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Electron-Transfer Reactions between the Perbromate Ion and Iron(II) Complexes of 2,2'-Bipyridine and Substituted 1,10-Phenanthrolines

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The kinetics of the reduction of the perbromate ion BrO_4^- by $[Fe(L-L)_3]^{2+}$ complexes in 0.05 mol dm^{-3} $NH_4H_2PO_4$, where L–L is 2,2'-bipyridyl, 1,10-phenanthroline, and the 5-nitro and 4,7-dimethyl derivatives of the latter, follow the rate law $-d[Fe(II)]/dt = k_1k_2[Fe(II)][BrO_4^-]/(k_{-1}[L-L] + k_2[BrO_4^-])$. This corresponds to rate-determining loss of L–L followed by faster electron transfer from the intermediate to BrO_4^-. It is substantiated by close correspondence between the rate constants k_1 and activation energies E_A to previously reported values for the ligand dissociation. For the four complexes, in the order listed, the rate constant 10^4k_1 (in s^{-1}) is 1.25 ± 0.05, 1.02 ± 0.03, 5.9 ± 0.1, and 0.34 ± 0.01 and E_A (in kJ) is 121 ± 2, 109 ± 5, 121 ± 3, and 134 ± 3. The almost constant ratio k_{-1}/k_2 (10–50) is discussed in terms of electron-transfer theory.

Introduction

The perbromate ion was discovered recently and a number of its thermodynamic and spectroscopic properties characterized.[1-9] Also the kinetics of the electrochemical reduction,[10-14] photochemical decomposition,[15] and reduction of BrO_4^- by several two-electron or oxygen-atom transfer reagents[16-18] in homogeneous solution have been reported, while the hydrated electron seems to be the only one-electron transfer reagent for which kinetic data are available.[19]

In this work we present data for the homogeneous reduction of BrO_4^- by $[Fe(L-L)_3]^{2+}$, where L–L represents 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and the 5-nitro- and 4,7-dimethyl derivatives of the latter. The purpose of this investigation is first to provide new kinetic data for one-electron reduction processes of BrO_4^-. In fact, detailed kinetic studies of the reduction of oxoanions are relatively limited, and the reduction processes furthermore proceed by different mechanisms. Of particular importance in relation to the present investigation are the observations that the mechanisms of reduction of the apparently closely related peroxodisulfate ($S_2O_8^{2-}$) and peroxodiphosphate ($P_2O_8^{4-}$) ions by $[Fe(L-L)_3]^{2+}$ are different.[20-26] In most cases direct electron transfer is thus rate determining for the former and ligand dissociation in $[Fe(L-L)_3]^{2+}$ for the latter.[23-25] Ligand dissociation is also the rate-determining step in oxidation of $[Fe(phen)_3]^{2+}$ by ClO_2^-.[26,27] Secondly, a notable feature of the electrochemical reduction of BrO_4^- (and of several other oxoanions) is that the transfer coefficient is small (0.05–0.1) over a wide potential range.[11-14] If the mechansim were direct electron transfer, this result would require special consideration in terms of electron-transfer theory, and comparison with a series of closely related homogeneous reactions, for which the free energy of reaction varies by almost 0.4 V, might provide a clue to these effects.

Experimental Section

A sample of $KBrO_4$ was kindly supplied by Dr. E. H. Appelman, Argonne National Laboratory, Argonne, IL. Solutions of the $[Fe(L-L)_3]^{2+}$ complexes were prepared by mixing analytical grade ligand (usually in slight excess compared with the equivalent amount) and ferrous ammonium sulfate recrystallized from water and checked spectrophotometrically with use of literature values of the molar extinction coefficients.[26,27] Doubly distilled water was used throughout, and all other materials were analytical grade and used without further purification.

The reactions were followed spectrophotometrically with a Beckman 24 spectrophotometer with recorder and thermostated quartz cells. The absorbance of Fe(II) complexes was followed typically over 1 or 2 half-lives and occasionally longer. The concentrations of Fe(II) and BrO_4^- were varied in the ranges (2.5–5) × 10^{-5} mol dm^{-3} and (2–20) × 10^{-4} mol dm^{-3}, respectively, and all individual rate constants are averages of at least two determinations differing by less than about 2%. For the $[Fe(phen)_3]^{2+}$ complex larger concentrations of Fe(II), in excess of the equivalent concentration of BrO_4^-, were also attempted, but during these runs a precipitate appeared that was identified spectrophotometrically as free phen. For a low concentration of Fe(II) (2.5 × 10^{-5} mol dm^{-3}), but still in excess of BrO_4^-, the absorbance change was inconveniently small due to the complicated stoichiometry (see below). However, the calculated rate constant for the first 25% of the reaction agreed with the value obtained when BrO_4^- was present in large excess.

All reactions proceeded in an atmosphere of argon scrubbed by solutions of chromium(II) ions, even though the effect of molecular dioxygen was found to be negligible. Apart from investigations of

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the stoichiometry and the effect of the ionic strength and pH, all data refer to solutions of ionic strength 0.05 mol dm^{-3} with respect to $NH_4H_2PO_4$. This solution ensures a constant pH 4.5 throughout the kinetic runs.

Results

Possible Side Reactions. In spite of its high standard redox potential (1.76 V[6]) BrO_4^- is a very inert reactant. Some attention was therefore given to possible side reactions involving the iron(II) complexes. These reactions are as follows.

(1) In acid solutions the iron(II) complexes are slowly dissociated, loosing the L–L ligands[28-31] and producing more reactive[32,33] partially aquated complexes. However, it was ascertained that for a pH in the range 4.0–6.2 adjusted by hydrochloric acid or $NH_4H_2PO_4/(NH_4)_2HPO_4$ mixtures, the rate of dissociation was negligible compared with the rate of reaction with BrO_4^-.

(2) The iron(III) complexes are rapidly reduced by hydroxide ions.[34] Moreover, in alkaline solutions the iron(II) complexes are autoxidized, forming eventually ferric hydroxide.[34,35] However, under the conditions of the present work, i.e., pH 4.5 and exclusion of dioxygen, interference of these processes is insignificant.

(3) The oxidation of both $[Fe(bpy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ by BrO_3^- has been investigated by several people.[26,32,33,36-38] The mechanism is complicated and depends on both $[H^+]$ and the ratio between the concentrations of the two reactants, being controlled either by aquation of $[Fe(L-L)_3]^{2+}$ or by an autocatalytic reaction path. The conditions of the present work correspond to reaction via aquation of $[Fe(L-L)_3]^{2+}$, but the reaction was found to be negligibly slow compared with the reaction of BrO_4^-. The reduction of the latter is therefore expected to proceed only to the stage of BrO_3^-, i.e., the overall process to be

$$2[Fe(L-L)_3]^{2+} + BrO_4^- + 2H^+ \rightarrow 2Fe^{III} + BrO_3^- + H_2O \tag{1}$$

where Fe(III) refers to the resulting iron(III) product.

Stoichiometry. The stoichiometry of the reaction with $[Fe(phen)_3]^{2+}$ was checked by letting the reaction go to completion and determining the concentration of the reactant in excess. For initial concentrations of $[Fe(phen)_3]^{2+}$ and BrO_4^- of 2.50×10^{-5} and 4.68×10^{-6} mol dm^{-3}, respectively, spectrophotometric determinations of excess $[Fe(phen)_3]^{2+}$ showed that only about 30% of the amount corresponding to eq 1 has been consumed (0.33×10^{-5} mol dm^{-3} as opposed to 0.94×10^{-5} according to eq 1). For initial concentrations of $[Fe(phen)_3]^{2+}$ and BrO_4^- of 4.99×10^{-5} and 3.70×10^{-4} mol dm^{-3}, respectively, $[H^+]$ was adjusted to 1.0×10^{-4} mol dm^{-3} with hydrochloric acid, i.e., to such a value that most iron(III) will be present as aqua or hydroxo complexes. After completion of the reaction a large excess of iodide was added to the resulting neutral solution. This rapidly converts excess BrO_4^- to BrO_3^- without interference from the iron species. The rate of the conversion can be measured spectrophotometrically by the rate of formation of I_3^-.[16,17] Calibration by means of neutral solutions of $KBrO_4$ thus showed, apart from a short "induction period", that the apparent rate of this process, $\Delta D/\Delta t$, where ΔD is the absorbance change and Δt the time interval, was constant over 30–60 s and proportional to $[BrO_4^-]$ for concentrations up to 1.7×10^{-4} mol dm^{-3}. When the reaction mixture was exposed to the same treatment as the standard solutions (after dilution to bring the excess $[BrO_4^-]$ into the range of the calibration), an excess BrO_4^- concentration of 2.92×10^{-4} mol dm^{-3} was found, while the value expected on the basis of eq 1 is 3.45×10^{-4} mol dm^{-3}, again corresponding to a consumption of about 30% of the stoichiometric amount of $[Fe(phen)_3]^{2+}$ according to eq 1. This feature is also observed for the oxidation of $[Fe(L-L)_3]^{2+}$ by $S_2O_8^{2-}$ and $P_2O_8^{4-}$ and likely ascribed to reduction of coordinated or liberated ligand with reactive free-radical intermediates.

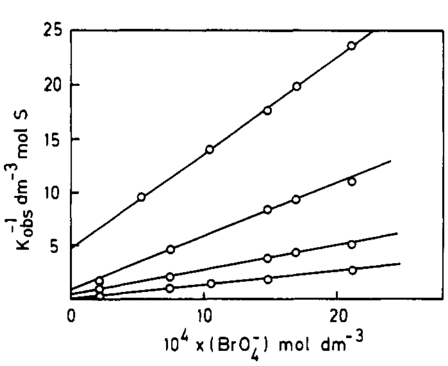

Figure 1. k_{obsd}^{-1} (s) plotted against $[BrO_4^-]$ (mol dm^{-3}). The four lines correspond to (from the bottom) 298.3, 303.3, 308.1, and 312.8 K.

Rates and Activation Parameters. The reactions were first order in $[Fe(L-L)_3]^{2+}$ over up to 2 half-lives. At longer times negative curvature from the first-order plots were observed. The apparent second-order rate constants, k_{obsd}, were independent of pH in the range 4.5–6.2, adjusted with $NH_4H_2PO_4/(NH_4)_2HPO_4$ mixtures of overall ionic strength 0.05 mol dm^{-3}, although addition of $(NH_4)_2HPO_4$ caused a drop in the rate constant of about 20%. For concentrations of $[Fe(phen)_3]^{2+}$ and BrO_4^- of 2.50×10^{-5} and 3.48×10^{-4} mol dm^{-3}, respectively, values of k_{obsd} were furthermore 0.396 for H_2O and 0.293 dm^3 mol^{-1} s^{-1} for 98% D_2O, corresponding to a kinetic deuterium isotope effect of 1.35. k_{obsd} displayed a slower variation with $[BrO_4^-]$ than corresponding to first order, but good linearity of plots of k_{obsd}^{-1} against $[BrO_4^-]$ was always found over a 10-fold variation of $[BrO_4^-]$, as shown in Figure 1. These observations are compatible with the following two mechanisms: (1) rapid preequilibrium involving outer-sphere complex formation between the reactants followed by rate-determining electron transfer within this complex; (2) rate-determining ligand dissociation followed by fast electron transfer between the partially aquated $[Fe(L-L)_2]^{2+}$ and BrO_4^-, i.e.

$$[Fe(L-L)_3]^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(L-L)_2]^{2+} + L-L \tag{2}$$

$$[Fe(L-L)_2]^{2+} + BrO_4^- \xrightarrow{k_2} [Fe(L-L)_2]^{3+} + BrO_3^- + O^- \tag{3}$$

where the iron(III) product rapidly decomposes. Also, in view of the high p*K* value of O^- (11.9[39]) the second step would most likely involve additional proton transfer.

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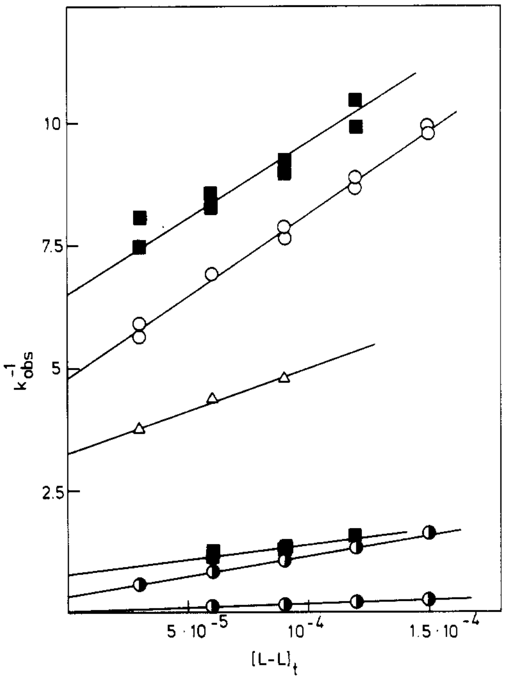

Figure 2. Plots of k_{obsd}^{-1} against excess $[L-L]_t$: (○) phen; (△) bpy; (◑) 5-NO_2phen; (■) 4,7-Me_2phen. The lower curves for 4,7-Me_2phen and 5-NO_2phen refer to 313.8 and 314.3 K, respectively, and all others to 303.3 K. [Fe(II)] = 2.5×10^{-5} mol dm^{-3} and $[BrO_4^-] = 9.35 \times 10^{-4}$ mol dm^{-3} for phen and bpy. For 5-NO_2phen $[BrO_4^-] = 5.76 \times 10^{-4}$ (upper) and 2.78×10^{-4} mol dm^{-3} (lower), and for 4,7-Me_2phen $[BrO_4^-] = 7.70 \times 10^{-4}$ (upper) and 2.78×10^{-4} mol dm^{-3} (lower). The scale of the top curve has been divided by 2.

The following observations now strongly favor the second mechanism.

(a) k_{obsd} showed an inverse linear dependence on [L–L] (Figure 2) corresponding to the overall rate expression

$$-\frac{d[[Fe(L-L)_3]^{2+}]}{dt} = \frac{k_1 k_2 [[Fe(L-L)_3]^{2+}][BrO_4^-]}{k_{-1}[L-L] + k_2[BrO_4^-]} \quad (4)$$

or

$$k_{obsd}^{-1} = \frac{k_{-1}}{k_1 k_2}[L-L] + \frac{1}{k_1}[BrO_4^-] \quad (5)$$

This is compatible with the second mechanism, but only with the first mechanism, if the preequilibrium involves substitution of L–L by BrO_4^-. In view of the high value of the corresponding equilibrium constant required for the interpretation of the kinetic data ($\approx 10^2$), and the low value for reported ligand dissociation constants,[21] the latter possibility is unlikely.

Table I. Rate Constants (s^{-1}) for the Reactions of $[Fe(L-L)_3]^{2+}$ with BrO_4^- and for the Ligand Dissociation Constants, k_2,[28] Standard Redox Potentials, $E°$ (V), and pK_a for the Ligands L–L[a]

L–L	$10^4 k_1$	$10^4 k_2$	$E°$	$k_{-1}K_a/(k_1k_2(K_a + [H^+]))$	pK_a	k_{-1}/k_2
bpy	1.25 ± 0.05	2.8	0.97	4.3 ± 0.2	4.5	10
phen	1.02 ± 0.03	1.63	1.06	6.8 ± 0.2	4.8	20
5-NO_2phen	5.9 ± 0.1	4.87	1.25	9.7 ± 0.5 4.1 ± 0.5	3.6	10
4,7-Me_2phen	0.34 ± 0.01	0.22	0.88	4.1 ± 0.2 2.3 ± 0.2	5.9	50

[a] The lower values for 5-NO_2phen and 4,7-Me_2phen refer to 314.3 and 313.8 K, respectively, and all others to 303.3 K.

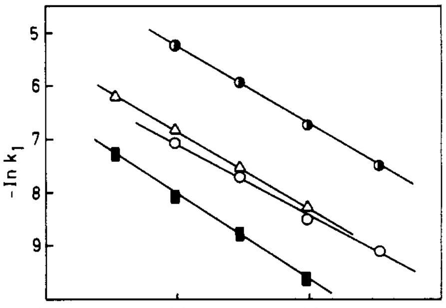

Figure 3. Arrhenius plot for k_1 (s^{-1}). Symbols are the same as in Figure 2.

(b) From the slopes of Figures 1 and 2 values of k_1 and the combination of constants $k_{-1}K_a/[k_1k_2(K_a + [H^+])]$, where K_a is the acid dissociation constant of L–L, could be found directly ($[L-L]_t$ is the total concentration of excess L–L). These data are shown in Table I, which also shows approximate values of (k_{-1}/k_2) calculated from literature values[-26,40] of K_a for the L–L ligands. In Table I are finally given literature values of the weakly acid-dependent standard redox potentials of the various Fe(II)/Fe(III) couples.[26] The free energy of the overall reaction thus varies by 0.37 V, and the 5-nitro- and 4,7-dimethyl-substituted complexes in fact represent the highest and one of the lowest redox potentials for $[Fe(L-L)_3]^{2+}$ commonly available. Figure 3 shows the Arrhenius plots for k_1 and Table II the activation parameters calculated from the theory of absolute rates. Within the experimental accuracy the intercepts of Figure 1 were independent of the temperature.

Tables I and II also show corresponding rate parameters for the direct ligand dissociation of the $[Fe(L-L)_3]^{2+}$ complexes taken from ref 28 (cf. ref 25). These two sets of rate parameters correspond so closely to each other that the second mechanism can be substantiated amost beyond doubt.

(c) k_1 is practically independent of the ionic strength up to 0.5 mol dm^{-3} ($NH_4H_2PO_4$), while the intercept (eq 4) decreases slightly with increasing ionic strength. This is expected for the second mechanism on the basis of previous extensive investigations of ionic strength effects on the ligand dissoication reactions,[29-31] whereas the rate constant for the first mechanism, which involves ion-pair formation, would be expected to be much more dependent on the ionic strength. The second mechanism is also in accordance with the observation that the overall rate constant, k_{obsd}, drops when $(NH_4)_2HPO_4$ is added. Addition of HPO_4^{2-} could thus interfere with the reactions of the partially aquated intermediates by complex formation, but these effects were not investigated further.

(d) The kinetic deuterium isotope effect of 1.35 is higher than values given in a previous report on the ($[H^+]$-independent) ligand dissociation of $[Fe(phen)_3]^{2+}$, according to which the isotope effect increases from 1.07 to 1.23 at 303.3 K, when $[H^+]$ increases from 0.01 to 1.0 mol dm^{-3}.[41] In view of the strong basicity of O^- this difference could reflect proton transfer in the second step. Since no explicit dependence between k_{obsd} and pH could be found, the proton donor would then most likely be water. On the other hand, separate direct measurements of the rate of ligand dissociation of $[Fe(phen)_3]^{2+}$ in H_2O and D_2O, 0.01 mol dm^{-3} with respect to hydrochloric acid and 2.5×10^{-5} mol dm^{-3} with respect to the iron(II) complex, in the present work gave values of the first-order rate constants of 1.74×10^{-4} and 1.35×10^{-4} s^{-1}, respectively, corresponding to an isotope effect of 1.29, i.e., quite close to the value for the perbromate reaction.

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Table II. Activation Parameters[a]

L-L	E_A	E_A^L	A	A^L	$\Delta H^‡$	$\Delta S^‡$	$\Delta G^‡$
bpy	121 ± 2	119	1.1×10^{17}	1.0×10^{17}	118 ± 2	75 ± 8	95 ± 2
phen	109 ± 5	125	1.3×10^{15}	6×10^{17}	106 ± 5	40 ± 15	96 ± 5
5-NO_2phen	121 ± 3	120	8.1 ± 10^{17}	1.3×10^{18}	118 ± 3	90 ± 10	91 ± 3
4,7-Me_2phen	134 ± 3	119	7.3×10^{18}	1.7×10^{16}	131 ± 3	110 ± 10	99 ± 3

[a] The activation energy, E_A, enthalpy, $\Delta H^‡$, and free energy of activation, $\Delta G^‡$, are in kJ mol^{-1}; the activation entropy, $\Delta S^‡$, is in J K^{-1} mol^{-1}. A (s^{-1}) is the Arrhenius preexponential factor. The superscript "L" refers to the corresponding values for the ligand dissociation from from ref 28.

Attempts were also made to measure the rates of oxidation of the 3,4,7,8-tetramethyl-substituted complex and of $[Fe(phen)_2(CN)_2]$ and $[Ru(phen)_3]^{2+}$. However, the rates of the former complex could not be measured because precipitation occurred during the reaction, and the latter two complexes did not react with BrO_4^- within several hours.

Discussion

We have provided kinetic data for the oxidation of the four $[Fe(L-L)_3]^{2+}$ complexes by BrO_4^-. The fact that the kinetics follow the rate expressions given by eq 1 and 5 and that the rate constants, activation parameters, kinetic deuterium isotope effect, and ionic strength dependence all correspond closely to those of the directly measured $[H^+]$-inpendent ligand dissociation of the $[Fe(L-L)_3]^{2+}$ complexes shows rather unambiguously that the rate-determining step is ligand dissociation. The process thus proceeds by the mechanism represented by eq 2 and 3, and in this respect BrO_4^- behaves similarly to $P_2O_8^{4-}$ and ClO_2^-, which oxidize $[Fe(L-L)_3]^{2+}$ by the same ligand dissociation mechanism.[23-25,27] In contrast, the mechanism of oxidation by $S_2O_8^{2-}$ apparently involves direct electron transfer in a bimolecular rate-determining step, although the complex containing the "electron-attracting" substituent NO_2 is reported to react by both reaction pathways.[21]

The different reactivity patterns of $P_2O_8^{4-}$ and $S_2O_8^{2-}$ were previously ascribed to the necessity of an unfavorable major solvent reorganization of the strongly charged $P_2O_8^{4-}$ ion in order for this ion to approach $[Fe(L-L)_3]^{2+}$ sufficiently closely prior to direct electron transfer.[25] BrO_4^- is neither protonated nor expected to be particularly strongly solvated compared with $S_2O_8^{2-}$. At least part of the reason for the apparently unfavorable direct electron transfer for BrO_4^- is rather that such a step would correspond to a quite endothermic elementary electron transfer. By combining the standard redox potentials for the BrO_4^-/BrO_3^- (1.76 V[6]), $[Fe(L-L)_3]^{2+/3+}$ (0.88–1.25 V[28]), and OH^-/OH (1.4 V[39]) couples and the ionic product of water, we thus find that the electron-transfer process

$$[Fe(L-L)_3]^{2+} + BrO_4^- + H_2O \rightarrow [Fe(L-L)_3]^{3+} + BrO_3^- + OH\cdot + OH^- \quad (6)$$

has a standard free energy of reaction ranging from +0.26 to +0.63 V. If these values are lower than for the reactions with $S_2O_8^{2-}$ (which, however, may be more likely to react via the sulfate radical anion[42,43]), this could be a reason for the different reactivity patterns of BrO_4^- and $S_2O_8^{2-}$.

The kinetic data represented by eq 2–5 refer to the first 1 or 2 half-lives of the reaction. However, the stoichiometry does not correspond to eq 1, but approximately 1 mol of $[Fe(L-L)_3]^{2+}$ rather than 2 mol is consumed for each mole of BrO_4^-. This is also observed for the reactions of $[Fe(L-L)_3]^{2+}$ with both $P_2O_8^{4-}$ and $S_2O_8^{2-}$.[21,25] In all cases the effects are undoubtedly caused by the formation of free-radical intermediates,[15,42,43] and we have suggested those to be O^- or OH in the reactions with BrO_4^-. These radicals have also been detected in the photolytic decomposition of BrO_4^-,[15] and they are known to attack both $[Fe(phen)_3]^{2+}$ and free phen in almost diffusion-controlled reactions forming OH adducts, which subsequently rapidly decay to several other products.[44]

We also notice that the ratio k_{-1}/k_2 depends weakly on the redox potential. The rates of electron transfer between $[Fe(L-L)_3]^{2+}$ and $S_2O_8^{2-}$ also vary weakly,[21] whereas their reactions with Ce(IV) and other one-electron transfer reagents exhibit a much larger variation,[45] in line with theoretical estimates,[46-48] according to which a 10^3-fold change is expected.

We have no direct way of separating k_{-1} and k_2, but the following rough estimates can be given. Taking for the bpy and phen complexes the values of k_{-1} obtained by stopped-flow techniques[49] (25 °C) as 1.4×10^5 and 1.5×10^6 dm^3 mol^{-1} s^{-1}, respectively, we find k_2 to be approximately 1.4×10^5 and 1×10^5 dm^3 mol^{-1} s^{-1}. For the 4,7-Me_2phen and 5-NO_2phen complexes the first consecutive stability constant $K_1 \approx 10^5$. For the former the overall stability constant $\beta_3 \approx 10^{23}$, while values around both 10^{18} and 10^{15} are reported for the latter.[40] If we use the former value, and if the ratio K_3/K_2 is not very different from the (calculated) value for the unsubstituted complex, then $k_2 \approx 3 \times 10^5$ and 2×10^4 dm^3 mol^{-1} s^{-1} for 4,7-Me_2phen and 5-NO_2phen complexes, respectively, while the value $\beta_3 \approx 10^{15}$ would give $k_2 \approx 5 \times 10^2$ dm^3 mol^{-1} s^{-1}. The data therefore indicate that the independence of k_2 on the free energy of reaction might be weak, but in view of the discrepancy between the reported equilibrium data, no firm conclusion can be reached.

We shall finally give a possible cause for low "transfer coefficients" in electron-transfer reactions[46-48] of BrO_4^- and (with suitable modifications) other oxoanions. When diffusion control can be excluded, this effect is expected when the process is accompanied by large structural reorganization involving in particular large vibrational frequency shifts of intramolecular nuclear modes, corresponding to the liberation of a molecular fragment from a bound to a free state or vice versa. The following expression for the activation energy can then be derived:[50]

$$E_A = u_i(R_c) + [E_s + u_f(R_c) - u_i(R_c) + \Delta G_o]^2/4E_s \quad (7)$$

E_s is the solvent reorganization energy, ΔG_o the free energy of reaction, R is a coordinate (set) that describes the motion of the molecular fragments, and $u_i(R)$ and $u_f(R)$ are the molecular potentials associated with the modes that undergo the large vibrational frequency increase and decrease, respectively. R_c is finally the particular value of R at which electron transfer occurs.

The transfer coefficient may now be small, for finite E_A, if $u_i(R_c) > E_s + u_f(R_c)$. Independence of the rate constant of ΔG_o can then be expected over a quite wide range around

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$-\Delta G_0 \approx E_s + u_f(R_c) - u_i(R_c) < 0$. For this to be possible, R_c must correspond to a considerable stretch of the Br–O bond, which in fact provides the dominating contribution to E_a, and the motion of the separated fragments must be restricted by a strong repulsive potential, so that $u_f'(R_c) >> u_i'(R_c)$. R_c is then the distance of closest approach of the two fragments, and $u_i(R_c)$ and $u_f(R_c)$ become reorganization energies along the mode R (the Br–O bond).

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Registry No. BrO_4^-, 16474-32-1; $[Fe(L–L)_3]^{2+}$, L–L = 2,2′-bipyridyl, 15025-74-8; $[Fe(L–L)_3]^{2+}$, L–L = 1,10-phenanthroline, 14708-99-7; $[Fe(L–L)_3]^{2+}$, L–L = 5-nitro-1,10-phenanthroline, 15245-50-8; $[Fe(L–L)_3]^{2+}$, L–L = 4,7-dimethyl-1,10-phenanthroline, 15226-33-2.

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Electron-Transfer Reactions of Copper(III)–Peptide Complexes with Hexacyanoferrate(II)

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The rate constants for the electron-transfer reactions of $Fe(CN)_6^{4-}$ with a series of copper(III)–peptide complexes vary from 2.6×10^5 M^{-1} s^{-1} to greater than 8×10^7 M^{-1} s^{-1}. The reactions proceed more slowly in the presence of alkali metal ions due to their association with $Fe(CN)_6^{4-}$. The reactions with $Cu^{III}(H_{-3}Aib_3a)$, where Aib_3a is di-α-aminoisobutyryl-α-aminoisobutyramide, permit the resolution of stability constants (M^{-1}, 25.0 °C) for $Fe(CN)_6^{4-}$ with alkali metal ions, Li^+ (16) ~ Na^+ (13) < K^+ (29) < Cs^+ (55), and redox rate constants (M^{-1} s^{-1}) for $Fe(CN)_6^{4-}$ (2.2×10^6) > $LiFe(CN)_6^{3-}$ (1.0×10^6) > $NaFe(CN)_6^{3-}$ (3.1×10^5) ≃ $KFe(CN)_6^{3-}$ (3×10^5) > $CsFe(CN)_6^{3-}$ (1.3×10^5). Most of the electron-transfer reactions with Cu(III) are 1–2 orders of magnitude faster than an outer-sphere mechanism predicts. This suggests a pathway in which cyanide bridges axially to the square-planar Cu(III) complexes facilitating the electron transfer from $Fe(CN)_6^{4-}$. The reaction products give evidence of a cyano bridge as quenching of the Cu(II)–peptide EPR signal occurs upon addition of $Fe(CN)_6^{3-}$. Bulky groups in the Cu(III)–peptide ligand serve to block the formation of the cyano bridge and give smaller electron-transfer rate constants, which are in agreement with an outer-sphere mechanism.

Introduction

Rapid electron-transfer reactions have been observed for copper(III, II)–peptide couples with several other redox couples.[1-4] Although the electrode potentials of the Cu(III, II) couples vary greatly with the peptide ligand (the values range from 1.02[5] to 0.37 V[6] vs. NHE), the self-exchange rate constant appears to be relatively insensitive to the nature of the coordinated peptide. Recently ^1H NMR line broadening was used[7] to determine directly the self-exchange rate constant for the $Cu^{III}(H_{-2}Aib_3)$–$Cu^{II}(H_{-2}Aib_3)^-$ complexes.[8] This value was in good agreement with values calculated from several Cu(III) peptide–Cu(II) peptide cross-exchange reactions by using the Marcus theory[9] and gave a self-exchange rate constant of 5×10^4 M^{-1} s^{-1} at 25 °C. The outer-sphere oxidation of ruthenium(II) ammine complexes[10] by Cu(III) peptides yield copper self-exchange rate constants that also are in good agreement with the NMR values and the values determined from the Cu(III)–Cu(II) cross reactions.

On the other hand, the very rapid reactions for the reduction[1] of Cu(III) peptides by $IrCl_6^{3-}$ and for the oxidation[4] of Cu(II) peptides by $IrCl_6^{2-}$ gave apparent self-exchange rate constants of 10^8 M^{-1} s^{-1} for the Cu(III, II) couples. Although these reactions show a Marcus correlation slope of 0.5, an inner-sphere mechanism with electron transfer occurring by a chloride bridge between Cu and Ir was proposed[1,4] to account for the 3 orders of magnitude increase in the apparent self-exchange rate constant.

In the present work the hypothesis of an inner-sphere electron-transfer mechanism for Cu(III, II) peptides is tested by using the reactions of $Fe(CN)_6^{4-,3-}$. The latter complexes have been shown in other reactions[11-13] to occur via a bridging cyano group as well as by outer-sphere electron transfer. The self-exchange rate constants are known[14,15] for $Fe(CN)_6^{3-,4-}$ so that the magnitude of the cross-reaction rate constants can be used to test for evidence of pathways more favorable than that expected from the Marcus correlation of the outer-sphere rate constants. The results indicate that the cyano group provides an inner-sphere bridge between iron and copper that is comparable to that found for the hexachloroiridate reactions.

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