactivity," J. H. Ridd, Ed., Methuen, London, 1966, Chapter 11.

(11) (a) D. W. Watts, *et al.*, *Australian J. Chem.*, **18**, 453 (1965); (b) *ibid.*, **19**, 935 (1966); (c) *ibid.*, **19**, 949 (1966); (d) *ibid.*, **20**, 53 (1967); (e) *ibid.*, **20**, 2623 (1967)..

(12) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 4614 (1962).

scribed and do not concern us here. K_1 and K_2, etc., will be used to represent the equilibrium constants of reactions 1 and 2, etc., and k_3 and k_{-3}, etc., the forward and reverse first-order rate constants of reaction 3, etc.

The second sequence of reactions is necessary to describe the reacting systems in which the displaced neutral ligand is not the solvent. It contains the following reactions in addition to those given above.

$$cis\text{-}[CoX(SOL_1)(en)_2]^{2+} + SOL_2 \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}}$$

$$cis\text{- and } trans\text{-}[CoX(SOL_2)(en)_2]^{2+} + SOL_1 \quad (6)$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \underset{k_{-7}}{\overset{k_7}{\rightleftarrows}} trans\text{-}[CoX(SOL_2)(en)_2]^{2+} \quad (7)$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} + Y^- \overset{K_8}{=\!=\!=}$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \cdot Y^- \quad (8)$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \cdot Y^- + Y^- \overset{K_9}{=\!=\!=}$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \cdot 2Y^- \quad (9)$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \cdot Y^- \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}}$$

$$cis\text{- and } trans\text{-}[CoXY(en)_2]^+ + SOL_2 \quad (10)$$

$$cis\text{-}[CoX(SOL_2)(en)_2]^{2+} \cdot 2Y^- \underset{k_{-11}}{\overset{k_{11}}{\rightleftarrows}}$$

$$cis\text{- and } trans\text{-}[CoXY(en)_2]^+ + SOL_2 + Y^- \quad (11)$$

In addition to the reactions omitted in the first sequence, we have simplified the second sequence by omitting a series of reactions comparable to eq 8–11 for the trans-[CoX(SOL_2)(en)_2]^{2+} species. We feel justified in making this simplification because all reactions of type 6 in these systems have produced predominantly cis products[15] and because the isomerization reaction 7 leads to 100% cis-[CoX(SOL_2)(en)_2]^{2+} in those systems for which results are interpretable. Even if this assumption should prove not to be true it will be seen that the main argument is not affected.

At this stage, neglecting the work in aqueous or part-aqueous media,[4,5] the published work fitting one of these two sequences is summarized in Tables I and II.

Table I

Se-quence	X⁻	Y⁻	SOL₁	SOL₂	Ref
1	Cl⁻	Cl⁻	DMF		11c
	Cl⁻	Cl⁻	DMA		16
	Cl⁻	Cl⁻	DMSO		6
	Cl⁻	Cl⁻	MeOH		8
	Br⁻	Br⁻	DMF		11b
	Br⁻	Br⁻	DMA		11b
	Cl⁻	SCN⁻	DMSO, DMF		11a, c
	Cl⁻	Br⁻	DMF		11e
2	NO₂⁻	Cl⁻	OH₂	DMF, TMS, acetone	7
	NO₂⁻	Br⁻			
	NO₂⁻	SCN⁻			
	NO₂⁻	NO₃⁻			
	Cl⁻	SCN⁻	DMSO	DMF	11a

Table II

Se-quence	X⁻	Y⁻	SOL₁	SOL₂
1	Br⁻	Br⁻	DMF	
2	Cl⁻	Cl⁻	DMSO	TMS, DMA, DMF, MeOH
	Br⁻	Cl⁻	DMSO	MeOH
	Br⁻	Br⁻	DMSO	DMA, TMS, MeOH
	Cl⁻	Cl⁻	DMA	MeOH

Experimental Section

Some complexes used in this work, cis-[CoBr(DMSO)(en)₂]-(ClO₄)₂, cis-[CoBr(DMF)(en)₂](ClO₄)₂, cis-[CoCl(DMSO)(en)₂]-(ClO₄)₂, cis- and trans-[CoBr₂(en)₂]ClO₄, and cis- and trans-[CoCl₂-(en)₂]ClO₄, were from batches used previously.[11b,16,17] The cis-[CoCl(DMA)(en)₂](ClO₄)₂ and cis- and trans-[CoBrCl(en)₂]ClO₄ samples were supplied by Dr. I. R. Lantzke, University of Southern California.

Tetraethylammonium chloride and tetraethylammonium bromide were recrystallized from hot dimethylacetamide, washed with acetone and ether, and dried under vacuum.

Dimethylformamide, dimethylacetamide, and sulfolane were purified as described in previous publications.[11b,13] Methanol was purified by the method of Vogel.[18]

Kinetic Technique. The reactions were followed spectrophotometrically by the techniques described previously.[11b] Measurements were made by use of an Optica 220 double-beam recording spectrophotometer and a Unicam S.P. 700 recording spectrophotometer. The molar absorptivities of the compounds in the various solvents at the wavelengths used to calculate rate constants are listed in Table III.

Results and Discussion

(a) Sequence 1 Reactions. The results for the system (X⁻ = Br⁻, Y⁻ = Br⁻, SOL₁ = DMF), that is, the anation of cis-[CoBr(DMF)(en)₂]²⁺ by bromide ion in DMF, have been discussed previously but are extended here because of the need for a model on which to base the discussion of the more complex reactions. We present (Figure 1) an analysis of the steric course of the anation reaction, expressed here by splitting (k_3
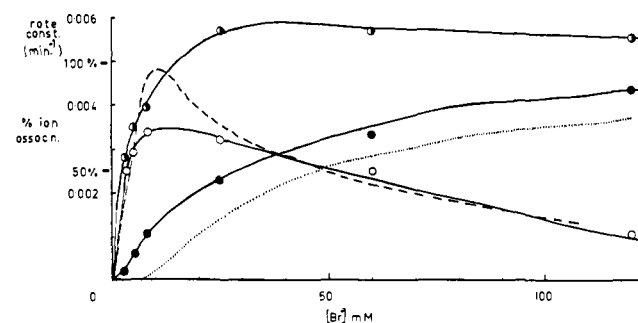

Figure 1. Dependence of the rate of anation of cis-[CoBr(DMF)-(en)₂]²⁺ by bromide, the rates of formation of cis- and trans-[CoBr₂(en)₂]⁺, and the percentage of cis-[CoBr(DMF)(en)₂]²⁺...Br⁻ and cis-[CoBr(DMF)(en)₂]²⁺...2Br⁻ on bromide concentration at 45° (total complex concentration 8 × 10⁻³ M): ◑, $k_3 + k_4$; ○, $(k_3 + k_4)_t$; ●, $(k_3 + k_4)_c$; – – – –, % ion pair; ······, % ion triplet.

(13) W. R. Fitzgerald and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 821 (1967).

(14) W. R. Fitzgerald and D. W. Watts, *Australian J. Chem.*, in press.

(15) I. R. Lantzke and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 815 (1967).

(16) I. R. Lantzke, Ph.D. Thesis, University of Western Australia, 1966.

(17) W. R. Fitzgerald and D. W. Watts, *Australian J. Chem.*, **19**, 1411 (1966).

(18) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1961, p 169.

Table III. Molar Absorptivities at the Wavelengths Used in the Determination of the Anation Rates

Complex	DMA 5490 Å	6250 Å	6590 Å	TMS 5420 Å	6200 Å	6550 Å	Methanol 5420 Å	6220 Å	6600 Å	DMF
cis-[CoBr₂(en)₂]⁺	121.5	80.0	58.0	112.5	82.0	59.8	110.5	75.0	53.5	
trans-[CoBr₂(en)₂]⁺	6.0	40.0	58.0	5.9	37.0	59.8	7.5	42.0	53.5	
cis-[CoBr(DMSO)(en)₂]²⁺	121.5	40.0	21.0	112.5	37.0	15.0	110.5	42.0	20.5	

Complex	5360 Å	5950 Å	5410 Å	5980 Å	5400 Å	5940 Å	5500 Å	6100 Å	5390 Å	5970 Å
cis-[CoCl₂(en)₂]⁺	110.5	77.5	100.0	71.0	95.5	67.0	94.0	57.5	105.3	75.5
trans-[CoCl₂(en)₂]⁺	5.0	37.5	5.0	35.5	7.0	34.5	11.3	39.0	7.0	35.3
cis-[CoCl(DMSO)(en)₂]²⁺	110.5	37.5	100.0	35.5	95.5	34.5			105.3	35.3
cis-[CoCl(DMA)(en)₂]²⁺							94.0	39.0		

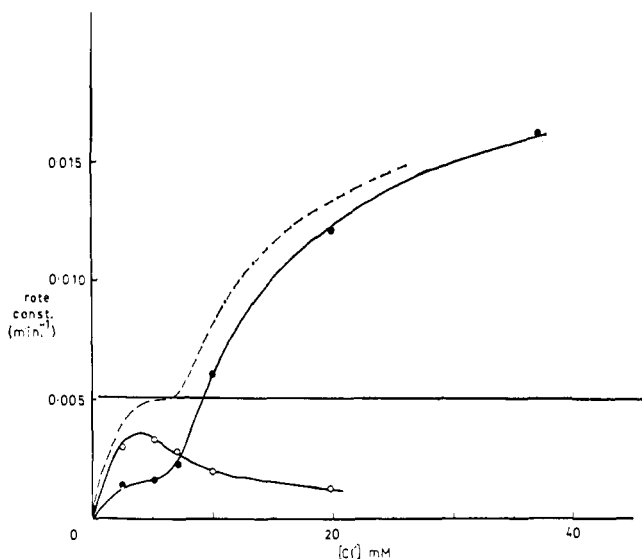| Complex	5530 Å	6200 Å	6460 Å
cis-[CoBrCl(en)₂]⁺	99.0	62.5	46.5
trans-[CoBrCl(en)₂]⁺	6.0	40.0	46.5
cis-[CoBr(DMSO)(en)₂]²⁺	99.0	40.0	24.5

Figure 2. Rates of formation of *cis*- and *trans*-[CoCl₂(en)₂]⁺ from chloride entry into *cis*-[CoCl(DMSO)(en)₂]²⁺ in DMA at 40.5° as a function of chloride concentration (total complex concentration 5 × 10⁻³ *M*): ○, rate of *trans* formation; ●, rate of *cis* formation; – – – –, summated rates; ———, rate of DMA entry into *cis*-[CoCl(DMSO)(en)₂]²⁺.
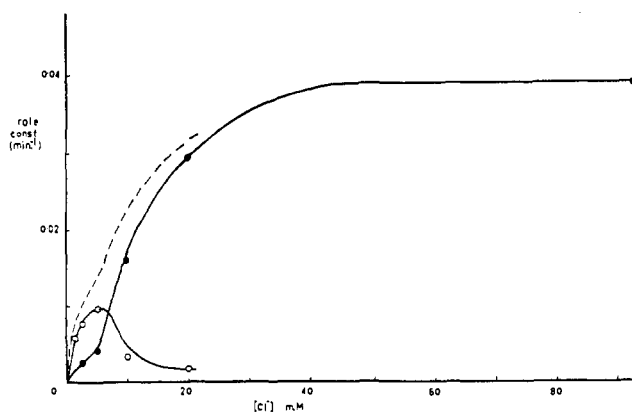

Figure 3. Rates of formation of *cis*- and *trans*-[CoCl₂(en)₂]⁺ from chloride anation of *cis*-[CoCl(DMSO)(en)₂]²⁺ in TMS at 50° (total complex concentration 5 × 10⁻³ *M*: ○, rate of *trans* formation; ●, rate of *cis* formation; – – –, summated rates.

intermediates with asymmetrically charged solvation spheres, closely resembling such ideal geometries.

It does seem, however, that in this system we are involved with a dissociative reaction and that, following the developing dissociation of the coordinated solvent molecule, the entry that follows depends on the conditions of the solvation sphere of the complex. If there is only solvent available, exchange occurs, which here is unnoticed. In the ion pair bromide entry occurs. The orientation of the ion-paired bromide is such as to favor the formation of *trans*-[CoBr₂(en)₂]⁺. The ion triplet also favors bromide entry, but in this case the arrangement of the outer sphere is such as to favor the formation of *cis*-[CoBr₂(en)₂]⁺.

It would be wrong to extrapolate from these results and to draw conclusions about the detailed geometry of the ion pair and the ion triplet since it must be remembered that these changes in steric course are also a function of the changing geometry of a dipolar transition state. At this stage we can only guess at the ion association properties and geometry of the transition state.

(b) Sequence 2 Reactions. It is convenient to discuss these systems in three groups, each group showing significantly different kinetic features.

(i) The first is the anation of *cis*-[CoCl(DMSO)-(en)₂]²⁺ by Cl⁻ in DMA and TMS (that is, X⁻ = Y⁻ = Cl⁻, SOL₁ = DMSO, SOL₂ = DMA and TMS). Figures 2 and 3 show the form of the dependence of anation rate (now in general $k_3 + k_4 + k_{10} + k_{11}$) on [Cl⁻] for these two solvent systems. The isomerization[12,13] reaction 5 is too slow to influence these rates during the first half-life of the reaction. Figure 2 also shows the known rate constant for reaction 6[15] in the SOL₂ = DMA system. The values of k_{10} and k_{11} have been determined previously[16] and are greater than the present rates by a factor of *ca.* 20. No values for k_6, k_{10}, and k_{11} are available for the TMS system since we have not been successful in isolating cobalt(III) complexes in which

TMS is a ligand, although we have succeeded in the preparation of the comparable chromium(III) complexes.

These reactions show essentially the same features as the bromination of *cis*-[CoBr(DMF)(en)₂]²⁺ in DMF. The limiting rate of *trans*-product formation is reached at approximately equimolar anion concentration as in the DMF system.

Although ion association constants will be higher in DMA and TMS than in DMF,[13,20] the difference will not be apparent here since, even in DMF, ion pairing is over 80% complete at equimolar complex and anion concentrations.

In the DMA system at least it seems that, once ion pairing is complete ([Cl⁻] *ca.* 5 × 10⁻³ *M*), the effects of reaction 6 are small and thus reactions 7–11 can also be omitted. Reexpressed this means that every dissociation of a DMSO ligand from the ion-paired species is followed by anation. In the region of [Cl⁻] where the complex reagent is only partially ion paired, anion entry will occur both through the *cis*-[CoCl(DMSO)-(en)₂]²⁺···Cl⁻ ion pair and through the *cis*-[CoCl-(DMA)(en)₂]²⁺ species following exchange.

Previous work[11b,13,14] has shown TMS to have less tendency than DMA to coordinate and thus, although no exchange data are available for TMS, it seems most unlikely that reactions 6–11 are significant once ion pairing of the starting material is complete. TMS exchange for DMSO may be occurring in the reactions of the free ion.

The flat section here in the graph of anation rate against [Cl⁻] in the region of complete ion pairing (*ca.* 5 × 10⁻³ *M*) suggests that in these systems K_1 and K_2 differ by more than in the previous system in DMF. The other difference between these systems and the previous system is that the rate of formation of *trans* product decreases to a significantly smaller fraction of the maximum value. Such a decrease in the *trans* rate is consistent with a greater degree of ion triplet formation in TMS and DMA, solvents in which ion association is known to be more extensive than in DMF.[13,20]

(ii) The second group consists of the anation of *cis*-[CoCl(DMSO)(en)₂]²⁺ by Cl⁻ in DMF and the anation

(20) W. A. Millen and D. W. Watts, *J. Am. Chem. Soc.*, **89**, 6858 (1967).
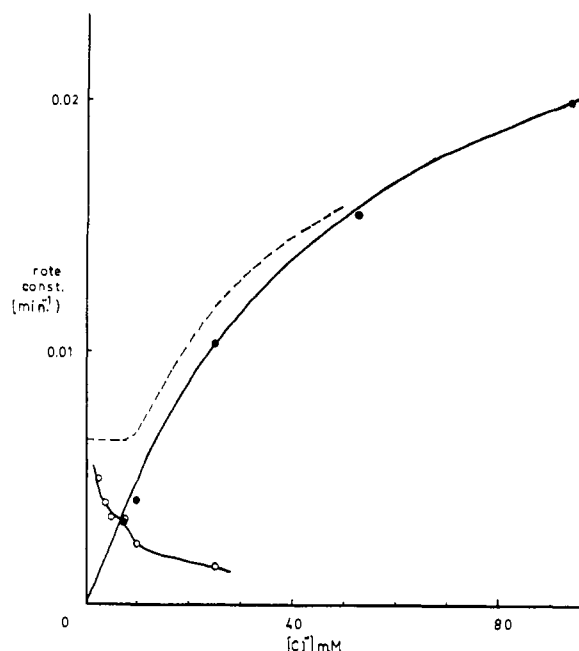
Figure 4. Rates of formation of cis- and trans-[CoCl₂(en)₂]⁺ from chloride entry into cis-[CoCl(DMSO)(en)₂]²⁺ in DMF at 45° (total complex concentration 5 × 10⁻³ M): O, rate of trans formation; ●, rate of cis formation; – – – – – –, summated rates.

Figure 6. Dependence of the rate of bromide entry into cis-[CoBr(DMSO)(en)₂]²⁺ and the rates of cis- and trans-[CoBr₂(en)₂]²⁺ formation on bromide concentration at 60° in TMS (total complex concentration 5 × 10⁻³ M): ◑, rate of cis-[CoBr(DMSO)(en)₂]²⁺ removal; O, rate of trans formation; ●, rate of cis formation.
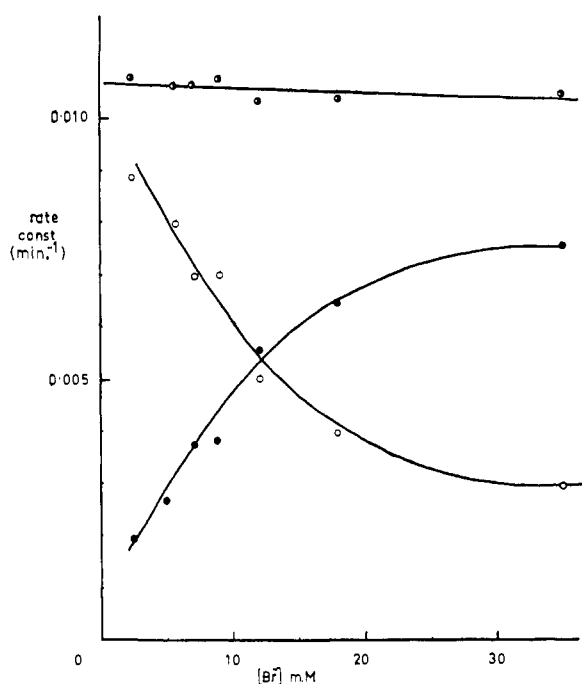

Figure 5. Dependence of the rate of bromide entry into cis-[CoBr-(DMSO)(en)₂]²⁺ and the rates of cis- and trans-[CoBr₂(en)₂]⁺ formation on bromide concentration at 45° in DMA (total complex concentration 5 × 10⁻³ M): ◑, rate of cis-[CoBr(DMSO)(en)₂]²⁺ removal; O, rate of trans formation; ●, rate of cis formation.

of cis-[CoBr(DMSO)(en)₂]²⁺ by Br⁻ in DMA and TMS. Figures 4–6 show the dependence of the anation rate constants on anion concentration. Comparison of these figures with Figures 1–3 shows that the dependence of the rate of formation of cis product on anion concentration is similar for all these systems. The rate of formation of trans product is quite different below the anion concentration required to complete the ion pairing
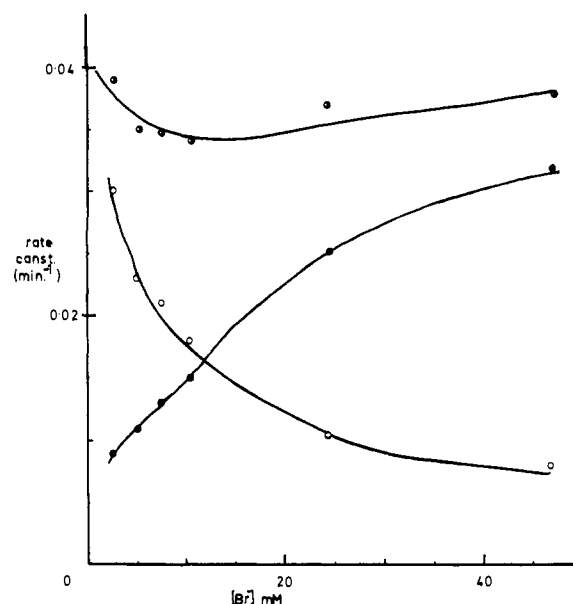
of the starting material. Such a dependence can only be accounted for in terms of a path to products which involves anion entry into the unassociated reactant. We must now consider whether this entry of anion into the free ion is dissociative in nature with free chloride competing with solvent interchange reaction,[15] or whether there is a bimolecular path.

It is meaningful to distinguish between a bimolecular mechanism and its accompanying transition state and the transition state formed by the dissociative reaction of an ion pair. The transition state in the second case must reflect the stereochemistry of the ion associated aggregate from which it is formed. At this stage it is unreasonable to assume that the path to a bimolecular transition state would necessarily involve the same orientation.

It can be seen in Figure 4 that the total initial rate constant ($k_3 + k_4 + k_{10} + k_{11}$) does not vary appreciably with anion concentration in the range where the ion-pair concentration is increasing. The total rate constant is the sum of two terms, one increasing and involving the ion pair, and the other decreasing and involving the free ion. None of the present systems gives sufficient precision to enable a distinction between a bimolecular and a unimolecular mechanism for the reaction of the free ion to be made on the basis of anion concentration dependence. We have attempted to measure the rate of reaction 6 for the system

$$cis\text{-[CoCl(DMSO)(en)}_2]^{2+} + DMF =$$

$$cis\text{- and } trans\text{-[CoCl(DMF)(en)}_2]^{2+} + DMSO$$
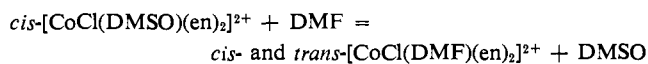
by a spectrophotometric method used on analogous systems.[15] Similarity in spectra make precise measurements impossible but a value of 0.03 min⁻¹ at 44.5° was obtained. This rate is greater (fivefold) than the rate of anion entry at 5 × 10⁻³ M chloride which contrasts markedly with the results for the previous system (Figure 2). For the rate of formation of the dissocia-

tive transition state to be so affected by ion association is quite reasonable and requires the difference in free energy between the ion and the transition state to change by only ca. 1 kcal mole[-1] upon association. The faster dissociative rate as measured by solvolysis means that the free anion in competition with the solvent must gain one in every five "embryo dissociations." It should be noted that the *trans* rate is over-estimated (*ca.* 10%) here because we cannot allow for *cis*-[CoCl(DMF)-(en)₂]²⁺ formed in the competing solvolysis reaction.

Since there is good evidence that all other reactions of this type are dissociative in nature and since the present results are not inconsistent with such a mechanism, provided the free ion dissociative solvolysis is relatively fast, we prefer to assign a dissociative rate to these systems.

It is worthy of note that the rates at higher anion concentrations in this system cannot be accounted for in terms of anation of *cis*-[CoCl(DMF)(en)₂]²⁺ following solvolysis because the rates for this anation reaction[11c] are considerably slower than the anation rates measured here.

In the systems *cis*-[CoBr(DMSO)(en)₂]²⁺ in DMA and TMS, product isomerization[11b,14] (reaction 5) interfered with the calculation of *cis*: *trans* product ratios for the anation process. In this case the *cis*: *trans* product ratio was extrapolated to zero time, after the method of Baldwin, Chan, and Tobe,[21] and the over-all rate of formation of products ($k_3 + k_4$) was divided into ($k_3 + k_4$)_c and ($k_3 + k_4$)_t. In the anation of *cis*-[CoCl(DMF)(en)₂]²⁺, reaction 5[11c] did not influence the rate plots over the first half-life of the reaction.

(iii) This group includes the anation of *cis*-[CoBr-(DMSO)(en)₂]²⁺ by Br⁻ and Cl⁻ and *cis*-[CoCl(DMSO)-(en)₂]²⁺ and *cis*-[CoCl(DMA)(en)₂]²⁺ by Cl⁻ in MeOH. The results for the first three of these systems, presented in Figure 7, are consistent with the general mechanism presented for the previous systems. Here, however, only *trans*-[CoXY(en)₂]⁺ product is observed because the isomerization of any *cis*-[CoXY(en)₂]⁺ (reaction 5) in these systems is fast[22] compared with the rate of anion entry. If anion entry into the free complex ion occurs, it is not likely to be seen because the methanolysis rate of the free ion (that is, the dissociative rate of the free ion), shown in Figure 7, is less than the anation rate in the ion pair.

In methanol, ion association constants have been shown to be considerably less than in the dipolar aprotic solvents used in this study (*e.g.*, K_{IP} for *cis*-[CoCl₂(en)₂]⁺···Cl⁻ in MeOH[23] at 25° equals 135 and in DMF[20] is 8060 at 25°). Thus complete ion pairing is reached here at much higher anion concentrations (*cf.* Figure 7 and previous figures). For this reason methanolysis (reaction 6) is an important feature in these systems and much of the anation occurs through reaction 10, reaction 11 being unimportant because of the negligible amount of ion triplet formed.

There will not be an appreciable buildup of the methanol-containing complex except at low anion concentrations because the anation of *cis*-[CoCl-(MeOH)(en)₂]²⁺ or the *cis*- and *trans*-[CoCl(MeOH)-
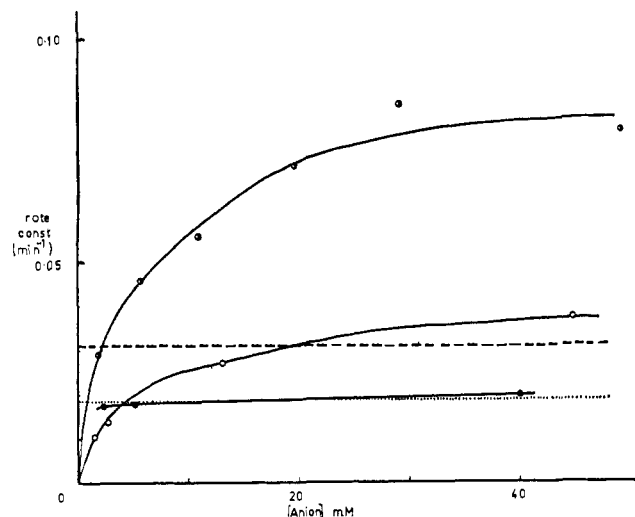

Figure 7. Rates of chloride and bromide entry into *cis*-[CoBr-(DMSO)(en)₂]²⁺ at 45° and the rate of chloride entry into *cis*-[CoCl(DMSO)(en)₂]²⁺ at 50° in methanol (total complex concentration 5 × 10⁻³ *M*): ◑, Cl⁻ entry into *cis*-[CoBr(DMSO)(en)₂]²⁺; ○, Br⁻ entry into *cis*-[CoBr(DMSO)(en)₂]²⁺; ●, Cl⁻ entry into *cis*-[CoCl(DMSO)(en)₂]²⁺; – – – –, MeOH entry into *cis*-[CoBr-(DMSO)(en)₂]²⁺ at 45° and zero anion concentration; ······, MeOH entry into *cis*-[CoCl(DMSO)(en)₂]²⁺ at 50° and zero anion concentration.

(en)₂]²⁺ mixture is fast as pointed out by Bosnich, Ferguson, and Tobe.[8] We have measured the rates of anation of the product of methanolysis of *cis*-[CoCl-(DMSO)(en)₂]²⁺ and *cis*-[CoBr(DMSO)(en)₂]²⁺ by dissolving these complexes as perchlorates and allowing five half-lives of methanolysis before introducing the anion as Et₄NCl and Et₄NBr. The rates of Cl⁻ entry at 25° are respectively 0.017 and 0.015 min⁻¹ and that of Br⁻ entry into the *cis*-[CoBr(MeOH)(en)₂]²⁺ is 0.020 min⁻¹, all anion concentrations being 2.5 × 10⁻³ *M*. These rates, which are consistent with Bosnich, Ferguson, and Tobe,[8] are clearly in excess of the other rates observed in these systems. Thus the rate-determining steps in all the reactions are either (i) methanolysis of the free ion, or (ii) anation in the ion pair following dissociation of coordinated DMSO.

Because in these systems the isomerization reaction 5 is relatively fast,[22] no indication of the steric course for either of these anation paths is found. The only product is *trans*-[CoXY(en)₂]⁺, the thermodynamically stable isomer.[22] We have thus looked briefly at the system *cis*-[CoCl(DMA)(en)₂]²⁺ in methanol in which the methanolysis ($k = 0.08$ at 25°) and anation are faster relative to the product isomerization. These results cannot be precise because of the buildup of methanol-containing complex but indicate that *cis*-[CoCl₂(en)₂]⁺ is definitely an initial product as is shown by the results in Table IV. That the anation rate of *cis*-[CoCl-

Table IV. Rates of Formation of *cis*- and *trans*-[CoCl₂(en)₂]⁺ from Chloride Entry into *cis*-[CoCl(DMA)(en)₂]²⁺ in Methanol at 30.1°

10³[Cl⁻], *M*	Rate constant for *cis* formation	Rate constant for *trans* formation
5.0	a	0.044
48.7	0.016	0.052

a MeOH entry into *cis*-[CoCl(DMA)(en)₂]²⁺ interferes with the calculation of this rate.

(21) M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4639 (1961).

(22) D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953).

(23) R. G. Pearson, P. M. Henry, and F. Basolo, *J. Am. Chem. Soc.*, 79, 5382 (1957).

Table V. Activation Energies for the Anation of cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ by Chloride Ion in DMA, TMS, and DMF

Reaction	[Cl] $\times 10^3 M$	E_a, kcal mole^{-1}	Solvent
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ $trans$-[CoCl$_2$(en)$_2$]$^+$	4.1	26.5 ± 0.3	DMA
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ cis-[CoCl$_2$(en)$_2$]$^+$	38.0	27.5 ± 0.3	DMA
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ $trans$-[CoCl$_2$(en)$_2$]$^+$	4.0	26.5 ± 0.3	TMS
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ cis-[CoCl$_2$(en)$_2$]$^+$	91.5	29.0 ± 0.3	TMS
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ $trans$-[CoCl$_2$(en)$_2$]$^+$	7.1	27.5 ± 0.3	DMF
cis-[CoCl(DMSO)(en)$_2$]$^{2+}$ ⟶ cis-[CoCl$_2$(en)$_2$]$^+$	53.0	27.5 ± 0.3	DMF

(DMSO)(en)$_2$]$^{2+}$ does not fall off at low Cl$^-$ concentrations, as in the other systems, is difficult to explain unless it is due to methanolysis competing favorably with anation under all conditions including in the ion pair.

Finally it can be said that anation reactions as exemplified by these systems require in general at least these 11 reactions for specification although under some conditions some are not relevant (e.g., sequence 1), some can be slow enough to be ignored, and some can be unimportant (e.g., reactions 4 and 11) because the concentration of the starting material (in this case the ion triplet) is exceedingly low.

In all systems in which the steric course has been followed without the interference of subsequent isomerization, trans product is favored in the reaction of the ion pair and cis product from the ion triplet. Thus as one expects, orientation effects in the solvation sphere are important in product determination. In most systems it seems that, once an ion is established in the inner solvation sphere, then its entry is preferred over solvent interchange or exchange.

Activation energies for those systems in which they were determined are collected in Table V. As the above discussion would predict they are found to be dependent on the degree of association and the dependence quite adequately accounts for the observed variation in rate of formation of the transition state in the assigned dissociative reaction.

Electron Transfer through Organic Structural Units. V. Reductions of Carboxamidopentaamminecobalt(III) Complexes[1a]

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Contribution from the Departments of Chemistry, San Francisco State College, San Francisco, California, and Kent State University, Kent, Ohio. Received September 11, 1967

Abstract: Pentaamminecobalt(III) complexes of seven N,N-disubstituted amides, and of the amide-like heterocycles 2- and 4-pyridone, have been prepared as their perchlorates, and the specific rates at which they are reduced with Cr(II) have been measured at 24.5°. In each of these, the amide is coordinated to Co(III) through oxygen rather than nitrogen. Ligand fields associated with coordinated acetamides and benzamides are weaker than those associated with formamides; the acetamido and benzamido complexes exhibit maxima near 520 mμ (as contrasted to 506 mμ for the formamido derivatives) and are labile to aquation in warm water. Separations, using cation-exchange chromatography, of the Cr(III)-containing products resulting from these reductions yielded Cr(H$_2$O)$_6$$^{3+}$, and, in all cases except that of the 4-pyridone complex, this aquo ion was the sole monomeric Cr(III) product, thus implying reduction through "outer-sphere" activated complexes for these amide derivatives. Unlike reduction of carboxylato derivatives via ligand transfer, which are retarded by steric crowding, reductions of the amide derivatives appear to be subject to steric assistance; reductions of the acetamido and benzamido complexes are more rapid than those of the formamido complexes. This suggests a partial relief of crowding during the activation process for these reductions. Reduction of Co(III) via ligand transfer was observed only for the complex of 4-pyridone. This mode of reduction, which yields an amide-bound Cr(III) species, competes here with outer-sphere reduction and proceeds about 1.5 times as rapidly as the latter.

Although the reductions, with Cr(II), of well over 100 different carboxylatopentaamminecobalt(III) complexes (I) have been studied,[2] only a handful of

(2) See, for example, (a) E. S. Gould and H. Taube, J. Am. Chem. Soc., 86, 1318 (1964); (b) D. K. Sebera and H. Taube, ibid., 83, 1785 (1961); (c) E. S. Gould, ibid., 87, 4730 (1965); (d) R. T. M. Fraser, ibid., 83, 4921 (1961); (e) E. S. Gould, ibid., 88, 2983 (1966).

carboxamide derivatives (II or III) in the (NH$_3$)$_5$Co^{III} series have been reported.

The reductions of complexes derived from N,N-dimethylformamide (IV, R = H) and 2-pyridone (VII)[3] are faster, by several orders of magnitude, than reductions of the hexaamminecobalt(III) complex[4] and the imidazolepentaammine complex,[2c] being,

(3) E. S. Gould, ibid., 89, 5792 (1967).
(4) A. Zwickel and H. Taube, ibid., 83, 793 (1961).