

Environmental Management Science Program

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Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation

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Research Objective

The broad objective of this project is to provide quantitative mechanistic information relevant to: (i) the extent and nature of radiation-induced chemical modification of the nuclear defense waste that occurs during storage, and (ii) the extent of accumulation of peroxynitrite in the waste and its potential use in remediation. Within this context, the specific goals are:

To determine the radiochemical yields of peroxynitrite in chemical mixtures simulating the various phases (salt cake, slurry, supernatant) of radioactive waste;

Through mechanistic studies of metal- and CO_2 -catalyzed oxidations by peroxynitrite, to estimate the extent of peroxynitrite-mediated oxidative degradation of organic waste components and determine the feasibility of using peroxynitrite in remediation technologies, e.g., for the destruction of organic complexants and the removal of chromium for more efficient vitrification.

Research Progress and Implications

This report summarizes work after the first year of a three-year project. The following studies either have been completed or are in progress:

Oxidation of Peroxynitrite by Radiolytically-Generated Inorganic Radicals (publication 1)

The reactivity of the peroxynitrite ion, ONOO^- , toward a number of inorganic radicals was determined using pulse radiolysis techniques. Rate constants for oxidation of the ONOO^- ion by the carbonate, azide, and chlorine dioxide radicals were measured from their decay kinetics to be 7.7×10^6 , 7.2×10^8 , and $3.2 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, respectively. For the hydroxyl radical, the rate constant of $4.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ was obtained using competition kinetic analysis. For the first time the oxidation potential of the ONOO^- ion was estimated as 0.8 V from kinetic data; the oxidation product decomposes to produce nitric oxide and molecular oxygen. Although thermodynamically favorable, oxidation of ONOO^- by the nitrogen dioxide radical was not observed; an upper limit of $2.5 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ could be set for this reaction.

The implications of these results for the waste chemistry are: (i) oxidation of peroxynitrite may be, at least in part, responsible for the generation of nitric oxide emitted by the waste tanks; (ii) nitrogen dioxide, which is the dominant oxidizing radical produced by radiation in the waste, does not scavenge peroxynitrite.

Mechanism of Peroxynitrite Decomposition (publications 2 and 3)

In order to resolve a long standing controversy about hydroxyl radical production via the proton-catalyzed decomposition of peroxynitrite, this reaction was studied in the pH range 5-10. While nitrate was the only product in the acidic solutions, in neutral and alkaline media nitrite and O_2 were also produced, with the oxygen yields reaching 80% of the stoichiometrically attainable at pH 10. Addition of the free radical scavengers (DMSO, alcohols, acetate, etc.) inhibited O_2 formation in a manner that was quantitatively consistent with their reactivity toward the $\cdot\text{OH}$ radical. Excess of nitrite reversed this inhibition at pH above 8, but was itself inhibitory under more acidic conditions. No O_2 was produced in the presence of CO_2 . An eight-step radical mechanism which requires a

generation of the free $\cdot\text{OH}$ radical with 30-35% yield was proposed to account for this unique reaction behavior. Upon numerical integration, the proposed mechanism accurately duplicated all experimental data. Because there are no adjustable parameters, the calculations provide a particularly stringent test of the mechanism unambiguously establishing that a free $\cdot\text{OH}$ radical is generated during proton-catalyzed peroxyxynitrite decomposition.

The implications of these results for the waste chemistry are: (i) decomposition of peroxyxynitrite can be an important source of oxygen within the alkaline waste; (ii) because upon protonation peroxyxynitrite generates an extremely reactive hydroxyl radical, it is capable of indirectly oxidizing virtually every organic compound found in the waste.

Oxidative Dissolution of Chromium(III) by Peroxyxynitrite (work in progress)

In strongly alkaline solutions, peroxyxynitrite rapidly oxidized freshly precipitated chromium(III) hydroxide to a soluble chromate with a stoichiometric ratio [chromate]:[ONOO \cdot] close to 1:3. Aging of the precipitate resulted in deceleration of the reaction and increase in the relative consumption of ONOO \cdot . Immediately upon initiation the reaction kinetics was first-order in both Cr(III) and ONOO \cdot , however the order in ONOO \cdot decreased during the course of reaction indicating a possible change in mechanism. The initial reaction rates were independent of the hydroxide concentration and ionic strength. A working hypothesis concerning the effect of aging is that a massive hydroxide is gradually formed making the inner Cr atoms inaccessible to the oxidant. A significant effect of additional transition metals on the reaction kinetics was observed. For example, in mixed Cr-Mn hydroxide the reaction was not only faster, but was also relatively insensitive to aging and did not decelerate with time. The reaction went to completion within tens of minutes, whereas for pure chromium hydroxide reaction took hours or days depending on the age of Cr hydroxide. Reaction rates linearly increased with [ONOO \cdot] and [Cr(III)] and showed a complex dependence upon the Cr/Mn ratio. In contrast, addition of Cu(II) in quantities comparable with that of Cr(III) inhibited formation of chromate, an effect that was attributed to a catalytic decomposition of peroxyxynitrite by copper ions. Importantly, Fe(III) hydroxide, which is abundant in the waste tanks, had no inhibitory effect on the rate of chromate formation.

The implication of these findings for the waste remediation is: it appears that peroxyxynitrite has a potential for being considered as an oxidant for removing precipitated chromium from waste sludges, which will improve their compatibility with vitrification methods for disposal.

Planned Activities

Second year: Studies of the yields and mechanisms of radiation-induced peroxyxynitrite generation in solid nitrate and nitrite and their concentrated solutions. Finishing studies of oxidative dissolution of chromium.

Third year: Mechanistic studies of metal- and CO₂-catalyzed oxidation of organic complexants by peroxyxynitrite. Developing generalized dynamical model for the peroxyxynitrite reactivity pathways in the radioactive waste.

Other Access To Information

1. Goldstein, S.; Saha, A.; Lymar, S. V., Czapski, G., "Oxidation of Peroxyxynitrite by Inorganic Radicals: A Pulse Radiolysis Study", J. Am. Chem. Soc., (1998), in press.
2. Lymar, S. V.; Hurst, J. K., "Radical Nature of Peroxyxynitrite Reactivity", Chem. Res. Toxicol. (1998), in press.
3. Coddington, J. W.; Hurst, J. K.; Lymar, S. V., "Hydroxyl Radical Formation During Peroxyxynitrous Acid Decomposition", Proc. Natl. Acad. Sci. USA, submitted.