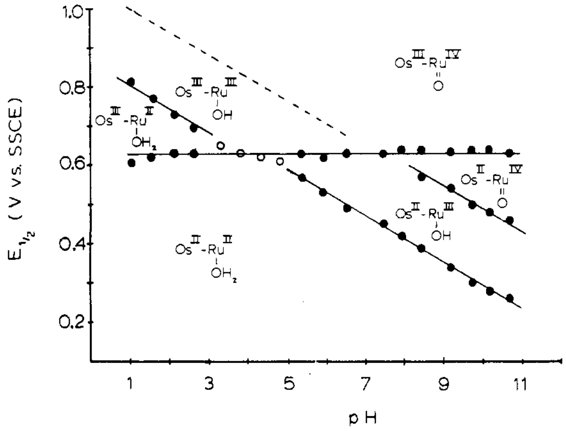


Figure 1. $E_{1/2}$ vs. pH diagram for the dimer [(trpy)(bpy)Os(4,4′-bpy)-Ru(H_2O)(bpy)$_2$]$^{4+}$. The oxidation state and pH contents of the dimer are indicated in those potential domains in which they are dominant. The dashed line for the Os^{III}–Ru^{IV}(O)/Os^{III}–Ru^{III}(OH) couple was calculated as described in the text. For the data shown as open circles, only a single electrochemical wave was observed because of the close proximity of the adjacent couples.

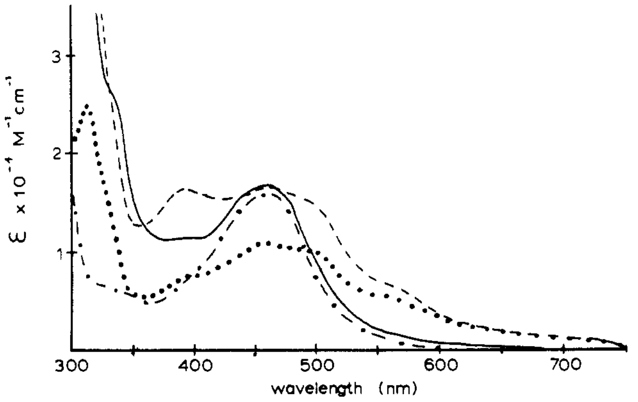


Figure 2. Visible spectra of [(trpy)(bpy)Os^{III}(4,4′-bpy)Ru^{II}(H_2O)-(bpy)$_2$]$^{5+}$ at pH 1.1 (—), [(trpy)(bpy)Os^{II}(4,4′-bpy)Ru^{III}(OH)(bpy)$_2$]$^{4+}$ at pH 8.9 (---), [(trpy)(bpy)Os^{II}(4,4′-bpy)]$^{2+}$ at pH 1.1 (···), and [(bpy)$_2$$Ru^{II}$($H_2O$)(4,4′-bpy)]$^{2+}$ at pH 1.1 (-·-).

Os^{II}–Ru^{IV}(O)/Os^{II}–Ru^{III}(OH) couples (0.19 V) to the potential of the Os^{III}–Ru^{III}(OH)/Os^{III}–Ru^{II}(OH_2) couple below pH 8.

Figure 1 shows that the oxidation-state distribution in the dimer is dependent on pH, suggesting that it should be possible to induce intramolecular electron transfer between the ligand-bridged metal sites by variations in the pH.[4] In Figure 2 are shown visible spectra of the once-oxidized, mixed-valence dimer at pH 1.1 and 8.9, as well as spectra for the related monomers [(bpy)$_2$(4,4′-bpy)Ru(OH_2)]$^{2+}$ and [(trpy)(bpy)Os(4,4′-bpy)]$^{2+}$. The spectra are dominated by Ru(II),Os(II) → π^*(bpy or trpy) metal to ligand charge-transfer transitions. The spectral shifts with pH clearly show that a pH jump from 1.1 to 8.9 induces net intramolecular electron transfer

$$[(\mathrm{trpy})(\mathrm{bpy})\mathrm{Os^{III}}(4{,}4'\text{-bpy})\mathrm{Ru^{II}}(\mathrm{H_2O})(\mathrm{bpy})_2]^{5+} \rightarrow [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Os^{II}}(4{,}4''\text{-bpy})\mathrm{Ru^{III}}(\mathrm{OH})(\mathrm{bpy})_2]^{4+} + \mathrm{H^+}$$

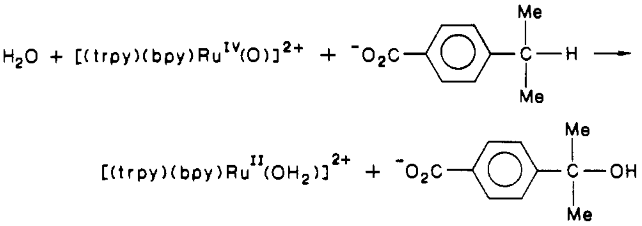
which is reversible if the pH is returned to 1. This is a significant result since it shows that long-range electron transfer between redox sites can be induced by local changes in the pH. In a related experiment, it was recently shown that long-range electron transfer across a redox-active polymeric film could be induced by pH changes in the external solution.[5] The results of both experiments suggest approaches to coupling electron-transfer processes to other, pH-dependent chemical processes.

A pH-induced intramolecular electron transfer above pH 7 also occurs in the twice-oxidized dimer

$$\mathrm{OH^-} + [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Os^{III}}(4{,}4'\text{-bpy})\mathrm{Ru^{III}}(\mathrm{OH})(\mathrm{bpy})_2]^{5+} \rightleftharpoons [(\mathrm{trpy})(\mathrm{bpy})\mathrm{Os^{II}}(4{,}4'\text{-bpy})\mathrm{Ru^{IV}}(\mathrm{O})(\mathrm{bpy})_2]^{4+} + \mathrm{H_2O}$$

which has the effect of concentrating both oxidative equivalents at the ruthenium site. Above pH 7 the twice-oxidized dimer contains a chemically reactive Ru^{IV}=O site for which studies on related monomers have shown an extensive stoichiometric and catalytic oxidation chemistry including oxidation of primary and secondary alcohols, cyclic ketones, and aldehydes,[6] epoxidation of olefins,[7] and allylic oxidation of olefins and aromatic hydrocarbons.[6,8]

Upon addition of *p*-isopropylbenzoate anion to the Os^{III}–Ru^{III} dimer at pH 5 at room temperature ($\mu = 0.1$), the mixed-valence dimer appears slowly followed by the even slower appearance of the Os^{II}–Ru^{II} dimer. Under pseudo-first-order conditions in the benzoate anion its oxidation by the Os^{III}–Ru^{III} dimer to give the Os^{II}–Ru^{III} dimer occurs with $k = (6.2 \pm 0.3) \times 10^{-3}$ M^{-1} s^{-1}. However, at pH 10, where the dimer is in the reactive Os^{II}–Ru^{IV}(O) form, $k = 5.0 \pm 1.0$ M^{-1} s^{-1}. Oxidation of the same substrate by [(trpy)(bpy)Ru^{IV}(O)]$^{2+}$ and [(trpy)(bpy)Ru^{III}-(OH)]$^{2+}$ occurs with $k_{IV} = 12.2 \pm 1.2$ M^{-1} s^{-1} and $k_{III} < 1 \times 10^{-4}$ M^{-1} s^{-1}.[8] For the Ru(IV) monomer the net reaction is



The enhanced reactivity of the oxo form of the dimer demonstrates that pH-induced electron transfer can be used to concentrate the "stored" redox equivalents in the twice-oxidized dimer at a single site, producing a considerable gain in chemical reactivity on demand by variations in pH.

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Heterolytic and Homolytic O-O Bond Cleavage Reactions of (Acylperoxo)manganese(III) Porphyrins

Sir:

Mechanistic studies of transition-metal-mediated reactions of peroxides have attracted attention for over a century.[1] Fenton's reagent, the prototype iron(II)–hydrogen peroxide system, has been inferred from detailed product studies to proceed by a one-electron homolysis of the O–O bond in acidic aqueous media to afford hydroxyl radicals,[2] whereas a heterolytic pathway to produce a reactive ferryl species [Fe^{IV}=O] was indicated in

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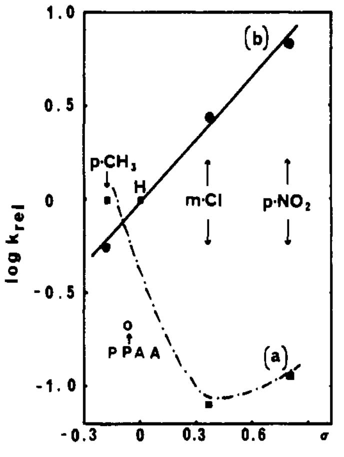
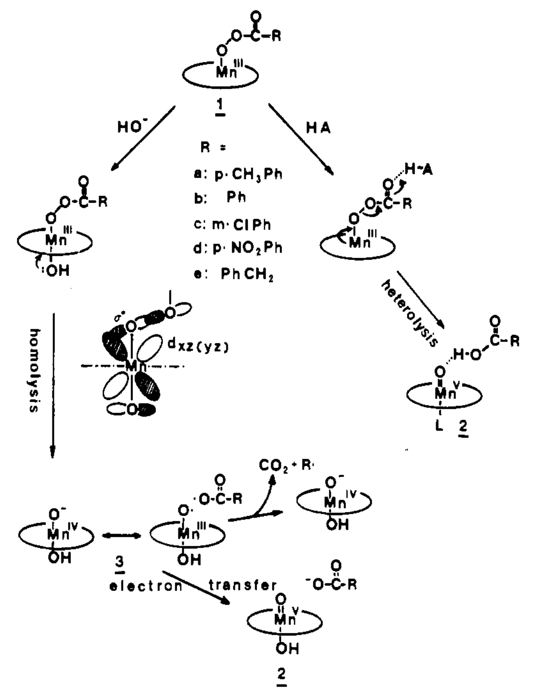


Figure 1. Substituent effects for the rate of O–O bond cleavage in **1a–e** obtained by the reaction of $Mn^{III}TMP(OH)$, (1) OH, with peracid: (a) in the presence of hydroxide ion in CH_2Cl_2 at -30 °C, (1) OH: Bu_4NOH:peracid = 1:1:1.2; (b) in the absence of hydroxide ion at -50 °C in CH_2Cl_2, (1)OH:peroxyacid = 1:3~8. Conditions: *p*-NO_2, 2.7 equiv; *m*-Cl, 4.0 equiv; H, 6.5 equiv; Tol, 8.1 equiv.

acetonitrile.[3] More recently, these reactions have received intense scrutiny since similar iron–peroxide reactions have been shown to form a central biological strategy for the manipulation of dioxygen. Of particular interest have been the processes of "oxygen activation" characteristic of the heme-containing monooxygenase, cytochrome P-450.[4] More generally, iron peroxide reactions in vivo may be involved in tissue-damaging effects of clinical iron overload[5] as well as the DNA-cleaving reactions typical of iron–EDTA[6] and iron–bleomycin complexes.[7] The direct observation of the O–O bond cleavage step in all these processes has been obscured by the instability of the reactive metal–peroxo and metal–oxo intermediates. We have recently described a manganese porphyrin model system that has allowed the observation of a (acylperoxo)manganese(III) complex and the corresponding oxomanganese(V) complex, the product of O–O bond scission.[8] We describe here a kinetic analysis of this process, which has revealed both homolytic and heterolytic pathways for O–O bond cleavage mediated by manganese(III).

A family of (acylperoxo)manganese(III) tetramesitylporphyrin (TMP) complexes (**1**) was prepared by the addition of peroxyacids to $Mn^{III}TMP(OH)$ in methylene chloride at -30 to -50 °C. The acidity of the medium was controlled by varying the relative stoichiometry of the peroxyacid and tetramethylammonium hydroxide ((TMA)OH). The kinetics of the reaction of **1** to produce the oxomanganese(V) intermediate **2** were derived from the dramatic changes observed in the visible spectra.[8] Figure 1a shows comparative rate data for five acylperoxymanganese(III) complexes, **1a–e**, obtained at -30 °C for solutions that were 1.34×10^{-5} M in manganese porphyrin and hydroxide ion formed with 1.2 equiv of peroxyacid. It is apparent from the results that the more electron-rich peroxyacids, **1a** and **1b**, were considerably *more reactive* than those with electron-withdrawing groups. This general pattern of reactivity is not what would be expected on the basis of leaving group tendencies, and it is unlike the relationship reported recently by Bruice et al. for a *catalytic* manganese(III) porphyrin system.[9] Indeed, the trend is strikingly similar to that observed for the thermal decomposition of diacyl peroxides for which a *homolytic* O–O bond scission certainly occurs.[10]

Scheme I



The oxidation of $Mn^{III}TMP(OH)$ (6.2×10^{-3} M) with 1.2 equiv of *m*-chloroperbenzoic acid (*m*CPBA) in 1 mL methylene chloride containing 2 equiv of (TMA)OH at -78 °C immediately produced a red-brown solution. The EPR spectrum of this freshly prepared solution initially showed no signals, but after a few minutes at -78 °C, signals characteristic of a manganese(IV) porphyrin[11] could be discerned. Accordingly, the initially formed oxidation product was EPR silent but decomposed readily under these conditions to manganese(IV). These observations are consistent with the initial formation of an unstable oxomanganese(V) species (**2**).

Further evidence for the homolytic cleavage of the O–O bond under basic conditions was obtained by the analysis of the reaction products from phenylperoxyacetic acid (PPAA). The rate of decarboxylation of arylcarboalkoxy radicals is known to be slow, 4.0 s^{-1} at -30 °C.[12a,b] By contrast, the rate of decarboxylation of alkylcarboalkoxy radicals is at least 10^7 s^{-1} under these conditions.[12c]

The reaction of PPAA with MnTMP(OH) and 1 equiv of (TMA)OH at -30 °C was kinetically well-behaved and displayed spectral changes similar to the aryl peroxyacids. However, whereas the oxidized intermediate (**2**) from aryl peroxyacids could be titrated with 2 equiv of iodide ion, titration of the solution obtained from PPAA required less than 1.4 equiv of iodide to generate $Mn^{III}TMP$. This titration corresponds to 36% oxomanganese(V) and 64% manganese(IV). In a similar preparative scale reaction at -78 °C in methylene chloride, phenylacetic acid was detected in 40% yield along with toluene (8%), benzyl chloride (3%), benzyl alcohol (5%), and benzaldehyde (7%).[13] All of the latter products are those expected to derive from initial decarboxylation of a carboalkoxy radical. Thus, consistent with the iodide titration, the reaction of PPAA with $Mn^{III}TMP(OH)$ must allow competing

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(13) Products analysis was performed by glpc vs. authentic samples.

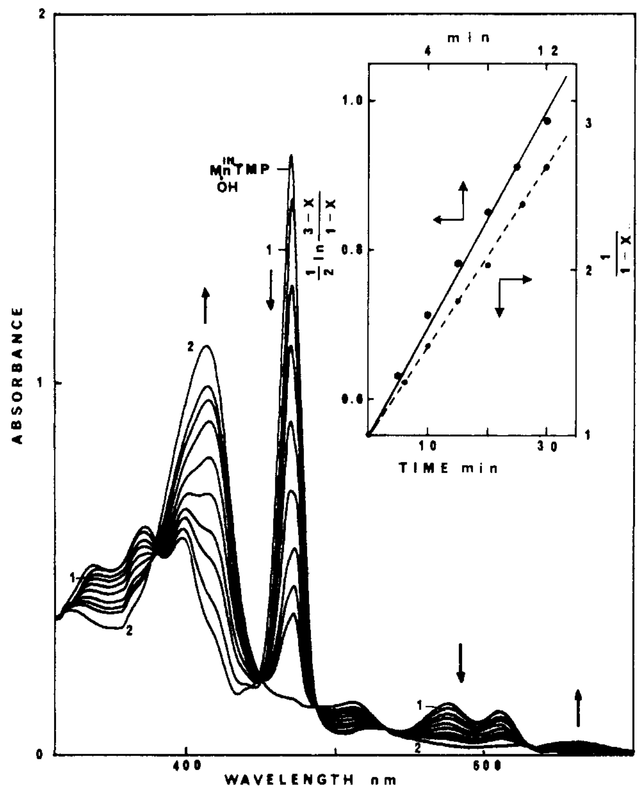

Figure 2. Visible spectral changes for the reaction of $Mn^{III}TMP(OH)$ [1.2×10^{-5} M] and 2.5 equiv of *m*CPBA at −48 °C in CH_2Cl_2; final spectrum of **2**. Inset: second order kinetic plots for the reaction of 2 equiv (- - -) and 4 equiv (—) of *m*CPBA.

electron transfer to give **2** and decarboxylation[14] (Scheme I).

The reaction of these peroxyacids with MnTMP(OH) under *protic* conditions was examined by using 2–8 equiv of the peroxyacids and no (TMA)OH. In all cases the visible spectral changes indicate an instantaneous ligand exchange to produce **1** followed by a slower production of **2** with kinetic order in [**1**] and [$ArCO_3H$] (Figure 2), similar to the same reaction under basic conditions.[8] However, there were two crucial differences between the basic and protic reactions: (i) the peroxyacid substituent effect showed a positive, linear Hammett correlation ($\rho = 0.9$) at −50 °C (Figure 1b); (ii) the temperature dependence of the rate constant for *m*CPBA under basic conditions indicated an activation energy of 14.7 ± 2.7 kcal/mol and $\Delta S^{\ddagger} = 2.6 \pm 0.3$ eu, while the protic reaction showed no discernible temperature effect.[15] We interpret these results for the protic reaction to be indicative of an acid-catalyzed heterolysis of the O–O bond in **1** to afford **2**. This second mode of reactivity is in accord with the conclusions derived by Bruice et al.[9] from a kinetic analysis of a catalytic manganese porphyrin/peroxyacid system in benzonitrile, and by Traylor et al.[16] for a related iron porphyrin/peroxyacid system.

These results demonstrate that the nature of the transition state for O–O bond cleavage in **1** is critically dependent on the reaction conditions.[17] Under basic conditions a hydroxide ion would be expected to coordinate to the sixth position of the manganese. The resulting antibonding interaction of the hydroxo lone pair should result in a higher energy level for the singly occupied manganese(III) d_{xz} and d_{yz} orbitals. The homolytic character of the transition state for O–O bond cleavage would then result from an interaction of one of these metal d orbitals with the vacant σ^* orbital of the coordinated peroxyacid. Subsequent electron transfer is required to afford the observed products (Scheme I). In the protic medium the strong trans ligand effect would be absent so that the acid-catalyzed heterolytic pathway predominates. Attempts to understand catalytic metal–peroxide systems must accommodate this effect of proton inventory and metal ligation on the nature of metal-mediated O–O bond cleavage. Efforts to elaborate the roles of axial ligand, metal d orbital occupancy and peroxide leaving group in these metalloporphryin reactions are under way.

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