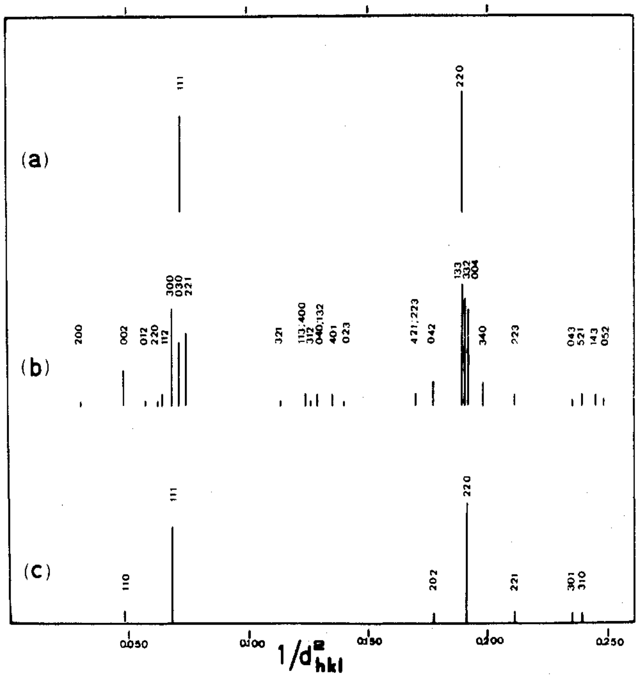

Figure 2. Schematic stick diagrams for the X-ray diffraction patterns obtained for the two allotropic forms of Mg_2NiH_4: (a) high-temperature cubic structure; (b) low-temperature orthorhombic structure; (c) calculated pattern assuming a tetragonal symmetry as reported in ref 1.

Å. The space group $P222_1$ is assumed from the systematic extinctions, resulting in conditions (001), $l = 2n$.

The measured density of Mg_2NiH_4 powder is 2.53 g/cm^3, leading to a value of 16 formula units per orthorhombic cell and to a calculated X-ray density of 2.56 g/cm^3.

It has been reported[1] that Mg_2NiH_4 has a tetragonal structure with $a = 6.464$ Å and $c = 7.033$ Å. The calculated reflections according to such a structure are presented schematically in Figure 2c, from which it is seen that most of the peaks appearing in the measured diffraction pattern (Figure 2b) cannot be indexed according to the tetragonal symmetry. Probably the X-ray measurements reported in ref 1 were performed with a Debye–Scherrer camera leading to a lower resolution pattern in which closely spaced triplet reflections coincided.

The high-temperature phase of Mg_2NiH_4 has a cubic pseudo-CaF_2-type structure where the Ni atoms occupy the cube edges and the cube face centers while the Mg atoms occupy the eight tetragonal positions. Table II summarizes the crystallographic data obtained for this structure. The stoichiometric nature of this hydride suggests the saturation of some 16 hydrogen equivalent interstitial sites. Such an arrangement is possible for the $F\bar{4}3m$ space group with four Ni atoms at sites a, four Mg atoms at sites c, four Mg atoms at sites d, and sixteen hydrogen atoms at sites e. However, without the supporting measurements of neutron diffraction it is not possible to determine unambiguously the positions of hydrogen atoms. Thus, the possibility of the $Fm3m$ space group where hydrogen atoms occupy part of the available interstitial sites in the CaF_2 structure (in the space group $Fm3m$) cannot be excluded.

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Registry No. Mg_2NiH_4, 12362-18-4.

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Linear Free Energy Relations in Redox Reactions. Oxidation of Iodide Ion by Poly(pyridine)–Iron(III) Complexes and Hexachloroiridate(IV) Ion

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The rates of oxidation of iodide ion by some poly(pyridine)–iron(III) complexes and by the hexachloroiridate(IV) ion have been measured in aqueous acidic solutions. For the 1,10-phenanthroline– and 2,2′-bipyridyl–iron(III) complexes and the hexachloroiridate ion, the reaction follows second-order kinetics, while for the less reactive substituted poly(pyridine)–iron(III) complexes, the rate law contains an additional term which is first order in the complex but second order in iodide ion. The reaction scheme proposed entails a fast formation of ion pairs between the reactants and a rate-determining intramolecular electron transfer from iodide to the iron(III) or iridium(IV) center or an electron transfer from another iodide ion to the ion pair. The immediate products of the electron-transfer steps are, respectively, the iodide atom or the iodine molecule radical and the reduced form of the complex ion. The variation of rate constants from one oxidant to the other is rationalized on the basis of Marcus' theory. From the results, the homonuclear electron exchange between I· and I^- was estimated as 7×10^7 M^{-1} s^{-1}. When the pertinent work terms are included in the Marcus equation for cross-reactions, excellent agreement between calculated and observed rate constants is obtained for all the oxidants. The higher rate constant often observed for the $[I^-]^2$ term relative to the $[I^-]$ term in iodide reactions is attributed to the more favorable $\Delta G°$ for the formation of I_2^{-}· from I^- and I·.

Introduction

Linear free energy relations have been demonstrated for a large number of redox reactions. The redox reactions of substitution-inert poly(pyridine) complexes of iron in either the ferrous or the ferric state are the most common reactants employed for these investigations.[1-8] Quite recently,[9] Davies and Earley found, using the oxidation of various polycyclic amino acid Cr(II) complexes by $Cr(NH_3)_5Cl^{2+}$, that such linear free energy relations also exist for reactions of the inner-sphere mechanism and, surprisingly, did obtain 0.5 as the slope of ΔG^* vs. $\Delta G°$ plots. The dependence of ΔG^* (the free energy of activation for the redox reaction) on $\Delta G°$ (the

Table I. Rate Parameters for the Oxidation of Iodide by $Fe(LL)_3^{3+}$ and $IrCl_6^{2-}$ [a]

oxidant	a, M^{-1} s^{-1}	b, M^{-2} s^{-1}	k_1,[b] s^{-1}	k_2,[c] M^{-1} s^{-1}
$Fe(phen)_3^{3+}$	$(1.54 \pm 0.09) \times 10^5$		1.9×10^4	
	$(1.45 \pm 0.03) \times 10^5$ [d]			
$Fe(5,6\text{-}(CH_3)_2\text{-}phen)_3^{3+}$	$(1.78 \pm 0.04) \times 10^4$	$(3.19 \pm 0.20) \times 10^6$	2.2×10^3	3.9×10^5
$Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3^{3+}$	$(5.04 \pm 0.43) \times 10^2$	$(2.66 \pm 0.08) \times 10^6$	6	3.2×10^5
$Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{3+}$	$(1.14 \pm 0.12) \times 10^2$	$(1.08 \pm 0.08) \times 10^5$	13.9	1.3×10^4
$Fe(bpy)_3^{3+}$	$(5.54 \pm 0.16) \times 10^4$		6.8×10^3	
	$(5.00 \pm 0.02) \times 10^4$ [d]			
$Fe(4,4'\text{-}(CH_3)_2\text{-}bpy)_3^{3+}$	$(2.73 \pm 0.31) \times 10^2$	$(5.15 \pm 0.20) \times 10^4$	33	6.3×10^3
$IrCl_6^{2-}$	$(1.38 \pm 0.07) \times 10^3$		2.5×10^3	

[a] Reaction medium 0.5 M H_2SO_4, $t = 25$ °C. The abbreviations used for the ligands (LL) are as follows: 1,10-phenanthroline, phen; 5,6-dimethyl-1,10-phenanthroline, $5,6\text{-}(CH_3)_2\text{-}phen$; 4,7-dimethyl-1,10-phenanthroline, $4,7\text{-}(CH_3)_2\text{-}phen$; 3,4,7,8-tetramethyl-1,10-phenanthroline, $3,4,7,8\text{-}(CH_3)_4\text{-}phen$; 2,2′-bipyridyl, bpy; 4,4′-dimethyl-2,2′-bipyridyl, $4,4'\text{-}(CH_3)_2\text{-}bpy$. [b] Obtained by dividing a by $2K_{IP}$ which has values of 8.2 M^{-1} for $Fe(LL)_3^{3+}$ and 0.56 M^{-1} for $IrCl_6^{2-}$. [c] Obtained by dividing b by $2K_{IP}$, which has the same values as in footnote b above. [d] Mean value obtained in 0.5 M $HClO_4$.

standard free energy of the reaction) has been given a semitheoretical treatment by Marcus and Sutin[10-13] and also, in a less elaborate manner, independently by Newton[14] and Earley.[9] The predicted linearity of such a plot and the slope of 0.5 are a consequence of the assumptions that are inherent in these semitheoretical treatments, and these assumptions are essentially equivalent in all the above treatments.

Apart from Irvine's work[1] and, more recently, the oxidation[15] of ascorbic acid by these iron(III) complexes and $IrCl_6^{2-}$, redox reactions that have been subjected to this free energy correlation are characterized by (a) possession of thermodynamically favorable rate-controlling electron-transfer steps and (b) transfer of an equal number of electrons (in most cases, one electron) between reactants to form final products; i.e., the reactions are complementary in redox reaction terminology.

As part of our continuing interest in phenomenological studies of the dynamics of redox reactions involving halogens, we have selected the title reactions with the hope of investigating linear free energy relations in reactions that do not have characteristics (a) and (b) above. Our previous experience in the kinetics of halogen redox reactions[16-19] and the reports of other workers[20-25] on the oxidation of halides to halogens have shown that, although halogen redox reactions entail a net transfer of two electrons, these reactions proceed by way of univalent changes involving the dihalogen radical ion $X_2^{-}\cdot$ or the halogen atom radical $X\cdot$ (X = Cl, Br, I) as the reactive intermediates. Reported estimates by independent researchers[26,40] of the redox potential for the $I\cdot/I^-$ and $I_2^-\cdot/I^-$ couples put the potentials in the ranges 1.38–1.42 and 1.08–1.18 V, respectively. The reduction potentials of the oxidants used in this work lie in the range 0.81–1.06 V.[3,15,27] Thus, the first electron-transfer step in the noncomplementary reduction by iodide is the oxidation of I^- to $I\cdot$ or I_2^-. This step, for which the above quoted values of the redox potentials show that $\Delta G° > 0$, is supposed to be rate determining. Therefore, these studies could provide a means of effecting empirical correlations of rate constants with the free energy of reaction for cases where $\Delta G° > 0$. In this work, the rates and mechanisms of the title reactions were investigated, and the rate constants for the rate-determining steps are shown to correlate with the equilibrium constants according to Marcus' theory for outer-sphere electron-transfer reactions.

Experimental Section

Materials. The iron(III) complexes were prepared by the oxidation of a dilute sulfuric acid solution of iron(II) complexes with ceric sulfate as reported by Ford-Smith and Sutin.[3] The perchlorate salts of the iron(III) complexes were precipitated from the sulfate solutions by addition of concentrated perchloric acid or saturated solutions of sodium perchlorate. The salts were purified by recrystallization from dilute perchloric acid. They were determined to be pure from the agreement of their spectral characteristics with previously published values.[3] The obtained absorption peaks and extinction coefficients in concentrated H_2SO_4 were as follows: $Fe(phen)_3^{3+}$, 600 nm, 872 cm^2 mol^{-1}; $Fe(5,6\text{-}(CH_3)_2\text{-}phen)_3^{3+}$, 600 nm, 780 cm^2 mol^{-1}; $Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3^{3+}$, 570 nm, 764 cm^2 mol^{-1}; $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{3+}$, 670 nm, 1590 cm^2 mol^{-1}; $Fe(bpy)_3^{3+}$, 620 nm, 321 cm^2 mol^{-1}; $Fe(4,4'\text{-}(CH_3)_2\text{-}bpy)_3^{3+}$, 595 nm, 395 cm^2 mol^{-1}. Standard solutions of the iron(III) complexes were prepared by dissolving known weights in predetermined volumes of solution.

The iron(II) complexes either were commercially available (G. F. Smith) or were made by adding stoichiometric amounts of the ligand to ferrous ammonium sulfate solution. Potassium hexachloroiridate (Alfa Inorganics) and lithium perchlorate, perchloric acid, and sulfuric acid (BDH products, AnalaR grade) were used without further purification.

Kinetics. The stoichiometry of the reaction was determined as follows: A known amount of the Fe(III) complex was alllowed to react with a slight excess (5–10%) of iodide ion. The iodine produced was extracted with three 10-mL portions of CCl_4, and its concentration was determined spectrophotometrically (λ_{max} (I_2 in CCl_4) 519 nm, ϵ_{max} 920 M^{-1} cm^{-1}). The Fe(II) complex produced was determined spectrophotometrically. For the two complexes investigated, $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{3+}$ and $Fe(phen)_3^{3+}$, the stoichiometry $2Fe(III) + 2I^- = 2Fe(III) + I_2$ was followed. It was assumed that this holds for all the other oxidants.

The rates of the reactions were measured with a Durrum-Gibson stopped-flow spectrophotometer in which temperature control was effected by circulating thermostated water from a bath through the temperature control units of the equipment. The absorbance changes for each reaction were monitored at the absorption peaks for the ferrous complexes. The wavelengths employed were as follows:[3] $Fe(phen)_3^{2+}$, 510 nm; $Fe(5,6\text{-}(CH_3)_2\text{-}phen)_3^{2+}$, 512 nm; $Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3^{2+}$, 533 nm; $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{2+}$, 500 nm; $Fe(bpy)_3^{2+}$, 522 nm; $Fe(4,4'\text{-}(CH_3)_2\text{-}bpy)_3^{3+}$, 529 nm. For the hexachloroiridate(IV) ion, the reaction was monitored[28] at λ 478 nm, the absorption peak for $IrCl_6^{2-}$. All kinetic runs were performed under pseudo-first-order conditions with the concentrations of iodide ion in at least tenfold excess over those of the oxidants. The reaction medium was either 0.5 M H_2SO_4 or 0.5 M $HClO_4$, and the temperature was maintained constant at 25.0 ± 0.1 °C.

Results

$Fe(LL)_3^{3+} + I^-$ Reactions. With the concentrations of iodide in at least tenfold excess over those of $Fe(LL)_3^{3+}$, plots of $\log(A_t - A_\infty)$ (A_t and A_∞ are respectively the absorbances at time t and at the end of the reaction) vs. t were linear to more than 90% reaction, thus confirming that the reaction is first order in $Fe(LL)_3^{3+}$. From the slopes of such linear plots, the pseudo-first-order rate constant k_{obsd} was determined at different initial concentrations of iodide. For $[Fe(phen)_3^{3+}] = (1.3\text{–}2.1) \times 10^{-5}$ M and $[I^-]$ in the range $(2.0\text{–}16.0) \times 10^{-4}$ M and for $Fe(bpy)_3^{3+} = 3.0 \times 10^{-5}$ M and $[I^-] = (4.0\text{–}24.0) \times 10^{-4}$ M, $k_{obsd}/[I^-]$ was constant and independent of $[I^-]$. This suggests that, in this range of iodide concentration, the data for the oxidation of iodide by either of these two complexes are consistent with the rate equation (1). Values of

$$-d[Fe(LL)_3^{2+}]/dt = 2d[I_2]/dt = a[Fe(LL)_3^{3+}][I^-] \qquad (1)$$

$k_{obsd}/[I^-]$ at different $[I^-]$ are presented in Figure 1, while

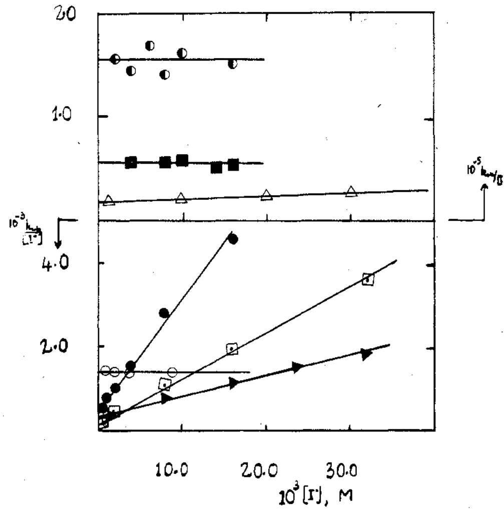

Figure 1. Variation of rate with iodide in the $Fe(LL)_3^{3+} + I^-$ and $IrCl_6^{2-} + I^-$ reactions. Plots of $k_{obsd}/[I^-]$ vs. $[I^-]$: (○) $Fe(phen)_3^{3+}$; (■) $Fe(bpy)_3^{3+}$; (▲) $Fe(5,6\text{-}(CH_3)_2\text{-}phen)_3^{3+}$; (□) $Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3^{3+}$; (●) $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{3+}$; (◐) $IrCl_6^{2-}$; (△) $Fe(4,4'\text{-}(CH_3)_2\text{-}bpy)_3^{3+}$ (reaction medium 0.5 M H_2SO_4, t = 25 °C).

values of k_a averaged over iodide concentration used are presented in Table I.

However, for $Fe(5,6\text{-}(CH_3)_2\text{-}phen)_3^{3+}$, $Fe(4,7\text{-}(CH_3)_2\text{-}phen)_3^{3+}$, $Fe(3,4,7,8\text{-}(CH_3)_4\text{-}phen)_3^{3+}$, and $Fe(4,4\text{-}(CH_3)_2\text{-}bpy)_3^{3+}$, values of $k_{obsd}/[I^-]$ increase as $[I^-]$ increases, but plots of $k_{obsd}/[I^-]$ vs. $[I^-]$ are linear with finite intercepts (Figure 1). Thus, for these four complexes, $[Fe(LL)_3^{3+}] = (1.0\text{–}2.0) \times 10^{-5}$ M and $[I^-] = (0.1\text{–}4.0) \times 10^{-3}$ M, the data are consistent with the rate equation (2).

$$-d[Fe(LL)_3^{2+}]/dt = 2d[I_2]/dt = (a + b[I^-])[Fe(LL)_3^{3+}][I^-] \quad (2)$$

Values of a and b with estimates of errors, as standard deviations obtained from mean linear least-squares analysis of the data, are presented in Table I. Equation 2 reduces to eq 1 for $b = 0$.

Effect of Added Sulfate Ions on the Rate Constants for the $Fe(LL)_3^{3+} + I^-$ Reactions. Ford-Smith and Sutin[3] have reported that the rates of oxidation of $Fe^{2+}(aq)$ by these iron(III) complexes differ by an almost constant factor in $HClO_4$ and H_2SO_4 solutions. The rate constant for the oxidation of iodide by $Fe(phen)_3^{3+}$ was therefore determined in 0.5 M $HClO_4$ without any added sulfate ion. The second-order rate constant obtained, averaged over five different iodide concentrations, was $(1.45 \pm 0.03) \times 10^5$ M^{-1} s^{-1}. Similarly, for $Fe(bpy)_3^{3+}$, the mean second-order rate constant obtained was $(0.50 \pm 0.02) \times 10^5$ M^{-1} s^{-1}. These values are essentially the same as those obtained in sulfuric acid, showing that the rate constants are unaffected by sulfate ions. This finding is consistent with their explanation that the higher rate of oxidation of $Fe^{2+}(aq)$ in sulfuric acid is due to the formation of sulfate–iron(II) complexes, and these complexes react at a faster rate than the aquo ion with $Fe(LL)_3^{3+}$. Since iodide ion does not form any sulfate complex, the rate of the reaction should be insensitive to perchloric acid medium, as was found in our investigations.

$IrCl_6^{2-} + I^-$ Reaction. For this reaction, pseudo-first-order plots were linear to more than 90% reaction, suggesting that the reaction is first order in $[IrCl_6^{2-}]$. Values of $k_{obsd}/[I^-]$ were independent of $[I^-]$ for $[IrCl_6^{2-}] = 4.1 \times 10^{-5}$ M and $[I^-] = (1.0\text{–}80.0) \times 10^{-3}$ M. Therefore, the reaction is also first order in $[I^-]$ in this range of iodide concentrations. The mean value of the second-order rate constants ($a = k_{obsd}/[I^-]$) obtained from eight different iodide concentrations is included in Table I, and values of $k_{obsd}/[I^-]$ as a function of $[I^-]$ are plotted in Figure 1.

Discussion

The rate equations obtained for these systems show that two paths[29] are concurrently operative in these reactions: one that is first order in the oxidant and first order in iodide, and another that is first order in oxidant but second order in iodide. The scheme proposed below (eq 3–7), although not unique, comfortably leads to the observed rate equations. Provided $k_3K_{IP}[Fe(LL)_3^{3+}][I^-] >> k_{-1}[Fe(LL)_3^{2+}]$ and $k_4K_{IP}[Fe(LL)_3^{3+}][I^-] >> k_{-2}[Fe(LL)_3^{2+}]$, eq 3–7 lead to eq 8.

$$Fe(LL)_3^{3+} + I^- \overset{K_{IP}}{\rightleftharpoons} Fe(LL)_3|I^{2+} \quad (3)$$

$$Fe(LL)_3|I^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Fe(LL)_3^{2+} + I\cdot \quad (4)$$

$$Fe(LL)_3|I^{2+} + I^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Fe(LL)_3^{2+} + I_2^-\cdot \quad (5)$$

$$Fe(LL)_3|I^{2+} + I\cdot \xrightarrow{k_3} Fe(LL)_3^{2+} + I_2 \quad (6)$$

$$Fe(LL)_3|I^{2+} + I_2^-\cdot \xrightarrow{k_4} Fe(LL)_3^{2+} + I_3^- \quad (7)$$

$$\text{rate} = -\frac{1}{2}\frac{d}{dt}[Fe(LL)_3^{2+}] = \frac{d}{dt}[I_2] = k_1K_{IP}[Fe(LL)_3^{3+}][I^-] + k_2K_{IP}[Fe(LL)_3^{3+}][I^-]^2 \quad (8)$$

Equation 8 is the same as eq 2 with $a = 2k_1K_{IP}$ and $b = 2k_2K_{IP}$. For $Fe(phen)_3^{3+}$ and $Fe(bpy)_3^{3+}$ under the experimental conditions of this work, steps 3, 4, and 6 will lead to the observed rate equation while for the less reactive iron(III) complexes, the experimental data are consistent with the proposed scheme from steps 3–7. As for $IrCl_6^{2-}$ as the oxidant, the relevant steps are steps 3, 4, and 6, with $Fe(LL)_3^{3+}$ being replaced by $IrCl_6^{2-}$ in the equations.

In the above scheme, the rate of formation of the precursor complex $Fe(LL)_3|I^{2+}$ is assumed to be rapid compared to rate for the subsequent electron-transfer steps. The precursor complex could be either (a) an ion-pair complex formed by a diffusion-controlled rate or (b) a π complex formed by the overlap of the π orbitals of the iodide ion and the π^* orbitals of the polypyridine ligands. A direct ligation of I^- to the metal ion is considered unlikely because the rate constants for the electron-transfer reactions are much higher than those obtained for anion-assisted substitution reactions of this type of complex. However, we prefer (a) on electrostatic considerations and on the grounds that aquo ions such as those of Co(III), Np(VI), Bi(V), and Cr(VI) and the binuclear complex ions $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$, $(NH_3)_4CoO_2,NH_2,Co(NH_3)_4^{4+}$, and $(en)_2CoO_2,NH_2Co(en)_2^{4+}$, which have no empty and low-lying π or π^* orbitals for bonding, do show in their reactions with halides the same type of rate equations as obtained in the $Fe(LL)_3^{3+}$ reactions,[20-24] and outer-sphere ion pairs have been invoked as the precursor complexes in these reactions.

The ion-pair formation constant K_{IP} can be estimated from eq 9,[30] where $U(a) = Z_1Z_2e^2/[Da(1 - \kappa a)]$ and $\kappa = [8\pi Ne^2\mu/(1000DRT)]^{1/2}$.

$$K_{IP} = (4\pi Na^3/3000)\exp[-U(a)/k_BT] \quad (9)$$

In eq 9, $U(a)$ is the Debye-Hückel interaction potential, a is the distance between the centers of the reactants, which is taken as the sum of the radii of the $Fe(LL)_3^{3+}$ (7.0 Å) or $IrCl_6^{2-}$ (4.3 Å) and I^- (2.16 Å).[31] Values of K_{IP} were estimated as 4.1 and 0.3 M^{-1} for the iron(III) complexes and the hexachloroiridate ion, respectively. With these, and from values of a and b, k_1 and k_2 were calculated for each oxidant, and the results are included in Table I.

Table II. Kinetic and Thermodynamic Parameters for the Oxidation of Iodide by $Fe(LL)_3^{3+}$ and $IrCl_6^{2-}$ [a]

oxidant	ϵ^0, V	k_{12}(exptl) ($a/2 = k_1K_{IP}$), M^{-1} s^{-1}	k_{12}(calcd),[b] M^{-1} s^{-1}	R_1[c]	k_{12}(calcd),[d] M^{-1} s^{-1}	R_2[c]
$Fe(phen)_3^{3+}$	1.06[e]	7.70×10^4	3.71×10^4	0.48	5.67×10^4	0.75
$Fe(5,6\text{-}(CH_3)_2\text{-phen})_3^{3+}$	0.97[e]	8.9×10^3	1.27×10^3	0.14	3.10×10^3	0.35
$Fe(4,7\text{-}(CH_3)_2\text{-phen})_3^{3+}$	0.87[e]	2.52×10^2	0.83×10^2	0.33	0.96×10^2	0.38
$Fe(3,4,7,8\text{-}(CH_3)\text{-phen})_3^{3+}$	0.81[e]	0.57×10^2	9.8	0.17	10.6	0.19
$Fe(bpy)_3^{3+}$	1.035[f]	2.77×10^4	1.77×10^4	0.64	2.6×10^4	0.94
$Fe(4,4'\text{-}(CH_3)_2\text{-bpy})_3^{3+}$	0.88[g]	1.37×10^2	1.17×10^2	0.43	1.41×10^2	1.04
$IrCl_6^{2-}$	0.957[h]	6.9×10^2	1.13×10^2	0.16	1.93×10^2	0.28

[a] Reaction medium 0.5 M H_2SO_4, $t = 25$ °C. Other constants not listed in the table but used in eq 10 and 16 are as follows: $I\cdot + e^- \rightarrow I^-$, $E^0 = 1.40$ V (mean values of 1.42, 1.40, and 1.38 V reported in the literature);[26,40] $k_{11}(I\cdot/I^-) = 6.8 \times 10^7$ M^{-1} s^{-1} (see text), $\Delta G_{11}{}^* = 6.77$ kcal mol^{-1}, $w_{11} = 0$; $k_{22}(Fe(LL)_3^{3+}/Fe(LL)_3^{2+}) = 3.3 \times 10^8$ M^{-1} s^{-1},[33] $\Delta G_{22}{}^*(Fe(LL)_3^{3+}) = 5.83$ kcal mol^{-1}, $w_{22}(Fe(LL)_3^{3+}) = 0.43$ kcal mol^{-1}, $\Delta G_{22}{}^{**}(Fe(LL)_3^{3+}) = 5.40$ kcal mol^{-1}, $w_{12}(Fe(LL)_3^{3+}) = -0.44$ kcal mol^{-1}; $k_{22}(IrCl_6^{2-}/IrCl_6^{3-}) = 2.3 \times 10^5$ M^{-1} s^{-1},[34] $\Delta G_{22}{}^*(IrCl_6^{2-}) = 10.14$ kcal mol^{-1}, $w_{22}(IrCl_6^{2-}) = 0.99$ kcal mol^{-1}, $\Delta G_{22}{}^{**}(IrCl_6^{2-}) = 9.15$ kcal mol^{-1}, $w_{12}(IrCl_6^{2-}) = 0.79$ kcal mol^{-1}. [b] k_{12}(calcd) is the calculated rate constant from eq 10. [c] R_1 is the ratio of k_{12}(calcd) by eq 10 to k_{12}(exptl). R_2 is the ratio of $k_{12}{}^{w}$(calcd) by eq 14 to k_{12}(exptl). [d] k_{12}(calcd) is the calculated rate constant after eq 14 is used for correction of work terms. [e] Values from ref 3. [f] Mean values of 1.05 V reported in ref 27 and 1.02 V in ref 15. [g] Mean values of 0.84 V quoted in ref 15 and 0.92 V in ref 27. [h] From ref 15b.

Correlation with Marcus' Theory. Marcus' equation for redox cross-reactions is

$$k_{12} = (k_{11}k_{22}K_{12}f)^{1/2} \tag{10}$$

or

$$\log k_{12} - 0.5 \log k_{22} - 0.5 \log f = 0.5 \log k_{11} + 0.5 \log K_{12} \tag{11}$$

where

$$\log f = (\log K_{12})^2/4 \log k_{11}k_{22}Z^{-2} \tag{12}$$

In the above equations, k_{12} ($=k_1K_{IP}$) and K_{12} are respectively the rate and equilibrium constants for the cross-reaction, k_{11} and k_{22} are respectively the homonuclear electron-exchange rate constants for the reducing ions ($I^- + I\cdot$) and the oxidizing ions ($Fe(LL)_3^{3+} + Fe(LL)_3^{2+}$ or $IrCl_6^{2-} + IrCl_6^{3-}$), and Z is the collision frequency for the uncharged reactant molecules in solution, usually taken as 10^{11} M^{-1} s^{-1}. In applying eq 11 to our system, we needed an estimate of k_{11}; k_{12}, k_{22}, and K_{12} (calculated from the $E°$ for the $Fe(LL)_3^{3+}/Fe(LL)_3^{2+}$ couple and estimated $E°$ for the $I\cdot/I^-$ couple) are known, but k_{11} is not. The estimate of k_{11} was obtained from an iterative procedure: viz., we guessed a value for k_{11} and plugged it into eq 12 to calculate f; then with the calculated value of $\log f$, plots of the left-hand side of eq 11 vs. $\log K_{12}$ were made, and from mean least-squares calculations, the intercept and slope of such plots were determined. From the intercept, a new estimated value of k_{11} was obtained, and this was then used to calculate a new $\log f$. The entire iterative process was repeated until successive estimates of k_{11} differed by less than 10%. The final result gave $\log k_{11} = 7.83$ and a slope of the linear plot as 0.44. The linear plot is presented in Figure 2. From these results, k_{11}, the elelctron-exchange rate constant between $I\cdot$ and $I_2^-\cdot$ was estimated as 7×10^7 M^{-1} s^{-1}. Although this estimate is comparable to the rate constants reported for electron transfer between $I_2^-\cdot$ and some aquo ions,[32,33] it is at least 1–2 orders of magnitude lower than what has been reported for the exchange rate constants between free radicals and parent organic molecules.[36] However, the large difference in charge and size between iodide ion and the atom radical ($r_I = 1.33$ Å, $r_{I^-} = 2.16$ Å)[31] suggests that the activation barrier (arising mainly from solvent reorganization) to electron exchange between this couple is higher than in the almost diffusion-controlled rates of electron exchange in organic radicals and their parent molecules. Using the estimated value $k_{11} = 7 \times 10^7$ M^{-1} s^{-1} and applying eq 10, we calculated the rate constants k_{12}(calcd) and the ratio k_{12}(calcd)/k_{12}(exptl) for each oxidant and present the results in Table II. From these, it is evident that values of k_{12}(calcd)/k_{12}(exptl) lie in the range 0.14–0.64 for all the oxidants.

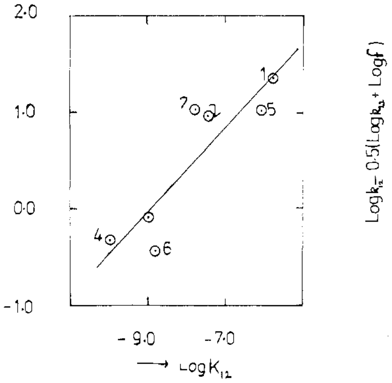

Figure 2. Marcus correlation for the $Fe(LL)_3^{3+} + I^-$ and $IrCl_6^{2-} + I^-$ reactions. Plot of $\log k_{12} - 0.5(\log k_{22} + \log f)$ vs. $\log K_{12}$: (1) $Fe(phen)_3^{3+}$; (2) $Fe(5,6\text{-}(CH_3)_2\text{-phen})_3^{3+}$; (3) $Fe(4,7\text{-}(CH_3)_2\text{-phen})_3^{3+}$; (4) $Fe(3,4,7,8\text{-}(CH_3)_4\text{-phen})_3^{3+}$; (5) $Fe(bpy)_3^{3+}$; (6) $Fe(4,4'\text{-}(CH_3)_2\text{-bpy})_3^{3+}$; (7) $IrCl_6^{2-}$ ($k_{22}(Fe(LL)_3^{3+}) = 3.3 \times 10^8$ M^{-1} s^{-1},[33] $k_{22}(IrCl_6^{2-}) = 2.3 \times 10^5$ M^{-1} s^{-1} [34]).

Recent reports by Haim and Sutin[37,38] have demonstrated that deviations from eq 10 could arise from the noncancelation of electrostatic work terms for reactions between ions, as in these reactions, and that a better agreement could be obtained if the work terms are included in eq 10. In such a situation, eq 10 could be written in terms of free energy as in eq 13 to include the work terms.[13]

$$\Delta G_{12}{}^{**} = \tfrac{1}{2}\Delta G_{12}{}^{**} + \tfrac{1}{2}\Delta G_{22}{}^{**} + \tfrac{1}{2}\Delta G_R{}^{\circ}(1 + \alpha) \tag{13}$$

$$k_{12} = \frac{k_BT}{h}[\exp(-\Delta G^*/RT)] \tag{14}$$

In eq 13 and 14

$$\alpha = \frac{G_R{}^{\circ}}{4[\Delta G_{11}{}^{**} + \Delta G_{22}{}^{**} - 2RT \ln(k_BT/hZ)]} \tag{15}$$

$$\Delta G_{12}{}^* = \Delta G_{12}{}^* - w_{12} + w_{21}$$

$$\Delta G_R{}^{\circ} = \Delta G^{\circ} - w_{12} + w_{21}$$

$$\Delta G_{11}{}^{**} = \Delta G_{11}{}^* - w_{11}$$

$$\Delta G_{22}{}^{**} = \Delta G_{22}{}^* - w_{22}$$

The w's are the electrostatic work terms, the suffixes 11, 22, and 12 refer to the reducing couple $I\cdot + I^-$, oxidizing couples $Fe(LL)_3^{3+} + Fe(LL)_3^{2+}$ or $IrCl_6^{2-} + IrCl_6^{3-}$, and the cross-reactions, respectively, k_B is Boltzman's constant, and h is Planck's constant, ΔG^{**} and ΔG^* are respectively the corrected and the experimental free energies (calculated from $k = k_BT/h \exp[-\Delta G_1{}^*/RT]$). The electrostatic work terms w were calculated with eq 16, with the symbols having the same meaning as those in eq 9.

$$w = Z_1Z_2e^2/[Da(1 + \kappa a)] \qquad (16)$$

Using eq 13–16, we calculated the values of ΔG, w, the rate constant k_{12} (k_1K_{IP}), and the ratio k_{12}(calcd)/k_{12}(exptl) for each oxidant; the values obtained are included in Table II. The results show that the inclusion of the work terms leads to a considerable improvement in the k_{12}(calcd) values, and the ratio of calculated rate constants to observed now lies in the range 0.17–1.04. Thus, in contrast to the $Fe^{2+} + Fe(LL)_3^{3+}$ reactions,[27] where calculated and experimental rate constants differ by a factor of 500, the systems under investigation in this work provide an excellent correlation with Marcus' theory. Moreover, differences in the adiabaticities of the exchange processes, and the cross-reaction, a probable cause of the large deviation in the $Fe^{2+} + Fe(LL)_3^{3+}$ reactions,[27] do not appear to be a feature of the $I^- + Fe(LL)_3^{3+}$ reactions.

A common characteristic of iodide redox reactions where rate equations of the type given by eq 2 are observed is that $b > a$. In this work, b/a lies within $(1.0–8.0) \times 10^2$ M^{-1} for the four complexes where this rate equation is applicable. Since reactivity differences in the reactions of these complexes seem to arise from changes in the free energy of the reaction, it can be concluded that differences in the magnitude of b and a may also be due to thermodynamic factors. The major difference in the steps leading to the $[I^-]$ and $[I^-]^2$ terms is in the oxidation product. In the $[I^-]$ term, the oxidation product is I· (eq 4), while in the $[I^-]^2$ term, it is $I_2^-\cdot$ (eq 5). The free energy change in these two steps differs by the free energy for the formation of $I_2^-\cdot$ from I· (eq 17). $K_{I_2^-}$ has been

$$I\cdot + I^- \overset{K_{I_2^-}}{\rightleftharpoons} I_2^-\cdot \qquad (17)$$

reported[39] as 10^5 M^{-1}. Thus, if in eq 10 f and k_{11} are the same for eq 4 and 5 for each oxidant, then k_2/k_1, and hence b/a $(=2k_2K_{IP}/2k_1K_{IP})$ should be approximately 3×10^2 M^{-1} and be independent of oxidant. The magnitude of this ratio lies within $(1.0–8.0) \times 10^2$ M^{-1} for the four iron complexes where eq 2 is the rate equation. In other systems[24,40] where the reported rate equation is of this form, values of this ratio are (M^{-1}) as follows: $(NH_3)_5CoO_2Co(NH_3)_5^{5+}$, 2.4×10^2; $(NH_3)_4CoO_2NH_2Co(NH_3)_4^{4+}$, 1.2×10^2; $(en)_2CoNH_2,O_2Co(en)_2^{4+}$, 6.0×10^2; $Os(bpy)_3^{3+}$, 4.7×10^2; $Os(phen)_3^{3+}$, 6.6×10^2. It can therefore be concluded that differences in b and a are due to the differences in $\Delta G°$ for the steps that lead to the $[I^-]^2$ and $[I^-]$ terms in the rate equation.

To summarize, our results do show that the rates of oxidation of iodide by these iron(III) complexes and by $IrCl_6^{2-}$ can be rationalized by Marcus' equation for cross-reactions and that Marcus' equation predicts the rate constants for these reactions to within a factor of 5. Thus, the Marcus equation is equally applicable for systems where $\Delta G° > 0$. The higher values of the third-order rate constants compared to the bimolecular rate constants in reactions of iodide where the two appear in the rate equation are attributed to the differences in the standard free energy of the two concurrent rate-determining steps.[40]

Registry No. I^-, 20461-54-5; $Fe(phen)_3^{3+}$, 13479-49-7; $Fe(5,6\text{-}(CH_3)_2\text{-phen})_3^{3+}$, 21924-26-5; $Fe(4,7\text{-}(CH_3)_2\text{-phen})_3^{3+}$, 17378-76-6; $Fe(3,4,7,8\text{-}(CH_3)_4\text{-phen})_3^{3+}$, 17378-81-3; $Fe(bpy)_3^{3+}$, 13479-48-6; $Fe(4,4'\text{-}(CH_3)_2\text{-bpy})_3^{3+}$, 34032-03-6; $IrCl_6^{2-}$, 16918-91-5.

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(40) At the time the revised form of this paper was being written, two papers appeared in this journal. The first (G. Nord, B. Pedersen, and O. Farver, *Inorg. Chem.*, **17**, 2233 (1978)) was on the oxidation of iodide and thiocyanate by $Os(phen)_3^{3+}$ and $Os(bpy)_3^{3+}$ and the other (M. Kimura and G. Wada, *Inorg. Chem.*, **17**, 2239 (1978)) concerned the kinetics of the $Fe(phen)_3^{3+} + I^-$ reaction in aqueous mixtures of methanol and ethanol. $Os(phen)_3^{3+}$ and $Os(bpy)_3^{3+}$ reactions with iodide have a rate law containing the $[I^-]$ and $[I^-]^2$ terms; b/a values from the results are 6.6×10^2 M^{-1} ($Os(phen)_3^{3+}$) and 4.7×10^2 M^{-1} ($Os(bpy)_3^{3+}$), which are in agreement with our predictions based on thermodynamic arguments. Their value of the second-order rate constant (1.60×10^5 M^{-1} s^{-1} at $[I^-] = 0.5$ M) reported for the $Fe(phen)_3^{3+} + I^-$ reaction is also in excellent agreement with that obtained in our study. k_{11} (for $I\cdot + I^-$) estimated from the data in the first paper is 10^7 M^{-1} s^{-1} which is also in good agreement with 7×10^7 M^{-1} s^{-1} obtained in our study.