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13. ABSTRACT (Maximum 200 words) All mononuclear peroxomolybdates and peroxovanadates, which form rapidly over virtually the entire pH range in aqueous solution, have been fully characterized and their formation constants determined. The reactivities of the mono- and diperoxo complexes have been examined; the peroxo ligands are strongly activated by Mo(VI) and mildly so by V(V). Mo(VI) and W(VI) are highly effective and robust catalyts for oxidations by hydrogen peroxide, and should find a number of practical uses in the near future. The system Mo(VI), H ₂ O ₂ , and base is probably the most promising chemical means of producing singlet oxygen known. Substantial progress has been made in elucidating the mechanistic aspects of these systems. Incorporation of heteroligands in peroxometallates does not appear to significantly the redox reactivity of the peroxo ligand(s), but can profoundly affect the lability of the peroxo ligand and also render the peroxo complex soluble in nonaqueous media. Preliminary experiments have revealed that calorimetry is the method of choice to determine formation constants for polynuclear peroxometallates. These species are of importance when relatively high concentrations of catalyst are employed, as will probably be the case in some practical applications. The formation constants are prerequisite to meaningful reactivity studies of these polynuclear complexes.				
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FINAL REPORT

"The Redox Chemistry of Some Peroxo and Superoxo Metal Ion Complexes"

Grant Number: DAAL03-91-G-0105

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Statement of Problem Studied

The water-dioxygen cycle is a fundamental yet complex process. Important intermediates often include peroxide and superoxide. It is well established that metal ions can profoundly affect both the rate and the mechanism of this cycle, often in a catalytic manner. We have thoroughly characterized peroxo complexes in aqueous solution in order to probe the mechanistic role played by the metal ion. In effect, we start in the middle of the water-dioxygen cycle with a well defined system. The early transition metals in their highest oxidation states are normally used as the metal ions for these studies. These d^0 ions rapidly form robust peroxo and superoxo complexes. We have examined the redox chemistry of these complexes. This chemistry is compared with that of the dioxygen analogues H_2O_2 (or HO_2^-) and HO_2 (or O_2^-) for the purpose of assessing in a detailed manner the role of the metal ion.

In a limited sense these studies are complementary to intensive research efforts by others on such topics as the use of peroxo complexes as oxygen atom transfer agents in synthesis, the development of singlet oxygen generators, the utilization of dioxygen in biological systems, the search for catalysts for the oxygen electrode component of fuel cells, and decontamination procedures that use hydrogen peroxide as the oxidant.

Summary of Important Results

Vanadium(V) and molybdenum(VI) form peroxo complexes over virtually the entire pH range. We and others have recently characterized all the mononuclear complexes, which predominate under the conditions of excess hydrogen peroxide and metal ion concentrations ≤ 0.05 M, and measured their equilibrium and kinetic parameters. Their absorption and metal ion NMR spectra have been determined, and in a number of cases single crystal X-ray structures are now available. Thus, under experimental conditions of practical importance, the distribution of peroxo complexes as a function of peroxide concentration and pH is known. We have been systematically studying the redox properties of these complexes. In general, the peroxomolybdates are among the

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most reactive complexes yet discovered, and their utility as oxygen atom transfer and one-electron oxidizing agents is only recently beginning to be exploited. We have determined that the *relative* reactivities of (water ligands omitted) $\text{MoO}(\text{O}-\text{O})_2$ (pK_a 1.9), $\text{MoO}(\text{OH})(\text{O}-\text{O})_2^-$ (pK_a 9.7), $\text{MoO}_2(\text{O}-\text{O})_2^{2-}$, and H_2O_2 are *substrate independent* and stand in the approximate order $10^5 : 10^4 : 10^3 : 1$. We are currently measuring the reactivities of $\text{MoO}(\text{O}-\text{O})_3^{2-}$ and $\text{Mo}(\text{O}-\text{O})_4^{2-}$ towards appropriate substrates. We have already found that the triperoxo complex is relatively unstable with respect to internal redox chemistry that produces singlet oxygen. The system $\text{Mo}(\text{VI})$, H_2O_2 , and base is certainly the simplest and probably the most promising *chemical* means of producing singlet oxygen known. $\text{Mo}(\text{VI})$ acts strictly as a catalyst capable of endless turnovers, and the only reagent that is consumed is hydrogen peroxide.

Peroxovanadates are only mildly more reactive than hydrogen peroxide, but are of considerable biological interest. They have close structural similarities to the peroxomolybdates; the principal difference is the stability of monoperoxovanadates in strongly acidic solution. We are in the process of measuring the unknown reactivities of the tri- and tetraperoxovanadates. Neither is effective as a singlet oxygen generator.

We have examined the effect of incorporating heteroligands into peroxo complexes. We have found in our early work that the redox reactivity of the peroxo ligand is not significantly affected by the heteroligands examined (dipic, nta, oxalate). However, we find that the lability of the peroxo ligand can be enormously affected. A striking example is $\text{MoO}(\text{O}-\text{O})(\text{nta})^-$, in which the dissociation rate of peroxide is 4 to 7 orders of magnitude slower than in diperoxomolybdates which form in the absence of the heteroligand. Thus, the monoperoxo complex retains its integrity for quite awhile following dissolution of its salt in aqueous media. Appropriate use of heteroligands allows peroxomolybdates to be used in nonaqueous media, and has allowed us to measure the redox activity of the otherwise inaccessible monoperoxomolybdates.

We have previously shown that inner-sphere attack of the substrate at the peroxo ligand is required for effective catalysis by peroxometallates. We have further tested this proposal by use of hexacyanoferrate(II) and hexacyanoruthenate(II) as substrates; inner-sphere attack at peroxide by the metal center is precluded due to the inertness of the complexes. What we find is that $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$ still catalyze the oxidation rate by hydrogen peroxide, not by direct attack but instead by an intricate catalytic cycle driven by trace and unavoidable metal ion impurities (iron being especially effective). Thus it is difficult to *prevent* $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$ from catalyzing oxidations by hydrogen peroxide, an observation that nicely illustrates the catalytic power of these metal ions.

It is important to remember, however, that $\text{Mo}(\text{VI})$ (or $\text{W}(\text{VI})$) is not a panacea for all applications involving hydrogen peroxide. For example, it was recently reported that a lanthanum(III) peroxo complex(es) dramatically accelerated the hydrolysis of the phosphate diester bonds in bis(nitrophenyl)phosphate. We do not understand how this occurs, but we would predict that peroxomolybdates would be inactive. We would love to be wrong for obvious practical reasons, but unfortunately our prediction was confirmed by appropriate experiments. This does reinforce the premise that solid mechanistic information greatly increases our predictive ability.

Hydrogen peroxide is a component of a number of oscillating reactions, especially when an open system such as a continuously stirred tank reactor (CSTR) is used. Several years ago we made the remarkable observation that solutions of H_2O_2 and Na_2SO_3 fed into a CSTR could show impressive bistability and even oscillatory behavior. This is an almost unbelievable result since the overall reaction simply involves oxygen atom transfer to form sulfate ion and water. We found that traces of a carbonate impurity in the sodium sulfite were essential. It appears that hydration of CO_2 (and its reverse) is a critical component of the bistability. If correct, this represents the first such oscillator discovered. The biological implications are considerable. However, we have not yet succeeded in modeling the system satisfactorily although we are frustratingly close.

Practical uses of peroxometallates may require the use of higher concentrations of the catalyst than we normally employ. Under these conditions polynuclear peroxo complexes are known to form in neutral and acidic solution, but little is known about the equilibrium constants and nothing about the relative reactivities of these condensed species relative to the mononuclear ones we have examined. The molybdenum(VI) system is probably the best one to study first since apparently only a dimer is of importance provided excess hydrogen peroxide is present. The problem is how to detect the dimer in the presence of monomer - cryoscopy, spectrophotometry, and Mo-95 NMR have all failed. Calorimetry, however, appears to provide the answer. The experimental difficulties are considerable, owing to significant heat contributions from trace decomposition of peroxide under the extreme conditions needed to form dimeric species. However, the preliminary results obtained this past summer are quite encouraging. The equilibrium data necessary before meaningful reactivity studies of the dimeric vs. the monomeric peroxomolybdates can be performed.

Publications and Technical Reports Published During Award Period

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