Oxidative Homolysis of the Superoxopentaaquachromium(III) Ion

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The polypyridine complexes of Ru^{III} and Fe^{III} react with $[Cr(H_2O)_5O_2]^{2+}$ to yield $[Cr(H_2O)_6]^{3+}$ and O_2 in the first reported case of chemically induced oxidative homolysis of a superoxo metal complex.

Oxygen activation by transition metal complexes is based on the increased tendency of O_2 to act as an oxidant once partially reduced. For example, both free and coordinated superoxide and peroxide are rapidly reduced by a number of reagents that are unreactive towards O_2 itself.[1]

Oxidations of superoxo and peroxo metal complexes have, however, been almost completely neglected.†[2,3] Here we present what we believe is the first kinetic and mechanistic study of chemically induced oxidative homolysis of a superoxo transition metal complex.

The reaction of the superoxochromium(III) complex, $[Cr(H_2O)_5O_2]^{2+}$[4] (hereafter $[CrO_2]^{2+}$), with an excess of $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) results in the appearance of the characteristic and intense spectrum of $[Ru(bpy)_3]^{2+}$.[5] A spectrophotometric titration yielded a ratio $\Delta[Ru(bpy)_3{}^{2+}]/[CrO_2{}^{2+}] = 0.92:1$, consistent with the one-electron oxidation of $[CrO_2]^{2+}$. After the completion of the reaction the concentration of the dissolved O_2 was determined with use of an oxygen electrode. A sample that originally contained 2.72×10^{-5} mol dm^{-3} $[CrO_2]^{2+}$ yielded 2.75×10^{-5} mol dm^{-3} O_2. The overall reaction is thus described by eqn. (1).

$$[CrO_2]^{2+} + [Ru(bpy)_3]^{3+} \rightarrow [Cr]^{3+} + [Ru(bpy)_3]^{2+} + O_2 \qquad (1)$$

The kinetics of the reaction with $[Ru(bpy)_3]^{3+}$ were monitored spectrophotometrically by observing the build-up of $[Ru(bpy)_3]^{2+}$ at 453 nm. The reaction followed mixed second-order kinetics and yielded the rate cosntant $k_{Ru(bpy)} = 2630$ dm^3 mol^{-1} s^{-1} in 0.1 mol dm^{-3} HCl at 25 °C. Two other oxidants, $[Fe(phen)_3]^{3+}$ and $[Ru(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$ (phen = 1,10-phenanthroline), reacted similarly with rate constants $k_{Fe(phen)} = 81.9$ dm^3 mol^{-1} s^{-1} and $k_{Ru(Me\text{-}phen)} = 1060$ dm^3 mol^{-1} s^{-1}.‡

Owing to the substitutional inertness of these polypyridine complexes, the oxidation probably takes place by outer-sphere electron transfer and the data should fit the Marcus equation. However, the reduction potential and the self-exchange rate constant for the couple $[CrO_2]^{3+/2+}$ are not known, which limits the analysis but still allows a comparison of the rate constants on a relative scale, eqn. (2).[6] Here k_{11} and k'_{11} represent the self-exchange rate cosntants for oxidants 1 and 1′, E and E′ are their reduction potentials, and k_{12} and k'_{12} are the rate constants for electron transfer from $[CrO_2]^{2+}$ to the oxidants 1 and 1′, respectively.

$$k_{12} = k'_{12}(k_{11}/k'_{11})^{\frac{1}{2}} \times 10^{(E-E')/0.118} \qquad (2)$$

With $[Ru(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$ used as the reference, the relative vlaues of k_{obs} are 2.5 $\{[Ru(bpy)_3]^{3+}\}:1.0:0.077$ $\{[Fe(phen)_3]^{3+}\}$. The calculated[7] ones are in the order 1.7:1.0:0.13. The apparent consistency with Marcus theory provides strong support for oxidative homolysis, whereby the rate-determining oxidation of $[CrO_2]^{2+}$ is followed by rapid homolysis of the Cr–O bond [eqn. (3)].

$$[CrO_2]^{2+} \xrightarrow{[Ru(bpy)_3]^{3+}} [CrO_2]^{3+} \xrightarrow{\text{fast}} [Cr]^{3+} + O_2 \qquad (3)$$

No build-up of an intermediate was observed in any of the reactions. Also, there was no obvious delay between the disappearance of the reactants and the apperance of O_2. These results demonstrate that the homolysis of $[CrO_2]^{3+}$ is indeed fast relative to its formation ($k_{hom} \gg k_{obs} > ca.\ 0.1$ s^{-1}). In fact, O_2 should be a better leaving group than an alkyl radical, and the homolysis of the Cr–O bond in $[CrO_2]^{3+}$ is expected to be faster than homolysis of the Cr–C bond in $[Cr\text{–}R]^{3+}$ (R = primary alkyl or benzyl). The latter complexes homolyse in <1 μs,[8] which suggests a lower limit of 10^6 s^{-1} on the rate constant for homolysis of $[CrO_2]^{3+}$. The one-electron oxidation of $[CrO_2]^{2+}$ has thus icnreased the homolysis rate of the Cr–O bond by at least ten orders of magnitude ($k_{hom} = 2.5 \times 10^{-4}$ s^{-1} for $[CrO_2]^{2+}$),[4] which makes this effect comparable to that observed upon oxidation[8] and reduction[9] of organo-transition metal complexes.

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Footnotes

† The electrochemcial oxidation of a macrocyclic $Co^{II}\text{–}O_2$ complex has been reported to yield the macrocyclic cobalt(III) complex lacking oxygen. It was suggested that a short-lived $Co^{III}\text{–}O_2$ intermediate had formed and then rapidly decomposed by the loss of O_2.[2] Similarly, the electrochemical oxidation of a binuclear, μ-peroxo complex $[\{Co(salen)\}_2O_2(dmso)_2]$ yields molecular oxygen and $[Co(salen)]^+$ (salen = bissalicylideneethylenediamine; dmso = dimethyl sulfoxide). The dissociation of O_2 was proposed to take place from the doubly oxidized dimeric complex.[3]

‡ The reaction with $[Ru(bpy)_3]^{3+}$ required the use of the stopped-flow technique (Durrum), whereas those with $[Fe(phen)_3]^{3+}$ and $[Ru(5,6\text{-}Me_2phen)_3]^{3+}$ used conventional spectrophotometry. The reaction with $[Fe(phen)_3]^{3+}$ was monitored at 510 nm [$\varepsilon(Fe^{II}) = 1.1 \times 10^4$ dm^3 mol^{-1} cm^{-1}] and that with $[Ru(5,6\text{-}Me_2\text{-}phen)_3]^{3+}$ at 453 nm [$\varepsilon(Ru^{II}) = 2.04 \times 10^4$ dm^3 mol^{-1} cm^{-1}].

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