

Research Objectives

This project provides information relevant to: (i) the extent of radiation-induced accumulation of peroxyxynitrite in the Hanford waste and its roles in waste chemistry and (ii) the potential applications of peroxyxynitrite in remediation technologies. These studies include: (1) Determinations of the peroxyxynitrite formation pathways and their radiation yields. (2) Time-resolved mechanistic investigation of the direct radiation effects in solid nitrates and their concentrated solutions. (3) Evaluation of using peroxyxynitrite for oxidative removal of chromium for more efficient vitrification.

Research Progress and Implications

This report summarizes work after 18 months of a 3 year project. Our studies during the previous funded period (i) have established that peroxyxynitrite, ONOO^- , is a major oxidant produced by radiation in waste tanks and (ii) have demonstrated that peroxyxynitrite could find applications in the pretreatment of the Hanford waste for disposal. Brief account of the new findings follows.

Peroxyxynitrite chemistry. A novel previously unrecognized pathway for the radiation-induced formation of peroxyxynitrite in Hanford wastes has been discovered. This pathway involves the radiolytic formation of nitroxyl, NO^- , through the reduction of nitric oxide, NO , followed by addition of the dissolved oxygen, i.e., the diffusion-controlled reactions



The major source of NO is the radiolytic decomposition of nitrite. Our preliminary studies have shown that the widely accepted description of this decomposition is incorrect; reinvestigation of this process has been initiated. The major source of dissolved O_2 is the radiolytic decomposition of nitrate, a process that was investigated in detail earlier in this project.

In oxygen-depleted environments, consecutive addition of NO becomes the major sink for radiolytically-formed nitroxyl, i.e., the reactions



The N_3O_3^- product is unstable and rapidly dissociates into nitrous oxide and nitrite:



An implication of these reactions is that they can be major contributors to formation of nitrous oxide. The origin of N_2O emitted from the waste tanks remains one of the least-understood aspects of the chemistry of Hanford wastes. A detailed description of nitroxyl chemistry has been published in: Shafirovich & Lymar (2002) *Proc. Natl. Acad. Sci. USA* **99**, 7340-7345.

The amount of chemical energy stored in the accumulated peroxyxynitrite depend upon its Gibbs energy of formation, $\Delta_f G^\circ(\text{ONOO}^-)$. This quantity has been accurately determined from the equilibrium constant, K_{eq} , for the homolysis reaction:



Pulse radiolysis experiments have shown that $K_{\text{eq}} = 3 \times 10^{-12}$ M and $\Delta_f G^\circ(\text{ONOO}^-) = 69$ kJ/mol. The latter value is 180 kJ/mol greater than the Gibbs energy of nitrate, a stable chemical isomer of ONOO^- . Thus, the radiation-induced conversion of NO_2^- to ONOO^- results in the large accumulation of chemical energy which can be released upon waste dissolution for retrieval. On the molar basis, this energy is comparable with the energy of hydrogen combustion. For the conjugate peroxyntrous acid, ONOOH , we derive $\Delta_f G^\circ(\text{ONOOH}) = 31$ kJ/mol. From this value, it follows that approximately 30% of ONOOH must decompose into the nitrogen dioxide and hydroxyl radicals. Being strong oxidants, these radicals contribute to organic waste degradation and tank corrosion.

The first experimental demonstration of radiation-induced ONOO^- formation in concentrated nitrate solutions has been made using γ -radiolysis of concentrated nitrate solutions. Our findings are as follows: (i) γ -radiolysis of 1-8 M nitrates in 0.1-1 M NaOH, which are typical concentrations in liquid Hanford waste, results in ONOO^- formation; (ii) the observed radiation yields of ONOO^- have been rationalized in terms of simultaneous ONOO^- formation via radiation absorption by nitrate (direct effect) and from the water radiolysis products (indirect effect). The corresponding radiation yields of $G_{\text{dir}} \approx 0.7$ and $G_{\text{indir}} \approx 0.06$ molecules/100 eV have been estimated from the dependence of G_{obsd} upon the nitrate concentration. Thus, the direct effect appears to be the predominant pathway to ONOO^- formation in solution. The main conclusion emerging from these studies is that radiation-induced generation of peroxyntrite can make a major contribution to the chemistry of nitrate-rich Hanford wastes. Indeed, the radiation yields determined for ONOO^- can be compared to a relatively low ~ 0.2 molecules/100 eV yield for hydrogen in concentrated nitrate solutions, which is sufficient in some tanks to create serious safety concerns.

Oxidative dissolution of chromium. A custom-build tandem quench-flow apparatus was used to prepare large quantities of concentrated peroxyntrite by reacting hydrogen peroxide with nitrite. This peroxyntrite was tested for its efficiency as an oxidant in dissolution of chromium contained in samples of real Hanford sludge. (The actual testing was performed by Dr. Brian Rapko of the PNNL). Peroxyntrite showed significant activity in the process, although it was less efficient than permanganate. The final assessment of the peroxyntrite utility will be done upon the completion of the transuranic element dissolution assays, that are now in progress.

Mechanistic studies of Cr(III) oxidation by ONOO^- have shown that the rate-determining step in this process involves an thermodynamically favorable oxygen atom transfer from ONOO^- to Cr. Based on thermochemical data, a prediction has been made that another peroxide anion, peroxymonosulfate (O_3SOO^-), should be even more efficient oxidant for Cr(III); the experimental testing of this conjecture is in progress.

Planned Activities

Time-resolved studies of radiation-induced peroxyntrite generation and decomposition; evaluation of the relative contributions from different formation pathways. Reinvestigation of the NO generation through radiation-induced decomposition of aqueous nitrite. Mechanistic investigation of chromium(III) oxidation by peroxymonosulfate.