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THE MECHANISMS FOR OXIDATION OF SOME d^6 LOW-SPIN METAL COMPLEXES BY TWO PEROXOANIONS

JOHN O. EDWARDS
Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912 (U.S.A.)

ABBREVIATIONS

phen	1,10-phenanthroline
bipy	2,2′-bipyridyl
terpy	terpyridyl
L	bidentate ligand

Our group has been studying the oxidation of a number of ferroin complexes by peroxodiphosphate ion. The unexpected difference between our initial results[1] and those in the literature[2,3] for oxidation by peroxodisulfate has necessitated a comparison of oxidation mechanisms by these two isoelectronic and isostructural oxidants. In this review, we present a summary of the data, a tentative hypothesis for the difference in mechanism type and a few notes on some unfinished aspects.

If one mixes a dilute ($\sim 10^{-4}$ M) solution of $Fe(phen)_3{}^{2+}$ with a solution containing a peroxodiphosphate salt★, one sees the gradual disappearance of the intense color of the complex. The rate law (when $[P_2O_8{}^{4-}] \geqslant 2 \times 10^{-3} M$) is

$$\frac{-d[Fe(phen)_3{}^{2+}]}{dt} = k_{obs}\,[Fe(phen)_3{}^{2+}] \qquad (1)$$

and the rate constant is, within a factor of two, equal to the rate constant for acid hydrolysis of the complex[4] under the same conditions. Study[1] of the peroxide oxidation over a wide range of concentrations led to the more complete kinetic law

$$\frac{-d[Fe(phen)_3{}^{2+}]}{dt} = \frac{k_1 k_2\,[Fe(phen)_3{}^{2+}]\,[P_2O_8{}^{4-}]}{k_{-1}\,[phen] + k_2\,[P_2O_8{}^{4-}]} \qquad (2)$$

which is in accord with the mechanism

★The peroxodiphosphate ion can exist in a number of protonated forms, in general, the tetranegative ion is the predominant species under our conditions.

$$\mathrm{Fe(phen)_3}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fe(phen)_2}^{2+} + \mathrm{phen}$$

$$\mathrm{Fe(phen)_2}^{2+} + \mathrm{P_2O_8}^{4-} \xrightarrow{k_2} \mathrm{products} \qquad (3)$$

That the observed reaction is indeed a redox process was proven by the following tests On addition of SCN^- to the reaction mixture after disappearance of the ferroin color, the color of the ferric–thiocyanate system is observed. Addition of sodium dithionite (a strong reducing agent) to another sample of the reaction mixture rapidly brought back the color of the ferroin reagent Further, the reactants together initiated polymerization of the olefin acrylonitrile, whereas neither of the reactants alone did so in comparable lengths of time. The polymerization reaction suggests the presence of a free radical intermediate in the oxidation process.

The stoichiometry is not without complications. Instead of the simple 2 to 1 ratio expected if only iron(II) is oxidized, approximately one mole of $\mathrm{Fe(phen)_3}^{2+}$ is consumed per mole of peroxide. This behavior also suggests that a free radical intermediate is formed in some step of the mechanism. The ferroins are one-electron reductants and peroxides are two-electron oxidants, with only one molecule of each in the transition state, a reactive intermediate is a mandatory product of the rate-determining step. The discrepancy between the theoretical consumption of two moles of ferroin by one of peroxodiphosphate and the observed ratio is ascribed to capture of this free radical by the phenanthroline molecules in the system. Addition of 2-propanol (which does not react with either reactant alone) widens the discrepancy between electrons gained by peroxide and lost by metal complex. In view of the known proclivity of 2-propanol to undergo hydrogen atom abstraction reactions of the type

$$\mathrm{RO}\cdot + \mathrm{HC(CH_3)_2OH} \rightarrow \mathrm{ROH} + \mathrm{(CH_3)_2\dot{C}OH} \qquad (4)$$

it is reasonable to assume that the phosphate radical-ion $\mathrm{PO_4}^{2-}$ is formed during the reaction This free radical has been suggested as an intermediate in other mechanism studies[5], and is almost certainly present in the photo-initiated oxidation of 2-propanol by peroxodiphosphate[6] There is little doubt that the iron(II) complex is oxidized to some iron(III) species, however, the amount of iron present in our reactions is so small as to preclude characterization of the nature of the species

Returning now to the kinetic aspects of the reaction, the same type of behavior is found for a number of ferroins and for analogous osmium(II) complexes. In Table I, a summary of the data for oxidation of complexes by peroxodiphosphate is presented. In Table 2, available data for hydrolysis of the same complexes are given. There can be no doubt about the identical nature of rate-determining steps for the two quite dissimilar reactions This step is

$$\mathrm{Fe(phen)_3}^{2+} \xrightarrow{k_1} \mathrm{Fe(phen)_2}^{2+} + \mathrm{phen} \qquad (5)$$

TABLE 1

Rates and activation parameters for the oxidation by $P_2O_8^{4-}$

Complex	k (sec^{-1})	E_a (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.mole^{-1} deg^{-1})	Ref.
$Fe(phen)_3^{2+}$	3.8×10^{-4} (35°)	30.9	+26	1[c]
$Fe(NO_2\text{-}phen)_3^{2+}$	3.1×10^{-3} (35°)[c]			13
$Fe(bipy)_3^{2+}$	1.0×10^{-4} (25°)	30.6	+24	
$Fe(terpy)_2^{2+}$	6.1×10^{-5} (35°, pH 5.9)	29.1	+13.4	13
$Os(bipy)_3^{2+}$	[a]			12
$Os(phen)_3^{2+}$	[b]			12
$Os(terpy)(bipy)Cl^+$	4.0×10^{-6} (60°)			12

[a] No reaction for 14 days at 60°.

[b] No reaction for 14 days at 60° in the presence of EDTA.

[c] The ligand in this case is 5-nitrophenanthroline.

TABLE 2

Rates and activation parameters for the dissociation

Complex	k (sec^{-1})	E_a (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal mole^{-1}.deg^{-1})	Ref.
$Fe(phen)_3^{2+}$	3.7×10^{-4} (34.6°)	32.1	+28	4
$Fe(bipy)_3^{2+}$	1.32×10^{-4} (25°)	28.4	+17	10
$Fe(terpy)_2^{2+}$	1.1×10^{-6} (35°, pH 6)	28.7		11
	7.3×10^{-3} (35°, 3 M H^+)	28.7		11
$Os(bipy)_3^{2+}$	Extremely slow at 100°			
$Os(phen)_3^{2+}$	Extremely slow at 100°			
$Os(terpy)(bipy)Cl^+$	4.0×10^{-6} (60°)			12

with capture of $Fe(phen)_2^{2+}$ by peroxide preventing reversal in the oxidation reaction and with capture of phen by hydrogen ion preventing reversal in the hydrolysis For the sake of simplicity, we have written the iron(II) intermediate as $Fe(phen)_2^{2+}$; this is not the only possible intermediate, but the data at present available do not indicate details about its nature (or natures).

Evidence that the rate-determining step in the oxidation process is indeed the release of ligand from the coordination sphere is easily obtained. The proposed step

$$Fe(phen)_3^{2+} \rightarrow Fe(phen)_2^{2+} + phen$$

generates an intermediate complex and a phen molecule Any particle which rapidly converts either to a non-reactive form can prevent reversal of this step. Irrespective of the nature of the overall reaction in the presence of an addend, the rate step can be the first loss of ligand from the tris complex. Protons rapidly react with the phenanthroline to form $phenH^+$, and cations such as Ni^{2+} and Cu^{2+} react with released phenanthroline to give stable complexes. The presumed iron(II) product of the rate step $Fe(phen)_2{}^{2+}$ reacts with complexing agents such as $P_2O_7{}^{4-}$ and EDTA to form other complexes not having the strong absorption of a ferroin. The influence on the oxidation rate itself by small amounts of phen is not unlike the behavior of $P_2O_7{}^{4-}$, except that for phen the capture of $Fe(phen)_2{}^{2+}$ regenerates the reactant $Fe(phen)_3{}^{2+}$. The rate behavior of the various addends with the tris complex is summarized in Table 3.

TABLE 3

Reaction of peroxodiphosphate and some substances with tris (1,10-phenanthroline) iron(II) in neutral solutions [a]

Substance	Concn., M_0	$10^4 k_{obs}$ (sec^{-1})
$Li_4P_2O_8$	1.0×10^{-2}	3.8
	6.0×10^{-3}	3.8
	5.0×10^{-3}	3.8
	2.4×10^{-3}	3.8
	2.0×10^{-3}	3.7
	1.0×10^{-3}	3.6 [b]
	5.0×10^{-4}	3.5 [b]
	3.0×10^{-4}	3.3 [b]
	2.0×10^{-4}	2.9 [b]
$CuSO_4$	2.0×10^{-3}	4.0
	1.0×10^{-3}	4.0
	5.0×10^{-4}	4.0
$NiSO_4$	1.0×10^{-2}	3.9
	5.0×10^{-3}	3.9
$Na_4P_2O_7$	5.0×10^{-2}	3.8
	2.5×10^{-2}	3.8
	1.0×10^{-2}	3.8 [b]
	5.0×10^{-3}	2.8 [b]
	2.5×10^{-3}	2.4 [b]
EDTA	5.0×10^{-3}	2.3 [b]
	2.5×10^{-3}	2.1 [b]

[a] Temp = 35°, ionic strength = 1.00, pH range 6–8, $[Fe(phen)_3{}^{2+}]_0 = 10^{-4}$ *M*.
[b] Initial first-order constants based on first 25–35% of reaction. Data from ref. 2.

Other complexes which react with peroxodiphosphate with behavior similar to that of $Fe(phen)_3{}^{2+}$ are listed in Table 1. The slow rates of oxidation of the three osmium(II) complexes are particularly noteworthy. The oxidation rates correlate well with rates of hydrolysis and ligand exchange.

By way of comparison, peroxodisulfate oxidizes these complexes rapidly by second-order kinetics

$$\frac{-d[\text{ferroin}]}{dt} = k[\text{ferroin}][S_2O_8{}^{2-}] \qquad (6)$$

In most of these reactions, oxidation is clearly faster than loss of first ligand[2,3,7], and the rate is not a strong function of metal ion or ligand The relevant data are presented in Table 4.

TABLE 4

Rates and activation parameters for the oxidation by $S_2O_8^{2-}$

Complex	k (l.mole^{-1}.sec^{-1})	E_a (kcal.mole^{-1})	$\Delta S^{\ddagger}$ (cal.mole^{-1}deg^{-1})	Ref.
$Fe(phen)_3^{2+}$	0.108 (25°)	13.5	−19	3
$Fe(Me_2phen)_3^{2+}$	1.87 (25°) [b]	6.9	−29	3
$Fe(bipy)_3^{2+}$	0.41 (25°)	10.3	−28	3
$Fe(terpy)_2^{2+}$	0.85 (35°)	10.7	−24	3
$Os(bipy)_3^{2+}$	49.0 (25°)			2
$Os(phen)_3^{2+}$	fast (25°)			12
$Os(terpy)(bipy)Cl^+$	[a]			12

[a] Too fast to measure by normal techniques at 0°C.

[b] The ligand in this case is 4,7-dimethylphenanthroline.

The mechanism of peroxodisulfate oxidation appears to be an electron transfer from the central metal to a closely situated peroxide The correlation of peroxodisulfate rates and metal complex redox potential has been clearly demonstrated[1] Some exemplary data are given in Table 5.

TABLE 5

Second-order rate constants, activation parameters and $\Delta E°$ values for the peroxodisulfate oxidations of ferroin complexes [a]

Complex	k_1 (l mole^{-1} sec^{-1})	$\Delta E°$ (V)	E_a (kcal mole^{-1})	$\Delta S^{\ddagger}$ (e.u.)
Fe^{2+}	~141	1.24	12.1	−10.1
$Os(bipy)_3^{2+}$	49.0	1.13	9.4	−22.0
$Fe(4,4\text{-}Me_2\text{-}bipy)_3^{2+}$	6.68	1.07	10.6	−21.7
$Fe(bipy)_3^{2+}$	0.55	0.89	12.4	−20.5
$Fe(phen)_3^{2+}$	0.30	0.87	13.3	−19.0
$Fe(5\text{-}Me\text{-}phen)_3^{2+}$	0.11	~0.86	12.6	−23.0
$Ru(bipy)_3^{2+}$	0.009	0.64	14.6	−20.7

[a] All rate constants at 25°C and zero ionic strength, data from ref. 13.

Using values from the tables plus activation energies, it has been estimated[8] that peroxodisulfate oxidizes $Os(bipy)_3^{2+}$ at a rate at least eight powers of ten faster than does peroxodiphosphate. This is, in energy terms, a difference of at least 11 kcal mole^{-1}.

The difference in oxidation rates by the two isoelectronic peroxoanions is so large as to demand an explanation. In part, the slower rates for oxidation by peroxodiphosphate can be correlated with the slower rate for homolytic scission of this peroxide This is an important part of the difference but it cannot be all, some oxidation rates are different by a factor of eight powers of ten whereas the homolytic scission rates of the two peroxoanions differ by a factor of about 200.

We have suggested[8] one possible contributing factor Usually the reactions of two ions having opposite charge sign are accompanied by a positive entropy of activation; this is not the case here, however, for the reaction of peroxodisulfate with ferroin complexes shows a negative value of $\Delta S^{\ddagger}$. One must conclude, therefore, that the geometry of the transition state is severely structured. Such would be the case if the peroxodisulfate ion were forced to come in between the planar (albeit not parallel) phen ligands A restricted geometry is required. The crux of the argument is then – why does not peroxodiphosphate do the same thing? The answer does not lie in the structure or size of the phosphate peroxide because there is very little difference between it and the peroxodisulfate. The charges on the peroxoanions would favor the phosphate peroxide.

We must, therefore, look elsewhere The charge on the peroxodiphosphate ion is –4 and on the peroxodisulfate –2 Peroxodiphosphate binds protons and metal ions much more strongly than does peroxodisulfate, and one would expect that solvation of the phosphate peroxide by protic solvents would be much stronger for related reasons If the amount of desolvation for peroxodiphosphate in order to allow it entry between the ligand planes is greater than peroxodisulfate by 11 kcal mole^{-1}, then the difference between oxidation rates is indeed explicable Evidently electron transfer from metal to peroxide can only occur when the two reactants are very close together.

It is important to consider the influence on rates of substituents placed on the phen ligands, for the observations can be explained in terms of three separate factors When the substituent is small and is electron-releasing, the bond between metal and ligand is stronger. It is then expected that the rate of oxidation by peroxodiphosphate will be slower because ligand release is slower By way of contrast, oxidation by peroxodisulfate will be more rapid, since the electron density at the metal atom will be higher and electron transfer from metal to peroxide more facile

It is to be expected, however, that the rate of peroxodisulfate oxidation will decrease with electron-withdrawal by the substituent only until the rate of dissociation of the complex is reached. At this point, a change in mechanism to that used by peroxodiphosphate will presumably obtain and the two rates should then be nearly the same at all higher degrees of electron withdrawal by substituent This changeover in mechanism has indeed been observed recently[9]. Some of the previously inexplicable large deviations in values reported can be resolved by a careful reinvestigation of these systems.

The data for $Os(terpy)(dipy)Cl^{+}$ indicate that, since Cl^{-} is the ligand released, only one coordination site in the octahedron needs to be opened in order to have peroxodiphosphate oxidation

The substituent effects are not solely electronic in nature. In order to come sufficiently close to the metal for electron transfer to take place, the peroxodisulfate ion must fit snugly into the slot between the ligands. If then a bulky substituent is placed on the ligand, the entry of the peroxide into the slot will be more difficult, and the rate of oxidation by peroxodisulfate will be diminished No comparable effect on the rate of oxidation by peroxodiphosphate is expected We hope to carry out a test of this prediction· the synthesis of 5-*t*-butyl phenanthroline and then of its ferrous complex is planned. A large decrease in the rate of oxidation by peroxodisulfate is expected, by way of contrast, the change in rate with peroxodiphosphate should be small and should correspond closely to the change in rate for acid hydrolysis.

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