urations.[26] We propose that an equivalent mechanism operates in the uranyl ion because, following the magnitudes of the static ligand fields, a much larger electron-phonon coupling should apply to the 6d orbitals, which constitute the intermediate states, as compared to that which applies to the 5f orbitals.

The TPA mechanism for the uranyl ion is then seen as two one-electron processes. The generation of the intermediate state corresponds to the $f_\sigma \rightarrow d_\pi$ transition. The same excited configuration is the source of the vibronic intensity in OPA. We note that this transition is polarized perpendicular to the UO_2 axis. The very strong linear dichroism in OPA indicates that the $f_\sigma \rightarrow d_\sigma$ transition occurs at much higher energies, as a result of the strong antibonding character of the d_σ orbital. In this model the second photon serves to complete the TPA transition through the $d_\pi \rightarrow f_\delta$ or $d_\pi \rightarrow f_\pi$ processes, depending on whether the polariation is y or z, respectively. It is now clear why the TPA intensity is dominated by the $\Delta_g(D_{\infty h})$ states which derive their intensity from the $\sigma\delta$ configuration. Moreover, this intensity will be largest in those states that have the largest singlet character. In our model calculations XIII and XIV have the largest singlet character and consequently relatively large transition probabilities. Qualitatively these states show by far the largest TPA intensity.

The much weaker TPA intensity in the xz and yz polarizations is a consequence of the relatively small role played by the $\sigma\pi$ configuration in the observed manifold. The spectrum of the neptunyl(VI) ion reveals that this configuration is approximately 15 000 cm^{-1} above $\sigma\delta$ and $\sigma\phi$,[25] and its contribution to the TPA intensity is then a second-order effect. The presence of this configuration must also be responsible for the x- and y-polarized magnetic-dipole intensity in OPA, and indeed the distribution of TPA intensity in origins I, II, V, VI, IX, and X closely follows the magnetic-dipole intensity in OPA.

Acknowledgment. We are indebted to the Science and Engineering Research Council for the support of T.J.B. and J.R.G.T. and to the staff of the Laser Support Facility at the Rutherford Appleton Laboratory for invaluable assistance.

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Contribution from the Department of Chemistry,
Rice University, Houston, Texas 77251

Stoichiometry and Kinetics for Reactions of Tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) with Oxygen, Hydrogen Peroxide, and Cyanide

Doan Trang Vu and David M. Stanbury*

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Fe^{II}(OHP)$_3$ (OHP = 4,7-dihydroxy-1,10-phenanthroline) reacts with O_2 rapidly in alkaline aqueous solution. A major product of the reaction is HO_2^-; O_2^- is a feasible intermediate in the reaction. Fe^{II}(OHP)$_3$ reacts with HO_2^- to produce a 1:1 mixture of Fe^{III}(OHP)$_3$ and "Fe^{III}(OHP)$_2$(OH)"; this reaction has a rate law that is first order in [Fe^{II}(OHP)$_3$] but zero order in [peroxide], with a rate constant of 1.8×10^{-2} s^{-1} at 22 °C, pH 13. The substitution reaction of Fe^{II}(OHP)$_3$ with CN$^-$ has the same rate law as the redox reaction with HO_2^- and a rate constant of 8×10^{-3} s^{-1}. Both the redox reaction of HO_2^- and the substitution reaction of CN$^-$ are interpreted as having loss of the ligand OHP as the rate-limiting step. A sensitive and specific HPLC method has been developed for determination of HO_2^- in complex mixtures.

Introduction

The ligand 4,7-dihydroxy-1,10-phenanthroline (OHP), which is used as a reagent for iron in alkaline media, is quite unusual among the phenanthrolines.[1] The iron(III)-tris complexes of most phenanthrolines are well-known as a graded series of substitution-inert one-electron oxidants that are stable only in acidic media; however, Fe^{II}(OHP)$_3$ is stable only in alkaline media, and it is a strong reducing agent. At pH 13 the hydroxo groups are fully deprotonated, rendering the ligand a dianion. But the unusual nature of Fe^{II}(OHP)$_3$ cannot be ascribed simply to a charge effect, since the comparable sulfonated complexes fall in the class of the normal phenanthroline complexes. Apparently an unusual type of conjugation occurs when OHP is complexed as its dianion, which leads to a very strong affinity for Fe(III).

The reaction chemistry of Fe^{II}(OHP)$_3$ has not been extensively explored, probably because of difficulties in handling. The complex is very sensitive to O_2, and the free ligand is difficult to purify because it is resistant to sublimation and insoluble in all solvents except strong acids and bases. There is a fascinating report of the kinetics of the reductions of O_2 and HO_2^- by the complex; the O_2 reaction was reported to proceed with simple bimolecular kinetics but without the intermediacy of free O_2^- or HO_2^-, and the HO_2^- reaction was reported to be first order in HO_2^- and second order overall.[2] In view of the reactions of O_2 with ruthenium(II) ammines, where O_2^- and H_2O_2 are formed,[3] a mechanism that avoids these species in the reaction with Fe^{II}(OHP)$_3$ would be rather unexpected. The bimolecular rate law for reduction of HO_2^- suggests an outer-sphere electron-transfer mechanism; as pointed out recently by Bakač and Espenson, reports of such a mechanism for reduction of H_2O_2 are extremely rare.[4] In the case of Cr(CN)$_6^{4-}$ the outer-sphere pathway was always a minor term in the rate law,[5] and in the case of Ru(NH$_3$)$_5$L^{2+} peculiar saturation effects were observed.[6] The present paper reports substantially different results for the reactions of Fe^{II}(OHP)$_3$ with O_2 and HO_2^-. The substitution reaction of Fe^{II}(OHP)$_3$ with CN$^-$ is also reported.

Experimental Section

Reagents and Solutions. 4,7-Dihydroxy-1,10-phenanthroline (OHP) was purchased from G. F. Smith, and purified by esterification. A 0.5-g sample of the crude ligand was refluxed for 1 h in 10 mL each of acetic anhydride and pyridine. The dark brown suspension was filtered, the filtrate collected, and the solvent removed by rotary evaporation. The

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orange-brown solid was dissolved in CH_2Cl_2 and purified by reverse-phase chromatography on a silica gel column (5 cm × 10 cm, elution with CH_3OH/CH_2Cl_2). The esterified ligand emerged in the 6–8% CH_3OH fraction. Removal of the solvent gave a light yellow powder, which, when dissolved and saponified in aqueous NaOH, yielded a dark yellow solution. A UV–vis spectrum of this solution corresponded to that of the deprotonated ligand as reported by Poe and Diehl.[7] Upon the addition of 1 M HCl, the free base precipitated from solution and was collected by suction filtration. The light yellow solid was washed with small portions of ethanol and anhydrous diethyl ether and then air dried (18% yield).

A 30% H_2O_2 solution containing 1 ppm $Na_2SnO_3{\cdot}3H_2O$ as preservative was obtained from J. T. Baker. The use of solutions made from 3% H_2O_2 containing organic preservatives gave irreproduceable kinetic results and was discontinued. Stock solutions of 1 M and 0.1 M H_2O_2 were standardized against MnO_4^-. $Fe(ClO_4)_2{\cdot}6H_2O$ was obtained from Alfa Products. A fresh solution (0.01 M) of Fe^{2+} was made on the day of each experiment and standardized against MnO_4^-. NaCN (Fisher Scientific) solutions were made up by weight as needed on the day of the experiment. NaOH pellets were obtained from MCB, and stock solutions of 0.2 M NaOH were standardized against 0.100 M HCl. All chemicals used were of reagent grade. Deionized water that was further purified by distillation in an all-glass still was used throughout.

Concentrated stock solutions of OHP were made in 0.1 M NaOH, stored in polyethylene vials, and protected from light. Solutions of the appropriate concentration were made on the day of the experiment, and the pH was adjusted by using NaOH or $HClO_4$ solutions. The use of $HClO_4$ was only necessary for experiments at pH less than 12.0. pH values were assigned not by measurement but by the calculated concentrations of free OH^-.

Argon scrubbed in a Cr(II) tower was used to degas air-sensitive solutions, which were transferred with glass Luer-tip syringes equipped with stainless-steel needles. Solutions of tris(4,7-dihydroxy-1,10-phenanthroline)iron(II) ($Fe^{II}(OHP)_3$ were prepared as needed by adding a deoxygenated solution of $Fe(ClO_4)_2{\cdot}6H_2O$ to a deoxygenated solution of OHP in a 1:3 molar ratio.

Reaction Studies. All kinetic studies except for those of the reaction of O_2 with $Fe^{II}(OHP)_3$ were performed on an all-glass hand-stopped-flow instrument equipped with Nylon stopcocks and a 1-cm quartz flow-through cuvette and monitored on a Cary 210 spectrophotometer. The hand-stopped-flow device was optimized for strict anaerobicity at the cost of temperature control; thus, rate constants are reported at room temperature. Reactions were carried out under pseudo-first-order conditions with either peroxide or cyanide in excess. The rates were followed by measuring the loss of $Fe^{II}(OHP)_3$ at 520 nm, except where noted, with $[Fe^{II}(OHP)_3]_0 = 5 \times 10^{-5}$ M.

The apparent rate of the reaction of $Fe^{II}(OHP)_3$ with HO_2^- decreased and became more consistent with improvements in technique. For example, experiments where H_2O_2 solutions were made in NaOH gave irreproducible results, all of which were faster than those obtained from experiments where H_2O_2 solutions were made in water. This observation could be attributed to the fact that HO_2^- decomposes rapidly in alkaline media to form O_2,[8,9] whose oxidation of $Fe^{II}(OHP)_3$ is many times faster than the corresponding reaction with peroxide. Other improvements included better airtight techniques, longer deoxygenating time, and the removal of all bubbles from the stopped-flow line.

For the studies of the variation of rate with pH, $HClO_4/NaClO_4$ was used to acidify the OHP solutions where necessary and to maintain the ionic strength at 0.11 M. NaCl was originally used in place of $NaClO_4$, but there was no noticeable effect on the rate upon changing the anions.

$Fe^{II}(OHP)_3$ was oxidized by bubbling with O_2 for various lengths of time, and the product solutions were analyzed for the presence of peroxide (HO_2^-) by using a Wescan ion analyzer. The method employed a 10-cm resin-based anion-exchange column (Wescan Anion/R-HS), a 100 μL sample loop, and amperometric detection at 500 mV vs. Ag/AgCl (Pt/Rh working electrode). A 0.006 M NaOH solution was used as the eluent, at a flow rate of 2 mL/min. The response of the instrument was first stabilized by injecting a sample of 0.001 M H_2O_2. Peroxide eluted very quickly ($\approx$1 min) presumably because hydrogen peroxide is only partially deprotonated at pH 11.8 ($pK_a(H_2O_2) = 11.8$). Concentrations of H_2O_2 in the analyte were determined by comparison of peak heights with a calibration curve (linear from 1×10^{-5} to 5×10^{-5} M H_2O_2). Attempts to determine $[HO_2^-]$ by various titration methods were found to be unreliable and were abandoned.

Table I. Absorptivity in the Visible Region of Iron Complexes

complex	color	λ_{max},[a] (nm)	absorptivity,[a,b] M^{-1} cm^{-1}
$Fe^{II}(OHP)_3$	rose red	510	1.34×10^4
		(520)	(1.48×10^4)
$Fe^{III}(OHP)_3$	gray	526	3.05×10^3
		(527)	(3.27×10^3)
		520[c]	2.71×10^3
		480[c]	1.35×10^3
"$Fe^{III}(OHP)_2(OH)$"	amber	464	2.96×10^3
		(465)	(3.10×10^3)
		520[c]	1.34×10^3
		480[c]	2.47×10^3
$Fe^{II}(OHP)_2(CN)_2$	bright yellow	435	1.19×10^4
$Fe^{III}(OHP)_2(CN)_2$	light yellow	none[d]	

[a] Values given in parentheses are those reported by Poe and Diehl.[7] [b] Absorptivity calculated on the basis of initial [Fe(II)], assuming a complete reaction. [c] Not a spectral peak; used for analysis of $Fe^{III}(OHP)_3$/"$Fe^{III}(OHP)_2(OH)$" mixtures. [d] No peak is observed within the range 400–600 nm; beyond 400 nm, the absorbance starts to increase very rapidly. The solution is almost colorless.

A cursory kinetic study (three sets of experiments) of the reaction of $Fe^{II}(OHP)_3$ with O_2 was performed on an Aminco-Morrow stopped-flow spectrophotometer as described previously.[10]

Cyclic Voltammetry. Electrochemical studies were performed with a BAS 27 voltammograph and C-1B cell stand. A one-compartment cell was used, with a glassy-carbon working electrode, a Ag/AgCl reference electrode (0.199 V vs. NHE),[11] and a Pt-wire counter electrode.

Results

According to Poe and Diehl[7] $Fe^{II}(OHP)_3$ forms rapidly and quantitatively from Fe(II) and OHP in base. The Fe(III) system is more complex. Gray $Fe^{III}(OHP)_3$ is stable between pH 8.8 and 12, but above pH 12 it slowly and reversibly converts to amber "$Fe^{III}(OHP)_2(OH)$". The structure of this amber species is uncertain, but it may be dimeric. If the pH is reduced below 10, the amber species rapidly converts to an unstable purple species. Thus, under the conditions of our experiments the gray and amber Fe(III) species are distinct, and interconvert only slowly. Electronic spectral data for the various species are given in Table I.

In cyclic voltammetry studies with 5×10^{-4} M $Fe^{II}(OHP)_3$ in 0.2 M NaOH the $Fe^{II/III}(OHP)_3$ couple gave $\Delta E_{p/p} = 320$ mV and $E_{1/2} = -0.066$ V when scanned at 20 mV/s, $\Delta E_{p/p} = 170$ mV and $E_{1/2} = -0.091$ mV at 5 mV/s, and $\Delta E_{p/p} = 100$ mV and $E_{1/2} = -0.101$ V vs. NHE at 1 mV/s. This dependence on scan rate implies that the system suffers from slow electrode kinetics. At the slowest scan rates the behavior approaches electrochemical reversibility, and so E_f is assumed to be −0.10 V vs. NHE. Poe and Eppen did not find such a severe scan-rate dependence, but their work was performed at pH 11.[12] Our E_f is just that obtained by Poe and Eppen (−0.10 V) in their study of the $Fe^{II/III}(OHP)_3$ couple.[12]

$Fe^{II}(OHP)_3$ with O_2. Despite the quasi-reversible electrochemistry of the $Fe^{II/III}(OHP)_3$ redox couple, addition of $Na_2S_2O_4$ to an air-oxidized solution of $Fe^{II}(OHP)_3$ yielded the same visible spectrum as that of the unoxidized material. Similar and other observations have been reported previously that confirm $Fe^{III}(OHP)_3$ as the product of the autoxidation reaction.[2,7]

Analysis of the product solution of the oxygen reaction gave variable yields of peroxide. Depending on the O_2 bubbling rate, the O_2 concentration, and the time between the addition of oxygen to a solution of $Fe^{II}(OHP)_3$ and the injection of the solution into the HPLC, the yield of HO_2^- ranged from 20% to 40% assuming a theoretical yield of one peroxide per two $Fe^{II}(OHP)_3$. For example, an oxygen-saturated solution of $Fe^{II}(OHP)_3$ gave a peroxide yield twice that of an air-saturated solution. Figure 1 shows the important role these factors play in determining the

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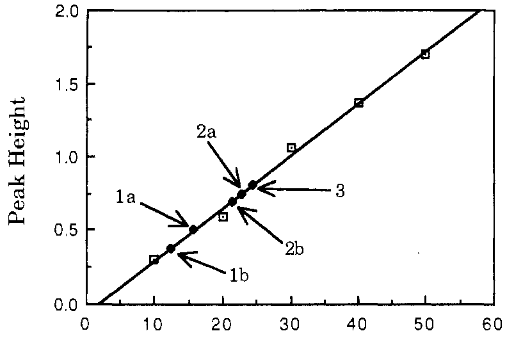

Figure 1. Peroxide analysis of the product solution of the reaction between $Fe^{II}(OHP)_3$ and O_2 using a Wescan HPLC. $[Fe^{II}(OHP)_3]_0 = 1.26 \times 10^{-4}$ M in 0.1 NaOH. Open squares = calibration points. Key: 1a = air-oxidized solution of $Fe^{II}(OHP)_3$; 1b = solution 1a after 15 min; 2a = O_2-bubbled solution of $Fe^{II}(OHP)_3$; 2b = solution 2a after 11 min; 3 = solution of $Fe^{II}(OHP)_3$ bubbled vigorously with O_2.

observed yield of peroxide. The low yield of peroxide, even under the best of conditions, can be attributed to two processes. One is that peroxide is unstable in the product solution. The other is that, as described below, $Fe^{II}(OHP)_3$ reacts with peroxide at a rate that can be comparable to the rate of reaction with O_2. In view of these complications, the stoichiometry

$$2Fe^{II}(OHP)_3 + O_2 + H_2O \rightarrow 2Fe^{III}(OHP)_3 + HO_2^- + OH^- \quad (1)$$

is a reasonable expression of the primary phase in the reaction. Numerical integration of the system consisting of rate laws 2 and 4 below indicates that the low yield of HO_2^- is adequately explained by reaction of peroxide with $Fe^{II}(OHP)_3$. This analysis is also consistent with Ng and Henry's measurements of O_2 consumption.[2]

Previous workers reported that peroxide was not a reaction product, being formed at less than 13% yield (as defined for the above stoichiometry).[2] We have found that their iodometric titration method is unreliable for several reasons: (1) the product solution contains oxidizing materials that affect the titration, but are not completely removed even by ion-exchange methods, (2) visual detection of I_2 formed from peroxide at such low concentrations (10^{-4} M) is very difficult, and (3) by the time that the peroxide is titrated, some of it will have decomposed. The HPLC method of peroxide analysis has advantages over iodometry in that it is rapid, very sensitive, and highly peroxide specific.[13]

Kinetics results obtained in the present study were similar to those of Ng and Henry: at $[Fe^{II}(OHP)_3]_0 = 1.0 \times 10^{-4}$ M and $[O_2]_0 = 5 \times 10^{-4}$ M, $k_{obsd} = 0.255 \pm 0.029$ s^{-1}, which compares favorably with the reported rate constant of 0.23 s^{-1}.[2] We have no reason to doubt that the rate law is

$$-d[Fe^{II}(OHP)_3]/dt = k_1[Fe^{II}(OHP)_3][O_2] \quad (2)$$

with $k_1 = 510$ M^{-1} s^{-1} as reported previously.[2]

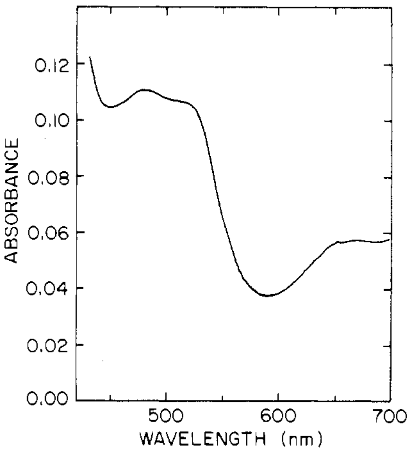

Figure 2. Spectrum of the product of the reaction between $Fe^{II}(OHP)_3$ and HO_2^-. The presence of two peaks arises from the formation of both $Fe^{III}(OHP)_3$ and "$Fe^{III}(OHP)_2(OH)$". $[Fe^{II}(OHP)_3]_0 = 4.99 \times 10^{-5}$ M; $[HO_2^-]_0 = 1.04 \times 10^{-3}$ M.

Table II. Kinetic Data for the Oxidation of $Fe^{II}(OHP)_3$ by HO_2^-[a]

$10^2[H_2O_2]$,[b] M	pH	10^2k_{obsd}, s^{-1}	$10^2[H_2O_2]$,[b] M	pH	10^2k_{obsd}, s^{-1}
0.05	13.0	2.1	5.00	13.0	3.6
0.10	13.0	1.8	10.0	13.0	3.4
0.50	13.0	2.2	0.10	12.7	2.1[c]
2.61	13.0	2.5	0.10	12.1	4.1[c]

[a] $[Fe^{II}(OHP)_3]_0 = 5 \times 10^{-5}$ M, $\mu = 0.13$ M (NaCl), monitored at 520 nm, $T \approx 22$ °C. [b] Concentration of total peroxide; at pH 13, peroxide exists predominantly as HO_2^-. [c] Rates obtained over the first 2 half-lives. See Experimental Section for details.

$Fe^{II}(OHP)_3$ with HO_2^-. Spectra of the oxidized complex obtained during this present study showed two peaks of nearly equal intensities at 520 and at 480 nm (Figure 2). The appearance of these two peaks suggests the presence of both the bis and tris iron(III) complexes. In order to verify this suggestion quantitatively, accurate extinction coefficients were required for both iron products at the same two wavelengths; thus, Table I reports data at 520 and 480 nm even though these wavelengths do not correspond to peak maxima. Careful analysis of the product spectrum ($[Fe^{II}(OHP)_3]_0 = 4.99 \times 10^{-5}$ M, $[HO_2^-]_0 = 1.04 \times 10^{-3}$ M, pH 13) using these spectra gave a one-to-one ratio of tris to bis complex with less than 2% error. Less than 5% error was observed between the initial iron(II) concentration and the combined concentrations of the bis and tris iron(III) complexes. These results imply that the reaction has the stoichiometry

$$2Fe^{II}(OHP)_3 + H_2O_2 \rightarrow Fe^{III}(OHP)_3 + \text{"}Fe^{III}(OHP)_2(OH)\text{"} + OHP + OH^- \quad (3)$$

Because of the decomposition of HO_2^- in alkaline media, kinetics studies were performed by mixing pure aqueous solutions of H_2O_2 with appropriate alkaline solutions of $Fe^{II}(OHP)_3$. Semilog plots of the raw data often yielded slight curves, giving slow initial k_{obsd} values (first 2 half-lives) and faster final k_{obsd} values. Evolution of oxygen by the decomposition of peroxide would account for this behavior, as the rate of consumption by evolved O_2 would be constant, whereas the rate of consumption of HO_2^- decreases exponentially with time. Some typical rate constants obtained from the first 2 half-lives are presented in Table II. For a 200-fold variation in HO_2^- concentration (5×10^{-4} vs. 1×10^{-1} M) at pH 13, the rates differed only by a factor of 2. The slight increase in rate with increasing $[HO_2^-]$ is attributable to an increasing degree of reaction with O_2 released by the decomposition of HO_2^-. Apart from this small effect the rate of oxidation of $Fe^{II}(OHP)_3$ by HO_2^- is independent of the peroxide concentration. Over the admittedly narrow range from pH 13 to pH 12.1 the rate constants varied by only a factor of 2. The reactions at low alkalinity showed increasing degrees of non-first-order behavior; this is as expected, because the decomposition of peroxide is accelerated by decreasing alkalinity in this pH range.[9] This negligible pH dependence is consistent with a rate law that is independent of total peroxide concentration. Thus the overall rate law is simply

$$-d[Fe^{II}(OHP)_3]/dt = 2k_2[Fe^{II}(OHP)_3] \quad (4)$$

with $k_2 = 1.1 \times 10^{-2}$ s^{-1}.

In an earlier paper[2] a brief study of this reaction yielded a direct dependence of the rate of oxidation on peroxide concentration, which is contrary to our observations. At $[HO_2^-] = 5 \times 10^{-2}$ M, our largest k_{obsd} was only 3.6×10^{-2} s^{-1}, whereas the prior study reported a rate constant that was 5-fold greater at a peroxide concentration that was 10-fold less.[2] It is possible that the

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(13) A modified iodometric determination of hydrogen peroxide that is very sensitive (≈0.2 µM) has recently been reported: Kieber, R. J.; Helz, G. R. *Anal. Chem.* **1986**, *58*, 2312–2315.

Table III. Kinetic Data for the Reaction of $Fe^{II}(OHP)_3$ with NaCN[a]

10^3[NaCN], M	pH	10^3k_{obsd}, s^{-1}	10^3[NaCN], M	pH	10^3k_{obsd}, s^{-1}
1.6	13.0	8.5	10.3	12.7	8.5
5.0	13.0	9.4	10.4	12.0	8.5
10.2	13.0	8.8	10.4	12.0	5.8[c]
10.5	13.0	7.4[b]	10.2	11.3	9.1[d]

[a] $[Fe^{II}(OHP)_3]_0 = 5 \times 10^{-5}$ M, $\mu = 0.11$ M (NaCl), monitored at 520 nm, $T \approx 22$ °C. [b] $T = 21.4$ °C. [c] $T = 19.0$ °C. [d] Monitored at 540 nm.

anomalous rates previously reported were obtained under conditions where oxygen formation due to rapid peroxide decomposition led to a corresponding increase in the rate of oxidation of $Fe^{II}(OHP)_3$.

$Fe^{II}(OHP)_3$ with CN^-. In alkaline media $Fe^{II}(OHP)_3$ reacts readily with CN^- to produce a bright yellow solution. The spectral features of the product of this reaction are presented in Table I. In a cyclic voltammetry study of this reaction a 5×10^{-4} M solution of the Fe(II)/CN^- product in 0.2 M NaOH gave a quasi-reversible wave at 5 mV/s with $\Delta E_{p/p} = 90$ mV and $E_{1/2} = 0.077$ V vs. NHE. The product is assumed to be $Fe^{II}(OHP)_2(CN_2)$; this species has been alluded to in previous work.[14] The reaction is given as

$$Fe^{II}(OHP)_3 + 2CN^- \rightarrow Fe^{II}(OHP)_2(CN)_2 + OHP \quad (5)$$

which is an ordinary substitution reaction.

Kinetic data in 0.1 M NaOH were obtained at three different cyanide concentrations. The reactions obeyed pseudo-first-order kinetics, and, as shown in Table III, the rate constants were independent of the concentration of CN^-. Over the range from pH 13.0 to 11.3, (limited by precipitation of free OHP at pH <11) the rate constants all lay within 7% of each other, and so the rate law is

$$-d[Fe^{II}(OHP)_3]/dt = k_3[Fe^{II}(OHP)_3] \quad (6)$$

with $k_3 = 8.63 \times 10^{-3}$ s^{-1}.

The product of the reaction of $Fe^{II}(OHP)_3$ with CN^- was sensitive to O_2. This autoxidation reaction displayed an isosbestic point at 528 nm for the first 3 half-lives (11 min), but it shifted by 5 nm after 3 h. Addition of $Na_2S_2O_4$ to the solution resulting from the autoxidation of $Fe^{II}(OHP)_2(CN)_2$ yielded a solution having the same visible spectrum as that of $Fe^{II}(OHP)_2(CN)_2$. The initial product of the autoxidation reaction is assumed to be $Fe^{III}(OHP)_2(CN)_2$, and its spectrum is reported in Table I. At $[O_2] = 5 \times 10^{-4}$ M the reaction showed first-order kinetics, with $k_{obsd} = 1.5 \times 10^{-3}$ s^{-1}.

In a cyclic voltammetry study of this autoxidation a 5×10^{-4} M solution of the Fe(II)/CN^- product in 0.2 M NaOH was saturated with O_2, allowed to react for 15 min, and then degassed with argon so as to avoid the electroreduction of O_2 to H_2O in strongly alkaline solution. $\Delta E_{p/p}$ and $E_{1/2}$ for the solution were not affected by the reaction with O_2, which confirms that $Fe^{III}(OHP)_2(CN)_2$ is the autoxidation product.

Discussion

The autoxidation of $Fe^{II}(OHP)_3$ proceeds with an ordinary second-order rate law. A key observation in assigning a mechanism to this reaction is that oxygen is reduced to hydrogen peroxide rather than directly to water. Additionally, the iron-containing product is $Fe^{III}(OHP)_3$, which is substitution-inert. These are the features characteristic of outer-sphere autoxidations, examples of which are already well established.[3] A reasonable mechanism is

$$Fe^{II}(OHP)_3 + O_2 \rightleftarrows Fe^{III}(OHP)_3 + O_2^- \quad k_1, k_{-1}, K_1 \quad (7)$$

$$2O_2^- + H^+ \xrightarrow{cat.} O_2 + HO_2^- \quad (fast) \quad (8)$$

bearing in mind the concurrent decomposition of HO_2^- and reaction HO_2^- with $Fe^{II}(OHP)_3$. These latter effects can lead to an observed stoichiometry that varies between two and four Fe(II)'s per O_2, depending on the conditions under which the data are collected.

Unlike the mechanism for autoxidation of $[Ru(NH_3)_5(isonicotinamide)]^{2+}$ in acidic media, wherein the free-radical HO_2 figures prominently,[3] eq 8 does not include HO_2 because the reactions are conducted in highly alkaline media. Our data are insufficient to specify the exact process by which O_2^- is reduced to HO_2^-; thus eq 8 is rather speculative and serves simply to represent a rapid consumption of O_2^-. The direct disproportionation of O_2^- is quite slow at pH 13, but the reaction is easily catalyzed by trace impurities.[15] Since in the present study no effort was made to prepare highly purified solutions (e.g., only reagent grade NaOH was used), the concentration of O_2^- should not become significant during the reactions. As long as O_2^- is consumed rapidly relative to electron back-transfer (k_{-1}) the mechanism leads to the observed rate law, eq 2. The equilibrium quotient, K_1, is calculated from the reduction potentials for $Fe^{III}(OHP)_3$ (see above) and O_2[16] (−0.15 V vs. NHE, 1 M O_2 as standard state) to give $K_1 = 0.14$. Since $K_1 = k_1/k_{-1}$, this mechanism implies that k_{-1} ($=7.2 \times 10^3$ M^{-1} s^{-1}) is rather slow, and so a variety of pathways could be envisioned to achieve the process represented in eq 8. In the previous report[2] a similar calculation indicated that k_{-1} would exceed the limit of diffusion control, but an erroneous reduction potential for O_2 was used. With the corrected reduction potential we find that a single-electron mechanism for reduction of O_2 by $Fe^{II}(OHP)_3$ is quite acceptable. If the cross relationship of Marcus theory (including work terms)[17] is applied to these results, we find that the product of the self-exchange rate constants for the O_2/O_2^- and $Fe^{II}(OHP)_3/Fe^{III}(OHP)_3$ couples, $k_{11}k_{22}$, is 7×10^4 M^{-2} s^{-2}. A case has been made that the O_2/O_2^- couple is very poorly behaved in terms of the cross relationship;[18] however, if a "reasonable" self-exchange rate constant of 1.0 M^{-1} s^{-1} is assumed, then the $Fe^{II}(OHP)_3/Fe^{III}(OHP)_3$ redox couple is predicted to have a self-exchange rate constant of 7×10^4 M^{-1} s^{-1}. The actual self-exchange rate constant for $Fe^{II}(OHP)_3/Fe^{III}(OHP)_3$ has not been reported. Our calculated value is some 4 orders of magnitude less than that for $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$, but the anomalous reduction potential for $Fe^{III}(OHP)_3$ suggests that there is a substantial change in bonding between the two oxidation states. In view of these uncertainties it can only be said that our results may well be consistent with the Marcus cross relationship.

In contrast with the normal behavior for the autoxidation of $Fe^{III}(OHP)_3$, oxidation of $Fe^{II}(OHP)_3$ by HO_2^- must proceed by a rather unusual mechanism in view of the first-order rate law and the 1:1 ratio of Fe(III) products. It is clear that the mechanism does not include rate-limiting outer-sphere electron transfer. In light of the present set of data, the following mechanism is proposed:

$$Fe^{II}(OHP)_3 \rightleftarrows Fe^{II}(OHP)_2 + OHP \quad k_2, k_{-2} \quad (9)$$

$$Fe^{II}(OHP)_2 + HO_2^- \rightarrow (OHP)_2Fe^{II}HO_2^- \quad k_3 \quad (10)$$

$$(OHP)_2Fe^{II}HO_2^- + Fe^{II}(OHP)_3 + H^+ \rightarrow \text{“}Fe^{III}(OHP)_2(OH)\text{”} + Fe^{III}(OHP)_3 + OH^- \quad (fast) \quad (11)$$

With use of the steady-state approximation for $[Fe^{II}(OHP)_2]$, the derived rate law is

$$\frac{-d[Fe^{II}(OHP)_3]}{dt} = \frac{2k_2k_3[HO_2^-][Fe^{II}(OHP)_3]}{k_{-2}[OHP] + k_3[HO_2^-]} \quad (12)$$

which reduces to the observed rate law for $k_3[HO_2^-] \gg k_{-2}[OHP]$. This last approximation is justified because k_3 and k_{-2} are expected to be comparable in magnitude, while the concentration of free

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peroxide vastly exceeds that of free OHP. Spectra of the products of the oxidation of $Fe^{II}(OHP)_3$ by HO_2^- are also consistent with the proposed mechanism.

An alternative mechanism would retain eq 9 (dissociative loss of OHP) and replace eq 10 and 11 with

$$Fe^{II}(OHP)_2 + H_2O_2 \rightarrow \text{“}Fe^{III}(OHP)_2(OH)\text{”} + OH \tag{13}$$

$$OH + Fe^{II}(OHP)_3 \rightarrow Fe^{III}(OHP)_3 + OH^- \tag{14}$$

where these steps would occur rapidly relative to formation of $Fe^{II}(OHP)_2$ through eq 9. This mechanism also yields the observed stoichiometry and rate law.

The rate of spontaneous loss of OHP from $Fe^{II}(OHP)_3$ in base as in eq 9 cannot be meausured directly, because of the high stability of the complex.[19] Such a measurement would provide an important test of either proposed mechanism. The substitution reaction by CN^- was undertaken to provide an indirect measure of this aquation, since CN^- has been shown to be an effective scavenger in such systems.[20] Our observed rate law is indeed independent of $[CN^-]$, which is consistent with a substitution reaction that proceeds by rate-limiting spontaneous loss of OHP. Since the rate constant for the CN^- reaction is approximately half that for the reaction with HO_2^-, we have strong support for the proposed mechanisms, because each HO_2^- consumes two $Fe^{II}(OHP)_3$. Thus, at this time all the data point toward a prior ligand dissociation reaction, which enables the HO_2^- to find a reactive form of iron(II) in the oxidation of $Fe^{II}(OHP)_3$.

It is not surprising that HO_2^- finds a pathway to oxidize $Fe^{II}(OHP)_3$ that does not involve direct outer-sphere electron transfer. The reason is that such a process would cleave the O–O bond as in

$$H_2O_2 + e^- \rightarrow OH + OH^- \tag{15}$$

Activation barriers for outer-sphere reductive cleavage have been discussed previously in the context of the $I_2^-/2I^-$ system.[21] By analogy the reduction of H_2O_2 could be written as having a first step

$$Fe^{II} + H_2O_2 \rightarrow Fe^{III} + HO,OH^- \tag{16}$$

and this step could be analyzed in terms of the Marcus cross relationship. An essential component of the analysis is then the hypothetical self-exchange reaction of H_2O_2 with HO,OH^-. To attain the transition state for this self-exchange reaction would require stretching the O–O bond of H_2O_2 by several tenths of an angstrom. Since the aqueous dissociation free energy of H_2O_2 is 184 kJ, the self-exchange reaction must have an enormous activation barrier. Hence, outer-sphere reduction of H_2O_2 is expected to occur only under rare circumstances. By contrast the barrier for I_2^- is much lower, and outer-sphere reductive cleavage of I_2^- is a common process. These same arguments may be applied to the second mechanism proposed for reduction of HO_2^- by $Fe^{II}(OHP)_3$ in which peroxide is cleaved by $Fe^{II}(OHP)_2$ (eq 13): such a mechanism, if it occurs, must involve cleavage of peroxide after it has become coordinated to Fe(II).

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Registry No. $Fe^{II}(OHP)_3$, 15053-63-1; $Fe^{III}(OHP)_3$, 18517-23-2; $Fe^{III}(OHP)_2(OH)$, 107890-90-4; $Fe^{II}(OHP)_2(CN)_2$, 107890-91-5; O_2, 7782-44-7; HO_2^-, 14691-59-9; CN^-, 57-12-5.

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Contribution from the Institut für Anorganische und Analytische Chemie, Universität Freiburg, 7800 Freiburg, FRG,
and Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 7900 Ulm, FRG

Formation of $[Pt^{2.25}]_4$–1-Methyluracil Blue through Silver(I) Oxidation of $[Pt^{2.0}]_2$ and Isolation of a Heteronuclear (Pt_2,Ag_2) Precursor

Bernhard Lippert,*[1a] Helmut Schöllhorn,[1b] and Ulf Thewalt[1b]

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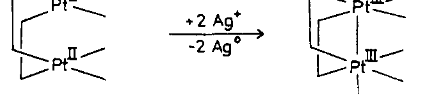
The oxidation of the diplatinum(II) complex (*head–head* isomer) *cis*-$[(NH_3)_2Pt(1\text{-}MeU)]_2(NO_3)_2$ (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$) to the mixed-valence-state complex $[(NH_3)_2Pt(1\text{-}MeU)]_4(NO_3)_5\cdot 5H_2O$ ($Pt^{2.25}$–1-MeU blue) in the presence of Ag^I, Fe^{III}, Ce^{IV}, and Cu^{II} has been studied. In the case of Ag^I, oxidation of Pt is coupled with reduction of Ag^I to Ag^0, as shown by a combination of potentiometric titration of Ag^I and visible spectroscopy. A heteronuclear complex of composition *cis*-$\{[(NH_3)_2Pt(1\text{-}MeU)]_2Ag\}(NO_3)_3\cdot AgNO_3\cdot 0.5H_2O$ (**1b**), obtained on cocrystallization of the diplatinum(II) starting compound and $AgNO_3$, appears to be a direct precursor of $Pt^{2.25}$–1-MeU blue. **1b** crystallizes in space group $P\bar{1}$, with $a = 13.470$ (4) Å, $b = 11.656$ (5) Å, $c = 10.185$ (3) Å, $\alpha = 104.89$ (3)°, $\beta = 107.29$ (2)°, $\gamma = 104.99$ (4)°, $V = 1374.9$ Å^3, and $Z = 1$. In this compound, the dinuclear Pt compound (Pt coordination through N3 and O4) has a Ag bound via the still available O2 sites, while a second Ag links two trinuclear Pt_2,Ag units without being directly coordinated to the 1-MeU rings. As a result, four Ag atoms take part in a 12-membered ring, which contains also bridging nitrate groups and in addition an aqua bridge. The intramolecular Pt–Pt distance in **1b** is 2.885 (1) Å, which is between the distances observed in the diplatinum(II) starting compound (2.937 (1) Å) and in $Pt^{2.25}$–1-MeU blue (2.802 (1) Å), while the intramolecular Pt–Ag separation is 2.860 (3) Å. It is suggested that the pronounced shortening of the Pt–Pt distance in **1b** as compared to the distance in the starting compound precedes the actual electron transfer from the Pt_2 core to the Ag^I and that oxidation of the diplatinum(II) starting compound by other transition metals may also occur via formation of heteronuclear intermediates.

Introduction

Ag^I occasionally has been applied as oxidizing agent for mono-[2] and dinuclear transition-metal complexes.[3-5] Among the latter, both Kuyper[3] and Bancroft et al.[5] have shown that Ag^I can remove two electrons from dinuclear Pt^{II} complexes to give diplatinum(III)

Scheme I



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(1) (a) Universität Freiburg. (b) Universität Ulm.

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