Reduction of Tris(2,2′-bipyridyl) and Tris(1,10-phenanthroline) Complexes of Iron(III) and Osmium(III) by Hydroxide Ion

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Reaction (i) (L = 1,10-phenanthroline, 2,2′-bipyridyl, and a series of methyl-substituted derivatives of these

$$4\,[M(LL)_3]^{3+} + 4\,OH^- \longrightarrow 4\,[M(LL)_3]^{2+} + O_2 + 2\,H_2O \qquad (i)$$

ligands; M = Fe and Os) has been studied in aqueous (1M) NaCl–NaOH from 6·5 to 35 °C. The rate law throughout is that reported earlier for the unsubstituted iron complexes, *i.e.* $d[Fe(LL)_3{}^{3+}]/dt = k[Fe(LL)_3{}^{3+}][OH^-]$. Phenanthroline complexes react faster than bipyridyl complexes, Fe^{III} complexes faster than the analogous Os^{III} complexes. A linear free-energy relation between the rates and standard free-energy changes of the metal couples, analogous to that known for other reducing agents, holds only for each metal and each ligand type. It is confirmed that the enthalpies of activation are less than those calculated for the standard enthalpy change of reaction (ii). From a consideration of the stopped-flow, potentiometric, and n.m.r. data, together with those from pulse-

$$[M(LL)_3]^{3+} + OH^- \longrightarrow [M(LL)_3]^{2+} + {}^{\bullet}OH \qquad (ii)$$

radiolysis and chemiluminescence studies for these and similar reactions, we conclude that the first-formed product is a highly reactive precursor complex and formulate this as $[M(LL)_2(R^{\bullet}\!-\!OH)]^{2+}$ where $R^{\bullet}$–OH is probably the pseudo-base of a radical formed by addition of an electron to a ligand which approaches the structure of a quaternary-nitrogen cation.

In an earlier publication[1] we showed that the rate of reduction of the tris(2,2′-bipyridyl) and tris(1,10-phenanthroline) complexes of iron(III) by hydroxide ion was first order in complex and hydroxide-ion concentrations.† We presented a reaction scheme which accorded with the suggestions of earlier workers[2,3] in that it also accounted for the final products {O_2 and $[M(LL)_3]^{2+}$}. We pointed out, however, that our data for $[Fe(bipy)_3]^{3+}$ over a range of temperature were accurate enough for us to show that the enthalpy of activation $\Delta H^{\ddagger}$ was less than that of $\Delta H^{\ominus}$ for the previously postulated rate-determining step k_1, thus necessitating an

$$[Fe(bipy)_3]^{3+} + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(bipy)_3]^{2+} + {}^{\bullet}OH \quad (i)$$

intermediate $[Fe(bipy)_3OH]^{2+}$ as the first reaction product. As rates of reduction of these reactant metal complexes {and of oxidation of the corresponding $[M(LL)_3]^{2+}$ complexes (M = Fe and Ru)}, together with variations in rate with substitution in the ligands, have been much used to test theories of outer-sphere electron-transfer mechanisms, any evidence for intermediate-complex formation is of obvious interest.[4] We have now extended our studies to complexes of Fe^{III} and Os^{III} with a series of such substituted ligands and have also accurately measured the temperature dependence of the reduction rate of $[Fe(phen)_3]^{3+}$.

The standard electrode potentials for the $[M(LL)_3]^{3+}$–$[M(LL)_3]^{2+}$ couples, used by earlier workers to construct linear free-energy–rate relations, have previously only been measured in acid solutions and have been said to be acid dependent. We have measured these for M = Fe^{III} and LL = phen and bipy in alkali. We have also investigated the ^1H n.m.r. spectra of the reactant $[Fe(phen)_3]^{3+}$ and product $[Fe(phen)_3]^{2+}$ in D_2O–NaOD solutions as another approach to the determination of the mode of attack of OH^- (OD^-) on the reactant complex.

EXPERIMENTAL

All reagents were either specially purified or were of AnalaR grade. Water doubly distilled from quartz glass was used throughout. Osmium tetraoxide was obtained from Drijfhout, Amsterdam, the ligands from G. F. Smith. and Co., U.S.A. The complexes were prepared by published methods. The absorption spectra of the 3+ and 2+ complexes were in excellent agreement with those given in the literature.

Kinetic measurements were made with a Cary 14 recording spectrophotometer and with a stopped-flow apparatus. The latter was the apparatus used in ref. 1 but was automated by attachment of a Biomation 802 Transient Recorder together with a Facit 4070 tape puncher. All solutions were 1·00M in NaCl or $NaNO_3$ (see Table) and rates of reaction were all measured under pseudo-first-order conditions, $[OH^-] \gg [M(LL)_3{}^{3+}]$.‡

N.m.r. measurements were made by Dr. Jonas Pedersen of Chemistry Department V of this institute. NaOD In D_2O was added to a solution of $[Fe(phen)_3]^{3+}$ in D_2O. The reduction reaction occurred rapidly (see above) and, before measurement of the product, $Na_2[S_2O_4]$ was added to remove O_2. This is necessary to stabilise the product solution for the n.m.r. measurements, since in the presence

$$4\,[Fe(LL)_3]^{3+} + 8\,OH^- + O_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)_3 + 12\,LL \quad (ii)$$

of O_2 the overall reaction (ii) is known to take place.[5,6] All operations were carried out in a glass apparatus under N_2.

Potentiometric titrations were carried out with a pH-stat (Radiometer) fitted with a gold electrode and a standard calomel electrode. The apparatus was thermostatted (25 ± 1 °C). Parallel experiments with solutions of the

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† The bidentate ligands 2,2′-bipyridine and 1,10-phenanthroline are referred to below as bipy and phen, respectively, and collectively as LL.

‡ 1M = 1 mol dm^{-3}.

[1] G. Nord and O. Wernberg, *J.C.S. Dalton*, 1972, 866.

[2] N. Sutin, unpublished work quoted in A. A. Green, J. O. Edwards, and P. Jones, *Inorg. Chem.*, 1966, **5**, 1858.

[3] M. Anbar and I. Pecht, *Trans. Faraday Soc.*, 1968, **4**, 744.

[4] J. N. Braddock and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 3158.

[5] G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.

[6] G. Nord, *Acta Chem. Scand.*, 1973, **27**, 743.

same composition were made using an O_2 electrode (Radiometer type E 5064). The apparatus was filled with either N_2 or H_2 and solutions were 1M in NaCl.

RESULTS

Rate Constants.—Pseudo-first-order rate constants were calculated from the rate of increase of optical density due to the $[M(LL)_3]^{2+}$ product at the wavelength of maximum absorbance in the visible range. These all increased linearly with (excess) $[OH^-]$ and were converted into second-order rate constants which were independent of the initial $[M(LL)_3{}^{3+}]$ (see Table). The activation parameters are also given in the Table. These were calculated from plots of $\ln k/T$ against $1/T$ using the expressions from reaction rate theory, $k = (k_BT/h)e^{-\Delta G^{\ddagger}/RT}$ and $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. Under the experimental conditions used (see Table), side reactions were negligible. This was not so for more concentrated solutions of complex and more dilute solutions of base, *cf.* the potentiometric measurements below.

Rate constants and activation parameters *

Ligand, LL	$\Delta G^{\ddagger}$ (25°C) / kJ mol^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	ln (k/dm^3 mol^{-1} s^{-1}) at 25 °C
(*a*) Reactants $[Fe(LL)_3]^{3+}$ and OH^-				
phen	57·92 (0·16)	46·5 (0·8)	−41·8 (2·8)	6·042 (0·06)
5-Mephen	60·00 (0·4)			5·25 (0·16)
5,6-Me_2phen	61·2 (0·3)	38·0 (0·6)	−78·0 (2·0)	4·76 (0·14)
4,7-Me_2phen	64·22 (0·08)	43·0 (0·6)	−71·5 (2·0)	3·55 (0·04)
3,4,7,8-Me_4phen	66 (2)	63 (8)	−12 (2)	2·83 (1·0)
bipy [a]	66·2	62·4 (0·8)	−17·0 (2·8)	2·76
4,4′-Me_2bipy	71·8 (0·2)	54 (6)	−60 (20)	0·50 (0·12)
(*b*) Reactants $[Os(LL)_3]^{3+}$ and OH^-				
phen	60·5 (0·2)	50 (5)	−35 (16)	5·05 (0·10)
5-Mephen	61·8 (0·2)	36 (4)	−80 (16)	4·53 (0·10)
bipy [b]	69·2 (0·3)	65·4 (1·6)	−13 (20)	1·54 (0·12)
4,4′-Me_2bipy	75·9 (0·3)	64·0 (1·6)	−46 (5)	−1·14 [c] (0·12)

$[OH^-] = 0{\cdot}005$—$0{\cdot}075$ and $[M(LL)_3{}^{3+}] = 1 \times 10^{-3}$—$1 \times 10^{-5}$M.

[a] From ref. 1. [b] Also in 1·00M-$NaNO_3$. [c] $k_{H_2O}/k_{D_2O} = 2{\cdot}25$ at 25 °C.

* Standard deviations (±) are given in parentheses.

N.M.R. Spectra.—The spectrum of the product $[Fe(phen)_3]^{2+}$ produced by treating OD^- with $[Fe(phen)_3]^{3+}$ in D_2O was identical with that of a sample dissolved in D_2O and prepared from iron(II) sulphate and ligand in H_2O, and agreed with the published spectrum.[7] The relative peak heights were easily measured. No D–H exchange thus occurs during the reduction of $[Fe(phen)_3]^{3+}$ by OD^-.

Potentiometric Studies.—Potential changes during the automatic addition of NaOH to maintain a constant concentration (1×10^{-4}—$2{\cdot}3 \times 10^{-4}$M) in rather concentrated solutions of $[Fe(phen)_3]^{3+}$ and $[Fe(bipy)_3]^{3+}$ (1×10^{-3}—2×10^{-3}M) were used to determine $E^{\ominus}$ values for the 2+–3+ couples. The pH-stat curves were reproducible and the overall stoicheiometry was as in (iii). The ligand

$$[Fe(LL)_3]^{3+} + 1{\cdot}38\,OH^- \longrightarrow 0{\cdot}81\,[Fe(LL)_3]^{2+} + 0{\cdot}19\,Fe(OH)_3 + (0{\cdot}57\,LL + 0{\cdot}20\,O_2) \quad \text{(iii)}$$

and O_2 concentrations are given in parentheses because the free ligand was not measured and the oxygen concentration measured with the oxygen electrode was only about one half that predicted. We hope to investigate whether or not this discrepancy is real by studying the corresponding Os^{III} systems in the presence of added ligand.† These are free from the competing product reaction (ii) (see above) and possibly also of any dissociation of the reactant $[M(LL)_3]^{3+}$.

The potential of the gold electrode in the reaction mixture was automatically recorded and from this curve the potential at the time corresponding to the first half-life of the reaction was obtained. It follows from the stoicheiometry that the concentration of $[Fe(LL)_3]^{3+}$ at this point is 50% and that of $[Fe(LL)_3]^{2+}$ is 40·5% of the initial $[Fe(LL)_3]^{3+}$ concentration. Thus the potential measured is $E = E^{\ominus} + (RT/F)\ln(50/40{\cdot}5) = E^{\ominus} + 5$ mV. The $E^{\ominus}$ values of the couples, *versus* the standard hydrogen electrode but in 1·00M-NaCl, were as follows:

$[Fe(phen)_3]^{3+}$–$[Fe(phen)_3]^{2+}$
$E^{\ominus}$/mV = 1 008, 1 026, 993, 1 040, 1 030, 1 015, and 1 026
(average 1 019 ± 6)

$[Fe(bipy)_3]^{3+}$–$[Fe(bipy)_3]^{2+}$
$E^{\ominus}$/mV = 976, 970, 987, 988, and 990
(average 982 ± 4)

DISCUSSION

Since the publication of our first paper[1] careful calculations[8] of the energetics of reaction (i) have given $\Delta H^{\ominus} = 102 \pm 15$ kJ mol^{-1} for bipy and 109 ± 15 kJ mol^{-1} for the corresponding reaction of phen. For the former, $\Delta H_0^{\ddagger}$ extrapolated (ionic strength→0) from our data[1] is 71 ± 5 kJ mol^{-1} giving $\Delta H^{\ominus} - \Delta H_0^{\ddagger} = 38 \pm 20$ kJ mol^{-1}, which is probably rather less than our estimate (50 kJ mol^{-1}) at I = 1M. For the phen reaction (see Table), using the same correction as that found for the bipy system, $\Delta H^{\ominus} - \Delta H_0^{\ddagger} = 58 \pm 20$ kJ mol^{-1}. Alternatively we note that the $E^{\ominus}$ values for the two metal complex couples are in agreement with literature values for acid solutions[9,10] and differ only by *ca.* 0·4 kJ mol^{-1}. Both couples are isentropic[11,‡] so that neither the differences in $\Delta H^{\ddagger}$ nor in $\Delta S^{\ddagger}$, 15·9 ± 1·5 kJ mol^{-1} and 24·8 ±

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† We showed in ref. 1 that addition of free ligand did not affect the rate of reduction, but did not determine its effect on the stoicheiometry.

‡ We thank J. C. Sullivan of the Argonne National Laboratory, U.S.A., for kindly bringing this reference to our notice.

[7] R. H. Prince and R. D. Miller, *J. Chem. Soc.*, 1965, 470; *J. Chem. Soc.* (*A*), 1966, 3185.

[8] P. B. Monkhouse, Chemistry Project Report, Queen Mary College, University of London, 1973.

[9] P. George, G. Hanania, and D. H. Irvine, *J. Chem. Soc.*, 1959, 2548.

[10] M. H. Ford-Smith and N. Sutin, *J. Amer. Chem. Soc.*, 1961, **83**, 1830.

[11] J. Lin and W. G. Brack, *Canad. J. Chem.*, 1965, **43**, 766.

5·6 J K^{-1} mol^{-1}, respectively, can be attributed to changes in $\Delta H^{\ominus}$ or $\Delta S^{\ominus}$ for the overall reaction (i).

Another approach is to assume that the thermochemical data for the reaction $OH \rightleftharpoons {}^{\bullet}OH + e^-$ are in error * and that the rate-determining step is in fact a reversible electron transfer with the product ·OH rapidly reacting further. In this context, pulse-radiolysis results [12] for the back reaction, $[Fe(phen)_3]^{2+} + {}^{\bullet}OH \longrightarrow$ Products, are relevant. It has been found that a product is formed at a rate close to the diffusion-controlled limit ($k = 9 \times 10^9$ dm^3 mol^{-1} s^{-1}). This, unlike the intensely absorbing radical product of the free ligand with ·OH, which was also measured, is stable in neutral solution (during the time scale of the experiments) but both decays in alkaline solution and has an intense spectrum very different from that of $[Fe(phen)_3]^{3+}$. The authors tentatively proposed a reaction involving attack on a ligand which remains bonded to the complex [equation (iv)] and which would decay as in equations (v) and (vi). There is thus additional evidence for the non-occurrence of a simple reversible electron-transfer mechanism.

$$[Fe(phen)_3]^{2+} + {}^{\bullet}OH \xrightarrow{k} [Fe(phen)_3OH]^{2+} \quad (iv)$$

$$[Fe(phen)_3OH]^{2+} \begin{cases} \longrightarrow [Fe(phen)_3]^{3+} + OH^- & (v) \\ \longrightarrow [Fe(phen)_2R^{\bullet}]^{2+} + H_2O & (vi) \end{cases}$$

Figure 1 illustrates that the dependence of rate on ligand type persists with complexes of the substituted ligands and also that it is larger than that found at 25 °C for the $[Fe(LL)_3]^{3+}$–Fe^{II} reaction which has been used to test the Marcus theory of outer-sphere electron transfer.[4] In both cases changes in rate from methyl substitution in either phen or bipy parallel changes in $E^{\ominus}$ for the metal couples. It is of interest that different activation energies, which are small but *negative*, have recently [4] been reported for the reduction of $[Ru(phen)_3]^{3+}$ and $[Ru(bipy)_3]^{3+}$ by $[Fe(OH_2)_6]^{2+}$ and that the similarity of the activation parameters to those for $[Fe(phen)_3]^{3+}$ with $[Fe(OH_2)_6]^{2+}$ is considered by the authors as evidence for a common mechanism. In both series it was necessary to invoke reaction by a ' non-Marcus ' path.

On replacing the metal centre Fe^{III} by Os^{III} rates of reduction consistently decreased (see Figure 2). For Ru^{III} complexes the rates are qualitatively known to be very fast [13] so that there is an overall increase in rate with increase in $E^{\ominus}$ for the three metal couples. Of particular interest here are the results of Lytle and Hercules [14] who found that addition of a concentrated solution of a strong base to concentrated solutions of $[Ru(bipy)_3]^{3+}$, formed *in situ* by PbO_2 oxidation of $[Ru(bipy)_3]^{2+}$, gave as an intermediate the same excited form of $[Ru(bipy)_3]^{2+}$ as that produced photochemically in $[Ru(bipy)_3]^{2+}$ solutions. These authors follow Fleischauer and Fleischauer [15] and suggest that an electron added to the π-system of the ligands is eventually transmitted to the metal-ion

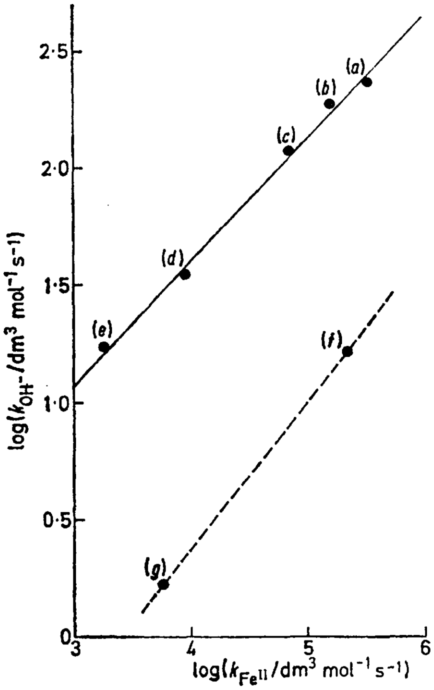

FIGURE 1 Plot of $\log_{10}$ (k/dm^3 mol^{-1} s^{-1}) for the reactions $[Fe(LL)_3]^{3+} + OH^-$ against $\log_{10}$ (k/dm^3 mol^{-1} s^{-1}) for the reactions $[Fe(LL)_3]^{3+} + Fe^{2+}$ at 25 °C (ref. 12 and this work in 0·5M-H_2SO_4): LL = phen (*a*), 5-Mephen (*b*), 5,6-Me_2phen (*c*), 4,7-Me_2phen (*d*), 3,4,7,8-Me_4phen (*e*), bipy (*f*), and 4,4′-Me_2bipy (*g*)

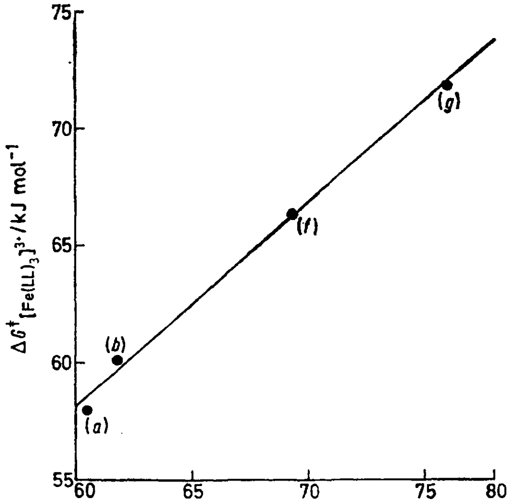

FIGURE 2 Plot of $\Delta G^{\ddagger}$ for the reactions $[Fe(LL)_3]^{3+} + OH^-$ against $\Delta G^{\ddagger}$ for rhe reactions $[Os(LL)_3]^{3+} + OH^-$. For key see Figure 1

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* Using $\Delta G^{\ominus}$ for reaction (i) to obtain K_1 ($=k_1/k_{-1}$), substitution of the measured k ($=2\ k_1$) would of course give an impossibly large value for k_{-1}.

[12] P. Pagsberg and K. E. Siekierska, Progress Report on the Redox Kinetics of Tris(*o*-phenanthroline)iron Ions Studied by Pulse Radiolysis, Symposium of Nordisk Forening for Strålingsforsøg og Strålingsindustri, Otaniemi, Finland, 1973.

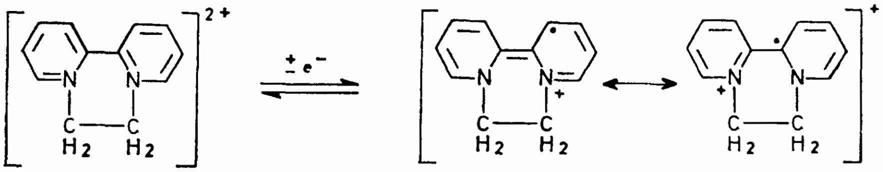
[13] J. D. Miller, Ph.D. Thesis, Cambridge University, 1965.

[14] F. E. Lytle and D. M. Hercules, *J. Amer. Chem. Soc.*, 1966, **88**, 4745.

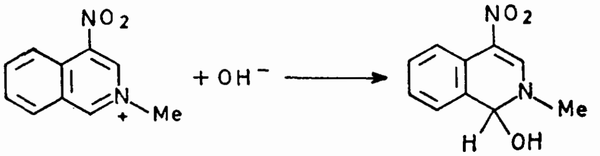
[15] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 1970, **70**, 199.

centre, the observed chemiluminescence corresponding to the intramolecular electron transfer ^3d–$\pi^*(t_{2g}{}^5\pi^*) \rightarrow {}^1d$–$d(t_{2g}{}^6) + h\nu$ [*cf.* stage (3a) in the reaction sequence given below]. It has previously been pointed out [4] that conceptually the chemiluminescent reactions of $[Ru(LL)_3]^{2+}$ are very similar to some oxidation-reduction reactions of Co^{III} complexes where ligand-reduced radical-anion intermediates have been postulated. However, for the reduction of $[M(LL)_3]^{3+}$ complexes by $[Fe(OH_2)_6]^{2+}$ the exothermicity associated with the formation of a precursor complex remains to be explained.[4]

We derived our scheme for the reaction sequence during OH^- reduction by first considering two typical reactions of quaternary cations formed from the ligands and similar molecules which we use as models * for the complexes $[M(LL)_3]^{3+}$. The reactions are reversible uptake of one electron, $A^{2+} + e^- \rightleftharpoons A^+$, *e.g.* as in equation (vii),[16] and reversible pseudo-base formation ($B^+ + OH^- \rightleftharpoons BOH$, $BOH + H^+ \rightleftharpoons B^+ + H_2O$) which in the example chosen is in the stopped-flow time range [equation (viii)].[17,†] We incorporated the two types of reaction in the following sequence using as illustrations *one example* of the resonance structures which would contribute to the electronic structures of the reactant complex, the postulated intermediate, and the product complex.



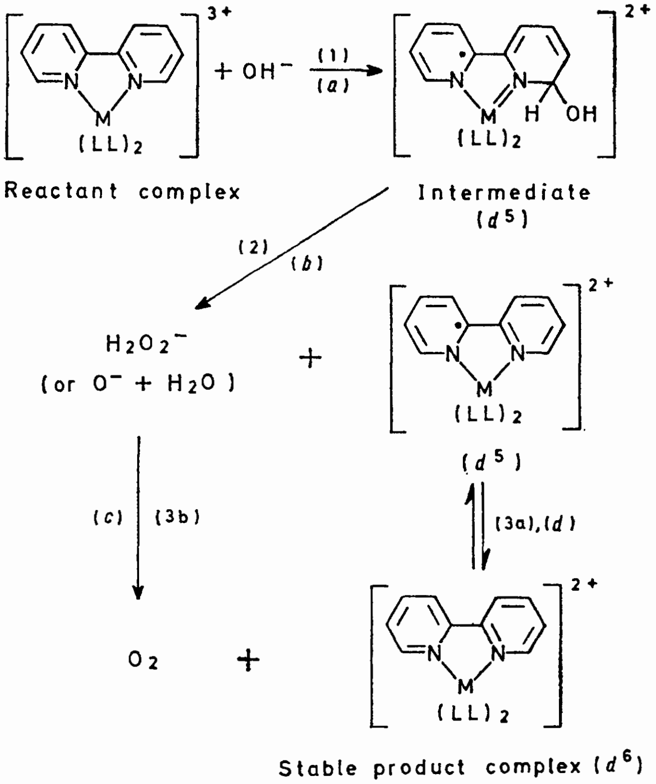
(vii)



(viii)

$\Delta H^{\ddagger}$: 17 kJ mol^{-1} and
$\Delta S^{\ddagger}$: −44 J K^{-1} mol^{-1}

The depiction of the intermediate as a radical can explain, in terms of increased conjugation, why reactions of the phen complexes are faster than those of the analogous bipy species, In accordance with this, changes in redox potentials for the couples A^{2+}–$A^{\dot{+}}$ with changes in ligand structure have been correlated [16] with the degree of resonance stabilisation due to the delocalisation of the free electron in the radical cation. Similarly, if the $E^{\ominus}$ sequence for the metal complex couples, Ru > Fe > Os, reflects decrease in the enthalpy of formation of $[M(LL)_3]^{3+}$ then this may be correlated with the degree of double bonding in both reactant and intermediate. The depiction of step (1) as rate determining together with the overall stoicheiometry gives the rate constant for this step as half the observed rate constants given in the Table, while the postulated pseudo-base formation could explain both the rate law and the activation parameters. Finally, step (2), the rapid reaction with further OH^-, can explain the observed effect of OH^- on the product of the $[Fe(phen)_3]^{2+} + {}^{\bullet}OH$ reaction [12] and also finds analogy with other reductions of $[M(LL)_3]^{3+}$ complexes. Thus the rate law for reduction of $[Fe(bipy)_3]^{3+}$ (ref. 18) and of $[Os(bipy)_3]^{3+}$ (ref. 19) by X^- (X = SCN and I) is as in equation (ix). We interpret the second term as due to formation of X_2^- and have therefore tentatively included $H_2O_2^-$ as a possible product in our postulated reaction scheme. The fast further stages involving peroxide radicals, (3b), as suggested in our first publication,[1] now account for the



(*a*), Rate-determining step k_1; (*b*), + OH^- (k_2); (*c*), further reaction with reactant complex according to ref. 1; (*d*), $t_{2g}{}^5\pi^* \rightarrow t_{2g}{}^6$

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* We are grateful to Professor Gerold Schwarzenbach of Zurich for suggesting this approach.

† We thank Professor Martin Ettlinger of Chemistry Department II of this institute for providing this reference.

[16] E. Steckhan and T. Kuwana, *Ber. Bunsengesellschaft. Chem.*, 1974, **78**, 253.

[17] J. W. Bunting and W. G. Meathrel, *Canad. J. Chem.*, 1973, **51**, 1965.

[18] W. K. Wilmarth, J. E. Byrd, and Jia-yong Chen, *Proc. 15th Internat. Conf. Co-ordination Chem.*, Moscow, 1973, p. 45.

[19] G. Nord and Britta Pedersen, unpublished work.

final product being oxygen. We were unable to detect radicals in the reacting solutions under our experimental conditions, but unidentified radicals have been detected by Gusenius [20] under undefined mixing conditions.

$$\frac{-\mathrm{d}[\mathrm{M(LL)_3}^{3+}]}{\mathrm{d}t} \cdot \frac{1}{c_{[\mathrm{M(LL)_3}]^{3+}}} = k_1 c_{\mathrm{X}^-} + k_2 (c_{\mathrm{X}^-})^2 \qquad \text{(ix)}$$

Reversible pH-dependent spectral changes have been reported for other bipy complexes. Murray and Nord [21] found that addition of sodium hydroxide to a red solution of $[\mathrm{Cr(bipy)_3}]^{2+}$ produced a blue solution, the spectrum of which corresponded to that reported for $[\mathrm{Cr(bipy)_3}]^{+}$. This fast colour change is reversed on immediate addition of acid without overall reduction of $[\mathrm{Cr(bipy)_3}]^{2+}$. In low-valent complexes such as those of $\mathrm{Cr^{I}}$ the presence of the ligand as an anion seems likely. Also, Gillard [22] has suggested that the reversible changes with pH in the u.v. spectrum of $[\mathrm{Pt(LL)_3}]^{2+}$ are due to OH addition at a carbon atom of the ligand. We also considered the possibility that a seven-co-ordinate intermediate is formed in the present reactions but note first that such complexes have only been reported for spin-free $\mathrm{Fe^{III}}$ and secondly that the increased rate of reduction of the phen complexes over those of bipy then becomes inexplicable.

Summarising, we find that the rate law and activation enthalpies for the reduction of $[\mathrm{M(LL)_3}]^{3+}$ with OH^- accord with the general equation (x). The rather large changes in $\Delta S^\ddagger$ are still unexplained. We find that

$$[\mathrm{M(LL)_3}]^{3+} + \mathrm{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{M(LL)_3OH}]^{2+} \xrightarrow[k_2]{+\mathrm{X}} \text{Products} \qquad \text{(x)}$$

succeeding fast steps involving peroxide radicals may be applicable as suggested earlier,[1] although we failed to point out previously that if the products include the hydroxyl radical then the equilibrium $^{\bullet}\mathrm{OH} + \mathrm{OH}^- \rightleftharpoons \mathrm{O}^- + \mathrm{H_2O}$ must be considered as the pK for $^{\bullet}$OH is 11·9.[23] For the decomposition of the intermediate, if $\mathrm{X} = \mathrm{OH}^-$ as in the reaction sequence given above, the observed rate constants become equal to $2k_1$, while in the other limiting case of $\mathrm{X} = \mathrm{H_2O}$ and a rapid pre-equilibrium, $k = 2K_1k_2$ where $K_1 = k_1/k_{-1}$. The D–H and $\mathrm{O_2}$ isotope [3] effects and also the salt effect [1] accord with either of these limiting cases.

We thank the Carlsberg Foundation for making available the stopped-flow apparatus, Statens naturvidenskabelige Forskningsråd for the award of a maintenance grant (to O. W.), Dr. R. H. Prince for kindly sending us photocopied sections of ref. 13, since such Ph.D. theses, although acceptable as references in *J.C.S.*, are not directly available outside the United Kingdom.

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[22] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.

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