

apical coordination of the fifth donor group must be assumed for 3.

Conclusions

The present study shows that rate constants and spectra of complexes can be obtained from EPR solution spectra.

The use of appropriate mathematical methods allows one to do the numerical evaluation in a straightforward manner even on a desk computer. Only initial estimates for the rate constants are necessary, while no information with regard to the spectra of the complexes is needed. No care has to be taken to select the data such that only distinct complexes give rise to a signal, since by doing the calculation on the complete data set simultaneously, all the information from the measurement is used.

Eigenvector representation not only yields the number of absorbing species but allows one to do the numerical treatment using minimal computer time and memory.

The spectra of the different chemical species are easily obtained, and valuable structural information can be derived from this. While this is also true for spectrophotometry, the EPR method has the advantage that the spin concentrations can be calculated for each complex, which helps to confirm the results of the mathematical analysis.

The results of this study show that EPR spectroscopy indeed is a useful method for the elucidation of reaction mechanisms. Because the mathematical evaluation of the data is straightforward, EPR measurements should be included in kinetic studies whenever possible.

Acknowledgment. Dr. M. Maeder provided the ligand, and Prof. F. Gerson allowed to use his EPR spectrometer (both from the University of Basel). This work was supported by the Swiss National Science Foundation (Grant No. 2.213-0.81).

Registry No. 1, 91994-70-6; 2, 91994-71-7; 3, 91994-72-8.

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Effect of Anions on Redox Reactions. 1. Chromium(II) Reduction of Bis(pentane-2,4-dionato)(ethylenediamine)cobalt(III) in the Presence of Chloride Ions

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Received October 25, 1983

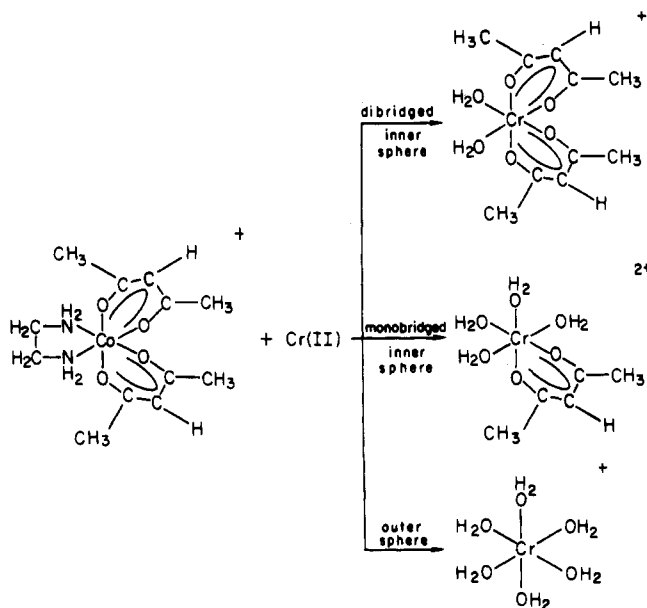
The effect of chloride ions on the Cr(II) reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$ was studied. The rate for the outer-sphere pathway was twice that of the uncatalyzed reaction ($k(25.0^\circ\text{C}) = (4.86 \pm 0.04) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 17 \pm 1 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -13 \pm 3 \text{ eu}$) whereas the rates for the inner-sphere pathways were practically unaffected. The kinetic parameters for the monobridged pathway were $k(25.0^\circ\text{C}) = (2.97 \pm 0.02) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and those of the dibridged path were $k(25.0^\circ\text{C}) = (1.46 \pm 0.02) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $\Delta H^\ddagger = 13 \pm 1 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -27 \pm 1 \text{ eu}$. No chloride could be detected in the inner-sphere electron-transfer products.

Introduction

It has been recognized for a very long time¹ that redox reactions between like-charged ions in solution may be markedly accelerated by the presence of ions of the opposite charge. It is generally assumed that the ion catalyst operates by coordinating to one of the reactants, thereby lowering the charge on this complex and reducing the Coulombic repulsion between the reacting species. The purpose of the present investigation was to see if there are substantial differences between the way the ion catalyst affects an outer-sphere as opposed to an inner-sphere process. The ultimate aim of this approach was to try to find a method involving ion catalysis that would allow one to distinguish between these two possible mechanisms of electron transfer, especially in cases in which the product criterion fails.²

The model reaction we have used to investigate this effect is the Cr(II) reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$ (where ptdn is the abbreviation used for pentane-2,4-dionato, also called acetylacetonato or acac) in the presence of chloride ions. This reaction was selected because, at least in perchlorate media,^{3,4} the reduction proceeded simultaneously by all three possible

mechanisms—outer sphere, monobridged inner sphere, and dibridged inner sphere.



Thus, we would be able to look at the effects of anions on all three mechanisms for identical reactants under identical

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conditions, making comparisons among the three pathways easy and meaningful.

Experimental Section

Reagents. The complex, bis(pentane-2,4-dionato)(ethylenediamine)cobalt(III) was made following a literature procedure⁵ and was purified by ion exchange on Sephadex (SP-C-25 120). The pure complex was eluted from the resin with 0.5 M NaClO₄ (G. Frederick Smith Chemical Co.). Addition of solid NaClO₄ caused the purple crystals of [Co(en)(ptdn)₂]ClO₄ to precipitate. This complex was recrystallized several times from purified water as described previously⁶ by addition of NaClO₄ to a concentrated aqueous solution of the crystals.

Anhydrous grade lithium chloride was obtained from G. Frederick Smith and was used as received to prepare stock solutions for ionic strength control. These solutions were standardized by determining titrimetrically the amount of hydrogen ion released from an Amberlite IR-120(H) analytical grade resin (BDH Chemicals Ltd.).

The acidity of the kinetic runs and product analyses was adjusted with a stock solution of HCl (1.000 M, Dilut-it, J. T. Baker Chemical Co.). The chromium(II) solutions were made by reducing chromic chloride in a 0.2 M HCl solution in the absence of air.

All standard solutions were stored under high-purity argon and were handled by using standard syringe techniques in an argon atmosphere.

Product Analyses. Two preliminary large-scale product analyses were performed at room temperature. In the first case, 830 μmol of [Co(en)(ptdn)₂]⁺ were reacted with 2175 μmol of Cr(II) in 100 mL of a 0.10 M HCl solution (μ = 1.00 M (LiCl)) for 13 h, and in the second instance 488 μmol of the same oxidant were reacted with 1100 μmol of the reductant. Each reaction mixture was then oxidized with a stream of air, diluted 10 times with distilled water, and ion exchanged on Dowex 500W-X8(200) in a cold room (5 °C). The eluent obtained upon charging the column and washing it with several column volumes of water was collected and analyzed spectrophotometrically for uncharged products. The UV spectrum showed the presence of the free ligand (ptdnH) followed by a neutral ptdn-substituted Cr(III) complex. The chromium species was contaminated with the free ligand, which absorbs at 277 nm (ε = 1900 M⁻¹ cm⁻¹).⁴ As a result, the complete UV spectrum of the metal complex could not be determined. However, it had an extinction coefficient of 7600 ± 300 at 330 nm where the absorption of the free ligand is negligible. The neutral [Cr(ptdn)₃] compound has an extinction coefficient that is double this value at 331 nm.⁹ It was therefore ruled out as a possible product of this reaction.

Increasing concentrations of a solution containing NaClO₄ and HClO₄ up to a maximum of 0.5 M NaClO₄ in 0.1 M HClO₄ were used to elute the chromium(III) inner-sphere products. Two distinct purple bands were observed on the column. These were removed and analyzed spectrophotometrically. A blue band of [Cr(OH₂)₆]³⁺ and the green chromium(III) dimer remained on the column. These were not estimated quantitatively.

The first of the two purple bands formed on the column was eluted as a monovalent ion and the second was eluted as a divalent species. The band eluted first may contain [Cr(ptdn)₂(OH₂)₂]⁺ and [Cr(ptdn)(Cl)(OH₂)₃]⁺. The UV spectra from this band are in good agreement with the published spectrum of [Cr(ptdn)₂(OH₂)₂]⁺ whereas, the chloride-substituted compound would be expected to have a spectrum very similar to that of [Cr(ptdn)(OH₂)₄]²⁺. This implies that very little of the chloride-substituted product was present. The band eluted as a divalent species may contain [Cr(OH₂)₅(Cl)]²⁺ and [Cr(ptdn)(OH₂)₄]²⁺. The former ion does not absorb in the UV region of the spectrum so that the quantity of this species present could easily be estimated by taking the difference between the total chromium present by analysis and the amount of [Cr(ptdn)(OH₂)₄]²⁺ present as determined from the UV spectrum. Chromium concentrations were determined spectrophotometrically as chromate.⁷ Several attempts were made to separate the [Cr(OH₂)₅(Cl)]²⁺ complex from the [Cr(ptdn)(OH₂)₄]²⁺ species. If the separation on the column were done very slowly, the green [Cr(OH₂)₅(Cl)]²⁺ band could be seen

forming under the purple 2+ band but a complete separation was never achieved.

The remainder of the product studies were carried out quantitatively in smaller batches. About 82–85 μmol of [Co(en)(ptdn)₂]ClO₄ were reacted with a 3- to 10-fold excess of Cr(II) in 10 mL of a 0.10 M HCl solution (μ = 1.00 M (LiCl)) for at least 5 half-lives at 25, 35, and 45 °C. After the reaction was completed, the solution was diluted to 200 mL and the excess Cr(II) was oxidized by bubbling a vigorous flow of air through the mixture for 5 min. The solution was further diluted to 500 mL and was ion exchanged on a Dowex 50W-X8 (200) column. The first purple compound, [Cr(ptdn)₂(OH₂)₂]⁺ came out by eluting with a mixture of 0.063 M NaClO₄ in 0.013 M HClO₄. The second purple band containing [Cr(ptdn)(OH₂)₄]²⁺, [Cr(OH₂)₅(Cl)]²⁺, and [Co(OH₂)₆]²⁺ was eluted with a solution of 0.5 M NaClO₄ in 0.10 M HClO₄.

A series of blank experiments was also performed at each of the temperatures at which the kinetics and product studies were done. In the blanks, no cobalt(III) complex was present. Instead, the free ligand, pentane-2,4-dione, was added in an amount equal to that which would have been present if all of the [Co(en)(ptdn)₂]⁺ had reacted by an outer-sphere pathway. The free ligand was added in five portions: half of the total was added at the beginning of the reaction, half of the remainder was added after the half-time, and the process was continued until the fifth half-time. This approximates an exponential generation of free ligand.

All UV spectra were run on a Perkin-Elmer Model 330 spectrophotometer.

Kinetic Measurements. The rates of reduction of [Co(en)(ptdn)₂]⁺ by Cr(II) in 1.0 M chloride media were determined by watching the decrease of the d → d absorption band of the oxidant at 537 nm, on a Hitachi EPS-3T spectrophotometer. The water temperature was maintained by a Lauda NB-D bath having an R2U electronic relay unit. A small probe was inserted into the metal cell holder and a YSI Model 72 proportional temperature controller sensed the temperature of this probe and controlled it to the desired value. The actual temperature of this probe was monitored by an ASTM thermometer calibrated from 0 to 50 °C (Fisher Scientific) inserted into a duplicate cell. All components of the reaction mixture were allowed to equilibrate in the cell before the reductant, Cr(II), was added to initiate the reaction. All reactions were carried out under pseudo-first-order conditions; i.e., the reductant was always present in greater than 20-fold excess over the oxidant. The ionic strength was controlled to 1.00 in each experiment with the standard LiCl solution.

Results

Product Analyses. The first mixtures for product analyses were allowed to react for 5 half-times at each of the three temperatures at which the kinetics were studied. Since there is a possibility of substitution of pentane-2,4-dione and chloride on the chromium(III) or aquation of these ligands from a chromium(III) product after the act of electron transfer, each set of analyses was also performed after about 10 half-lives. If no substantial differences are observed, then it is reasonably safe to assume that neither substitution nor aquation of chromium(III) products occurs during the time frame of this experiment.

The results are given in Table I. Although no startling differences were observed between the two sets of data indicating that neither substitution nor aquation of the Cr(III) products is a serious problem, a set of blank experiments was also performed at each temperature. These studies showed that a surprising amount of uncharged Cr(III) species are formed. Chloride does not add to Cr(III) alone to give an uncharged chromium(III) complex in the time interval employed in these experiments,⁸ and pentane-2,4-dione also does not produce an uncharged chromium(III) species in such a short time.⁴ The chromium(III) uncharged product, then, likely contains both ligands. The UV spectra (λ, nm (ε)) of this material from the electron-transfer experiments (330 (7500 ± 300)) and from the blank studies (330 (7600 ± 300))

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Table I. Product Analysis Data for the Chloride-Assisted Cr(II) Reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$ in $[\text{H}^+] = 0.10 \text{ M}$ (HCl) and $\mu = 1.00 \text{ M}$ (LiCl)

temp, °C	time, min	[Co(III)], μmol used	[Cr(II)], μmol used	[uncharged Cr(III)], μmol recovered	[monopositive Cr(III)], μmol recovered	[dipositive Cr(III)], ^a μmol recovered	
						CrO ₄ ²⁻ anal.	UV
25.0	90	84.8	827	14.7	13.5	54.0	26.8
	90	84.5	827	14.8	13.2	52.3	27.6
	240	82.3	827	12.1	13.5	52.3	27.7
	240	84.0	827	10.4	12.1	50.3	25.1
	90	blank	827	8.0	1.80	25.3	1.1
	90	blank	827	11.2	1.76	18.6	0.96
35.0	31	82.5	827	14.7	11.7	52.3	23.0
	31	82.9	827	14.5	11.9	54.0	24.1
	60	83.5	832	11.5	12.3	52.3	30.1
	60	83.1	827		13.0	54.0	28.6
	31	blank	827	8.10	2.99	19.4	1.52
	31	blank	827	6.76	3.12	30.7	1.47
45.0	16	81.0	827	17.4	9.20	54.0	22.5
	16	82.4	827	13.8	11.6	55.7	22.8
	30	83.0	827	13.8	9.30	59.8	31.0
	30	82.8	827	12.9	10.8	60.6	36.1
	16	blank	832	8.00	2.80	24.9	1.49
	16	blank	832	8.40	2.50	27.4	1.75

^a The difference in values obtained by CrO₄²⁻ analysis and UV spectroscopy reflects the fact that considerable $[\text{Cr}(\text{OH}_2)_5(\text{Cl})]^{2+}$ is present in this band, as well as $[\text{Cr}(\text{OH}_2)_4(\text{ptdn})]^{2+}$. The CrO₄²⁻ procedure gives the sum of these two species whereas the UV method measures only the inner-sphere product, $[\text{Cr}(\text{OH}_2)_4(\text{ptdn})]^{2+}$ (see Experimental Section).

indicate that it is likely $[\text{Co}(\text{ptdn})(\text{Cl})_2(\text{OH}_2)_2]$ since the spectrum is very similar to that of the known compound $[\text{Cr}(\text{ptdn})(\text{OH}_2)_4]^{2+}$ (326 (8150 ± 70), 253 (4310 ± 30))⁴ and is very different from that of $[\text{Cr}(\text{ptdn})_3]$ (335 (15800))⁹ and $[\text{Cr}(\text{ptdn})_2(\text{OH}_2)_2]^+$ (328 (14000 ± 300), 256 (9200 ± 200)).⁴

The $[\text{Cr}(\text{ptdn})(\text{Cl})_2(\text{OH}_2)_2]$ in the blank studies does not arise from substitution of these ligands on Cr(III). In the time frame of these experiments, and under the same conditions of temperature and concentration, no $[\text{Cr}(\text{ptdn})(\text{Cl})_2(\text{OH}_2)_2]$ was formed from a mixture of $[\text{Cr}(\text{OH}_2)_6]^{3+}$, pentane-2,4-dione, and chloride ions. The uncharged product must, therefore, arise from the capture of a pentane-2,4-dione ligand and two chloride ions in the first coordination sphere of the excess Cr(II) in the reaction mixture as it was being oxidized by bubbling air through the solution. From Table I, the amount of uncharged product arising from the blank experiments can be seen to be always less than was recovered from the kinetic experiments. However, these lower values and the rather large variability in the results from the blank experiments are undoubtedly due to the difficulties encountered in reproducing these air-oxidation experiments exactly. Similar substitution results were observed in the uncatalyzed experiments, with the monosubstituted pentane-2,4-dionato product again being the predominant species formed.⁴ It seems likely that the $[\text{Cr}(\text{ptdn})(\text{Cl})_2(\text{OH}_2)_2]$ recovered from the kinetic experiments is from the capture of these ligands during the air-oxidation process, and we therefore do not account for this product as a result of electron transfer. If we do in fact make corrections for the presence of this species and other substitution products, the final values of ΔH^\ddagger and ΔS^\ddagger do not change significantly and the final conclusions remain unchanged.

There are two possible ptdn-containing species that may appear in the band that elutes as if it is composed of monopositive cations, i.e. $[\text{Cr}(\text{ptdn})_2(\text{OH}_2)_4]^+$ and $[\text{Cr}(\text{ptdn})(\text{OH}_2)_3(\text{Cl})]^+$. From the UV spectrum of the eluent from this band and assuming that replacement of water by chloride ion does not affect the spectrum appreciably in this region, we infer that the complex is $[\text{Cr}(\text{ptdn})_2(\text{OH}_2)_4]^+$.

Again, two possible compounds may be present in the band of dipositive ions— $[\text{Cr}(\text{ptdn})(\text{OH}_2)_4]^{2+}$ and $[\text{Cr}(\text{OH}_2)_5(\text{Cl})]^{2+}$.

The relative amounts of each of these is easily estimated from the UV spectrum since the spectral characteristics of $[\text{Cr}(\text{OH}_2)_4(\text{ptdn})]^{2+}$ are known⁴ and $[\text{Cr}(\text{OH}_2)_5(\text{Cl})]^{2+}$ does not absorb in this region (see Experimental Section).

Kinetic Results. Kinetic data for the reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$ in a 1.0 M chloride medium are given in Table II. Contributions from each pathway were evaluated by using the results of the product studies, and these are summarized in Table III. No corrections were made for symmetry since it cannot be determined whether all oxygens are equivalent or not.

Discussion

The effect of added chloride on redox reactions involving substitution-inert oxidants and substitution-labile reductants has been investigated in several systems.¹¹⁰⁻¹¹⁶ The conclusions reached by early workers was that rate accelerations were substantial for outer-sphere reactions such as that between hexaamminecobalt(III) and -chromium(II) whereas only small enhancements were noted for the inner-sphere chromium(II) reductions of the fumarate¹⁷ and (acetato) pentaamminecobalt(III)⁷ complexes. Pennington and Haim¹⁵ were further able to show that, in the chloride-catalyzed reduction of $[\text{Co}(\text{NH}_3)_5(\text{Cl})]^{2+}$ by Cr(II), the nonbridging chloride is more effective from the trans than from the cis position in promoting the electron transfer to the cobalt(III) center.

Sutin and Forman¹⁶ noted that the reaction of cytochrome c^{III} with Cr(II) was markedly catalyzed by thiocyanate ions whereas chloride has a negligible effect on this process. To understand this, they looked at the Fe(II) reductions of $[\text{Fe}(\text{phen})_3]^{3+}$ and $[\text{Fe}(\text{bpy})_3]^{3+}$ in the presence of Cl⁻, Br⁻, I⁻, N₃⁻, and SCN⁻. Their conclusion from these experiments was that added anions have very different effects on the rates of reduction of these complexes than they have on "ordinary" electron-transfer reactions. These studies suggested that the

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Table II. Kinetic Data for the Chloride-Assisted Cr(II) Reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$, $\mu = 1.00 \text{ M}$ (LiCl)

temp, ^a °C	$[\text{H}^+]$, ^b M	$10^3[\text{Co(III)}]$, ^b M	$10^2[\text{Cr(II)}]$, ^b M	10^3k_{overall} , $\text{M}^{-1} \text{s}^{-1}$	10^3k_{mono} , $\text{M}^{-1} \text{s}^{-1}$	10^3k_{di} , $\text{M}^{-1} \text{s}^{-1}$	10^3k_{outer} , $\text{M}^{-1} \text{s}^{-1}$
25.0	0.08	8.16	1.85	9.14	2.89	1.45	4.80
					2.99	1.42	4.73
	0.10	8.15	1.90	9.12 ^c	2.88	1.45	4.79
					2.98	1.42	4.72
	0.10	8.15	1.90	9.35 ^c	2.95	1.49	4.91
					3.06	1.46	4.83
	0.10	8.15	1.90	9.35 ^c	2.95	1.49	4.91
					3.06	1.46	4.83
	0.10	8.18	1.82	9.40	2.97	1.49	4.94
					3.07	1.46	4.87
	0.10	8.16	1.86	9.43	2.98	1.50	4.95
					3.08	1.47	4.88
	0.10	8.16	1.80	8.95	2.83	1.42	4.70
					2.93	1.39	4.63
	0.20	8.16	1.86	9.30	2.94	1.48	4.88
					3.04	1.45	4.81
	0.50	8.16	1.86	8.92	2.82	1.42	4.68
					2.92	1.39	4.61
	0.80	8.16	1.88	9.13	2.89	1.45	4.79
					2.99	1.42	4.72
0.80	8.15	1.90	9.23 ^c	2.92	1.47	4.84	
				3.02	1.44	4.77	
0.10	8.16	2.82	9.09	2.87	1.45	4.77	
				2.97	1.42	4.70	
0.10	8.16	9.37	9.54	3.01	1.52	5.01	
				3.12	1.49	4.93	
35.0	0.10	8.16	1.87	23.2	6.47	3.29	13.4
					6.75	3.34	13.1
	0.10	8.16	1.88	22.3	6.22	3.17	12.9
					6.49	3.21	12.6
	0.10	8.15	1.90	22.4 ^c	6.25	3.18	12.8
				6.52	3.23	12.7	
0.10	8.15	1.90	22.8 ^c	6.36	3.24	13.2	
				6.63	3.28	12.9	
45.0	0.10	8.15	1.90	45.6 ^c	12.7	5.20	27.7
					12.6	6.42	26.6
	0.10	8.15	1.90	52.1	14.5	5.94	31.7
					14.4	7.35	30.4
				14.5	5.94	31.7	
				14.4	7.35	30.4	

^a Temperatures are controlled to within ± 0.1 °C. ^b Concentrations are initial values in molar units. ^c These sets of data were obtained with CrCl_3 as the source of Cr(II).

Table III. Summary of the Rate Constants and Activation Parameters for the Chloride-Assisted Cr(II) Reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$

path	medium	k , ^a $\text{M}^{-1} \text{s}^{-1}$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
mono	Cl^-	$(2.97 \pm 0.02) \times 10^{-3}$	13.8 ± 0.9	-24 ± 3
di	Cl^-	$(1.46 \pm 0.02) \times 10^{-3}$	13 ± 2	-27 ± 5
outer	Cl^-	$(4.86 \pm 0.04) \times 10^{-3}$	17 ± 1	-13 ± 3
mono ^b	ClO_4^-	$(2.5 \pm 0.2) \times 10^{-3}$	13.7 ± 0.9	-24 ± 3
di ^b	ClO_4^-	$(2.1 \pm 0.2) \times 10^{-3}$	13 ± 1	-28 ± 5
outer ^b	ClO_4^-	$(2.0 \pm 0.2) \times 10^{-3}$	10 ± 2	-36 ± 7

^a k , the second-order rate constant, was determined at 25.0 °C.

^b These data were taken from ref 3.

porphyrin-ring system of cytochrome *c* is the site of electron transfer with Cr(II).

The most comprehensive set of experiments on anion-assisted outer-sphere reactions was reported by Przystas and Sutin in 1973.¹⁰ They looked at the reductions of $[\text{Co}(\text{en})_3]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{Co}(\text{phen})_3]^{3+}$ by Cr(II) and V(II) in the presence of perchlorate, chloride, and thiocyanate. The results were interpreted in terms of the orbital symmetries of the electron donor, the electron acceptor, and the added anion. These investigators proposed that the anion was coordinated to the reducing agent and that it was between the two metal centres, i.e. in the outer coordination sphere of the oxidizing agent. Their reasoning was based on the idea that it is very favorable electrostatically to have the anion between the positively charged metals.

In our experiments, we were interested in comparing the magnitude of the catalytic effect of anions on inner-sphere and outer-sphere processes occurring in the same system. Table III lists the rate constants and activation parameters for the reduction of $[\text{Co}(\text{en})(\text{ptdn})_2]^+$ in both perchlorate and chloride media. Within experimental error, the two inner-sphere paths have identical activation parameters regardless of the anion present, whereas significant differences were found for the values of the outer-sphere path in the Cl^- -catalyzed and -uncatalyzed experiments. The product studies were especially interesting since we were unable to find any conclusive evidence for the presence of chloride in the inner-sphere products, except for that which arose from substitution on the excess Cr(II) during oxidation and also appeared in the blank experiments (see Results). Evidently, little if any chloride was incorporated into these products as a result of electron transfer. The fact that the rate constants and activation parameters are the same as they were in the perchlorate studies also supports the idea that chloride was not involved in these inner-sphere reactions.

The rate enhancement for the outer-sphere pathway was unexpectedly small. For example, the Cr(II) reduction of $[\text{Co}(\text{en})_3]^{3+}$, in perchlorate medium,¹⁸ proceeds with a rate constant $k = 3.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ whereas, in a chloride medium,¹⁹ $k = 25 \text{ M}^{-1} \text{ s}^{-1}$, both values measured at 25 °C. Thus, a 10^7 increase in rate was observed for the reduction of $[\text{Co}$

Table IV. Comparison of Rates of Outer-Sphere Electron-Transfer Reactions in Chloride and Perchlorate Media

reaction	$k_2(\text{ClO}_4^-)$, $\text{M}^{-1} \text{s}^{-1}$	$k_2(\text{Cl}^-)$, $\text{M}^{-1} \text{s}^{-1}$	$k_2(\text{Cl}^-)/$ $k_2(\text{ClO}_4^-)$
$\text{Cr(II)} + [\text{Co(en)(ptdn)}_2]^+ \text{ }^a$	2.0×10^{-3}	4.86×10^{-3}	2.4
$\text{Cr(II)} + [\text{Co(en)}_3]^{3+}$	3.4×10^{-4}	1.5×10^{-3}	4.4
$\text{Cr(II)} + [\text{Co(phen)}_3]^{3+}$	3.0×10^1	1.7×10^2	5.6
$\text{Cr(II)} + [\text{Co(NH}_3)_6]^{3+}$	1.0×10^{-3}	1.1×10^{-2}	11
$\text{V(II)} + [\text{Co(en)}_3]^{3+}$	7.2×10^{-4}	1.9×10^{-3}	3.7
$\text{V(II)} + [\text{Co(phen)}_3]^{3+}$	3.8×10^3	6.0×10^3	1.6
$\text{V(II)} + [\text{Co(NH}_3)_6]^{3+}$	1.0×10^{-2}	2.4×10^{-2}	2.4
$\text{Fe(II)} + [\text{Co(phen)}_3]^{3+}$	5.3×10^2	2.0×10^4	3.6

^a This work. All other values taken from ref 10.

$(\text{en})_3]^{3+}$ upon changing the medium from ClO_4^- to Cl^- whereas a factor of only about 2 resulted from a similar change in medium for the reduction of $[\text{Co(en)(ptdn)}_2]^+$ in the present investigation.

In contrast, drastic changes were noted in the outer-sphere path. An unexpected observation is that the ΔH^\ddagger is actually higher in the chloride-catalyzed outer-sphere process by almost 7 kcal/mol (Table III), compared to the perchlorate values. This means that the enthalpic barrier to electron transfer is much higher when chloride is present, and this chloride-assisted reaction is faster only because of the more favorable entropy associated with this process. The ΔS^\ddagger is more positive by about 20 eu in the chloride study due presumably to the addition of Cl^- to the activated complex.

The rate constants for a number of chloride-catalyzed outer-sphere reactions are listed in Table IV. In all cases, the rate in the chloride medium is at least twice that in the corresponding perchlorate mixture. The possibility of determining the mechanism of a redox process by looking at the effect of chloride on the rate of reduction has some potential. Since the rate enhancement is small, however, our results indicate that a comparison of the activation parameters in the catalyzed and uncatalyzed media may provide a more sensitive mechanistic probe. Obviously, more work needs to be done in this area with other systems before any definite statements can be made concerning the magnitude of the changes to be expected in ΔH^\ddagger and ΔS^\ddagger as chloride is added, but the present results predict more positive values for both of them by fairly substantial amounts.

This study poses some interesting questions, especially concerning the role of the catalytic chloride ion in mediating electron transfer. The assumption that the function of the chloride is simply to lower the Coulombic repulsion in the transition state cannot be the total explanation since the same effect should be felt in the inner-sphere process, which is indifferent to the presence of chloride.

The lack of involvement of chloride in the inner-sphere reaction might be explained if it is assumed that the chloride ion must be between the two metals to be effective, and this is clearly impossible for an inner-sphere process. However, Pennington and Haim¹⁵ have shown that the chloride can function as a catalyst from either a cis or trans position, with the latter being more effective.

It may be that in inner-sphere reactions the two metals are already strongly coupled electronically so that the entropic stabilization realized by adding a chloride ion to the transition state is not large compared to the total free energy of activation. In outer-sphere reactions, however, the coupling between the metal centers is generally much weaker so that the additional stabilization available when a chloride ion is incorporated in the transition state may become significant.

These ideas are unable to explain why Pennington and Haim were able to observe the incorporation of chloride in the products of the inner-sphere reaction of $\text{Cr(II)} + [\text{Co(NH}_3)_5(\text{Cl})]^{2+} + \text{Cl}^-$. Nevertheless, the effect is small, with only a few percent of the transition states having a chloride ion present. Our experiments are not sufficiently sensitive to detect similar small quantities of chloride-containing product, and unfortunately, it is impossible to measure the rates or activation parameters of the system involving $[\text{Co(NH}_3)_5(\text{Cl})]^{2+}$ as oxidant. It would be instructive to find a system where chloride catalysis is observed for a purely inner-sphere reaction that proceeds at a convenient velocity such that activation parameters could be measured. We are presently searching for such a system.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of New Brunswick Research Fund for grants supporting this research.

Registry No. $[\text{Co(en)(ptdn)}_2]^+$, 46934-01-4; Cr, 7440-47-3; Cl^- , 16887-00-6.