CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS 02215

Inner-Sphere Electron-Transfer Reactions of Cobalt(III). Nonbridging Ligand Effects, Activation Energies, and Precursor Complex Formation[1]

BY RAMESH C. PATEL, RICHARD E. BALL, JOHN F. ENDICOTT,[2] AND R. GRAHAM HUGHES

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The rates of Cr^{2+} reductions of various $Co(en)_2ACl^{2+}$ complexes have been determined. The observed rates are relatively insensitive to the ligand A. Several of these reactions exhibit negative apparent energies of activation. Such behavior is consistent with the existence of precursor Cr^{II}–X–Co^{III} complexes whose formation and dissociation influence the observed reaction rates. Activation parameters are compared for inner-sphere and outer-sphere electron-transfer reactions.

Introduction

In electron-transfer reactions of simple chemistry, the ligands coordinated to the metal center can dramatically affect the reaction rate. In reactions of the inner-sphere type, where a ligand is shared in the coordination spheres of the reactant metal centers, it is convenient to formulate the reaction in terms of a series of steps

$$ML_6^{2+} + {}^*ML_5X^{3+} \rightleftarrows L_5M^{2+}\text{–}X\text{–}{}^*M^{3+}L_5 + L \qquad (1)$$

$$L_5M^{2+}\text{–}X\text{–}{}^*M^{3+}L_5 \rightleftarrows L_5M^{3+}\text{–}X\text{–}{}^*M^{2+}L_5 \qquad (2)$$

$$L_5M^{3+}\text{–}X\text{–}{}^*M^{2+}L_5 + L \rightleftarrows ML_5X^{3+} + {}^*ML_6^{2+} \qquad (3)$$

These steps represent the formation (eq 1) and dissociation (eq 2) of binuclear species which in alternative formulations may be regarded as the activated complex[3,4] for the electron-transfer step (eq 2) or simply as a binuclear intermediate of finite lifetime.[3,5–7] Taube[8] has recognized that formation of a genuine binuclear intermediate can have a pronounced effect on the over-all activation parameters of reaction and has cited the relatively low activation energies of some Cr^{2+}–Co(III) reactions as strong evidence for the formation of such intermediates. Unfortunately, the merit of this argument has been somewhat obscured by the recognition that a large free energy of reaction (such as occurs for most Cr^{2+}–Co(III) reactions) can also lower the activation barrier for the electron-transfer reaction,[8–11] by recognition of the fact that transfer of a bridging ligand alters the free energy of reaction[12–14] and by the observation that "nonbridging"[15] ligands can greatly alter the free energy of activation for any specified "bridging" ligand.[12,16–19] To some extent this ambiguity has resulted in the neglect of the energetics of precursor complex formation (eq 1) in the elaborate discussions of the function of the bridging ligand in promoting electron transfer[20] and even in discussions which specifically focus on comparisons of the energetics of inner-sphere reactions (where precursor complexes may occur) and outer-sphere reactions (where precursor complexes cannot occur).[12,21]

It has been observed that inner-sphere reactions should have relatively negative entropies of activation.[22] Attempts to correlate $\Delta S^{\ddagger}$ with the geometry of the activated complex have been notoriously unsuccessful.[20,23] The formation of precursor complexes would complicate the comparison.

The present study was commenced as a complement to our earlier study of "nonbridging" ligand effects in outer-sphere reactions.[12] The Cr^{2+} reductions of $Co^{III}(en)_2AX$ complexes were chosen for this study because the activated complex for these reactions is unambiguously of the inner-sphere type. As the reactivity patterns began to evolve, this original purpose was necessarily modified. As a result, the present report both contributes to the recent discussion of nonbridging ligand effects and forms a part[24] of an examination of the role of precursor complexes in Cr^{2+} reductions of cobalt(III) complexes.

Experimental Section

Reagents.—The preparations of most of the complexes employed in this study have been described previously.[12] The preparations of *cis*-$Co(en)_2FOH_2^{2+}$, *cis*-$Co(en)_2ClF^{+}$, *trans*-Co-

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[2] Author to whom correspondence may be addressed at the Department of Chemistry, Wayne State University; Detroit, Mich. 48202.

[3] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[4] (a) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956); (b) J. Halpern and L. G. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960).

[5] J. F. Endicott, *J. Phys. Chem.*, **73**, 2594 (1969).

[6] M. P. Liteplo and J. F. Endicott, *J. Am. Chem. Soc.*, **91**, 3982 (1969).

[7] It should be noted that in the "activated complex" formulation, reaction 3 should involve the immediate products of reaction which are not necessarily (*e.g.*, in the case of reductions of cobalt(III)) identical with the equilibrated product species.

[8] N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

[9] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[10] R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

[11] N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

[12] R. C. Patel and J. F. Endicott, *J. Am. Chem. Soc.*, **90**, 6364 (1968).

[13] J. Halpern, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 123.

[14] A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966); **87**, 4210 (1965)

[15] Since this effect is present in both inner-sphere and outer-sphere reactions, the terms "bridging" and "nonbridging" are somewhat ambiguous here. See footnote 14 of ref 12.

[16] P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).

[17] C. Bifano and R. G. Linck, *ibid.*, **89**, 3945 (1967).

[18] R. G. Linck, *Inorg. Chem.*, **7**, 2394 (1968).

[19] P. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969).

[20] For a recent review see: A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1967).

[21] A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

[22] W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, **29**, 49 (1960); W. C. E. Higginson, *ibid.*, **29**, 123 (1960).

[23] J. P. Candlin, J. Halpern, and D. T. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

[24] For other relevent discussion and experimental evidence see ref 3 and 4 and Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 146.

$(en)_2F_2^+$, and $Co(tetraaen)Br^{2+}$ are to be found in the literature.[25,26] Perchlorate or chloride salts of these complexes were recrystallized from aqueous solution until their absorption (infrared, visible, and uv) agreed with literature values.[27]

All reaction solutions were made with distilled water which had been passed through a deionizing resin.[28] Stock $NaClO_4$ and $LiClO_4$ solutions were prepared by neutralizing weighed aliquots of the respective carbonate salts with $HClO_4$. Stock solutions of NaCl and LiCl were prepared from the reagent grade salts. All solutions containing reactants were deaerated by means of a stream of Cr^{2+} scrubbed N_2.

The preparation and handling of $Ru(NH_3)_6^{2+}$ solutions has been discussed previously.[12] The Cr^{2+} used in reactions described in this paper was prepared from the reduction of Cr^{3+} with zinc amalgam in perchloric acid. This reduction was performed in relatively concentrated ($\sim 10^{-3}$ *M*) solution. Aliquots of stock Cr^{2+} solutions were transferred to the storage vessels of the stopped-flow apparatus by means of a syringe. The stock $Cr(ClO_4)_3$ solutions were prepared by the H_2O_2 reduction of purified $Na_2Cr_2O_7$ in $HClO_4$. The concentration of Cr^{2+} was monitored by the reduction of $Co(NH_3)_5Br^{2+}$ as determined at the uv absorbance maximum at 2525 Å (ϵ_{max} 1.65×10^4). In such determinations of reducing titer, the absorbance of $Co(NH_3)_5Br^{2+}$ was determined within a few minutes after adding an aliquot of the reducing agent and was compared to the absorbance (measured at the same time) of an appropriately diluted stock solution of $Co(NH_3)_5Br^{2+}$. This procedure minimized errors due to the aquation of $Co(NH_3)_5Br^{2+}$.

Techniques for Kinetic Runs.—The $Ru(NH_3)_6^{2+}$ reactions were carried out using the syringe technique.[11] For the Cr^{2+} reactions it was necessary to use a stopped-flow technique. The apparatus used was basically that described by Dulz and Sutin[8] and purchased from Atom Mech Machine Co. The apparatus was designed so that all parts in contact with reactant solutions could be purged of O_2 by means of Cr^{2+}-scrubbed nitrogen.[11] The tubes leading to the Teflon mixing chamber, as well as the quartz observation tube emerging from it, were sealed tightly by means of "O" rings. With these precautions Cr^{2+} solutions as dilute as $\sim 10^{-6}$ *M* could be handled fairly safely (Table I). In the actual kinetic runs $[Co(III)] > [Cr^{2+}]$ and the actual $[Cr^{2+}]$ in the reaction mixture was determined from observed absorbance changes.

We attempted to design the experiments so that reaction half-lives were ≥30 msec. In order to check the functioning of the stopped-flow apparatus at different temperatures we determined the rate of formation of $FeCl^{2+}$ in acidic (0.311 *M*) solutions of unit ionic strength ($NaClO_4$–$HClO_4$) with $[Cl^-] = 4.7 \times 10^{-3}$ *M* and $[Fe^{3+}] = 7.9 \times 10^{-3}$ *M*. Our values of $\bar{k} = 42 \pm 4$ M^{-1} sec^{-1} (20°) and $\bar{k} = 193 \pm 28$ M^{-1} sec^{-1} (31°) compare satisfactorily with 40.5 ± 4 M^{-1} sec^{-1} (21°) and 155 ± 15 M^{-1} sec^{-1} (31°) reported by Connick and Coppel.[29]

The temperature of solutions at the point of observation was determined using a calibrated differential thermocouple in the exit stream of solution from the quartz observation tube. The stopped-flow apparatus was generally operated with a 5 ± 1 msec "deadtime." The accuracy of transmittances measured from the oscilloscope traces was determined by comparison with the absorbancies of reactant and product solutions using a Cary 14 spectrophotometer.

Second-order rate constants were calculated using a Fortran IV least-squares program.[12,27] Since cobalt(III) oxidants were in excess, it was possible to check the calculated second-order constants by comparing them with rate constants obtained from a pseudo-first-order treatment of the observed spectral changes (also using a Fortran IV least-squares program).[27] In those cases where the concentrations of cobalt(III) and chromium(II) were not very different only the first 10–25% of reaction was used in the calculations of pseudo-first-order rate constants. In order to obtain reasonable estimates of the second-order rate constant, these approximate pseudo-first-order rate constants were divided by an "average" effective concentration of cobalt(III)

$$[Co(III)]_{av} = \frac{[Co(III)]_{t=0} + [Co(III)]_{t=\infty}}{2}$$

Such approximate rate constants are reported in the last column of Table I to provide a check on the calculation of second-order rate constants. In addition, the validity of the treatment of data was periodically checked by a standard graphical treatment of the data.[30] The rate constants calculated by these different methods generally agreed to better than 5%. Only in the most difficult cases (*i.e.*, reactions with low signal to noise ratios or reactions with very short half-lives) did the second-order rate constants differ by more than 15%. Such deviations are reflected in the data recorded below. In the case of the Cr^{2+} reactions, at least three determinations of each reaction were made and only if these were nearly superimposable did we use data to calculate rate constants. As a check on the accuracy of the calculated rate constants, several determinations were repeated using independently prepared solutions. These duplicate determinations suggest that the rate constants in Table I are generally reproducible to within 10–20%.

Radioactive Tracer and Chromatographic Studies.—Owing to the high reactivity of *trans*-$Co(en)_2OH_2Cl^{2+}$ with other reagents[9,12] we attempted to determine the rate of its Cr^{2+} reduction by competition with the reduction with $Co(NH_3)_5{}^{36}Cl^{2+}$. In these tracer studies a 1-ml aliquot of the reaction mixture was mixed with 10 ml of a dioxane solution of "Omnifluor" scintillator (New England Nuclear Corp.). Counting was performed using a Tracerlab PD-20 D solid scintillation counter with a Tracerlab Versa-Matic II scalor. Four to six separate counts, each of 5-min duration, were taken.

To determine the stoichiometry of the Cr^{2+}–*trans*-$Co(en)_2OH_2Cl^{2+}$ reaction, the $CrCl^{2+}$ was separated from the reaction mixture using a Bio-Rad Ag 50 W-X4 (acidic form, 200–400 mesh) cation-exchange resin and eluting with 0.5 *M* $HClO_4$. $CrCl^{2+}$ was the first cationic species eluted from the resin. Total chromium in the eluent was determined as the CrO_4^{2-} produced by peroxide oxidation.

Results

A. The Cr^{2+} Reaction.—The results of our investigations of Cr^{2+} reductions of cobalt(III) complexes are presented in Table I. Owing to several unusual features these data are presented in some detail. Duplicate determinations involving separately prepared solutions are entered individually.

B. The Cr^{2+}–*trans*-$Co(en)_2OH_2Cl^{2+}$ Reaction.—Since the $Ru(NH_3)_6^{2+}$–*trans*-$Co(en)_2OH_2Cl^{2+}$ reaction has such a large specific rate,[12,27,31] we originally felt that an accurate value for the Cr^{2+}–*trans*-$Co(en)_2OH_2Cl^{2+}$ reaction could only be obtained from a competition study. In order to establish the mechanism of the latter reaction Cr^{2+} was added to an acidic ($HClO_4$) solution containing an excess of *trans*-$Co(en)_2OH_2Cl^{2+}$. The amount of Co^{2+} produced from the reduction (there was always some Co^{2+} present in the stock *trans*-$Co(en)_2OH_2Cl^{2+}$ solution) was found to be equal to the amount of $CrCl^{2+}$ separated chromatographically. Two determinations involving different

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(25) W. R. Matoush and F. Basolo, *J. Am. Chem. Soc*, **78**, 3972 (1956).

(26) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966); **6**, 272 (1967).

(27) For details see: R. C. Patel, Ph.D. Dissertation, Boston University, 1969.

(28) C. G. Swain and D. F. Evans, *J. Am. Chem. Soc.*, **88**, 383 (1966).

(29) R. E. Connick and C. P. Coppel, *ibid.*, **81**, 6389 (1959).

(30) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

(31) The second-order rate constant for this reaction is 7×10^4 M^{-1} sec^{-1} at 13.5°.[27]

TABLE I

Cr^{2+} REDUCTION OF VARIOUS $Co(en)_2AX^{2+}$ COMPLEXES[a]

Complex[b]	Temp, °C	Initial concn, M		$10^{-5}k_{obsd}$, M^{-1} sec^{-1} [c,d]	$10^{-5}k_{obsd}$, M^{-1} sec^{-1} [d,e]
		10^{-5}[Co(III)]	10^{5}[Cr(II)]		
cis-$RClNH_3^{2+}$	13.5 ± 0.4	11.6	4.78	2.6 ± 0.1	2.4 ± 0.1
	13.5 ± 0.4	11.6	5.02	2.8 ± 0.1	2.8 ± 0.1
	13.5 ± 0.4	11.6	4.16	2.6 ± 0.2	2.7 ± 0.2
	18.6 ± 0.4	11.4	5.35	2.3 ± 0.1	2.2 ± 0.1
	25 ± 0.4	11.4	4.61	2.5 ± 0.1	2.3 ± 0.1
	25 ± 0.4	11.6	4.78	2.3 ± 0.1	2.3 ± 0.1
	25 ± 0.4	11.6	3.60	2.4 ± 0.1	2.5 ± 0.1
cis-$RClH_2O^{2+}$	13.5 ± 0.4	7.48	0.46	3.9 ± 0.1	3.9 ± 0.3
	18.6 ± 0.4	7.48	2.53	3.1 ± 0.2	3.1 ± 0.3
	25 ± 0.4	7.48	2.04	3.8 ± 0.1	3.6 ± 0.1
	25 ± 0.4	7.48	2.08	4.6 ± 0.1	4.6 ± 0.2
cis-$RClNC_5H_5^{2+}$	13.5 ± 0.4	2.20	0.34	5.0 ± 0.1	5.0 ± 0.1
	18.6 ± 0.4	2.20	0.44	9.1 ± 0.5	8.8 ± 0.4
	18.6 ± 0.4	2.20	0.33	11.7 ± 1	11.9 ± 1
	25 ± 0.4	2.20	0.28	9.4 ± 0.5	9.3 ± 0.2
cis-$RClNH_2C_6H_{11}^{2+}$	13.5 ± 0.4	19.2	18.4	13.6 ± 2	...
	18.6 ± 0.4	19.2	18.2	9.6 ± 1	...
	25 ± 0.4	19.2	16.1	4.5 ± 0.2	3.9 ± 0.1
cis-$RClNH_2CH_2CO_2H_2^{2+}$	18.6 ± 0.4	8.89	7.76	26 ± 3	...
cis-RCl_2^{+}	13.5 ± 0.4	2.21	0.92	11.0 ± 0.4	11.3 ± 0.2
	18.6 ± 0.4	2.21	0.75	10.0 ± 0.2	10.3 ± 0.2
	25.0 ± 0.4	2.21	0.34	7.7 ± 0.2	7.8 ± 0.2
cis-$RClF^{+}$	13.5 ± 0.4	2.58	1.32	16.7 ± 0.5	16.6 ± 0.2
	13.5 ± 0.4	2.58	1.10	17.1 ± 0.5	16.2 ± 0.3
	18.6 ± 0.4	2.58	0.42	14.0 ± 1	14.0 ± 1
	25 ± 0.4	2.58	0.38	8.6 ± 0.6	8.7 ± 0.6
	25 ± 0.4	2.58	1.44	9.3 ± 0.5	9.6 ± 0.4
trans-RCl_2^{+}	13.5 ± 0.4	0.59	0.27	82 ± 6	84 ± 4
	18.6 ± 0.4	0.59	0.23	66 ± 4	67 ± 4
trans-RF_2^{+}	13.5 ± 0.4	5.44	0.97	4.2 ± 0.1	4.2 ± 0.1
	18.6 ± 0.4	5.44	0.50	3.5 ± 0.2	3.5 ± 0.1
	25 ± 0.4	5.44	0.68	4.3 ± 0.1	4.3 ± 0.1
cis-RFH_2O^{2+}	13.5 ± 0.4	7.00	2.64	1.3 ± 0.1	1.3 ± 0.1
	18.6 ± 0.4	7.00	1.04	1.6 ± 0.1	1.6 ± 0.1
	25.0 ± 0.4	7.00	1.98	1.4 ± 0.1	1.4 ± 0.1

[a] $[H^+] = 10^{-2}$ M; $NaClO_4$–$HClO_4$ medium of ionic strength 0.10. [b] R = $Co(en)_2$. Two to four determinations were made for each datum entered in the table. An entry has been made only if the duplicate decay curves were nearly superimposable. [c] Calculated as a second-order rate constant using the Fortran IV program. [d] Errors are based on 95% confidence limits for the slopes: C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley & Sons, Inc., New York, N. Y., 1954. [e] Calculated from the pseudo-first-order rate constants. [f] $[Cl^-] = 2.6 \times 10^{-2}$ M.

TABLE II

ACTIVATION PARAMETERS FOR SOME $Ru(NH_3)_6^{2+}$–Co(III) REACTIONS[a]

Oxidant	pH	Temp range,[c] °C	Log A	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu
$Co(NH_3)_5Br^{2+}$	3	15–35 (9)	11.6 ± 1	10.9 ± 1.4	−8.4 ± 4.6
$Co(NH_3)_5Cl^{2+}$ [b]	2	9–30 (4)	7.6 ± 0.9	6.9 ± 1.2	−26.6 ± 4.2
Co(tetren)Br^{2+} [b,d]	1	13–33 (6)	9.0 ± 0.5	8.4 ± 0.7	−20.2 ± 2.2
cis-$Co(en)_2pyCl^{2+}$ [b]	2	9–30 (7)	9.5 ± 0.3	8.4 ± 0.4	−17.9 ± 1.5
cis-$Co(en)_2OH_2Cl^{2+}$ [b]	2	9–30 (5)	8.2 ± 0.5	7.2 ± 0.6	−24.1 ± 2.2

[a] $\mu = 0.1$ ($NaClO_4$, except as indicated). [b] NaCl medium. [c] Total number of determinations in parentheses. Determinations were made at approximately 5° temperature intervals. [d] tetren = tetraethylenepentamine; $k = 234$ M^{-1} sec^{-1} (20°, $\mu = 0.10$).

concentrations of reactants gave ratios of $\Delta[Co^{2+}]/[CrCl^{2+}]$ that were 1:1 to within 5%.

The competition reactions were run in high ionic strength medium ($\mu = 0.1$ ($NaClO_4$, $HClO_4$)) and we encountered some difficulty owing to the precipitation of NH_4ClO_4 in the dioxane mixtures prepared for counting. As a result of the difficulty our assays of $[Cr^{36}Cl^{2+}]/[CrCl^{2+}]$ in the product were not sufficiently reproducible to permit accurate estimation of a rate constant. In the only useful determination $[Co(NH_3)_5{}^{36}Cl^{2+}] = 2.9 \times 10^{-3}$ M, [*trans*-$Co(en)_2OH_2Cl^{2+}$] $= 1.6 \times 10^{-3}$ M, and $[Cr^{2+}] = 1.2 \times 10^{-3}$ M. In this experiment $[Cr^{36}Cl^{2+}]/[CrCl^{2+}] \geq {}^1/_3$ implying that *trans*-$Co(en)_2OH_2Cl^{2+}$ is no more than 5.6 times as reactive as $Co(NH_3)_5Cl^{2+}$ toward Cr^{2+}.

C. Activation Parameters for $Ru(NH_3)_6{}^{2+}$–Co(III) Reactions.—Table II contains activation parameters for some $Ru(NH_3)_6{}^{2+}$ reactions. Specific rates for these reactions at 25° and the techniques for calculating activation parameters are reported elsewhere.[12,27]

TABLE III

IONIC STRENGTH DEPENDENCE OF THE ACTIVATION PARAMETERS OF THE REACTION

$$Co(NH_3)_5Br^{2+} + Ru(NH_3)_6^{2+} \xrightarrow{[H^+]} Co^{2+} + Ru(NH_3)_6^{3+} + 5NH_4^+ + Br^-$$

$10^3\mu$[a]	Log A	$\Delta H^\ddagger$, kcal	$\Delta S^\ddagger$, eu	$\Delta G^\ddagger$, kcal	Temp range,[b] °C
1.27	9.0 ± 0.9	8.6 ± 1.3	−20 ± 4	14.7	18–38 (6)
5.5	9.9 ± 0.8	9.5 ± 1.1	−16 ± 4	14.3	15–36 (9)
110	11.6 ± 1.0	10.9 ± 1.4	−8 ± 5	13.4	15–35 (9)
400	13.8 ± 0.9	13.5 ± 1.3	1.6 ± 4.3	13.0	16–37 (6)

[a] $NaClO_4$–$HClO_4$. [b] Total number of determinations in parentheses. Determinations were made at approximately 5° temperature intervals.

Table III summarizes the ionic strength dependence of the activation parameters of the $Ru(NH_3)_6^{2+}$–$Co(NH_3)_5Br^{2+}$ reaction.

Discussion

The Cr^{2+} reductions of $Co(en)_2ACl^{2+}$ complexes (Table I) vary only about 30-fold in their apparent specific reactivities. This is to be contrasted to the 10^4-fold range of reactivity exhibited by these same oxidants toward $Ru(NH_3)_6^{2+}$, an outer-sphere reducing agent. Some of the Cr^{2+} reactions are very rapid, particularly with *trans*-$Co(en)_2Cl_2^+$ as oxidant, and the rate of substitution of the bridging chloride into the first coordination sphere of Cr^{2+} may be nearly rate limiting in these cases.[32–39] Thus the upper limit on the range of observable reactivities (for an inner-sphere mechanism) may be ~10^7 M^{-1} sec^{-1}. However, the reactivity scale is relatively compressed even when these few very fast reactions are eliminated. It has been pointed out by Sutin[8,9,40] that when the free energy of reaction becomes sufficiently large, the potential energy surfaces of the reactants and products should overlap in such a way that small changes in the free energy of reaction or in shapes of the potential curves will not produce as large a change in the rate of reaction as when $\Delta G° \approx 0$. Thus the compressed reactivity range in the Cr^{2+} reactions (compared to reactions of $Ru(NH_3)_6^{2+}$)[41] could in principle result from the ~10 kcal more negative $\Delta G°$ for the Cr^{2+} reactions. If this argument is carried to the limit ($\Delta G_2^{\ddagger}$ [42] ≤ 0), then the observed rate of reaction becomes limited by the rate of formation of the binuclear intermediate. In this limit the observed rate constant is equal to the diffusion rate ($k_{obsd} \rightarrow k_d \approx 10^9$ M^{-1} sec^{-1})[36] and a typical activation energy for diffusion ($E_{a,d}$ = 1-3 kcal) should be observed.[43–45] As noted by Taube, an additional contribution to the observed activation energy should arise from the dissociation of a water molecule from Cr^{2+}. This latter contribution is probably greater than 3 kcal,[37] so observed activation energies for reactions whose rate is limited by the rate of formation of a binuclear intermediate should exceed 4 kcal. This is clearly not the case for many of the reactions in Table I. If the binuclear reaction intermediates, $(H_2O)_5Cr^{II}$–X–$Co^{III}(am)_5$ (II, III) and $(H_2O)_5Cr^{III}$–X–$Co^{II}(am)_5$ (III, II), have sufficiently long lifetimes[46] their formation and decomposition kinetics (eq 1–3) can profoundly affect the observed specific reaction rate constants. In the case of Cr^{2+} reduction of cobalt(III) complexes, step 2 is analogous to the nonradiative decay of a charge-transfer excited state (II, III) to the ground state (III, II) of the binuclear intermediate. The energy difference between states (II, III) and (III, II) can be estimated to be in excess of 10 kcal[47] and therefore step 2 is essentially irreversible. A steady-state treatment of (1) and (2) gives for the observed specific rate constant: $k_{obsd} = [k_1/(k_{-1} + k_2)]k_2$. There are two limiting cases: if $k_{-1} \gg k_2$, then $k_{obsd} \rightarrow K_1k_2$, and if $k_{-1} \ll k_2$, $k_{obsd} \rightarrow k_1$. Since steric, solvation, and electrostatic factors may vary from complex to complex both k_1 and K_1 may be expected to exhibit a variety of values for the systems reported here. However, as noted above, k_1 is expected to have $\Delta H_1^{\ddagger} \geq$ 4 kcal while $\Delta H_1°$ may be less than 0 for K_1.[48] The sections below analyze and compare a variety of relevant activation parameters for reduction of cobalt(III) complexes.

A. Enthalpies of Activation for Cr^{2+}–Co(III) Reactions.—Enthalpies of activation (Table IV) have been obtained using a Fortran IV least-squares program to

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(32) M. Orhanovic and N. Sutin, *J. Am. Chem. Soc.*, **90**, 538, 4286 (1968).

(33) O. J. Parker and J. H. Espenson, *ibid.*, **91**, 1968 (1969).

(34) See also footnote 16 of ref 35.

(35) M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

(36) If the lifetime of the outer-sphere collision complex, $[Co(en)_2ACl^{2+}]$-$[Cr(OH_2)_6^{2+}]$, is taken to be of the order of 10^{-11}–10^{-12} sec and the rate of substitution for water in $Cr(OH_2)_6^{2+}$ is of the order of 10^9 sec^{-1},[37] then a bridged species will be formed in only about 1% of the outer-sphere collision complexes. If the diffusion-controlled rate of approach of two +2 cations is ~10^9 sec^{-1},[38] then the limiting rate of formation of a bridged intermediate is ~10^7 M^{-1} sec^{-1} for Cr^{2+}.

(37) (a) C. W. Merideth and R. E. Connick, paper presented at 149th National Meeting of the American Chemical Society, Detroit, Mich., April (1965); (b) M. Eigen, *Ber. Bunsenges. Physik. Chem.*, **67**, 753 (1963).

(38) For comparison note that the diffusion-controlled rate of reaction of e_{aq}^- with $Co(NH_3)_6^{3+}$ is ~10^{10} M^{-1} sec^{-1}.[39]

(39) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc.* (London), **A286**, 320 (1965).

(40) N. Sutin, paper presented at the Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D. C., Feb 1969. Some of the points touched upon by N. Sutin during his talk were debated later that evening with J. F. Endicott in a dark, dingy restaurant.

(41) For the present argument we are confining the comparison only to reactants containing halogens as bridging ligands. The over-all reactivity range of Cr^{2+}–Co(III) reactions is of course greater than range of reactivity exhibited by $Ru(NH_3)_6^{2+}$–Co(III) reactions.[12,30]

(42) Where $\Delta G_2^{\ddagger} = RT \ln k_2$, for k_2 the rate of electron transfer within the binuclear intermediate. See (2) above.

(43) S. R. Logan, *J. Phys. Chem.*, **73**, 227 (1969); *Trans. Faraday Soc.*, **63**, 1712 (1967).

(44) R. A. Marcus, "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 138; *J. Chem. Phys.*, **43**, 3477 (1965).

(45) M. Anbar, *Quart. Rev.* (London), **22**, 578 (1968).

(46) Note that in this context the lifetime of the intermediates is kinetically significant if it exceeds characteristic vibrational lifetimes. It is also to be borne in mind that present discussion is limited to reactions which can only proceed subsequent to the formation of M–X–*M bridged species. Rapid preequilibrium to form a reactive intermediate is of course a well-documented and frequently observed type of kinetic behavior. See for example: S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960. In the present discussion it is necessary (due to the short lifetimes involved) to regard the establishment of the labile equilibrium as one limiting case and reaction immediately on formation of a bridged species as the other limiting case. See detailed discussion below.

(47) W. Latimer, "Oxidation Potentials," Prentice Hall, Inc., Englewood Cliffs, N. J., 1952.

(48) For example see R. D. Cannon and J. E. Earley, *J. Am. Chem. Soc.*, **87**, 5264 (1965); **88**, 1872 (1966).

TABLE IV

ACTIVATION PARAMETERS FOR THE Cr^{2+} REDUCTIONS OF Co(III) COMPLEXES

Complex[a]	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal[b]
cis-$RClNH_3^{2+}$(7)	-2.0 ± 3	-41 ± 4	10.0
cis-$RClH_2O^{2+}$(4)	1 ± 4	-29 ± 11	9.8
cis-$RClpy^{2+}$(4)	8 ± 7	-3 ± 24	9.2
cis-$RClNH_2C_6H_{11}^{2+}$(3)	-17 ± 5	-90 ± 15	9.7
cis-RCl_2^{+}(3)	-6 ± 4	-51 ± 10	9.4
cis-$RClF^{+}$(5)	-10 ± 3	-65 ± 13	9.3
trans-RCl_2^{+}(2)	-8 ± 6	-53 ± 30	8.3
trans-RF_2^{+}(3)	-0.1 ± 3	-33 ± 11	9.8
cis-RFH_2O^{2+}(3)	0.0 ± 6	-34 ± 20	10.4

[a] Number of experiments in parentheses. R = Co(en)$_2$. Using data from Table I. [b] At 25°.

calculate the slopes and intercepts of log (k_{obsd}/T) *vs.* $1/T$[27] using data from Table I. These calculations have been independently checked in each case by determining the slopes graphically using the mean values of lines of maximum and minimum slopes drawn through the data points. Activation parameters calculated by these two techniques agree to within the stated error limits. The limited temperature range of the observations and the relatively large errors (10–15%) in the stopped-flow determination are reflected in relatively imprecise $\Delta H^{\ddagger}$ values (±5–6 kcal). Even taking account of the maximum possible errors, no more than four of the nine Cr^{2+}–Co(III) reactions represented in Table IV can possibly have $\Delta H \geq 4$ kcal. Many of these reactions clearly have $\Delta H^{\ddagger} < 0$. It can only be concluded that the formation and dissociation of precursor complexes (II, III) are very important features of these reactions.

TABLE V

COMPARISON OF ACTIVATION PARAMETERS FOR ELECTRON-TRANSFER REACTIONS OF COBALT(III)

	Reductant									
	Cr^{2+}	V^{2+}	Fe^{2+} [a]	Cu^{+} [b]	$Ru(NH_3)_6^{2+}$	Cr^{2+}	V^{2+}	Fe^{2+} [a]	Cu^{+} [b]	$Ru(NH_3)_6^{2+}$
Oxidant	$\Delta H^{\ddagger}_{obsd}$, kcal					$\Delta S^{\ddagger}_{obsd}$, eu				
$Co(NH_3)_5F^{2+}$	...	...	14 ± 1	12.4 ± 0.3	13.4 ± 0.4[c]	...	...	-23 ± 5	-17 ± 1	-17 ± 1[c]
$Co(NH_3)_5Cl^{2+}$	...	...	12 ± 1	0.3 ± 0.3	6.9 ± 1	...	...	-30 ± 5	-19 ± 1	-27 ± 4
$Co(NH_3)_5Br^{2+}$	...	9.1[d]	13 ± 1	3.9 ± 0.2	11 ± 1	...	-22[d]	-28 ± 5	-20 ± 1	-8 ± 5
$RClNH_3^{2+}$ [e]	-2 ± 3	...	...	...	12 ± 1	-41 ± 4	...	...	...	-15 ± 3
$RClpy^{2+}$ [e]	8 ± 7	...	...	...	8.4 ± 0.4	-3 ± 24	...	...	...	-18 ± 2
$RClOH_2^{2+}$ [e]	1 ± 4	...	...	...	7.2 ± 0.6	-29 ± 11	...	...	...	-24 ± 2

[a] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965). $\mu = 1.0$. [b] Reference 33. [c] Reference 27. $\mu = 0.20$. [d] Reference 24. $\mu = 1.0$. [e] This work and ref 12. R = *cis*-Co(en)$_2$.

B. Comparisons of Activation Parameters in Reductions of Cobalt(III) Complexes.—Activation parameters for a number of reductions of cobalt(III) complexes are compared in Table V. The entropies of activation for the $Ru(NH_3)_6^{2+}$ reactions (Table II, this work; Table IV, ref 9) seem to be relatively reliable. It is clear that the observed values are far from constant, exhibiting a range of 20 ± 8 eu for reactions run under similar conditions; however, the average value of $\Delta S^{\ddagger}$ for these reactions is -18 ± 5 eu. This rather small amount of scatter (only two reactions are as much as two standard deviations from the mean value) suggests that factors contributing to $\Delta S^{\ddagger}$ do not vary much for these outer-sphere reactions. Since charge types and dipolar character are similar for all of these reactants, this seems a reasonable observation. At an ionic strength of 1, $\Delta S^{\ddagger} > 0$ for the $Ru(NH_3)_6^{2+}$–$Co(NH_3)_5Br^{2+}$ reaction (Table III).

The values of $\Delta S^{\ddagger}$ for the Cr^{2+}–Co(III) reactions (Table IV) have about one-third the precision of the corresponding $Ru(NH_3)_6^{2+}$ reactions. Despite the larger uncertainties involved, the Cr^{2+} reactions generally have more negative values of $\Delta S^{\ddagger}$ (for the nine values cited in Table IV, $\Delta S^{\ddagger} = -44 \pm 16$ eu). The generally more negative entropies of activation are consistent with the inner-sphere mechanism for the Cr^{2+} reactions.[22] It is likely that the lack of correlation of $\Delta S^{\ddagger}$ with the mechanism of reactions noted previously [20,23] was partly the result of comparing reactions which are very dissimilar (*e.g.*, with different bridging groups). However, the very large *range* of $\Delta S^{\ddagger}$ values (±40 eu) for the Cr^{2+} reactions suggests that another reason for the frequently poor correlation of $\Delta S^{\ddagger}$ and activated complex geometry may arise from the variable limiting behavior (*i.e.*, $k_{obsd} \rightarrow K_1k_2$ or $k_{obsd} \rightarrow k_1$) possible in Cr^{2+} reactions. Finally it is likely that the geometry of the activated complex is not the only factor contributing to $\Delta S^{\ddagger}$. Thus if the V^{2+}–$Co(NH_3)_5Br^{2+}$ reactions proceed by means of an outer-sphere mechanism,[19,23] then the greater than 22-eu difference in $\Delta S^{\ddagger}$ for the V^{2+} and $Ru(NH_3)_6^{2+}$ reactions suggests that other than purely electrostatic factors make large contributions to $\Delta S^{\ddagger}$ even in outer-sphere reactions.

For those reactions whose mechanism is inner sphere, there are two important factors to consider in comparing activation parameters. Firstly, both $\Delta H^{\ddagger}_{obsd}$ and $\Delta S^{\ddagger}_{obsd}$ may have contributions due to precursor complex formation.[49] Thus if Fe^{2+} and Cu^{+} react by means of an inner-sphere mechanism and if precursor complexes have negative enthalpies of formation (as often seems to be the case in the Cr^{2+} reactions), then the enthalpy of activation, $\Delta H_2^{\ddagger}$, for the electron-transfer step may be much greater than $\Delta H^{\ddagger}_{obsd}$.[3]

In order to examine the comparison of inner-sphere and outer-sphere reactions in greater detail, it is useful to break (1) up into the additional components (4)–(6).[50]

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(49) That is, in the limit that $k_{obsd} = K_1k_2$, $\Delta H^{\ddagger}_{obsd} = \Delta H_1^{\circ} + \Delta H_2^{\ddagger}$ and $\Delta S^{\ddagger}_{obsd} = \Delta S_1^{\circ} + \Delta S_2^{\ddagger}$.

(50) In eq 4–6 the species formulated as $[L_6M^{2+}]\cdot[X\text{-}{}^*M^{3+}L_5]$ is to be regarded as a pair of reactants "trapped" by the solvent matrix at less than the critical reaction distance. The formation of such species is to be regarded as diffusion controlled and their lifetimes are expected to be in the range 10^{-11}–10^{-12} sec.

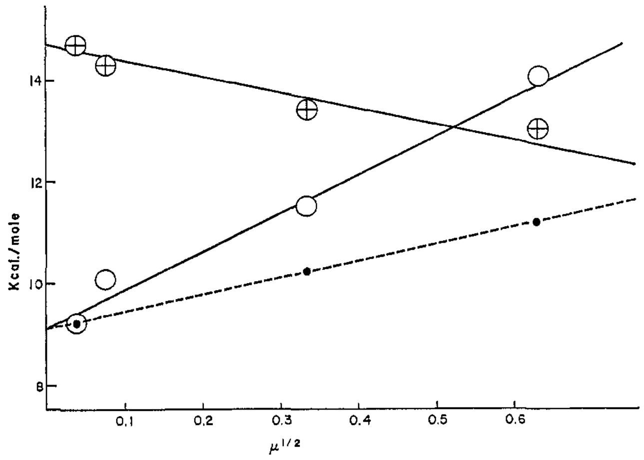

Figure 1.—Ionic strength dependence of activation parameters for the $Ru(NH_3)_6^{2+}$ reduction of $Co(NH_3)_5Br^{2+}$. Observed quantities: ○, E_a; ⊕, $\Delta F\dagger$. Theoretical (Debye-Hückel): ●, E_a.

$$ML_6^{2+} + {}^*ML_5X^{3+} \rightleftharpoons [L_6M^{2+}]\cdot[X-{}^*M^{3+}L_5] \qquad (4)$$

$$[L_6M^{2+}]\cdot[X-{}^*M^{3+}L_5]\begin{cases} \rightleftharpoons L_5M^{2+}-X{}^*M^{3+}L_5 + L & (5)\\ \rightleftharpoons [L_6M^{3+}]\cdot[X-{}^*M^{2+}L_5] & (6)\end{cases}$$

Then for an outer-sphere reaction $k_{obsd} = K_4k_6$ while in the limiting case of precursor complex formation in inner-sphere reactions $k_{obsd} = K_4K_5k_2$. It is not an unreasonable assumption that some of the factors determining the magnitudes of k_6 and k_2 are the same.[12,51] Thus for cobalt(III) complexes with the same "bridging ligand" the ratios k_{obsd}(inner sphere)/k_{obsd}(outer sphere) would be expected to vary partly in their values of K_5. It must be at least partly this parameter which gives rise to the different patterns in "nonbridging ligand" effects.

Unfortunately comparisons involving the Cr^{2+} reactions are ambiguous owing to the different possible limiting kinetic behavior discussed above. This point may be illustrated by consideration of the Cr^{2+} reductions of *cis*-$Co(en)_2pyCl^{2+}$ and *cis*-$Co(en)_2NH_2C_6H_{11}Cl^{2+}$. These two reactions differ only by a factor of ~2 in their values of k_{obsd} at 25° (Table I), but they exhibit a difference of at least 10 kcal in their values of $\Delta H^{\ddagger}_{obsd}$. The maximum value of $\Delta H^{\ddagger}_{obsd}$ for the *cis*-$Co(en)_2NH_2C_6H_{11}Cl^{2+}$ reaction is ~ −10 kcal. If the factors affecting $\Delta H_4°$ and $\Delta H_2^{\ddagger}$ are similar to those affecting the analogous outer-sphere reactions, then $(\Delta H_4° + \Delta H_2^{\ddagger}) > 0$ kcal and $\Delta H_5° < 10$ kcal for cyclohexylamine complex. If the entropies of activation (*i.e.*, $\Delta S_2^{\ddagger}$) are about the same for these two cobalt(III) complexes, then actual values of $\Delta H_2^{\ddagger}$ differ by more than 10 kcal and the actual values of k_2 could be vastly different (*i.e.*, by a factor of ~10^7).[52] This would indeed be a very large nonbridging ligand effect. However it is possible that both of these reactions do not meet conditions for the $k_{obsd} \approx K_4K_5k_2$ limit. In fact the value of $\Delta H^{\ddagger} \geq 1$ kcal/mol for the Cr^{2+}–*cis*-$Co(en)_2pyCl^{2+}$ reaction suggests that this system may be approaching the $k_{obsd} \approx K_4k_5$ limit. Thus it is likely (using (1) to describe the over-all formation of a binuclear intermediate) that k_{-1} for *cis*-$Co(en)_2NH_2C_6H_{11}Cl^{2+}$ is much greater than k_{-1} for *cis*-$Co(en)_2pyCl^{2+}$. The variations of specific rates k_{obsd} and values of $\Delta H^{\ddagger}_{obsd}$ suggest that the Cr^{2+}–$Co(am)_5Cl^{2+}$ reactions span the range of rate-determining behavior, *i.e.*, that $K_4K_5k_2 \leq k_{obsd} \leq K_4k_5$.

A final difficult point is raised by the ionic strength dependence of activation parameters. Some variation of activation energy is to be expected from the theory of ionic interactions in polar media.[53] The observed variation of E_a for the $Ru(NH_3)_6^{2+}$–$Co(NH_3)_5Br^{2+}$ reaction is greater than predicted (see Figure 1). This may indicate that in concentrated ionic media a few kilocalories of energy are expended rearranging the ionic atmosphere of the reactants before electron transfer. There is no reason to expect the same kind of ionic strength dependence of the activation parameters for inner-sphere and outer-sphere reactions. Not only is there an additional step (involving change of dipole moment) in the former mechanism, but the reactants do not have to approach the collision complex (step 4) in any sense activated; *i.e.*, activation energy can be accumulated in the precursor complex after its formation.

C. Concerning Linear Free Energy Reactions.—

We recently suggested a means of correlating inner-sphere and outer-sphere reactions by means of a free energy relation.[12] Our approach has been modified by Guenther and Linck,[19] who suggested a more general correlation of the form[54]

$$\log k_{red} = a \log k_{Ru(NH_3)_6^{2+}} + b \qquad (7)$$

for the specific rates of reduction of various cobalt(III) complexes by $Ru(NH_3)_6^{2+}$ and by some other reducing agent, "red." The present study suggests that precursor complex formation must seriously limit the precision of any correlation such as (7). This limitation should be most severe for reactions such as those of Cr^{2+} where a variety of limiting kinetic behavior is possible as discussed above. However within the limits of applicability of the $k_{red} \approx K_4K_5k_2$ limit and setting $k_{Ru(NH_3)_6^{2+}} = K_4'k_6'$

$$\log k_2 \simeq a \log k_6 + (\log (K_4')^a/K_4) - \log K_5 + b$$

or for $a \approx 1$ and $K_4' \approx K_4$

$$\log k_2 \approx a \log k_6 - \log K_5 + b$$

If the lifetime of the precursor complexes is always short compared to the lifetime (*i.e.*, $1/k_2$) for electron transfer, then our previous calculations (Tables V and VI, ref 12) should be corrected in the amount of $\log K_5$. Examination of data in Table VI of ref 12 suggests that often $K_5 \approx 10^{1\pm1}$ (assuming $a \approx 1$) for Cr^{2+} reactions. However inversion of the orders of reactivity of some of the Cr^{2+} (compared to $Ru(NH_3)_6^{2+}$) reactions, the large range of different temperature coefficients, and the ambiguities noted above imply that our original opto-

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(51) It is necessary to keep account of the differences in the free energy changes involved in inner-sphere and outer-sphere reactions.[11]

(52) Values of $\Delta S_2^{\ddagger}$ are expected to vary, by analogy with the cases of outer-sphere reactions discussed above.

(53) See E. A. Moelwyn-Hughes, "Physical Chemistry," Pergamon Press, New York, N. Y., 1957.

(54) In (7) k_{red} is the value of k_{obsd} for some reducing agent "red," $k_{Ru(NH_3)_6^{2+}}$ is k_{obsd} for $Ru(NH_3)_6^{2+}$, and a and b are experimental correlation parameters depending on "red."

mism concerning the generality of linear free energy relations was premature. Of course such correlations are helpful in understanding some of the grosser features of patterns of reactivity.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA—DULUTH, DULUTH, MINNESOTA 55812

Dissociation Kinetics of Metal Ion–2,6-Dicarboxypiperidineacetic Acid Complexes: Nickel(II) and Cadmium(II)

BY T. J. BYDALEK, T. M. STOKICH, AND D. M. COLEMAN

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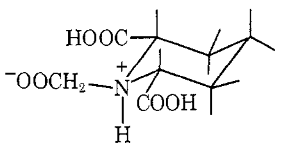
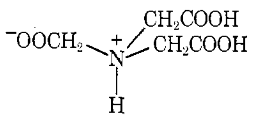
The kinetics of the dissociation of the nickel(II) and cadmium(II) complexes of 2,6-dicarboxypiperidineacetic acid (DPA) have been measured. For the NiDPA dissociation, the results are consistent with the rate law $-d[\mathrm{NiDPA}]/dt = (k_{\mathrm{Cu}}{}^{\mathrm{NiDPA}} \cdot [\mathrm{Cu^{2+}}] + k_{\mathrm{H}}{}^{\mathrm{NiDPA}}[\mathrm{H^+}] + k_{\mathrm{H^2}}{}^{\mathrm{NiDPA}}[\mathrm{H^+}]^2)[\mathrm{NiDPA}]$. The values of the rate constants at 25.0 ± 0.1° and the activation energies are, respectively: $(3.0 \pm 0.3) \times 10^{-3}\ M^{-1}\ \mathrm{sec}^{-1}$, 12.2 ± 1 kcal mol^{-1}; $(8.0 \pm 0.2) \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$, 14.3 ± 1 kcal mol^{-1}; $(2.95 \pm 0.09) \times 10^{2}\ M^{-2}\ \mathrm{sec}^{-1}$, 12.1 ± 0.5 kcal mol^{-1}. For the CdDPA dissociation, the rate law is $-d[\mathrm{CdDPA}]/dt = (k^{\mathrm{CdDPA}} + k_{\mathrm{H}}{}^{\mathrm{CdDPA}}[\mathrm{H^+}] + k_{\mathrm{H^2}}{}^{\mathrm{CdDPA}}\ [\mathrm{H^+}]^2)[\mathrm{CdDPA}]$. The values of the rate constants at 25.0 ± 0.1° are $4.9 \pm 0.4\ \mathrm{sec}^{-1}$, $(3.3 \pm 0.3) \times 10^{5}\ M^{-1}\ \mathrm{sec}^{-1}$, and $(5.1 \pm 0.2) \times 10^{9}\ M^{-2}\ \mathrm{sec}^{-1}$, respectively.

Introduction

Recently the preparation and metal ion stability constants of 2,6-dicarboxypiperidineacetic acid (DPA) have been reported.[1] The ligand possesses the same bonding groups as nitrilotriacetic acid, but the nitrogen and the α carbons of two of the three acetate groups form part of a six-membered saturated ring. Nmr data[1b] indicate that the three substituents on the ring are all in equatorial positions as shown. Models suggest that the ring holds these two acetate groups in close proximity to the central metal ion and therefore the dissociation of the metal complex may be hindered.



DPA



NTA

The present study investigates the effect of the ring structure on the dissociation reactions of the nickel(II) and cadmium(II) complexes. The rates of dissociation of these complexes can be compared to the rates of dissociation of the nitrilotriacetate (NTA) complexes, which have previously been measured. In the case of nitrilotriacetatonickelate(II)[2] and other nickel systems,[3,4] the reaction has been postulated to proceed through dinuclear intermediates with the breaking of the nickel–nitrogen bond being the rate-determining step. Studies of the nitrilotriacetatocadmate(II)[5] dissociation suggest that the reaction pathways are similar to those observed with nitrilotriacetatonickelate(II), but the rate-determining step has not been elucidated.

The dissociation of the nickel(II) complex was followed by conventional spectrophotometry, measuring the exchange with copper(II). The data are consistent with the chemical system

$$\mathrm{NiDPA^-} + \mathrm{Cu^{2+}} \xrightarrow{k_{\mathrm{Cu}}{}^{\mathrm{NiDPA}}} \mathrm{CuDPA^-} + \mathrm{Ni^{2+}} \qquad (1)$$

$$\mathrm{NiDPA^-} + \mathrm{H^+} \xrightarrow{k_{\mathrm{H}}{}^{\mathrm{NiDPA}}} \mathrm{Ni^{2+}} + \mathrm{HDPA^{2-}} \qquad (2)$$

$$\mathrm{NiDPA^-} + 2\mathrm{H^+} \xrightarrow{k_{\mathrm{H^2}}{}^{\mathrm{NiDPA}}} \mathrm{Ni^{2+}} + \mathrm{H_2DPA^-} \qquad (3)$$

$$\mathrm{Cu^{2+}} + \begin{bmatrix}\mathrm{HDPA^{2-}}\\ \mathrm{H_2DPA^-}\end{bmatrix} \xrightarrow{\text{rapid}} \mathrm{CuDPA^-} + \begin{bmatrix}\mathrm{H^+}\\ \mathrm{2H^+}\end{bmatrix} \qquad (4)$$

The dissociation of the cadmium(II) complex is much faster and was followed by the analysis of the kinetic wave observed in conventional polarography. The data can be expressed by the equations

$$\mathrm{CdDPA^-} \xrightarrow{k^{\mathrm{CdDPA}}} \mathrm{Cd^{2+}} + \mathrm{DPA^{3-}} \qquad (5)$$

$$\mathrm{CdDPA^-} + \mathrm{H^+} \xrightarrow{k_{\mathrm{H}}{}^{\mathrm{CdDPA}}} \mathrm{Cd^{2+}} + \mathrm{HDPA^{2-}} \qquad (6)$$

$$\mathrm{CdDPA^-} + 2\mathrm{H^+} \xrightarrow{k_{\mathrm{H^2}}{}^{\mathrm{CdDPA}}} \mathrm{Cd^{2+}} + \mathrm{H_2DPA^-} \qquad (7)$$

$$\begin{tikzcd} \underbrace{\mathrm{Cd^{2+}} \rightleftharpoons \mathrm{CdOAc^{+}}} \arrow[d, "+2e"] \\ \mathrm{Cd(amal)} \end{tikzcd} \qquad (8)$$

In acetate media, free $\mathrm{Cd^{2+}}$ (produced in eq 5–7) and cadmium acetate complexes are in rapid equilibrium and these species undergo rapid electrochemical reac-

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[1] (a) S. K. Kundra and L. C. Thompson, *J. Inorg. Nucl. Chem.*, **30**, 1847 (1968); (b) L. C. Thompson and S. K. Kundra, *Inorg. Chem.*, **7**, 338 (1968).

[2] T. J. Bydalek and M. L. Blomster, *Inorg. Chem.*, **3**, 667 (1964).

[3] T. J. Bydalek and D. W. Margerum, *ibid.*, **2**, 678 (1963).

[4] T. J. Bydalek and A. H. Constant, *ibid.*, **4**, 833 (1965).

[5] J. Koryta, *Collection Czech. Chem. Commun.*, **24**, 3057 (1959).