

Redox considerations for a ruthenium complex catalysis of substrate oxidation by hydrogen peroxide in aqueous solution

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The pH dependence of the redox chemistry of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ has been measured (dmphen = 2,9-dimethyl-1,10-phenanthroline). Comparison of the results with those for similar complexes illustrates the unique acidity of the co-ordinated waters and the large oxidizing strength of the ruthenium. The reaction of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ with H_2O_2 has been studied as a function of pH and the results are used to provide a mechanism for the catalysis of alkane oxidation by this complex.

The metal-catalysed oxidation of organic substrates is a subject of intensive research. Che,¹ Meyer,² Takeuchi³ and Groves⁴ and co-workers have extensively examined the synthesis, reactivity and electrochemical properties of a large number of ruthenium complexes. They exist in a wide range of oxidation states and can form stable oxo and dioxo species in solution through proton-coupled electron-transfer reactions. These properties are attractive for oxidation catalysts.

Our research has focused on a unique sterically hindered ruthenium complex, $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$, where dmphen is 2,9-dimethyl-1,10-phenanthroline. In acetonitrile, this complex is oxidized by hydrogen peroxide and dioxygen to form oxoruthenium(IV) and by hydrogen peroxide to form *cis*-dioxoruthenium(VI). It is a catalyst for oxidizing alkenes and alkanes with O_2 and H_2O_2 . The sterically hindering ligands prevent the formation of both μ -oxo dimers and the *trans*-dioxo species. In other polypyridyl complexes the dimers are not very reactive and the *trans*-dioxo complex is a weaker oxidant than the *cis* complex.^{1d,2a,d,g,5}

An earlier paper^{6a} proposed a mechanism for ruthenium-catalysed oxidation of alkenes and alkanes with dioxygen and hydrogen peroxide. This paper focuses on the inorganic chemistry of the catalyst. The kinetics of formation and thermodynamic oxidization potentials of the various aqua- and oxo-complexes of $\text{Ru}(\text{dmphen})$ involved in the catalytic oxidation cycle are studied. The pH dependences of the ruthenium potentials in aqueous solution are reported and compared to the pH-dependent potentials required for the activation of dioxygen and hydrogen peroxide. The use of Pourbaix plots for the prediction of feasible metal complex intermediates is examined. A kinetic study of the reaction of the ruthenium(II) complex with hydrogen peroxide is also reported and the effect of pH examined. The implications of this chemistry on aqueous and non-aqueous catalytic oxidation mechanisms are discussed.

Experimental

Materials

Ruthenium(III) chloride, 2,9-dimethyl-1,10-phenanthroline, LiClO_4 and LiCl were all used as received from Aldrich. Potassium hydrogenphthalate (Fisher) was dried overnight at 100 °C under vacuum. 30% Hydrogen peroxide (Fisher) was diluted as appropriate for the kinetic studies and the peroxide concentrations were measured by iodometric titration. The KOH solution used in the pH measurements was prepared by dilution of a stock solution made from KOH pellets (Fisher), followed by standardization with potassium hydrogenphthalate.

Measurements

The UV/VIS measurements were performed on a Perkin-Elmer Lambda-6 spectrophotometer, pH measurements with a Fisher Accumet model 630 pH meter. Cyclic voltammetry was done with a PAR 173 potentiostat/galvanostat attached to a PAR 175 universal programmer, a PAR 179 digital coulometer and a Houston Instrument Omnigraphic 2000 XY-recorder. The reference was a Corning Ag–AgCl general-purpose electrode and the working electrode a Cypress Systems glassy carbon minielectrode. Cyclic voltammetry measurements were done in aqueous solution with 0.1 mol dm⁻³ LiClO_4 as the supporting electrolyte and 1.0×10^{-4} mol dm⁻³ ruthenium(II) complex. The pH was adjusted by adding small amounts of dilute KOH. Volume changes were negligible. Cyclic voltammograms were obtained at many different pH levels ranging from 2.42 to 9.90, with a scan rate of 200 mV s⁻¹.

Synthesis

The complex $[\text{Ru}(\text{dmphen})_2\text{Cl}_2]$ was synthesized as previously described⁵ (Found: C, 55.70; H, 3.95; N, 8.95. Calc: C, 55.45; H, 4.30; N, 9.25%).

The complex $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$ was synthesized by a modification of the literature procedures:^{5,6a} $[\text{Ru}(\text{dmphen})_2\text{Cl}_2]$ (0.5 g) was suspended in distilled water (200 cm³) and then heated to 70 °C. At the higher temperature water displaces the chloride ligand to give the orange diaqua complex. A saturated NaPF_6 solution (50 cm³) in 0.1 mol dm⁻³ HPF_6 was added to the orange solution, which was then cooled in an ice-bath to precipitate the product. The resulting orange-red microcrystals were filtered off, rinsed with 0.1 mol dm⁻³ HPF_6 solution, and then with water. Rinsing was continued until the filtrate was free of chloride (AgNO_3 test).

Determination of the oxidation rate of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$

The rate of oxidation of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$ by H_2O_2 was measured by placing a solution (aqueous) (3 cm³) containing a known concentration of the complex (pH 3.3 for the rate-law study) in a spectrophotometer cell, and then adding aqueous hydrogen peroxide solution (0.5 cm³). The cell was capped, shaken thoroughly to ensure complete mixing and then placed in the spectrophotometer. The ruthenium(II) absorbance at 495 nm was determined as a function of time and the ionic strength was assumed to be constant. Experiments demonstrated that a ten-fold increase in ionic strength by addition of KCl does not significantly alter the rates and that addition of an excess of chloride to the reaction solution does not alter the reactant complex in the time frame of the experiments; pH changes in the reaction with H_2O_2 were negligible.

In order to determine the change in concentration of ruthenium(II) a correction accounting for the absorbance of oxidized ruthenium species was made. Ref. 6(b) shows that ruthenium(III) is first formed when peroxide is added to ruthenium(II). Ruthenium-(IV) and -(VI) are formed sequentially as the amount of added peroxide increases. Isosbestic points are observed for each step and molar absorption coefficient, ϵ , values for the ruthenium-(II) and -(IV) species can be obtained from analysis of the UV/VIS data. These are 6870 and 3540 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, respectively. The concentration of ruthenium(II) and the approximate rate constants result from the measured absorbance, A , using equation (1), where

$$[\text{Ru}^{\text{II}}]_t = \frac{A - \epsilon_{\text{IV}}[\text{Ru}^{\text{II}}]_i}{\epsilon_{\text{II}} - \epsilon_{\text{IV}}} \quad (1)$$

A_t = absorbance at time t , $[\text{Ru}^n]_t$ = concentration of ruthenium(n^+) at time t , $[\text{Ru}^{\text{II}}]_i$ = initial concentration of ruthenium(II) and ϵ_n = molar absorption coefficient of ruthenium(n^+). Since $A_t = [\text{Ru}^{\text{II}}]_t \epsilon_{\text{II}} + [\text{Ru}^{\text{IV}}]_t \epsilon_{\text{IV}}$ and $[\text{Ru}^{\text{II}}]_i = [\text{Ru}^{\text{II}}]_t + [\text{Ru}^{\text{IV}}]_t$, combining these equations gives $A_t = [\text{Ru}^{\text{II}}]_t (\epsilon_{\text{II}} - \epsilon_{\text{IV}}) + [\text{Ru}^{\text{II}}]_i \epsilon_{\text{IV}}$ which rearranges to equation (1).

Results

Three separate experiments were performed to characterize the reactivity of the $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ complex. An electrochemical study was performed in aqueous solution to determine the change in reduction potentials as the pH was changed. Similar experiments have yielded useful insights about the reactivity of other ruthenium complexes.^{1a,c,f,g,2l,3b} A pH titration of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ with aqueous potassium hydroxide was carried out to determine the $\text{p}K_a$ of the coordinated water. A pH titration was used because this complex does not exhibit large pH-dependent changes in the UV/VIS spectrum. The reaction of the ruthenium(II) *cis*-diaqua complex with hydrogen peroxide was also studied and an empirical rate law determined.

Electrochemistry

Fig. 1 shows a typical cyclic voltammogram for the complex at pH 9.9. While the separations between the cathodic and anodic peaks for both couples between 0 and 1 V are slightly greater than 60 mV, the equality of the cathodic and anodic peak currents suggests reversibility, as $i_{\text{p,a}}/i_{\text{p,c}} \approx 1$.^{3b} Other reports of electrochemical studies with a glassy carbon electrode on similar complexes^{1g} reveal quasi-reversible or irreversible couples. The $\text{Ru}^{\text{VI}}\text{-Ru}^{\text{IV}}$ couple was irreversible.

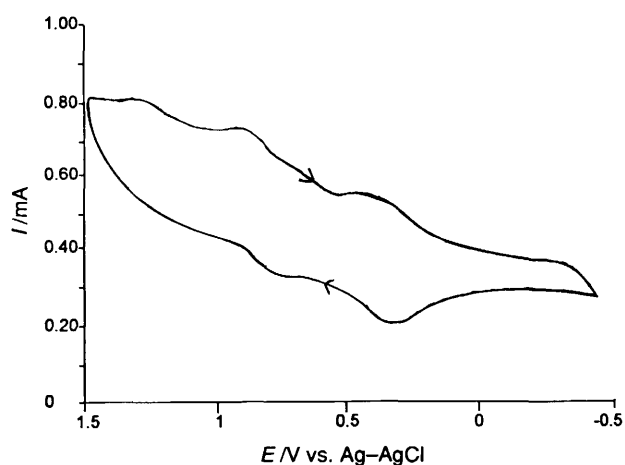


Fig. 1 A typical cyclic voltammogram for the $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ complex at pH 9.90. Reversible couples at 0.55 and 0.85 V and an irreversible reduction at 1.3 V are evident

The $E_{1/2}$ values for the ruthenium redox couples over a wide pH range are shown in Table 1. They have been adjusted to standard reduction potentials by adding 0.197 V to the values obtained with the Ag-AgCl reference.⁷ These are reported as reduction potentials for a $1.0 \times 10^{-4} \text{mol dm}^{-3}$ solution of the metal complex. At $\text{pH} \geq 5.8$ oxidations attributed to the II-III, III-IV and IV-VI couples are observed. At lower pH values only two redox steps are distinguished. The II-III and IV-VI couples are sensitive to pH and the other couples are relatively insensitive. The column labelled IV-II in Table I refers to the $E_{1/2}$ value where the III-II and IV-III couples merge into one peak.

Electrochemical measurements of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ in aqueous solution at $\text{pH} < 3$ have been previously reported.⁵ We were not able to see the clear separation of the III-II and IV-III oxidations reported at low pH nor did we observe V-IV reduction. The reported $E_{1/2}$ values are in good agreement with ours and their change with pH will be discussed subsequently.

Titration

The solution pH changes for the $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2][\text{PF}_6]_2$ complex as it was titrated with standardized KOH(aq) solution, are shown in Fig. 2. The curve exhibits two inflection points, one at the addition of 1 mol of KOH(aq) per mol of ruthenium complex and the second after 2 mol. The measured $\text{p}K_a$ values are 4 and 6 for the sequential deprotonation of two aqua ligands. The first conjugate base produced is $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})(\text{OH})]^+$ and the species observed after removal of the second proton is proposed to be $[\text{Ru}(\text{dmphen})_2(\text{OH})_2]$. The small change in the UV/VIS spectrum with pH does not permit a correlation of the $\text{p}K_a$ values to direct spectral changes.

The $\text{p}K_a$ values for $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ are much lower than those reported by Meyer^{2,8} and Che^{1c,d,f,g} and co-workers for water co-ordinated to other ruthenium(II) centres and are closer to those reported by Che *et al.*^{1g} for co-ordinated water in *trans*-diaquaruthenium(III) complexes. Steric problems cause the dmphen ligand to be more weakly bound, making the ruthenium centre more electrophilic and binding the water more strongly. The electrochemical results are consistent with more weakly bound dmphen ligands. The reduction potentials for high-valence *cis*-dioxoruthenium(VI) complexes are known to be higher (by over 200 mV)^{1c,d} than those of the *trans* species. The dmphen complex of ruthenium shows an unusually high VI-IV reduction potential compared to the *cis*-bipyridine complexes of ruthenium.^{1c} Less stabilization of the high oxidation state indicated by the electrochemical results is consistent with a weak interaction between the ruthenium centre and the dmphen ligand.

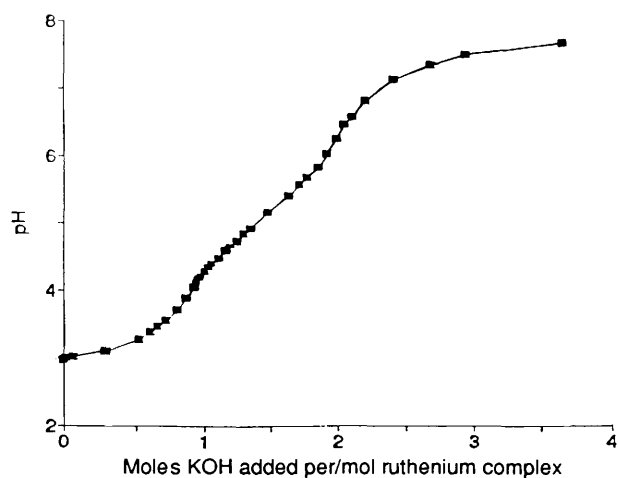


Fig. 2 Titration curve for $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ with KOH in water. Note the inflection points which give $\text{p}K_a$ values for the coordinated water as 4 and 6

Table 1 The E_1 values for the different pH levels examined, adjusted to reflect voltages vs. normal hydrogen electrode

pH	Ru ^{III} -Ru ^{II}	Ru ^{IV} -Ru ^{II}	Ru ^{IV} -Ru ^{III}	Ru ^{VI} -Ru ^{IV}
9.90	0.747	—	1.05	1.52
8.24	0.747	—	1.05	1.52
7.12	0.772	—	1.05	1.52
6.49	0.847	—	1.05	1.52
5.78	0.872	—	1.05	1.52
5.19	—	1.02	—	1.52
4.60	—	1.02	—	1.52
3.74	—	1.05	—	1.52
3.09	—	1.06	—	1.60
2.42	—	1.06	—	1.70

Table 2 Results of initial rate measurements. All concentrations are in mol dm⁻³, initial rates in mol [Ru²⁺] dm⁻³ s⁻¹. Initial rates were determined by a linear regression performed on the data from the first 10 s of the kinetic runs. In all cases the R^2 value was 0.99 or better, insuring linearity

Run	[H ₂ O ₂]	10 ⁴ [Ru(dmphen) ₂ (H ₂ O) ₂] ²⁺	10 ⁷ Initial rate
1	0.066 0	1.15	19.0
2	0.026 4	1.15	9.85
3	0.010 6	1.15	4.15
4	0.005 77	1.15	2.24
5	0.002 11	1.15	1.05
6	0.026 4	0.69	6.55
7	0.026 4	0.46	3.50
8	0.026 4	0.33	2.15

Oxidation of the ruthenium complex by hydrogen peroxide

The spectral changes that occur in the reaction between the [Ru(dmphen)₂(H₂O)₂]²⁺ complex and hydrogen peroxide lead to a decrease in the strong absorbance at 495 nm for the ruthenium(II) complex in aqueous solution.^{6b} The initial rates for different ruthenium and peroxide concentrations are given in Table 2. The initial rate is expressed as the decrease in concentration of the ruthenium(II) species over the first 10 s of the reaction. From these initial rates, the empirical rate law⁹ is found to be first order in peroxide and ruthenium concentrations, equation (2), where $k = 0.32 \pm 0.04$ dm³ mol⁻¹ s⁻¹ at 23 °C.

$$-d[\text{Ru}^{\text{II}}]/dt = k[\text{Ru}^{\text{II}}][\text{H}_2\text{O}_2] \quad (2)$$

The reaction of [Ru(dmphen)₂(H₂O)₂]²⁺ with hydrogen peroxide was observed over a range of pH values. As can be seen from the slopes of the lines in Fig. 3, the initial rate of oxidation changes only slightly as the pH changes. The equilibrium concentrations of aqua and hydroxo species apparently are compensated for by changes in the concentrations of H₂O₂ and HO₂⁻ leading to a small change in rate with pH. As can be seen in Fig. 3, when the pH is increased from 3.33 to 9.13, the net loss of absorbance at 495 nm decreases substantially. At pH ≤ 4 the Ru^{II} is almost completely oxidized to Ru^{VI}. However, as the pH increases the reaction seems to proceed to only the ruthenium(IV) species. The conclusion about the species formed is based upon the values for ϵ obtained from the data in ref. 6b. Since the molar absorption coefficient of Ru^{IV} is between those of Ru^{II} and Ru^{VI} a smaller decrease in absorbance is expected when Ru^{IV} is the product.

A more detailed kinetic analysis of the time dependence of the data in Fig. 3 would involve fitting these curves by rate constants for oxidation and reduction reactions of all the hydroxo- and oxo-ruthenium species present at each pH. The pK_a values for higher-oxidation-state complexes would also have to be solved. With so many unknown parameters, the added quantitative insights obtained from such an analysis

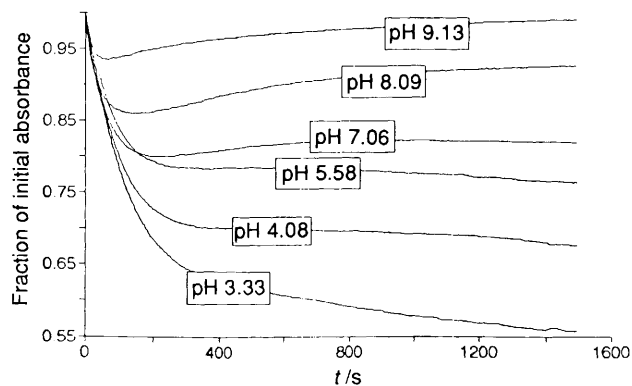


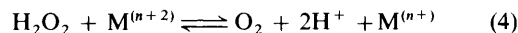
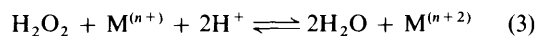
Fig. 3 Kinetic curves for ruthenium(II) oxidation by H₂O₂ at different pH. Note the similarity of initial rates, and the inability of the peroxide completely to oxidize the complex at higher pH values

about the species involved in catalytic reactions are limited so the data fit was not attempted.

Discussion

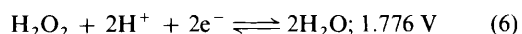
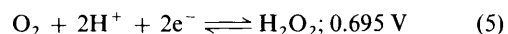
Metal complex activation of H₂O₂

The reactivity of H₂O₂ with [Ru(dmphen)₂(H₂O)₂]²⁺ and the ability of the resulting system to catalyse substrate oxidation is governed by the dependence of the reduction potentials of the metal complex and hydrogen peroxide on the hydrogen-ion concentration. In peroxide activation the insights from electrochemical data become even more important because hydrogen peroxide can act as both a reductant and an oxidant, as shown in equations (3) and (4).



Peroxide reduction and metal oxidation, equation (3), is involved in substrate oxidation by Class III (metal oxide formed from peroxides) or Class V (high-valent metal-centred oxidants) mechanisms.¹⁰ One-electron oxidation can be involved in some Class V mechanisms or in alkyl peroxide decomposition by a Class IVa (Fenton-type) mechanism. In a Class III reaction the metal undergoes the two-electron change shown in equation (3), but the product is an oxo metal complex. Catalysis (or peroxide activation) by the metal complex occurs when the oxidized metal complex, peroxy metal or oxo metal species is kinetically more reactive than peroxide in the oxidation of substrate. In addition, depending on the potentials, the oxidized complex may oxidize hydrogen peroxide as shown in equation (4). When the oxidized and reduced forms of a given metal complex catalyst lead to both peroxide reduction and oxidation the catalysed decomposition of hydrogen peroxide to water and dioxygen occurs.

The reduction potentials¹¹ in acidic (pH 0) aqueous solution for the half-reactions involving hydrogen peroxide are given in equations (5) and (6). The pH dependences of these potentials (a



Pourbaix plot), as calculated by the Nernst equation, are shown in Fig. 4. The potential for peroxide being reduced (*i.e.* the peroxide half-reaction when it oxidizes the transition-metal complex) is given by line A. The reduction potential for the two-electron reduction of O₂ to H₂O₂ is given by line B in Fig. 4.

The redox considerations presented above are not new.¹⁻³

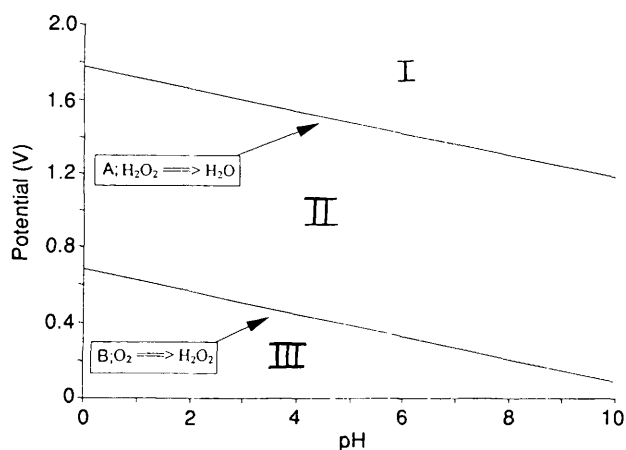


Fig. 4 The pH dependence of the half-reaction potentials for reduction (A) and oxidation (B) of hydrogen peroxide

However, we do recommend a more consistent use of Fig. 4 as a template upon which metal redox potentials can be plotted to predict the reactivity of a prospective catalyst with hydrogen peroxide. In aqueous solution, metal complexes with two-electron reduction potentials falling in region I of Fig. 4 will act only as stoichiometric oxidants, because even hydrogen peroxide is not strong enough an oxidant to reoxidize the reduced form of the metal complex. Metal catalysts with two-electron reduction potentials falling in region II of Fig. 4 will activate hydrogen peroxide, but also have a thermodynamic tendency to decompose the peroxide. Those falling in region III will not decompose hydrogen peroxide, and will produce relatively mild oxidants that activate hydrogen peroxide with high utilization efficiency.

Based on the above thermodynamic considerations, any metal complex which utilizes hydrogen peroxide to produce a high-oxidation-state metal complex *cannot be*, on thermodynamic grounds, both as strong an oxidant as hydrogen peroxide and also efficiently use hydrogen peroxide in aqueous solution. Kinetic factors have to exist that slow peroxide reduction of the complex in order to obtain an efficient catalyst.

Fig. 4, while admittedly simplistic, also explains the behaviour of metal oxidases. Under standard conditions O_2 is not able to oxidize any metal complex having a reduction potential above line B in Fig. 4, and as a result these complexes cannot participate in metal-catalysed activation of O_2 . If a sacrificial two-electron reducing agent can be used to convert O_2 into H_2O_2 , any metal complex with a reduction potential below line A in Fig. 4 can be oxidized and can function as a catalyst for substrate oxidation. These thermodynamic considerations explain the role of the sacrificial reducing agent in monooxygenase-type systems. Without the sacrificial reducing agent to form peroxide, O_2 is not able to oxidize metal complexes having reduction potentials in region II of Fig. 4. These considerations have general applicability for eliminating metal species proposed as aqueous oxidizing agents in catalytic cycles. Unfortunately, the necessary redox potentials in non-aqueous solvents are not available to permit an analysis under these conditions.

pH Dependence of peroxide activation by $[Ru(dmphen)_2(H_2O)_2]^{2+}$

In this section the discussion presented above will be applied to the possibility of using $[Ru(dmphen)_2(H_2O)_2]^{2+}$ as a catalyst for substrate oxidation in aqueous solution. Fig. 5 shows the ruthenium reduction potentials (indicated by solid lines) superimposed on the peroxide potential template (dashed lines) of Fig. 5. The oxidation of ruthenium(II) to ruthenium(IV) by H_2O_2 is spontaneous at all pH values shown. The reduction

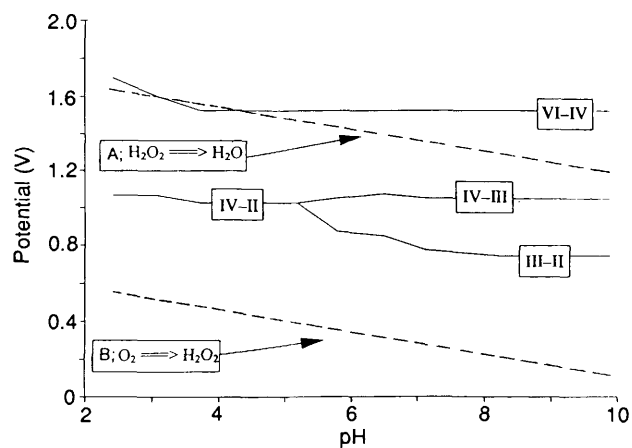


Fig. 5 Comparison of the ruthenium reduction potentials (solid lines) and the potentials for oxidation and reduction of hydrogen peroxide (dashed lines)

potentials for the $Ru^{IV}-Ru^{II}$ and $Ru^{III}-Ru^{II}$ couples are both lower than that of hydrogen peroxide, but still high enough to be in region II, where hydrogen peroxide decomposition can occur. As we get to higher pH levels the reduction potential of H_2O_2 is too low (*i.e.* H_2O_2 is not a good enough oxidizing agent) to oxidize ruthenium(IV) to ruthenium(VI). The ruthenium(VI) complex is formed in diminishing amounts as the pH rises above 5. This chemistry accounts for the pH dependence of the oxidation of $[Ru(dmphen)_2(H_2O)_2]^{2+}$ by peroxide shown in Fig. 3. From pH 5.5 to 9 the absorbance decrease is attributed to the formation of Ru^{IV} . The increase in absorbance with time after 150–200 s above pH 5.6 results from the reduction of ruthenium(IV) to ruthenium(II) by H_2O_2 . As the pH decreases below 5.6 the amount of Ru^{VI} formed increases, and a larger decrease in absorbance is observed.

In catalysed oxidations with this complex⁶ efficient use of peroxide results from a slow kinetic pathway for peroxide oxidation/metal reduction. The nucleophilic oxygen of peroxide is more likely to displace water from the ruthenium(II) than to displace aqua or hydroxo ligands from the ruthenium(IV) complex and reduce it. The aqua and/or hydroxide ligands on the ruthenium(IV) are not likely to be removed when it is oxidized to Ru^{VI} . Rather, it is likely that a proton-coupled electron transfer occurs at this point. Proton-coupled electron transfer has been seen in similar complexes.^{1e,2a,b} Thus, for kinetic reasons the ruthenium(II) complex is oxidized faster by peroxide than the ruthenium-(IV) or -(VI) complex is reduced.

Conclusions on the rates of competitive reactions cannot be based on thermodynamic considerations alone. For example, the potentials (Fig. 5) show that at pH 3 the reaction of hydrogen peroxide with ruthenium(IV) is spontaneous to form either ruthenium-(II) or -(VI). The reaction of the ruthenium(IV) complex and hydrogen peroxide to form the ruthenium(II) complex, and oxidize peroxide, is favoured thermodynamically over the reduction of the peroxide to form the ruthenium(VI) complex. However, the spectrophotometric studies in Fig. 3 show that the reaction to form the ruthenium(VI) species is favoured. Thus, kinetic factors must facilitate the reaction to produce ruthenium(VI).

Applications of the analysis presented above in catalytic oxidations can provide insights about the metal oxidants generated in catalytic cycles for peroxide and for dioxygen activation in aqueous solution. If the reduction potential for metal complex oxidation becomes significantly more positive than the peroxide or dioxygen reduction potential, substrate oxidations through Class III and V mechanisms are not possible. If substrate oxidation is found to occur a Class IV

mechanism involving nucleophilic attack on a co-ordinated peroxide is suggested. The metal complex must remain soluble for these considerations to be relevant and this is often a problem at higher pH, as transition-metal hydroxides and oxides often form under basic conditions.

Oxidation of alkenes by $[\text{Ru}(\text{dmphen})_2(\text{solv})_2]^{2+}$ and O_2 (solv = H_2O or MeCN)

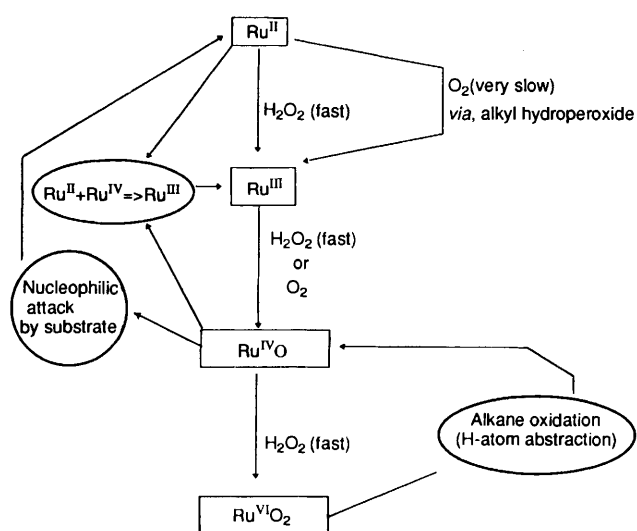
The epoxidation of alkenes by O_2 occurs in acetonitrile solution.⁶ In the absence of peroxides the reaction has a 24 h induction period. This induction period is eliminated when 3 equivalents of an alkyl hydroperoxide or hydrogen peroxide are added. Previously we had concluded that alkyl hydroperoxide is formed in the induction period, and this reacts to form ruthenium(IV). It was proposed that ruthenium(IV) is oxidized to ruthenium(VI) by dioxygen and ruthenium(VI) is the oxygen-atom-transfer agent. The addition of peroxides eliminated the induction period by oxidizing ruthenium(II) to ruthenium(IV).

The redox considerations presented above are not directly applicable to acetonitrile. Sauvage and Collins⁵ report that the $\text{Ru}^{\text{III}}-\text{Ru}^{\text{II}}$ reduction potential for $[\text{Ru}(\text{dmphen})_2(\text{solv})_2]^{2+}$ changes from 1.0 V in water to 1.7 V in MeCN. Unfortunately, the reduction potentials of O_2 in most non-aqueous solvents are not known. However, in view of the high reduction potential in aqueous solution, the generation of ruthenium(VI) by O_2 in non-aqueous solutions is suspect. The following scheme can be proposed as an alternative to the generation of a ruthenium(VI) species. Ruthenium(II) is oxidized to ruthenium(III) by alkyl hydroperoxide formed slowly in the induction period from alkene autoxidation. The formation, and subsequent decomposition, of the alkyl hydroperoxide is indicated by the small amounts of ketone and alcohol formed during the induction period when the alkene epoxidation is carried out with O_2 .^{6a} These products are not formed after the induction period. Radicals formed during the metal-catalysed peroxide decomposition which lead to ketone and alcohol have been identified¹² by spin-trapping experiments. During the induction period the ruthenium(III) concentration slowly increases. Once a significant concentration of ruthenium(III) forms (probably containing co-ordinated water) it can be oxidized to the oxoruthenium(IV) species by dioxygen in acetonitrile solvent. Nucleophilic attack on an alkene by $\text{Ru}^{\text{IV}}\text{O}$ results in oxygen-atom transfer to form epoxide and reduction of the metal to ruthenium(II). The ruthenium(II) complex can react with ruthenium(IV) to produce two ruthenium(III) complexes which then react with dioxygen to produce oxoruthenium(IV). The reaction becomes catalytic after the required steady-state concentration of ruthenium(III) forms. This mechanism is shown in Scheme 1.

Conclusion

The complex $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ undergoes a reaction with hydrogen peroxide which is first order in both ruthenium and peroxide concentration. At $\text{pH} > 4$ the acidic protons of the aqua ligands are neutralized ($\text{p}K_a$ 4 and 6). The electrochemical experiments confirm this transformation by showing breaks in the plot of E_1 vs. pH at the deprotonation pH values. The $\text{p}K_a$ values illustrate the weak binding of the dmphen ligand and the high partial positive charge on the ruthenium centre in this complex. Kinetic studies of the reaction of the ruthenium complex with H_2O_2 show that significant amounts of the active *cis*-dioxoruthenium(IV) complex are not formed above pH 5.

Fig. 4 is proposed as a template upon which substrate and metal-ion potentials can be superimposed to predict and explain the reactivity of hydrogen peroxide with a transition-metal complex in aqueous solution. As with any thermodynamic



Scheme 1 An alternative mechanism for oxidation of alkanes and alkenes with the $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ complex in the presence of H_2O_2 and O_2

argument, the only certain prediction about reactivity is that reactions with large positive free energies will not occur. The inability of $[\text{Ru}(\text{dmphen})_2(\text{H}_2\text{O})_2]^{2+}$ to form $[\text{Ru}(\text{dmphen})_2\text{O}_2]^{2+}$ by reaction with hydrogen peroxide in aqueous solution at higher pH levels is described using this template. The procedures discussed can be used to screen transition-metal complexes as peroxide-activation catalysts in aqueous solutions of different pH. When free-energies are applied in aqueous solution under other than standard conditions or in non-aqueous solvents, qualitative estimates of the influence of these conditions on the relevant potentials must be made.

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