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OXIDATION OF COORDINATED DIIMINE LIGANDS IN BASIC SOLUTIONS OF TRIS(DIIMINE)IRON(III), -RUTHENIUM(III), AND -OSMIUM(III)

O. MØNSTED and G. NORD

Department of Inorganic Chemistry, University of Copenhagen, H.C. Ørsted Institute,
DK-2100 Copenhagen, Denmark

I. Introduction

The possibility of the practical application of the catalytic photodecomposition of water based on the reactivity of the excited states of tris(2,2′-bipyridine) complexes of ruthenium(III) and ruthenium(II) has attracted considerable interest, but it is now clear that the efficiency of this process is limited not only by the lack of efficient catalysts, particularly for the dioxygen-evolving path, but also by both thermal and photochemical ligand oxidation (*1, 2*) and ligand substitution reactions (*3*) of the 2,2′-bipyridine complexes. The stoichiometrically analogous tris(2,2′-bipyridine) and tris(1,10-phenanthroline) complexes of both iron(III) and osmium(III) have also been found to undergo thermal redox and substitution reactions, particularly in aqueous base (*4–6*), and the data from the literature for these reactions are critically examined in this review article. Figure 1 shows ligand structures and ligand numbering schemes, and the ligand name abbreviations are given in Table I.

When tris(diimine)iron(III), -ruthenium(III), or -osmium(III) salts are dissolved in water, reduction to the intensely colored tris(diimine)metal(II) complexes soon becomes apparent. In acid solution this process is slow, but in alkaline solution it appears to be significantly accelerated. It is known that the kinetics of this reduction process is a complicated plethora of parallel and consecutive reactions (*2, 4–6*), and that metal(II) complexes of differently oxidized diimine ligands are formed in addition to the dominant tris(diimine)metal(II) product. These different metal(II) complexes frequently have similar visible absorption spectra, and the accurate stoichiometry of the reactions is therefore not easily established. Mixed monomeric and polymeric complexes containing diimine, hydroxo, and oxo ligands are also formed by diimine ligand aquation and polymerization reactions, and although the accurate compositions of these hydrolyzed solutions are not known, it has been found that one or more species in such solutions are responsible for the observed production of dioxygen in such systems. Figure 2 illustrates this for the tris(2,2′-bipyridine)iron(III) complex in basic solution. The figure also shows that this dioxygen-producing reaction is not catalytic, and that dioxygen is not produced in the absence of hydrolysis products. Destruction of the partly hydrolyzed (diimine)-iron(III)complex, which is responsible for the dioxygen production, by reduction to a stoichiometrically similar but much more labile (diimine)iron(II) complex would be in accord with these observations.

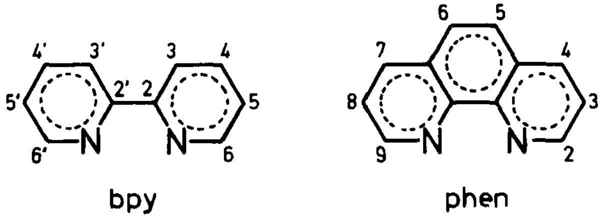


FIG. 1. 2,2′-Bipyridine and 1,10-phenanthroline.

TABLE I

LIGAND NAME ABBREVIATIONS

Abbreviation	Ligand
diim	Diimine Ligand in general
bpy	2,2′-Bipyridine
4,4′-me_2bpy	4,4′-Dimethyl-2,2′-bipyridine
phen	1,10-Phenanthroline
5-mephen	5-Methyl-1,10-phenanthroline
5,6-me_2phen	5,6-Dimethyl-1,10-phenanthroline
4,7-me_2phen	4,7-Dimethyl-1,10-phenanthroline
3,4,7,8-me_4phen	3,4,7,8-Tetramethyl-1,10-phenanthroline
py	Pyridine
trpy	2,2′:6′, 2″-Terpyridine

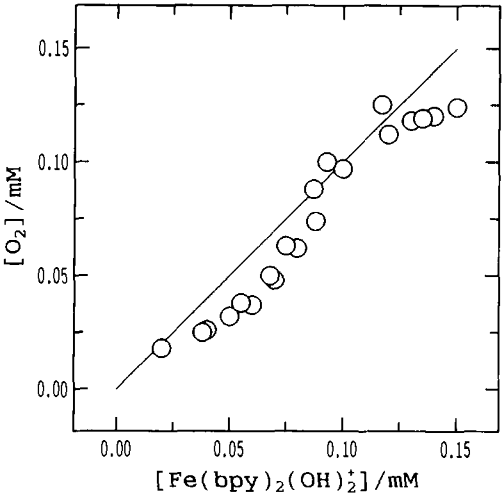


FIG. 2. Concentration of dioxygen produced as function of the concentration of Fe$(bpy)_2(OH)_2{}^+$. The experiments were performed by rapidly adding base to an acid solution of $Fe(bpy)_3{}^{3+}$ that had been allowed partly to hydrolyze. C[Fe(III)] = 1.00 m*M* and C[OH^-] = 0.100 *M* in the reacting solution (*5*).

II. Rate Law and Stoichiometry for the Reduction of Dilute Solutions of Tris(diimine)iron(III), -ruthenium(III), and -osmium(III) in Base

Reduction of these tris(diimine)metal(III) complexes in basic solution is easily monitored by conventional spectrophotometry in the visible range. The molar absorption coefficients of the reduced species are very large, and at most wavelengths are significantly larger than for the tris(diimine)metal(III) initial reactants. The traditional experimental approach within this field of chemistry has therefore been stopped-flow visible spectrophotometry, pseudo-first-order conditions with base in large excess over complex, and complex concentrations in a range between 1 and 0.01 m*M*. Under such conditions there is usually a range of concentrations wherein the experimental rate law corresponds to

$$-d[\mathrm{M(III)}]/dt = d[\mathrm{M(II)}]/dt = k'[\mathrm{M(III)}][\mathrm{OH^-}] \qquad (1)$$

This rate law requires a rate-determining formation of an intermediate that has either added hydroxide or lost a proton (cf. Section IV,B), and as the overall stoichiometry to a good approximation conforms to Eq. (2)

$$n\mathrm{M(III)} \rightarrow (n-1)\mathrm{M(diim)_3}^{2+} + \mathrm{M(diim)}_{3-x}(\text{oxidized diim})_x{}^{2+} \qquad (2)$$

the initially formed intermediate is required to be oxidized in a number of rapid successive steps. In sufficiently dilute solution, n has a value around 6, but this appears to be a lower limit, and in solutions of a higher metal ion concentration, n has been found to increase significantly (cf. Section III), in particular for the most oxidizing systems. Table II contains rate constants, k', and activation parameters as well as the reagent concentration ranges for which the rate law conforms to Eq. (1) and the stoichiometry conforms to Eq. (2) with n about 6.

The oxidized ligand(s) have not been well characterized in most systems, but from the limited evidence available (*2, 7*), introduction of hydroxy groups in the aromatic ring systems according to the generalized stoichiometry

$$-\mathrm{H} + 2\mathrm{OH^-} \rightarrow -\mathrm{OH} + \mathrm{H_2O} + 2e^- \qquad (3)$$

is not an unreasonable supposition. In view of the fact that n is about 6, introduction of one hydroxy group in each of the three diimine ligands is a distinct possibility (cf. Section III).

TABLE II

KINETIC AND THERMODYNAMIC PARAMETERS FOR THE REACTION OF TRIS(DIIMINE) METAL(III) COMPLEXES IN BASIC SOLUTION[a]

Complex	k' (25°C) (M^{-1} sec^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1}mol^{-1})	$E°$ [Eq. (4)] (V)	Ref.
$Fe(bpy)_3^{3+}$	15.8(0.1), 12, 8[b]	62.4(0.8)	−17(3)	0.98	*4, 6*
$Ru(bpy)_3^{3+}$	148[b]	64(4)	+12(13)	1.25	*1, 2*
$Os(bpy)_3^{3+}$	4.7(0.6)	65.4(1.6)	−13(6)	0.84	*4, 6*
$Fe(4,4'\text{-}me_2bpy)_3^{3+}$	1.65(0.21)	54(6)	−60(20)	—	*6*
$Os(4,4'\text{-}me_2bpy)_3^{3+}$	0.32(0.04)[c]	64(1.6)	−46(5)	—	*6*
$Fe(phen)_3^{3+}$	420(25)	46.5(0.8)	−42.(3)	1.01	*4, 6*
$Os(phen)_3^{3+}$	156(16)	50(5)	−35(16)	0.84	*4, 6*
$Fe(5\text{-}mephen)_3^{3+}$	191(33)	—	—	1.02	*6*
$Os(5\text{-}mephen)_3^{3+}$	93(10)	36(4)	−80(16)	—	*6*
$Fe(5,6\text{-}me_2phen)_3^{3+}$	117(17)	38.0(0.6)	−78(2)	0.97	*6*
$Fe(4,7\text{-}me_2phen)_3^{3+}$	35(1.2)	43.0(0.6)	−72(2)	—	*6*
$Fe(3,4,7,8\text{-}me_4phen)_3^{3+}$	17(1.2)	63(8)	−12(2)	0.81	*6*

[a] See Eqs. (1) and (2). Standard deviations are given in parentheses. Conditions for kinetic experiments: C[Fe(III)], 0.1–1mM; C[OH^-], 0.005–0.10 M; C[Os(III)], 0.01–0.1 mM; C[OH^-], 0.005–0.075 M; C[Ru(III)], 0.03–0.17 mM; C[OH^-], 0.01 M.

[b] Ionic strength adjusted to 1 M with Na_2SO_4, others with NaCl.

[c] H/D isotope effect: $k'(H_2O)/k'(D_2O) = 2.25$.

III. Stoichiometry and Identification of Oxidized Reaction Products in Concentrated Solutions

Detailed information on mechanistic aspects of the ligand oxidation reactions is limited by the fact that well-defined tractable kinetics is only found for systems so very dilute in the metal ion reactants that stoichiometric studies including isolation of reaction products have not yet been practicable. Some selected systems have, however, been studied in some detail, but at significantly higher metal ion concentrations than used for the kinetic studies. It is relevant to recall, however, that under such conditions the rate usually does not follow Eq. (1) and the stoichiometry does not conform to Eq. (2) with a value of n about 6.

A. IRON(III) COMPLEXES

Iron(III) complexes are generally more labile than analogous complexes of both ruthenium(III) and osmium(III), and this also holds for the diimine complexes discussed here. In acidic and neutral solution, there is thus an acid-independent diimine ligand aquation reaction of tris(diimine)iron(III) complexes to give diaquabis(diimine)iron(III) or deprotonation products thereof. This puts a lower limit on the hydroxide concentration if complications due to ligand dissociation reactions competing with the metal ion reduction reactions are to be avoided. In sufficiently basic solution, however, this is not a problem, as demonstrated by the data in Table III.

When the basic solutions are allowed to stand, the product iron(II) complexes dissociate and eventually iron(III)hydroxide precipitates. From such solutions, free diimine ligand and a free oxidized ligand product, which has not been further characterized, were isolated. In solutions in which dioxygen was formed (cf. Fig. 2), free diimine-*N*-oxide was also detected *(4)*.

B. RUTHENIUM(III) COMPLEXES

Tris(diimine)ruthenium(III) complexes are significantly more oxidizing than the analogous complexes of both iron(III) and osmium(III). This correlates well with the observation that rates of reduction in base are also faster for the tris(diimine)ruthenium(III) complexes. The tris(1,10-phenanthroline)ruthenium(III) reduction is significantly faster than the tris(2,2′-bipyridine)ruthenium(III) reduction, and this may be the reason why it is only the latter reaction that has been investigated in detail *(1, 2)*. This system is particularly complex, and the rate law given by Eq. (1) holds only for very small concentrations of ruthenium complex. In contrast to the iron(III) systems, simple kinetics

TABLE III

COMPARISON OF KINETIC DATA FOR LIGAND DISSOCIATION AND METAL ION REDUCTION REACTIONS[a]

Reaction		Medium	Half-life (Seconds)
$Fe(bpy)_3^{3+}$	$\rightarrow Fe(bpy)_2(OH_2)_2^{3+}$	0.030 *M* HCl	8.6×10^3
$Fe(phen)_3^{3+}$	$\rightarrow Fe(phen)_2(OH_2)_2^{3+}$	0.030 *M* HCl	15.0×10^3
$Fe(bpy)_3^{2+}$	$\rightarrow Fe(bpy)_2(OH)_2$	0.100 *M* NaOH	6.9×10^2
$Fe(phen)_3^{2+}$	$\rightarrow Fe(phen)_2(OH)_2$	0.100 *M* NaOH	7.6×10^2
$Fe(bpy)_3^{3+}$	→ Fe(II) [cf. Eq.(2)]	0.100 *M* NaOH	0.44
$Fe(phen)_3^{3+}$	→ Fe(II) [cf. Eq.(2)]	0.100 *M* NaOH	0.017

[a] Reactions take place in aqueous acidic and basic solutions at 25°C. Data from Pedersen *(5)*.

has also an upper limit in the hydroxide concentration, as there is an extra term second order in hydroxide, which even in $0.01M$ hydroxide accounts for about 1% of the observed rate of reduction (*2*).

Increase in the ruthenium concentration increases the stoichiometric factor, n in Eq. (2), from about 6 up to about 20, and in these more concentrated solutions rates of ruthenium(III) reduction are no longer first order in ruthenium(III). Under these conditions reaction products depend on the hydroxide concentration and include hydroxy-aromatic ligands [cf. Eq. (3)], carbonate, and trace amounts of dioxygen. Ruthenium complexes of ligands in which one pyridine ring had been completely oxidized were also characterized (*2*). This accounts for the carbonate, and the minor dioxygen yields could originate from complexes oxidized to ruthenium(IV) (*8*). Unlike the iron(III) system, neither free 2,2′-bipyridine nor the *N*-oxide was detected.

C. OSMIUM(III) COMPLEXES

The osmium(III) complexes are very robust and the free ligand has never been observed as a reaction product. Under the conditions wherein Eq. (1) holds, so does Eq. (2) with the value of n about 6. Increase in the osmium complex concentrations results in the formation of relatively long-lived intermediates with osmium in a higher oxidation state, and this seems to be a characteristic difference from the iron and ruthenium systems. The formation of higher oxidation states of osmium were studied in some detail using a 0.5 mM solution of tris(2,2′-bipyridine)osmium(III) in 0.1 M sodium hydroxide (*5*). Kinetic studies were combined with a multitude of physical measurements, which were interpreted with three intermediates. The initial intermediate, formed according to Eq. (1), was further oxidized to give an osmium(IV) product, which in turn decomposed to give (2,2′-bipyridine)dihydroxodioxoosmium(VI). This latter complex has subsequently been characterized further (*9*).

IV. Intimate Mechanism of Formation of the First Intermediate

The present review is chiefly concerned with the mechanism of the formation of the first intermediate and not with the very complicated kinetics of its further fast oxidation. In this section an attempt will be made first to analyze relevant data for the initial slowest step for all the three metal centers with the ligands shown in Table II, and second, to discuss mechanisms that have been suggested in the literature.

A. EMPIRICAL CORRELATIONS OF RATE AND EQUILIBRIUM DATA

As illustrated in Fig. 3, there is a linear correlation between the free energy of activation for the conversions as in Eq. (1) and the corresponding standard reduction potentials

$$\mathrm{M(diim)_3}^{3+} + e^- \rightarrow \mathrm{M(diim)_3}^{2+}; \qquad \mathrm{M} = \mathrm{Fe, Ru, Os} \tag{4}$$

Rates constants are seen to be consistently higher for the tris(1,10-phenanthroline) complexes of iron(III) and osmium(III) than for the analogous tris(2,2′-bipyridine) complexes, in accord with the fact that the reaction of tris(1,10-phenanthroline)ruthenium(III) is known to be qualitatively faster than that of tris(2,2′-bipyridine)ruthenium(III) (*10*). Figure 4 illustrates that the variation in rate with diimine ligand is the same for iron(III) as for osmium(III) complexes, and that there is a good linear free-energy relationship between the two sets of data with a slope of 1. These correlations all point toward significant mechanistic similarities between the reactions independent not only of the ligand system but also of the metal center. Figure 5 shows correlation of the rate constant for reduction with the acid dissociation constants of the di- and monoprotonated diimine ligands. The left part of the figure illustrates that, within the limits of available experimental data, the

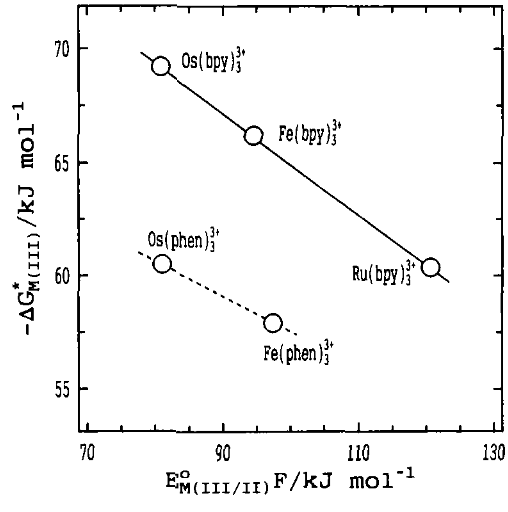


FIG. 3. Correlation between the free energies of activation for the reactions given by Eq. (2) and the standard reduction potentials for the tris(diimine)metal(III) complexes [cf. Eq. (4)]. The data are from Table II.

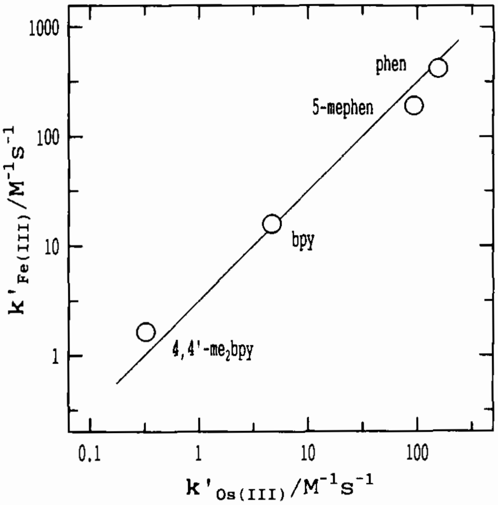


FIG. 4. Linear free energy correlation between the rates of reduction of iron(III) and osmium(III) complexes [cf. Eq. (2)]. The line is drawn with a slope of 1.00. The data are from Table II.

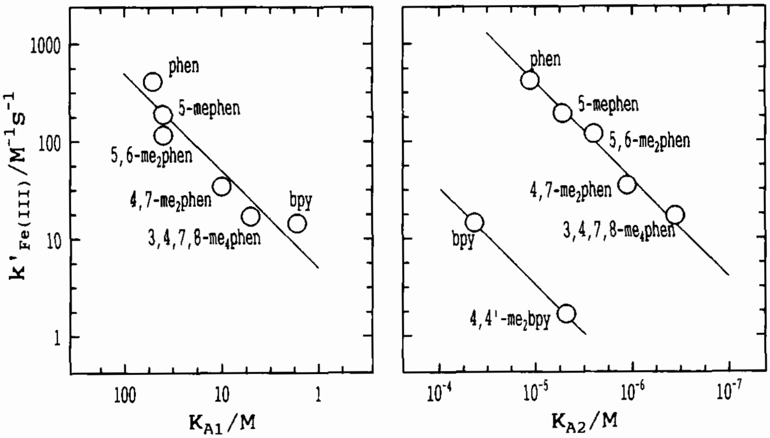


FIG. 5. Free energy correlations between the rates of reduction of tris(diimine)iron(III) complexes [cf. Eq. (2)] and the acid dissociation constants of the di- and monoprotonated free ligands. The lines are drawn with slopes of 1.00. The data are from McBryde (*11*) and from Table II.

difference between the 2,2′-bipyridine and the 1,10-phenanthroline complexes apparent in Fig. 3 disappears when the reduction rates are correlated with the first acid dissociation constant of the diprotonated diimine ligand. In the right part of the figure, however, the differences between the two ligand types are again apparent, and it is tempting to correlate this difference with the stereochemical rigidity of the 1,10-phenanthroline ligand in contrast to the rotational freedom around the C(2) — C(2′) bond in the 2,2′-bipyridine ligand system, which particularly for the acid dissociation constant of the monoprotonated 2,2′-bipyridine gives an energy contribution not present for the 1,10-phenanthroline system. This is illustrated in Fig. 6.

B. SURVEY OF LITERATURE MECHANISMS

The suggested literature mechanisms for the first step of the diimine ligand oxidation in basic solution include (1) simple electron transfer, (2) dissociation of a ligand proton, (3) adduct formation at a ligand carbon atom, and (4) dissociation of a metal–nitrogen bond. These four mechanistic possibilities are shown in Scheme 1 and are discussed below.

Mechanism 1 is a simple rate-determining outer-sphere electron transfer between hydroxide and the tris(diimine)metal(III) reactant. This mechanism is, however, not very plausible for the reactants in Table II, because, first, the enthalpy of activation is significantly less than the enthalpy of reaction (*6*). Second, the standard reduction potential for Eq. (5)

$$OH + e^- \rightarrow OH^-; \qquad E^\circ = 1.89\text{V} \tag{5}$$

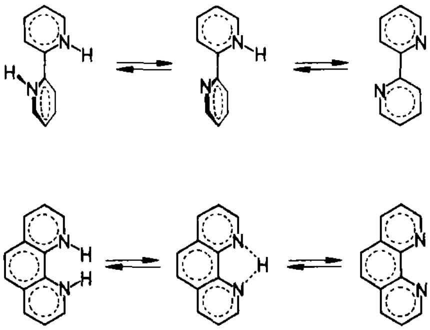
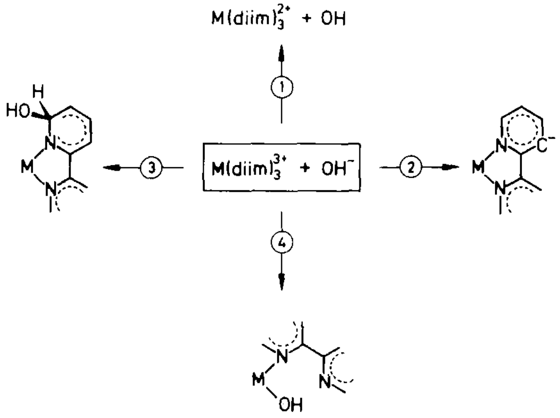


FIG. 6. Illustration of the difference in the conformational behavior of 2,2′-bipyridine and 1,10-phenanthroline on protonation.



SCHEME 1.

in combination with the standard reduction potentials for the tris(diimine)metal(III) reductions [cf. Eq. (4)] and Table II gives reaction rates for the reverse process, rates that are all much greater than the value usually ascribed to a diffusion-controlled process. Third, the general increase in rate for the tris(1,10-phenanthroline) complexes over that of the tris(2,2′-bipyridine) complexes is significantly larger than that generally found for outer-sphere electron transfer reactions of such reactants. For these latter reactions, the small increase in rate for complexes of 1,10-phenanthroline over 2,2′-bipyridine presumably derives from the small difference in standard reduction potentials. Two such examples are oxidation of hexaaquairon(II) for which $k[\mathrm{Fe(phen)_3}^{3+}] = 3.0 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ and $k[\mathrm{Fe(bpy)_3}^{3+}] = 2.2 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$ (*6*), and oxidation of iodide for which $k[\mathrm{Os(phen)_3}^{3+}] = 26\ M^{-1}\ \mathrm{sec}^{-1}$ and $k[\mathrm{Os(bpy)_3}^{3+}] = 17M^{-1}\ \mathrm{sec}^{-1}$ (*5*), respectively. Thus the rate constant ratios for these two pairs of tris(diimine) reactants are significantly smaller than the ratios of reduction rate constants for the same tris(diimine) reactants in Table II, which are both more than 10 times larger.

Mechanism 2 requires deprotonation of a ligand, and dissociation of the hydrogen bound to the C(3) atom was suggested to be the slow step for the reaction of tris(2,2′-bipyridine)ruthenium(III) in base (*12*). This would require a mechanism for the 1,10-phenanthroline complexes different from that of the 2,2′-bipyridine complexes, but, from the data in Table II as illustrated in Figs. 3–5, this seems unlikely. The requirement of a different mechanism is based upon the significant differences in rates of D/H exchange as measured by ^{1}H NMR for the tris(diimine) complexes of ruthenium(II) and osmium(II) (*13,14*), under the assumption that these rates reflect the relative acidities of the ligand hydrogens. For both tris(2,2′-bipyridine)ruthenium(II) and -osmium(II), the hydrogen atoms at the C(3) and C(3′) atoms exchange much faster than do the hydrogen atoms at the other carbon atoms, when measured in basic mixtures of D_2O and nonaqueous solvents. The much slower rates of exchange at the other positions of the 2,2′-bipyridine ligands are comparable with all the rates seen for coordinated 1,10-phenanthroline, the largest difference being exchange of the 1,10-phenanthroline ligand C(2) and C(9) hydrogen atoms, which is about five times as fast as exchange at the C(6) and C(6′) atoms of coordinated 2,2′-bipyridine (*13, 14*). In aqueous solution, the rate of exchange at all positions in the tris(diimine)metal(II) complexes is very slow and has not been measured. In the tris(diimine)metal(III) systems it is likely that the acidity of the ligand hydrogen atoms is increased, but it would seem unlikely that the relative rates will be very different from those found for the metal(II) systems.

Mechanism 3 was originally suggested to explain the kinetics and stoichiometry of tris(diimine)iron(III) and -osmium(III) reactions in base (*6*) and has recently been discussed in some further detail for the tris(2,2′-bipyridine)ruthenium(II) system (*2*). It has the reversible nucleophilic addition of hydroxide to a carbon atom of the coordinated diimine ligand as the first step. This is then supposed to be followed by an intramolecular ligand-to-metal electron transfer and rapid further oxidation of the generated radical ligand. This mechanism was also considered for the overall two-electron reduction in aqueous base of the ruthenium(IV) complexes: $Ru(trpy)(phen)O^{2+}$, $Ru(trpy)(bpy)O^{2+}$, and $Ru(bpy)_2(py)O^{2+}$ (*7*). The first of these was studied in some detail and a number of similarities with the presently considered reactions are apparent. First, the rate law was analogous to that for the reduction of tris(2,2′-bipyridine)ruthenium(III) in base; second, the activation parameters were similar to those shown for the systems in Table I; and third, a ligand was oxidized. This mechanism requires the hydroxide adduct to be formed reversibly, and because there is at present no convincing evidence for such adducts in the present or other similar systems and also the lack of structural evidence for these "covalent hydrates" has earlier been discussed in some detail (*12, 15*), mechanism 3 seems at present highly speculative.

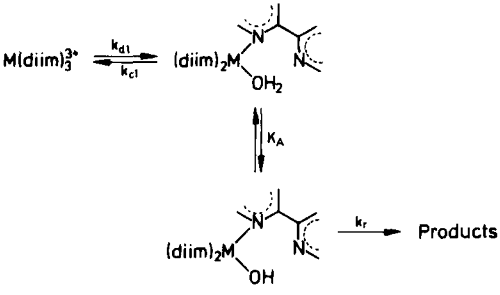
Mechanism 4 requires substitution at the metal center with concomitant dissociation of a metal nitrogen bond as the first step. It is generally accepted that complete dissociation of a bidentate chelate ligand is a two-stage process, and that breaking of the second bond in stereochemically rigid systems is frequently the slow step. The steric arguments that were earlier much used against the tendency of 1,10-phenanthroline to behave as a monodentate ligand were, however, nullified when the nitrate salt of the cation $[Pt(phen)_2(CN)]^+$ was found to have one of the platinum nitrogen bonds about 0.7 Å longer than the remaining three bonds from platinum to the 1,10-phenanthroline ligands (*16*). Also, singly bonded diimine intermediates have been invoked to explain the photosubstitution of not only tris(2,2′-bipyridine)ruthenium(II) but also of the tris(1,10-phenanthroline) complex (*3*). Two-step dissociation is in general agreement with data for the kinetics of complex formation of 1,10-phenanthroline (*17*), and this mechanism is discussed further in the next section.

C. METAL–LIGAND BOND RUPTURE AS A PREREQUISITE FOR LIGAND OXIDATION

The mechanism depicted in Scheme 2 involves two main steps. Rupture of the first metal–nitrogen bond accompanied by coordination of a water ligand at the metal center is followed by reversible deprotonation and intramolecular reduction of the metal center. Under the experimental conditions wherein the concentration of base is much larger than the concentration of tris(diimine) complex, and, applying the steady-state approximation to the concentration of the intermediate species with the monodentate diimine ligand, Eq. (6) can be derived as

$$k' = n(k_{d1}/k_{c1})k_r(K_A/K_W) \tag{6}$$

which holds for the condition $k_{c1} >> k_rK_A(OH^-)/K_W$, K_W being the ionic product of water. Comparison of Eq. (6) with the empirical correlations in Fig. 3–5 makes it likely that differences in ligands are pri-



SCHEME 2.

marily exhibited by differences in the k_{d1}/k_{c1} ratio, and that changes in the metal center are reflected by ligand-independent contributions to the parameters.

The consistent variation of k' with diimine ligand at different metal centers apparent in Fig. 4 and the correlation between k' and the equilibrium constant for dissociation and uptake of the second proton of the diprotonated ligand support the mechanism shown in Scheme 2. A further discussion along such lines is, however, impossible at present, because very little detailed information is available about complex formation of these diimine ligands at the metal centers under discussion. The iron(III) complexes are the most labile, but even for these systems there are no kinetic or equilibrium data for the uptake of the third ligand. This is because formation of the dimeric complex $(\text{diim})_2\text{-Fe(OH)}_2\text{Fe(diim)}_2^{4+}$ effectively competes with formation of Fe-(diim)_3^{3+}. This is also the reason why the tris(diimine) complexes of iron(III), ruthenium(III), osmium(III), and also chromium(III) are synthesized by oxidation of the stoichiometrically analogous divalent metal complexes. The dissociation rates given in Table III chiefly reflect a fast equilibrium between the monodentate and the bidentate diimine ligand followed by a rate-determining breaking of the second metal–nitrogen bond. Consequently, there seems at present no way of reasonably estimating the k_{d1}/k_{c1} ratio for the different ligands.

The acid dissociation constant of a coordinated water molecule is dominated by the overall charge of the metal complex, as demonstrated by the data in Tables IV and V (*18–21*). It is, however, doubtful whether the acidities of the complexes in these tables are representative of the acidities of the complexes with monodentate diimine ligands. This may be seen from a consideration of data for the hydrolysis of tris(2,2′-bipyridine)chromium(III), a complex that in both charge and size resembles tris(2,2′-bipyridine)iron(III). In the acidity range from 1 down to about 10^{-11} M this chromium(III) complex hydrolyzes in a manner that, if considered as arising from formation of a monodentate diimine complex, would lead to a K_A value of about $10^{-7.5}$ M (*22*). This is smaller than the values for tripositive species in Tables IV and V and could reflect significant hydrogen bonding stabilization of the acid form in the monodentate species.

The rate constant for the redox step, k_r, is unlikely to reflect a simple electron transfer from the monodentate diimine ligand to the metal center because replacement of coordinated water with coordinated hydroxide would be expected to decrease the oxidizing power of the metal(III) center. This is well documented by the standard reduction potentials of the aqua and hydroxo complexes in Table IV, and it would seem

TABLE IV

STANDARD REDUCTION POTENTIALS AND ACID DISSOCIATION CONSTANTS FOR SOME AQUAPENTAKIS(IMINE)RUTHENIUM AND -OSMIUM COMPLEXES AT 25°C[a]

M(III)–OH_2 complex	$E°$(M–OH_2) (V)	Ionic medium (*M*)	$-\log[K_A$(M(III)] (*M*)	$-\log[K_A$(M(II)] (*M*)	$E°$(M-OH) (V)[b]
(trpy)(bpy)Os(OH_2)$^{3+}$	0.65	1.0	2.0	7.8	0.32
(trpy)(bpy)Os(OH_2)$^{3+}$	0.60	0.10	—	—	—
(trpy)(bpy)Ru(OH_2)$^{3+}$	1.03	0.10	1.7	9.7	0.56
(trpy)(phen)Ru(OH_2)$^{3+}$	1.05	0.10	1.7	10.0	0.56
(trpy)(phen)Ru(OH_2)$^{3+}$	—	1.0	—	10.2	—
$(bpy)_2$(py)Ru(OH_2)$^{3+}$	1.02	1.0	0.9	10.8	0.42
$(bpy)_2$(py)Ru(OH_2)$^{3+}$	1.04	0.10	0.9	10.2	0.49

[a] See Eq. (4). Data from Roecker *et al.* (*7*), Gilbert *et el.* (*9*), and Pipes and Meyer (*19*).

[b] Standard reduction potentials for M(III)OH^{2+} + e^- → M(II)OH$^-$ calculated from the standard reduction potentials for the aquapentakis(imine) species and the acid dissociation constants.

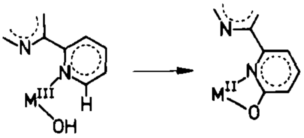
unlikely that the water ligand in the metal(II) intermediates is more acid than in the metal(III) intermediates, as would be required for the hydroxometal(III) complex to be more oxidizing than the analogous aqua complex. Instead, the formal hydrogen atom transfer mechanism depicted in Scheme 3 may operate, in which the reduced oxidizing power of the metal center is compensated for by the presence of a base to accept a proton from a ligand carbon atom. The suggested intermediate is analogous to that detected as a bidentate ligand in bis(2,2′-bipyri-

TABLE V

ACID DISSOCIATION CONSTANTS FOR SOME DIAQUABIS(DIIMINE) METAL(III) COMPLEXES[a]

Complex	$-\log(K_{A1})$ (*M*)	$-\log(K_{A2})$ (*M*)	Ref.
cis-$(bpy)_2Os(OH_2)_2^{3+}$	1.9	5.4	*19*
trans-$(bpy)_2Os(OH_2)_2^{3+}$	0.5	4.4	*19*
cis-$(phen)_2Cr(OH_2)_2^{3+}$	3.4	6.0	*18*
cis-$(bpy)_2Cr(OH_2)_2^{3+}$	3.5	6.1	*18*
cis-$(phen)_2Co(OH_2)_2^{3+}$	4.5	6.8	*20*
cis-$(bpy)_2Co(OH_2)_2^{3+}$	4.7	7.1	*21*

[a] Reaction takes place in a 1 *M* ionic medium at 25°C.



SCHEME 3.

dine)(2-hydroxypyridine)ruthenium(II) (*7*). Also, the D/H isotope effect (cf. Table II) would fit such a mechanism.

V. Conclusion

The rates of oxidation of diimine ligands in basic solutions of tris(diimine)iron(III), -ruthenium(III), and -osmium(III) are in accord with a common mechanism for the first step. A detailed consideration of this is limited at present not only by the complicated and only partly unraveled stoichiometries, but also by the paucity of detailed kinetic and equilibrium data.

A consideration of alternative mechanisms for the common slowest step in the ligand oxidation has led to the conclusion that a metal–ligand dissociation reaction may well operate. It would seem worthwhile to test this by using the newly developed cage complexes (*23, 24*) in which the coordination sphere is effectively unchanged but in which metal–ligand bond breaking would be very difficult. It would seem possible that such caged tris(diimine)ruthenium complexes could be useful for the catalytic photodecomposition of water, but the consequences of the fact that the standard reduction potentials are about 0.3 V higher than for the tris(2,2′-bipyridine)ruthenium(III/II) system (*25*) are not easily foreseeable. Thus, although this higher potential means that production of hydroxyl radicals by electron transfer from hydroxide ions to the metal(III) center is now a distinct possibility (cf. mechanism 1 in Scheme 1, and Section IV,B), and ideally these radicals could form peroxide and finally dioxygen in an uncatalyzed system, they could also cause ligand oxidation. This latter possibility would be in accord with the results of pulse radiolysis studies with tris(1,10-phenanthroline)iron(III) and tris(2,2′-bipyridine)iron(III) and -ruthenium(III), which are known to form "hydroxyl radical adducts." These adducts, on dimerization, disproportionation, or further oxidation, are converted stoichiometrically into hydroxy-substituted aromatic compounds [cf. Eq. (3)]. One obvious way of decreasing the oxidizing power of these new caged diimine ligand complexes would be to replace the ruthenium(III) center by iron(III) or osmium(III), but this would mean that production of dioxygen would still require a catalyst. Alternatively, one of the imine coordination positions could be replaced with a ligand that lowers the standard reduction potential of the ruthenium(III) species. The combination of this aspect with the possibility of direct substrate binding to the metal center, preferably in a multicentered system, remains, however, an intriguing intellectual and synthetic challenge.

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