bidentate ligand (22.7 vs 15 for DMB or 20.0 for mimosine[19]), making these ligands the most effective bidentate iron(III)-chelating agents extant. These binding subunits are excellent iron chelators, even before incorporation into a macrocyclic or macrobicyclic structure.

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Supplementary Material Available: Figures S1–S4, showing sample Y_{obs} and Y_{calc} for MTA ligand titration (Y is a linear combination of the absorbance data), calculated extinction coefficient spectra for the MTA ligand, sample Y_{obs} and Y_{calc} for titration of ferric complexes of MTA, and calculated extinction coefficient spectra for ferric complexes of the MTA ligand (4 pages). Ordering information is given on any current masthead page.

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Effects of Anions on Redox Reactions. 2. Chromium(II) Reduction of $[Co(sep)]^{3+}$ (sep = Sepulchrate) in the Presence of Halide Ions

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Temperature-dependence studies on the Cr(II) reduction of $[Co(sep)]^{3+}$ (I = 0.5 M ($LiClO_4$)) provided the activation parameters $\Delta H^{*} = 9 \pm 2$ kcal mol^{-1} and $\Delta S^{*} = -43 \pm 5$ eu. In a chloride medium (I = 0.5 M (LiCl + $LiClO_4$)) the reaction was markedly accelerated, with $\Delta H^{*} = 11 \pm 2$ kcal mol^{-1} and $\Delta S^{*} = -28 \pm 5$ eu. The reaction was also carried out in the presence of bromide and iodide ions, showing significant rate enhancements. Analysis of experimental parameters suggests that the anion catalysis is best explained in terms of reduction of the entropic contribution to the activation energy through hydrogen-bonding interactions, originating from outer-sphere complexation of the reactants with the anions. The catalyzed rate constants for electron transfer seem to be the same for all the halides, with a value of $(2.5 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}, whereas the ion-pairing formation constants at I = 0.5 M were estimated to be 5.5, 2.3, and 1.7 M^{-1} for Cl^-, Br^-, and I^-, respectively.

Introduction

Ever since the earliest studies on electron-transfer processes, the role of anions and specifically halides has attracted the attention of reseachers working in this field.[1-20] The original workers reported some remarkable catalytic effects, but interest in these studies faded after a fairly simple mechanism was suggested.[21] However, later investigations[22-26] in biologically interesting systems suggested that more detailed information on simple systems would be welcome. Our earlier studies[27] in this area were concerned with a comparison of the magnitudes of the catalytic effect of anions on inner-sphere and outer-sphere processes occurring in the same system. We found that inner-sphere paths in the Cr(II) reduction of $[Co(en)(ptdn)_2]^+$ (where ptdn is the abbreviation for pentane-2,4-dionato, also called acetylacetonato or acac) did not show any catalysis in the presence of chloride ions but the outer-sphere path was accelerated in the same medium. Our objective in the present work was to determine the role of the anion in the activated complex for electron transfer; specifically, we wished to determine if it functions simply to reduce the Coulombic repulsion between the cationic redox partners, as some have suggested, or if it functions by complexing to the labile reductant $[Cr(OH_2)_6]^{2+}$ to create a different reductant, $[Cr(OH_2)_5Cl]^+$, for example. In the case of Cr(II) reductions of proteins[26] such as cyt *c*, azurin, and cyt *a*, electrostatic interactions were considered to be inferior in importance to the symmetry and degree of orbital overlap between the reactants, facilitated by the anion, as the factor that determines the electron-transfer rate.

The synthesis of (*S*)-(1,3,6,8,10,13,16,19-octaazabicyclo-[6.6.6]eicosane)cobalt(III), or $[Co(sep)]^{3+}$ (sep = sepulchrate), reported by Sargeson and co-workers in 1977[28] provided an oxidant that is ideal for our purposes since it is symmetrical, is an obligate

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outer-sphere agent,[29] and is reduced at a convenient rate by most common reductants. Thus, we report the Cr(II) reduction of $[Co(sep)]^{3+}$ in the presence of Cl^-, Br^-, and I^- anions.

Experimental Section

Reagents. All reagent solutions were prepared in water that was purified in a Barnstead Nanopure II system and then distilled from alkaline permanganate in an all-glass apparatus. High-purity argon (Liquid Carbonic) was used in the manipulation of air-sensitive reagents. The lithium perchlorate, perchloric acid, and chromium(II) solutions were prepared and standardized as described earlier.[27]

The LiCl, LiBr, and LiI stock solutions were made by dissolving a calculated amount of each salt (reagent grade, G. Frederick Smith Chemical Co.) in a small quantity of purified water and filtering the resulting solution through a 0.22-μm Durapore hydrophilic filter (Millipore Filter Corp.). The solutions were then diluted quantitatively to prepare standard solutions. Standardization was accomplished by taking triplicate aliquots of each solution and determining the amount of hydrogen ions released upon passage of each through an Amberlite 120 IR(H) cation-exchange resin (BDH) that was extensively purified with 3 M $HClO_4$ before use. The LiCl solution was also standardized by a gravimetric procedure with excellent agreement between the two methods. The LiI solution was prepared and standardized immediately before use. It was stored under argon in the dark at low temperature and was discarded if any coloration appeared.

Preparation of $[Co(sep)](ClO_4)_3$. The complex was prepared as the chloride salt by following the published procedure.[28,29] To convert it to an analytically pure perchlorate salt, a solution of $[Co(sep)]Cl_3$ was passed through a Bio-Rex 5 anion-exchange resin (Bio-Rad) which had been converted to the ClO_4^- form. The ion-exchanged solution was evaporated under vacuum to dryness at 50 °C. Spectral data and elemental analysis showed the product to be 99.5% pure.

Kinetic Measurements. Spectral scan runs of each system were performed on a Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer. The rate of reduction of $[Co(sep)]^{3+}$ by Cr(II) was followed on a Cary 17 instrument using standard thermostated cell holders. Temperature control to within 0.1 °C was achieved with a Masterline 2095 water bath (Fisher Scientific). The temperature in the cell was monitored with an ASTM thermometer calibrated from 0 to 50 °C (Fisher Scientific).

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 in each experiment was controlled to 0.50 M with the standard lithium perchlorate and lithium halide solutions. The acid concentration was 0.10 M in each case. The kinetic data were obtained by monitoring the course of the reaction at the longest wavelength d–d transition for $[Co(sep)]^{3+}$ (473 nm). First-order plots were linear for at least 3 and usually 5 half-lives (>30 points). Rate constants were calculated by fitting the absorbance data to an exponential function. For the nonlinear least-squares fitting the Marquardt algorithm[30] was used.

Product Analyses. These studies were performed by reacting the oxidant and reductant in 1:1, 1:2, and 1:3 ratios under anaerobic conditions with an excess of both chloride and acid. Due to the slowness of the electron-transfer process, the temperature employed was 45 °C in order to avoid interference by side reactions at lower temperatures (vide infra). After completion of the reaction, the excess Cr(II) was consumed by bubbling oxygen through the solution for 5 min and the resulting products were separated quantitatively on a strong cation-exchange resin (Dowex 50W-X8 (200)).

In a typical run, 300 mg of $[Co(sep)](ClO_4)_3$ (466 μmol) was reacted with 1400 μmol of $[Cr(OH_2)_6]^{2+}$ in 30 mL of a solution that was 0.1 M in LiCl and 0.1 M in $HClO_4$. The solution, in a 10-cm quartz cell, was monitored at an absorbance of 473 nm by the Cary 17 spectrophotometer until it reached a constant value (>5 half-lives). Separation of the reaction products was achieved on a Dowex 50W-X8 (200) column by eluting with increasing concentrations of the stock eluting solution (0.1 M $HClO_4$ in 0.5 M $NaClO_4$), starting at one-eighth strength and continuing up to its maximum value. The separated species were characterized by UV–vis spectroscopy on the Lambda 9 spectrophotometer. The chromium content of each band was estimated by using a standard chromate analysis[31] allowing the calculation of extinction coefficients. Control experiments were carried out by using the same conditions, except that the oxidant was absent or substituted by $[Cr(H_2O)_5Cl](ClO_4)_2$, which was prepared and characterized according to a procedure in the literature.[32]

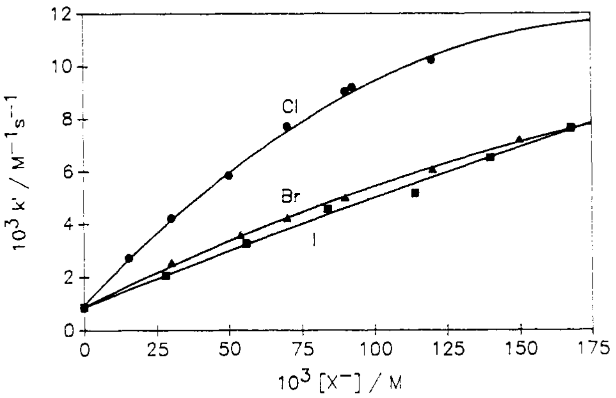

Figure 1. Plots of second-order rate constants against anion concentrations for the Cr(II) reduction of $[Co(sep)]^{3+}$. The solid lines were calculated with the parameters listed in Table III.

Table III. Rate and Equilibrium Constants for Halide Catalysis of the Cr(II) Reduction of $[Co(sep)]^{3+\,a}$

	Cl^-	Br^-	I^-
$10^4 k_0{}^b$	8.7 ± 0.1	8.7 ± 0.1	8.7 ± 0.1
$10^2 k_X{}^c$	2.5 ± 0.3	2.6 ± 0.3	2.5^f
$K_X{}^d$	5.5 ± 0.8	2.3 ± 0.3	1.7^g
$10^2 k_X K_X{}^e$	14 ± 2	5.8 ± 0.9	4.3 ± 0.1^h

[a] Intervals are standard errors. [b] Uncatalyzed second-order rate constant, M^{-1} s^{-1}. [c] Catalyzed second-order rate constant, M^{-1} s^{-1}. [d] Formation constant, M^{-1}. [e] Catalyzed third-order rate constant, M^{-2} s^{-1}. [f] From the average for Cl^- and Br^-. [g] From the experimental value of $k_I K_I$ and k_X. [h] From a linear least-squares fit.

Results

Rate constants for the uncatalyzed reaction between Cr(II) and $[Co(sep)]^{3+}$ are listed in Table I (supplementary material). The value at 25 °C is in excellent agreement with the literature value.[33] Temperature-dependence measurements gave the activation parameters, $\Delta H^\ddagger = 9 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = -43 \pm 5$ eu.

Although the low solubility of the oxidant forced us to work at relatively low ionic strengths, the rate of electron transfer was markedly enhanced by the addition of halides, especially Cl^-. Rate constants for the reduction process were measured in the presence of Cl^-, Br^-, and I^- at different concentrations ranging from 0.0155 to 0.168 M, and the results are listed in Table II (supplementary material). In the presence of higher concentrations of the catalysts, the reaction was characterized by nonreproducible kinetics and/or precipitation of the complex.

The plots of these rate constants against their respective anion concentrations are depicted in Figure 1. Even with the limited concentration range, it is obvious from the figure that there is not a linear dependence of the rates, especially for Cl^- and Br^-. Specifically, the rate for the uncatalyzed reaction, which was independently measured by two different laboratories, would be very difficult to include in any linear plot. Even when differences in the activity coefficients between LiCl and $LiClO_4$[34] are taken into account, the uncatalyzed point does not lie on a straight line drawn through the other points. The data were best fitted to a function of the form of eq 1 (see Discussion), where k' is the

$$k' = \frac{k_0 + k_X K_X [X^-]}{1 + K_X [X^-]} \tag{1}$$

experimental rate constant, k_0 is the uncatalyzed rate constant, k_X is a second-order rate constant for the reaction catalyzed by

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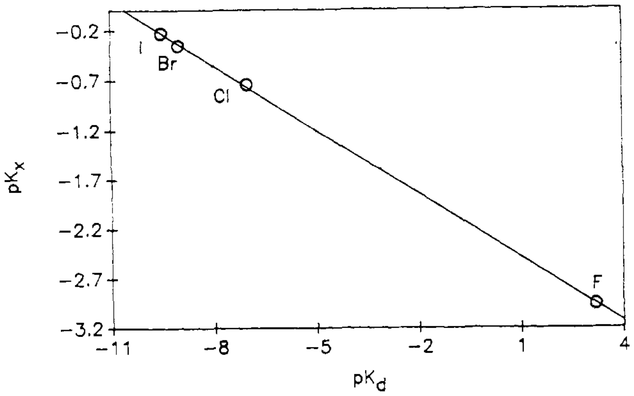

Figure 2. Correlation between the third-order rate constants for halide catalysis and the basicities of the halides, where $pK_d = -\log([H^+][X^-]/[HX])$. The pK_d values are 3.18, −7.0, −9.0, and −9.5 and the pK_X values are −2.96, −0.74, −0.354, and −0.23 for F^-,[35] Cl^-, Br^-, and I^-, respectively.

anion X, and K_X is the formation constant of the reacting species in the catalyzed path. The constants k_{Cl}, k_{Br}, K_{Cl}, and K_{Br} at 25 °C were resolved by a nonlinear least-squares fit[30] to eq 1, and the results are listed in Table III. The solid lines in Figure 1 were calculated by using those results, and the agreement with the experimental points is very good. The data for I^- however did not yield a curved line of statistical significance, and thus it was fit to the linear equation

$$k' = k_0 + k_I K_I[I^-] \qquad (2)$$

where k_I and K_I cannot be resolved directly.

The rate of electron transfer was also measured at 35 and 45 °C at a constant chloride concentration of 0.0925 M, and the data are included in Table II. Calculation of the activation parameters in the presence of chloride yields $\Delta H^\ddagger = 11 \pm 2$ kcal mol^{-1} and $\Delta S^\ddagger = -28 \pm 5$ eu. This gives a significant decrease in the magnitude of the entropy of activation with respect to the uncatalyzed reaction, which seems to be a common feature of the anion catalysis and will be discussed later.

The results of the nonlinear least-squares fits indicate that the intrinsic rate of electron transfer k_X is the same for both the Cl^-- and Br^--catalyzed reactions. The average value is $(2.5 \pm 0.3) \times 10^{-2}$ M^{-1} s^{-1}. The intrinsic rate constant could not be separated from the ion-pairing constant for I^-, since when this anion was employed, the observed rate constant was of the form given in eq 2. If it is assumed that the intrinsic rate constant is the same for the I^-- and F^-[35]-catalyzed reactions as for the Cl^-- and Br^--catalyzed processes, then ion-pairing constants may be estimated for these reactions from eq 2. Confirmation that this is a reasonable assumption is given in Figure 2, which shows that the calculated pK_X for all four halides ion pairing with the reactants in the electron-transfer process, plotted against the pK_d for dissociation of the corresponding halo acid, produces an excellent straight line. The calculated values of K_X were 5.5 ± 0.8, 2.3 ± 0.3, and 1.7 ± 0.2 M^{-1} for Cl^-, Br^-, and I^-, respectively.

Table III also reveals that the contribution to the rate by the chloride-catalyzed term is much greater than the one by the uncatalyzed reaction in the case of the Cr(II) reduction of $[Co(sep)]^{3+}$. Although the other amine complexes reported in the literature, $[Co(en)_3]^{3+}$ and $[Co(NH_3)_6]^{3+}$, were reduced much more slowly[2,10,36] by Cr(II) in the presence of chloride, the relative rate enhancements were similar. For instance, the quotient k_XK_r/k_0 for $I = 0.5$ M would be 158, 34, and 136 M^{-1}, for the three oxidants listed above, respectively.

In order to probe the detailed nature of the reaction mechanism, several spectral scans and product analyses were run for the chloride-catalyzed process under essentially the same conditions as the kinetic runs. Four isosbestic points were initially observed at 663, 537, 411, and 388 nm when the medium had a low acid content (0.02 M) and no chloride, but these disappeared as the reaction progressed. These points were not observed in more acidic media (0.1 M $HClO_4$). This is in agreement with the postulate of an acid decomposition reaction of $[Co(sep)]^{2+}$ following electron transfer as reported by Sargeson.[29]

Only one isosbestic point at 422 nm was observed when Cl^- was added. Also, upon mixing of the Cl^- and $[Cr(OH_2)_6]^{2+}$, the broad band at 710 nm, which is characteristic of the fully aquated species in perchlorate media, shifted slightly red, presumably as a result of formation of a species different from $[Cr(OH_2)_5Cl]^{2+}$, which has a peak at 608 nm. To check this point, an acidic solution of $CrCl_3{\cdot}6H_2O$ was left equilibrating over a long period of time, such that any formed $[Cr(H_2O)_5Cl]^{2+}$ should be hydrolyzed, which was verified by ion exchange on a Sephadex column. Upon reduction of this solution the same small shift (ca. 4 nm) was observed.

Contrary to what was found in previous works,[2,4,5] the product analyses did not show any signs of a chlorochromium(III) species. This implies that the equilibrium constant for formation of the chlorochromium(II) species may be quite low, and the experiments were repeated several times with increasing amounts of reactants in order to ensure detection of any minor amount of chloride-substituted product. For example, assuming that the equilibrium $Cr^{2+} + Cl^- \rightleftharpoons CrCl^+$ is rapidly achieved and the value of the formation constant of $CrCl^+$ has an upper limit of 5, the reaction should have produced about 80 μmol of $CrCl^{2+}$ at 25 °C for the maximum concentrations of Cr(II) and Cl^- employed, which were at the solubility limit.

In all cases in which the reaction mixture was quenched after the electron-transfer process was completed in the presence of Cl^- ions, the only products observed were a pink band that eluted first and was identified as $[Co(OH_2)_6]^{2+}$ and a dark blue band that eluted later and was found to be $[Cr(OH_2)_6]^{3+}$. A dark green band remaining on the top of the column was partially eluted with 3 M $NaClO_4$ and was identified as the chromium(III) oxo dimer formed during the quenching step.

We attempted to circumvent this problem by performing the experiment at 45 °C. At this temperature $[Cr(H_2O)_5Cl]^{2+}$ is known to be still very stable[31] toward acid-promoted decomposition ($t_{1/2}$ ca. 2 days at $[H^+] = 0.1$ M), whereas the time of completion for the reaction reported in the present work is much shorter (6 h), thus improving the chances of detecting minor amounts of the possible product. However, the control experiments showed that even large amounts of $[Cr(H_2O)_5Cl]^{2+}$ disappear very rapidly under these conditions to produce $[Cr(H_2O)_6]^{3+}$, probably via fast Cr(II)-catalyzed decomposition of the former.[37] The electron transfer is too slow to obtain conclusive information from the product analyses, and it is not possible to determine if Cl^- is present in the first coordination sphere of the Cr(II) labile reactant during the act of electron transfer or if it is brought into the activated complex as an ion pair.

Discussion

Kinetics in the Presence of Anions. The exact mechanism by which anions affect the rate of outer-sphere electron transfer is not clear. Originally, it was postulated that there would be less Coulombic repulsion between the cationic partners due to the presence of the anion in the transition state.[21,38] However, in 1973, Przystas and Sutin[10] in an elegant paper proposed an alternative mechanism in which the effectiveness of anion catalysis was rationalized in terms of orbital symmetry. In all cases, formation of an inner-sphere complex between the anion and the reductant was considered very important.

Later work using electrochemical methods has shown,[39,40] however, that the formation constants for inner-sphere complexes of Cr(III) with several anions are very small, whereas the values for the outer-sphere complexes (i.e. ion pairs) are at least 1 order of magnitude larger. Moreover, the anions with the largest effects

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on the electron-transfer rates (e.g. SCN^-) had the highest ion-pairing constants. It is thus difficult to reconcile these experimental facts with an explanation involving orbital symmetry concepts.

As an example, the formation constant of the inner-sphere chromium(III) complex, chlorochromium(III), from Cr(III) and Cl^- was estimated[40] from electrochemical methods to be around 0.1 M^{-1} at an ionic strength of 1 M, whereas the value reported[41] for the presumed outer-sphere or ion-pairing constant of the Cr(II) complex, calculated from the Cr(II) reduction of hydrazine, hydroxylamine, and hydrazoic acid in the same medium, was 1.5 M^{-1}. It is also known that the value at 0.5 M ionic strength[42] of the inner-sphere chromium(III) complex increases from 0.1 M^{-1} at 1.0 M ionic strength to 0.4 M^{-1} at 0.5 M ionic strength. Therefore, an upper limit to the value of the inner-sphere chromium(II) complex may be set at 0.4 M^{-1} at 0.5 M ionic strength. However, the value observed from our kinetics was 5.5 M^{-1} under these conditions. This implies that the main contributing factor to the measured equilibrium constant is outer-sphere complexation.

If the chloride is not in the first coordination sphere of Cr(II), it may be brought into the transition state as an ion pair by either the reductant or the oxidant.

$$[Cr(H_2O)_6]^{2+} + X^- \rightleftharpoons [Cr(H_2O)_6,X^-]^+ \quad K_r$$

$$[Co(sep)]^{3+} + X^- \rightleftharpoons [Co(sep),X^-]^{2+} \quad K_o$$

If the idea of a direct termolecular collision is discarded, there are at least three possible pathways by which the chloride ion may enter the transition state, viz.

$$[Cr(OH_2)_6,X]^+ + [Co(sep)]^{3+} \rightarrow \text{products} \quad k_x$$

$$[Cr(OH_2)_6]^{2+} + [Co(sep),X]^{2+} \rightarrow \text{products} \quad k_y$$

$$[Cr(OH_2)_6,X]^+ + [Co(sep),X]^{2+} \rightarrow \text{products} \quad k_z$$

In addition, we describe the uncatalyzed path having the rate constant k_0.

$$[Cr(OH_2)_6]^{2+} + [Co(sep)]^{3+} \rightarrow \text{products} \quad k_0$$

Previous studies[29] have shown that $[Co(sep)]^{2+}$ undergoes an acid-catalyzed decomposition reaction with a $t_{1/2}$ of 10 min in 0.1 M $HClO_4$, which is very large compared to the electron-transfer rate. Thus, the latter is the rate-determining step in our studies. There was no interference by the decomposition of $[Co(sep)]^{2+}$ in the spectral region in which our kinetic studies were performed.

If all of the above equilibria and pathways are considered to be important, the following expression may be developed for the rate of the reaction:

$$\text{rate} = k'[Cr(OH_2)_6]^{2+}[Co(sep)]^{3+}$$

where

$$k' = \frac{k_0 + k_xK_r[X^-] + k_yK_o[X^-] + k_zK_rK_o[X^-]^2}{(1 + K_r[X^-])(1 + K_o[X^-])} \qquad (3)$$

Since this equation is rather complicated, it is normally assumed[2,4,10,16-20] that the formation constant for ion association with the oxidant (K_o) is negligible. With this simplification, the measured rate constant takes the form given in eq 1, which is a relatively simple expression.

In their 1973 paper, Przystas and Sutin[10] proposed that the ion-pairing constant with the oxidant, K_o in our formalism, was very small for their complexes and could be neglected. This is somewhat surprising since even by then experimental data were already available which, albeit variable, suggested that the ion-pairing constants for Co(III) complexes were much larger[43-45] than their assumed limit of 0.2 M^{-1} at 1 M ionic strength. Moreover, since they considered K_r an inner-sphere complexation constant, they logically assumed it to be small, thus arriving at eq 4, which is the rate law most commonly used for anion catalysis.

$$\text{rate} = (k_0 + k_rK_r[X])[Cr(II)][Co(III)] \qquad (4)$$

It would be difficult, however, to justify from the experimental evidence available that K_r is much greater than K_o, especially for Cr(II) (vide supra). On the other hand, it should not be surprising that k_x and k_y were very similar if not the same, since they describe the rate of the electron transfer itself, independently of any preceding equilibria. If the latter argument is correct, by substituting k_c for k_x and k_y and dropping the squared terms in eq 3, it is easily shown that

$$k' = \frac{k_0 + k_c(K_r + K_o)[X^-]}{1 + (K_r + K_o)[X^-]} \qquad (5)$$

which is identical with eq 1 with $k_X = k_c$ and $K_X = K_r + K_o$. There are several methods of choice for the calculation of formation constants from kinetic data employing functions like (1) and (5), and their critical review can be found elsewhere.[46] Generally, nonlinear least-squares fitting is regarded as the best one, although linear double-reciprocal plots can be reliable if proper weighting procedures are used, and hence they have been extensively employed. In our particular case the nonlinear least-squares analysis showed that k_X is practically the same for Cl^- and Br^- catalysis, with K_X being the only variable.

The reasoning presented so far is borne out not only by our experimental results but also by those of other researchers. For example, many years ago, Wells and Salam[41,47,48] considered the possibility of a rate law like (1). We calculate that their values for the catalyzed rate constants k_X of the Cr(II) reduction of N_3^- at 25 °C and $I = 1$ M in the presence of F^-, SO_4^{2-}, and Cl^- were 14 ± 2 M^{-1} s^{-1}, whereas the formation constants K_X were 7.3, 4.1, and 1.5 M^{-1}, respectively,[41] for the three anions.

It is very likely then that most reports on anion catalysis have used somewhat limited rate laws and that the values calculated with them represent composite parameters. This would explain why some of the uncatalyzed rate constants reported by Przystas and Sutin[10] (estimated by extrapolation to $[X^-] = 0$) were much higher than other reliable values quoted in the literature.

Nonlinear plots such as those shown in Figure 1 only may be observed at low ionic strengths. This is a consequence of the fact that the formation constants for the outer-sphere complexes become lower at higher ionic strengths. For example, the value of the formation constant for the outer-sphere complex of Cr(II) and Cl^- at $I = 1.0$ M is only 1.5 M^{-1}. This would require a prohibitively high anion concentration in order to see any leveling effect. In our experiments, we were forced to use $I = 0.5$ M because of the poor solubility of the oxidant. Lower ionic strengths could not be employed because it is generally assumed that this would violate the constant ionic strength principle.[49]

Activation Parameters for the Uncatalyzed Reaction. The relatively low value for the enthalpy of activation of the uncatalyzed reaction is not unexpected for an outer-sphere electron-transfer reaction in which bond breaking and bond making are unnecessary. Negative entropies of activation are normally observed; this is explained in terms of the ordering felt by the solvent molecules as the precursor complex forms.[50] However, the very

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Table IV. Activation Energies[a] for Cr^{2+} Reductions of Co(III) Compounds

	$[Co(NH_3)_6]^{3+}$	$[Co(ptdn)_2en]^{3+}$	$[Co(en)_3]^{3+}$	$[Co(sep)]^{3+}$
$k_{Cl}K_{Cl}/k_0$[b]	136	2	34[c]	158
ΔH_{unc}^*	14.7	10 ± 2	6.4[c]	9 ± 2
ΔS_{unc}^*	−30	−36 ± 7	−57[c]	−43 ± 5
ΔG_{unc}^*	23.7	21 ± 4	23.4[c]	21 ± 3
ΔH_{cat}^*	12.4	17 ± 1	*d*	11 ± 2
ΔS_{cat}^*	−25	−13 ± 3	*d*	−28 ± 5
ΔG_{cat}^*	19.8	21 ± 2		19 ± 3
ref	*e*	*f*	*g*	*h*

[a] In kcal mol^{-1} for ΔG^* and ΔH^* and cal deg^{-1} mol^{-1} for ΔS^*. [b] In units of M^{-1}. [c] The value at 25 °C was quoted in ref 36, and the value at 50 °C was given in ref 66. The activation parameters were calculated from these data. [d] Not reported. [e] Reference 2. [f] Reference 27. [g] References 36 and 66. [h] This work.

large negative value obtained in the present work was unexpected because of the large size of the oxidant; disruption of the solvent sheath should be greater in small molecules.[54] Values below −40 cal deg^{-1} mol^{-1} are rare in the literature and usually involve a rare earth or a labile reactant.[51-53] Very negative values have been considered as partial evidence for nonadiabaticity.[50] Sargeson and co-workers[33] have measured the kinetics of electron transfer between various sepulchrate and related complexes reacting with each other and have found that the results correlated very well with the Marcus theory. They therefore concluded that the steric hindrance of these compounds was not affecting their adiabaticity. The Marcus theory, however, usually gives good results for reactions in which the two redox partners are structurally similar.[55-59] In a cross-reaction, both reactants need not be nonadiabatic in order to see a low transmission coefficient for the redox process. It may well be that the reaction of $[Co(sep)]^{3+}$ with Cr(II) is intrinsically nonadiabatic and therefore slow due to the distorted nature of the latter in solution, which would require extra reorganizational energy prior to electron transfer.[51]

The large decrease in entropy can also be interpreted in terms of a high degree of solvent structuring, following the suggestions of Weaver and co-workers.[60-65] They have found evidence that the entropy changes depend strongly on the extent of interaction with the solvent primarily due to hydrogen bonding, which is expected to be important for both of our highly charged reactants. From their data[60] on standard reaction entropies for the self-exchange reactions of $Cr^{2+/3+}$ and $[Co(sep)]^{2+/3+}$, which are −49 and 19 eu, respectively, a $\Delta S°$ of −30 eu may be calculated for the cross-reaction involving the Cr(II) reduction of $[Co(sep)]^{3+}$. With the electromotive data for the self-exchange reactions, $\Delta G°$ can be estimated as −2.8 kcal mol^{-1}. From that value and the entropy of reaction, the $\Delta H°$ is calculated to be −11.7 kcal mol^{-1}. Since the standard entropy datum is also available for the reaction involving $[Co(en)_3]^{3+}$ as an oxidant, the same calculations were performed as a comparison, and the results are listed in Table IV. The complete activation profiles are shown in Figure 3. Both reactions are found to be highly exothermic, but this parameter is counterbalanced by a large decrease in the entropy, thus reducing the driving force. This effect appears to be especially dramatic for $[Co(en)_3]^{3+}$, whose extremely slow electron-transfer reaction with Cr(II) has been known for a long time.[36,66,67] It is clear that $[Co(sep)]^{3+}$ is reducing the entropic barrier in both the ground state and the activated complex perhaps because solvent molecules such as water are excluded from the interior of the ligand whereas, in the $[Co(en)_3]^{3+}$ complex, they are able to fit between the chelate rings. In the latter case, these solvent molecules would require extra energy for reorganization within the activated complex. This proposal was first made many years ago,[68] and recently some theoretical arguments have been advanced to estimate its contribution to the reorganization energy.[69-71]

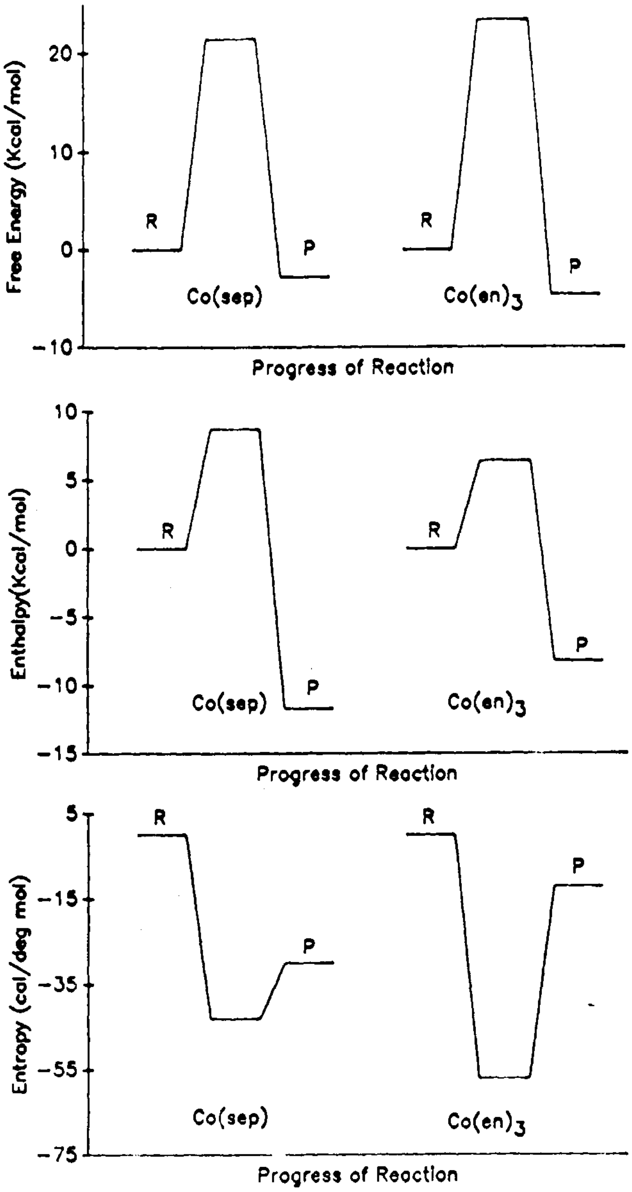

Figure 3. Quantitative comparison of the activation parameter profiles for the Cr(II) reductions of $[Co(sep)]^{3+}$ and $[Co(en)_3]^{3+}$. In the profiles, the reactants have been assumed to be at the zero level in their ground states.

Activation Parameters in the Presence of Anions. A general characteristic of anion catalysis is that there is always a substantial decrease in the magnitude of the entropy of activation. We were unable to measure the rate constant for electron transfer, k_{et}, directly at each temperature so the calculated ΔS^* comes from a composite of rate and equilibrium constants, as is usually the

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case for outer-sphere electron-transfer reactions. Therefore, the data can be helpful in describing qualitatively the catalytic process.

Wells and Salam[41,47,48] suggested that the catalytic capacity of a given anion was related to its ability to cause changes in solvent structure. Hence, hard, structure-forming anions like F^- were expected to be much better catalysts than soft, structure-breaking anions like I^-. However, they assumed that their experimental formation constants were for the inner-sphere complexes and that the release of water from the first coordination sphere of Cr(II) reduced the activation energy. Weaver and co-workers[60] have suggested that the interactions of transition-metal complexes with water molecules are not limited to the first coordination sphere, which is likely to produce a larger reorganization energy. Thus, outer-sphere complexation may be a more efficient way of disrupting those interactions, since fewer solvent molecules would be coupled to the motions of the activated complex.

Model for Anion Catalysis of Electron Transfer. Ion pairing of the halides with $[Cr(H_2O)_6]^{2+}$ and $[Co(sep)]^{3+}$ plays a very important role during the course of the reaction. Recently, strong hydrogen bonding with halides has been experimentally demonstrated[72] in solution by using vibrational circular dichroism (VCD) for the related compound $[Co(en)_3]^{3+}$. It was found that conformational changes are induced in the complex by the halides in the order $Cl^- > Br^- > I^-$, which is the same order reported in the present work. Furthermore, each halide was able to interact with more than one amino hydrogen from the complex at the same time. Even though we could not detect the ion pairs $[Co(sep),X]^{2+}$ spectroscopically in solution, evidence for such species has been reported in the literature,[73] at least for I^-.

A general explanation is that interaction with the halide displaces water bound to the positive metal complexes, thereby making a positive contribution to the entropy of activation. This lowers the entropic barrier.[41,74] The mechanism for this is 2-fold: first, the halide may occupy the hydrogen-bonding sites of the complex, and second, the halide will reduce the overall positive charge felt by the free water molecules in solution. There is an intrinsic advantage in using the halides in this study, since the orbital symmetry arguments are expected to be the same for all of them, as is their charge and many other chemical properties. When the ion-pair constants are plotted against the basicities[75] of the ionized halides (as indicated by their pK_d values in water at 25 °C, where K_d is the dissociation constant of the haloacid), a good correlation is found (Figure 2). This lends support to our model for the catalysis, since this parameter is an indirect measure of the hydrogen-bonding ability of each halide.

Conclusions

Ion pairing may play a very significant role in catalysis of redox processes, especially at medium to low ionic strengths. This can be of importance for electron transfer in biological systems, since many of the compounds used in such studies exhibit very poor solubilities, thus forcing the use of low ionic strengths. The possibility exists that the role of anions in previous catalysis studies may have been disguised by the use of high strength and/or complexing media.

At least in the present work, anion catalysis appears to be facilitated by outer-sphere complexation of the anions with reactants that are prone to hydrogen-bond formation, since the resulting decrease in entropy for the ionic species in solution translates into less rearrangement to reach the transition state. Even though this is a rather simple argument, it readily explains why anion catalysis is still effective when direct contact with the metals is difficult to rationalize for steric reasons.

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Supplementary Material Available: Tables I and II, giving the temperature dependence of the uncatalyzed reaction and kinetic data in the presence of halides (3 pages). Ordering information is given on any current masthead page.

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