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Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation

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This project provides information relevant to: (i) extent and nature of radiation-induced chemical modification of Hanford waste during storage and (ii) potential applications of peroxynitrite in remediation technologies.

Research objectives: 1. To determine the extend of radiation-induced peroxynitrite generation in mixtures simulating the various phases of nuclear waste. 2. Through mechanistic studies of catalyzed peroxynitrite reactions to estimate their contribution to the degradation of organic waste components and to determine the feasibility of using peroxynitrite for the destruction of organic complexants and for the removal of chromium for more efficient vitrification.

Research progress and implications: This report summarizes work after 2.5 years of a 3 year project. Peroxynitrite, $ONOO^-$, is a powerful oxidant when protonated or combined with CO_2 or metal ions. These reactivity pathways have been investigated, starting with the catalyzed decomposition reactions. Mechanistic studies has demonstrated that ONOOH undergoes homolysis producing the strongly oxidizing $^\$NO_2$ and $^\$OH$ radicals with a 28% yield. An extensive oxidation of EDTA was found in the presence of excess of ONOOH. Similarly, CO_2-catalyzed oxidations by peroxynitrite proceeds via formation of the $^\$NO_2$ and $^\$CO_3^-$ radicals with a 35% yield. The carbonate radical has shown to be a strong acid, contrary to the previous reports of low radical acidity. The pulse radiolysis studies have shown that both $^\$OH$ and $^\$CO_3^-$ rapidly oxidize $ONOO^-$, generating an unstable $^\$ONOO$ radical, which decomposes into $^\$NO$ and O_2. Collectively, these studies have clarified all significant issues concerning the H^+- and CO_2-catalyzed reactivities of peroxynitrite. It is concluded that $ONOO^-$ can be an important source of oxygen within Hanford waste and may contribute to the generation of $^\$NO$ and N_2O emitted from the storage tanks. Reactive radicals produced in the H^+- and CO_2-catalyzed peroxynitrite reactions can contribute to the chemical modification of the waste during its storage.

Oxidation of Cr(III) by peroxynitrite has been investigated in concentrated alkaline solutions. This reaction cleanly produces Cr(VI) in the form of highly soluble chromate, with the stoichiometric ratio $Ä[ONOO^-]/Ä[Cr(III)] = 3/2$, indicating that the oxidation equivalent of $ONOO^-$ is utilized completely. The rate-determining step of this reaction is an S_{N2} nucleophilic attack of $ONOO^-$ on $Cr(OH)_4^-$, for which a rate constants of 6.5 $M^{-1}s^{-1}$ has been determined. Comparative studies showed that peroxynitrite is significantly better oxidant for Cr(III) than hydrogen peroxide, frequently used for this purpose. Above the solubility limit of Cr(III), the oxidation rate depends upon the solution aging due to formation of polymeric species; the hydrolysis of the polymer becomes the rate-limiting step under these conditions. The oxidation of

Cr(III) is strongly promoted by the presence of Mn(II), which not only accelerates the reaction, but also virtually eliminates the effects of aging. Several transition metals have been tested as catalysts for EDTA oxidation in alkali. Remarkably, even in the absence of a catalyst, EDTA was degraded simultaneously with the decay of ONOO$^-$ during 5-10 hours. Copper(II)-based catalysts (CuEDTA and Cu on SiO_2) were the most active causing ~80% oxidation within one hour. Thus, applications of peroxynitrite for the destruction of the waste organics and for the oxidative removal of chromium appear to be promising.

Both UV- and ã-radiation generate ONOO^B in solid nitrates, as shown by the optical and Raman spectral changes and the chemical analyses upon dissolution. Similarities between photolysis and radiolysis suggest that ONOO^B is produced via isomerization of an electronically excited NO_3^- ion. Although the initial radiation yields of ONOO$^-$ are significant (~1 molecule per 100 eV of absorbed energy), the accumulation decelerates with time reaching a steady-state levels due to competing radiolytic decomposition of ONOO$^-$; the data indicate that a long-range electron transfer and an unusual radical chain reaction are involved in the decomposition process. ã-radiolysis of concentrated nitrate solutions, also generates ONOO$^-$ via both direct radiation absorption by NO_3^- and an indirect pathway. The main conclusion from these studies is that the radiation-induced generation of peroxynitrite is an efficient process in both solid nitrates and their concentrated solutions, which can contribute very significantly to the chemistry of Hanford wastes.

Planned activities: Mechanistic time-resolved studies of radiation-induced peroxynitrite generation and decomposition in solid nitrates. Development of protocols for oxidative destruction of complexants and dissolution of chromium.

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