The formulation and equilibrium parameters of a number of peroxocomplexes of transition metal ions have been determined; an empirical model is presented to correlate the various structures observed. The redox reactions of these complexes with a number of substrates have been studied, and the results are compared to the corresponding reactions of hydrogen peroxide. Enormous catalytic activation of peroxide is observed with group 6 metal ions. In some cases superoxocomplexes have been formed from precursor peroxocomplexes, and their redox chemistry is compared to that of protonated superoxide.

The final report contains a statement of work, a summary of the most important results, a list of publications, and a list of all participating scientific personnel.
THE REDOX CHEMISTRY OF SOME PEROXO AND SUPEROXO METAL ION COMPLEXES

FINAL REPORT

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Statement of Work

The mechanisms for the interconversion of the various dioxygen species have been extensively studied. The principal species in acidic solution are shown below.

\[ H_2O \leftrightarrow H_2O_2 \leftrightarrow HO_2 \leftrightarrow O_2 \]

It is well established that metal ions can profoundly affect both the kinetics and mechanisms of these conversions, often in a catalytic manner. We have used peroxocomplexes of certain metal ions to probe the mechanistic role played by the metal ion. In effect, we start in the middle of the water-oxygen cycle with a well defined system. The redox chemistry of these complexes is compared to that of hydrogen peroxide itself to assess the specific effect of the metal ion on the interconversions. In a few cases we have been able to generate superoxocomplexes and to compare their redox behavior with that of the dioxygen analogue HO_2.

The early transition metals in their highest oxidation states have been used extensively in these studies. These d^0 ions rapidly form peroxo and superoxo complexes with large formation constants. A critical component of our studies has been to characterize these complexes with respect to formulation, stability constants, rates of formation and dissociation, acid-base properties, and spectra.

A variety of substrates have been examined in the redox studies. Some react with hydrogen peroxide in a non-radical manner, often with oxygen atom transfer from peroxide to the substrate. Other substrates selected show classical Fenton type
chemistry in their reactions with peroxide, with formation of radical intermediates. In most cases the reference reactions with \( \text{H}_2\text{O}_2 \) and/or \( \text{HO}_2 \) have been previously characterized by other investigators.

**Summary of the Most Important Results**

Very little was known about the formulation of and particularly the equilibria associated with the peroxocomplexes of interest at the beginning of our project. This data base has been expanded considerably. We may summarize as follows, where the peroxocomplex listed is formed from the indicated metal ion or complex under appropriate experimental conditions: \( \text{Ti}(\text{O}_2)^{2+} \) from \( \text{TiO}^{2+} \), \( \text{Zr}_4(\text{O}_2)_2(\text{OH})_4^{8+} \) from \( \text{Zr}^{4+} \), \( \text{VO}(\text{O}_2)^{+} \) from \( \text{VO}_2^{+} \), \( \text{VO}(\text{O}_2)_2^{-} \) from \( \text{VO}(\text{O}_2)^{+} \), \( \text{CrO}(\text{O}_2)_2 \) from \( \text{HCrO}_4^{-} \), \( \text{MoO}(\text{O}_2)_2 \) from \( \text{HMOO}_3^{+} \), and \( \text{WO}(\text{O}_2)_2 \) from ? In addition, \( \text{UO}_2(\text{O}_2) \) may be formed from \( \text{UO}_2^{2+} \), and no peroxocomplexes have been reported for \( \text{Th}^{4+} \) and \( \text{ReO}_4^{-} \).

We have been able to correlate these observations by means of the following empirical model. We first note that replacement of an oxo group on the precursor by \( \text{O}_2^{2-} \) from \( \text{H}_2\text{O}_2 \) is an acid independent process, whereas replacement of \( \text{H}_2\text{O} \) or \( \text{OH}^{-} \) (not shown in the above formulations) has an inverse acid dependence. Second, we propose that the most stable oxo-peroxo
structure is $\text{MO(O}_2\text{)}_2^-$, but that this form may not be realized in many cases due to proton requirements and acid-base properties of the precursor.

For example, according to this scheme $\text{Ti(O}_2\text{)}^{2+}$ is readily formed from $\text{TiO}_2^{2+}$ in acidic solution, but to add a second peroxide and/or an oxo group would require a high pH outside the stability region of either oxotitanium(IV) or peroxotitanium(IV). The complex $\text{VO(O}_2\text{)}^+$ is readily formed in acidic solution, but replacement of the second oxo ligand would not be expected instead, the stable $\text{VO(O}_2\text{)}_2^-$ species is formed but requires a higher pH, in accord with experiment. The group 6 metal ions form the $\text{MO(O}_2\text{)}_2$ structure directly even in strongly acidic solution, with no evidence for a mono-peroxo complex. $\text{UO}_2(\text{O}_2)$ is formed only in nearly neutral solution, as would be predicted; the reason the oxo groups are not replaced in acidic solution is presumably due to the extremely slow oxygen exchange rate of $\text{UO}_2^{2+}$. As a final illustration, we rationalize the reluctance of $\text{ReO}_4^-$ to form a peroxocomplex due to the $[\text{H}^+]^2$ dependence required to form $\text{ReO(O}_2\text{)}_2^+$ and the small tendency of the perrhenate ion to protonate.

Raman spectroscopy has been a valuable tool for determining the solution structure of the peroxocomplexes. The use of oxygen-18 enriched solvent or peroxide has enabled us to assign metal-oxo, metal-peroxo, and peroxo stretching frequencies with
a high degree of certainty.

The rates of oxidation of the peroxocomplexes with most oxidants examined are slower than the corresponding rates with hydrogen peroxide. Relative reduction rates are enormously dependent on the identity of the metal ion. For example, the rates for Ti(O₂)²⁺, H₂O₂, and MoO(O₂)₂ with a specific reductant stand in the approximate order 10⁻³ : 1 : 10⁴ for a wide variety of substrates. The impressive activation afforded by molybdenum(VI) and tungsten(VI) is strictly catalytic provided hydrogen peroxide is present in excess. Under this condition the metal ion is maintained in the active MoO(O₂)₂ or WO(O₂)₂ form due to the rapid formation rate of the oxodiperoxocomplex.

The group 6 metal ions form peroxocomplexes over the entire pH range, although the formulations and equilibria in basic solution have not been established. If the enormous reactivity enhancement observed in acidic solution persists at higher pH, these metal ions should prove to be versatile catalysts in certain practical applications. We have found that all the group 6 MO(O₂)₂ complexes undergo hydrolysis to form MO(OH)(O₂)₂⁻⁻⁻, the pKa values are 0.8, 1.9, and 3.4 for M = W(VI), Mo(VI), and Cr(VI), respectively. The hydrolyzed complexes for Mo(VI) and W(VI) are about ten times less reactive than the neutral forms, but the relative rates at pH values where the MO(OH)(O₂)₂⁻⁻⁻ species predominates, referenced to H₂O₂ at that pH, remain at 10⁴ - 10⁵. These results are encouraging, but the
investigation must be extended into the basic region to assess fully the potential usefulness of these metal ions towards peroxide activation over the entire pH range.

It is important to decipher the mechanism by which these reactions occur. It is reasonable to assume that oxygen transfer from coordinated peroxide to the substrate occurs in many cases; this has been established for H₂O₂ and we are currently extending the studies to selected peroxocomplexes. The probable mechanism would then appear to be either direct attack at the coordinated peroxide by the substrate, or prior coordination of the substrate at the metal ion center followed by oxygen transfer from the adjacent peroxy group. The latter situation appears to apply for reactions with organic substrates in non-coordinating solvents, but does not necessarily hold in aqueous solution. We have recently completed a study of the oxidation of Co(en)₂(SCH₂CH₂NH₂)₂⁺ and Co(en)₂(S{O}CH₂CH₂NH₂)₂⁺ by MoO₂⁻ and WO₂⁻. These reactions involve oxygen transfer to the coordinated sulfur atom. The idea is that both the charge and structure of the substrate mitigate against coordination to the Mo(VI) or W(VI) center. We find that the relative rates compared to H₂O₂ are again ca. 10⁴, and tentatively conclude that direct attack at the coordinated peroxide occurs.

Oxidation of Ti(O₂)₂⁺ by Ce(IV) rapidly produces a transient intermediate that we identify as superoxotitanium(IV), although the precise formulation of this species has not been established.
We have studied its redox reactions with a variety of substrates by multi-mixing, stopped-flow procedures and have found that it is somewhat less reactive than its dioxygen analogue, HO₂. We have initiated studies aimed at forming superoxocomplexes from other peroxocomplexes by similar procedures. It will be fascinating to determine if the redox properties of these complexes show a similar, enormous dependence on the identity of the metal ion as is seen with the corresponding peroxocomplexes.

It may be possible to extend our studies to peroxo and superoxocomplexes of certain nonmetals. For example, peroxoborates are commercially used in some cleansing powders, although their structure in solution is uncertain. A crystal structure of sodium peroxoborate revealed the \( B_2(O_2)_2(OH)_4^{2-} \) ion; two peroxide ions bridge the borons in the dimeric unit. This species is similar in some respects to the peroxocomplex of zirconium(IV) that we have characterized. The principal point of interest to us is that we may be able to characterize the redox properties of bridging peroxo groups by use of these species; the peroxocomplexes of the d⁰ transition metal ions normally show the \( \eta^2 \), or triangular, structure.

It is possible that our results may provide some insights into the intricate dioxygen chemistry so important in a number of biological systems; however, it is premature at this stage to speculate in a meaningful fashion.
Publications Citing ARO Support


Other Related Publications During Contract Period


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