Research Objectives

This project provides information relevant to: (i) the extent of radiation-induced accumulation of peroxynitrite in the Hanford waste and its roles in waste degradation and (ii) the potential applications of peroxynitrite in remediation technologies. These studies include: (1) Determinations of the peroxynitrite radiation yields in chemical mixtures simulating the various phases of Hanford waste. (2) Time-resolved mechanistic investigation of the direct radiation effects in solid nitrates and their concentrated solutions. (3) Determination of the optimal conditions for catalyzed oxidation of organic complexants by peroxynitrite. (4) Evaluation of the feasibility of using peroxynitrite for oxidative removal of chromium for more efficient vitrification.

Research Progress and Implications

This report summarizes work after 5 months of a 3 year project. Our studies during the previous funded period (i) have established that peroxynitrite, $ONOO^-$, is a major oxidant produced by radiation in solid nitrates present in waste tanks and (ii) have demonstrated that peroxynitrite solutions could find applications in the pretreatment of the Hanford waste for disposal. Brief account of the new findings and their implications follows.

Peroxynitrite thermochemistry. Both the reactivity and the amount of chemical energy stored in the accumulated peroxynitrite depend upon its Gibbs energy of formation, $Ä_fG^o(\mathrm{ONOO^-})$. We have determined this quantity by measuring an equilibrium constant, K_{eq}, for the homolysis reaction:

$$ONOO^- \;^{o}\; {}^{\bullet}NO + {}^{\bullet}O_2^- \qquad Ä_fG^o(\mathrm{ONOO^-}) = Ä_fG^o({}^{\bullet}\mathrm{NO} + {}^{\bullet}\mathrm{O_2^-}) + RT\ln K_{eq}$$

An efficient selective superoxide scavenger, methylviologen radical (${}^{\bullet}MV^+$) generated by pulse radiolysis, was used in these experiments:

$${}^{\bullet}MV^+ + {}^{\bullet}O_2^- (+H_2O) \;!\; MV^{2+} + HO_2^- + OH^- \qquad k = 2.8\times10^9\ M^{-1}s^{-1}$$

Because ${}^{\bullet}MV^+$ does not react with ${}^{\bullet}NO$, the above equilibrium continuously shifts to the left as superoxide is being scavenged and ${}^{\bullet}NO$ accumulates. This results in a highly specific ${}^{\bullet}MV^+$ decay pattern, as shown in Figure 1, whose salient features are the strongly non-exponential character and the half-life dependence upon initial ${}^{\bullet}MV^+$ concentration. The numerical data analysis gives $K_{eq} = 3\times10^{-12}$ M and $Ä_fG^o(\mathrm{ONOO^-}) = 69$ kJ/mol. The latter value is 180 kJ/mol greater than the Gibbs energy of nitrate, a more stable chemical isomer of $ONOO^-$. This means that the radiation-induced conversion of nitrate to peroxynitrite can result in large chemical energy accumulation that can be released upon waste dissolution for retrieval. On the molar basis, this energy is comparable with 230 kJ/mol, the energy of hydrogen combustion.

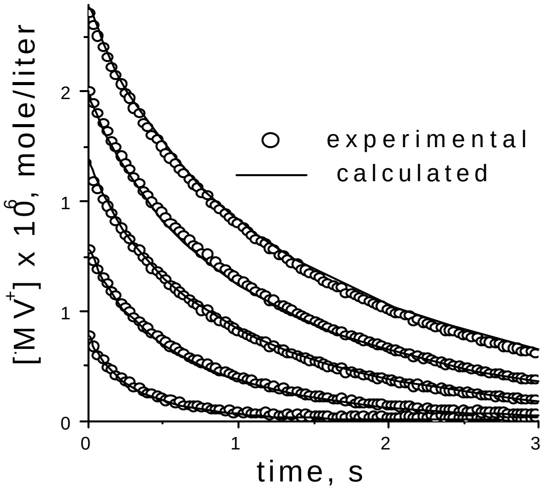

Figure 1. Decay kinetics of ${}^{\bullet}MV^+$ in the presence of 1×10^{-4} M of $ONOO^-$

Based on the pK_a = 6.6 of a conjugate peroxynitrous acid, ONOOH, we derive $Ä_fG^o$(ONOOH) = 31 kJ/mol. From this value and other well-established characteristics of ONOOH, it follows that approximately 30% of ONOOH must decompose into the nitrogen dioxide and hydroxyl radicals. Being strong oxidants, these radicals can contribute to organic waste degradation and tank corrosion.

Radiolytic peroxynitrite formation in solutions. For decades it has been widely accepted that NO_2^- and O_2 are the only end products from radiolysis of concentrated aqueous solutions of nitrate. Analysis of published studies shows that they have been done mostly in neutral and acidic media where peroxynitrite is unstable and its formation could easily be overlooked. We have therefore initiated reinvestigation of ã-radiolysis of concentrated nitrates, specifically analyzing for $ONOO^-$. Our findings are as follows:

(i) ã-radiolysis of 1-8 M nitrates in 0.1-1 M NaOH, which are typical concentrations in liquid Hanford waste, results in $ONOO^-$ formation. The accumulation curves do show saturation, but only at the relatively large $ONOO^-$ concentration levels of 1-5 mM. These data provide the first experimental demonstration of radiation-induced $ONOO^-$ formation in concentrated nitrate solutions.

(ii) The observed radiation yields of $ONOO^-$, G_{obsd}, have been rationalized in terms of simultaneous $ONOO^-$ formation via radiation absorption by nitrate (direct effect) and from the water radiolysis products (indirect effect), i.e.,

$$G_{obsd} = f_N @ G_{dir} + f_W @ G_{indir}$$

where f_N and f_W are the fractions of radiation energy absorbed by nitrate and water, respectively. Radiation yields of G_{dir} . 0.7 and G_{indir} . 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 peroxynitrite 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.

Planned Activities

Time-resolved studies of radiation-induced peroxynitrite generation and decomposition; evaluation of the relative contributions from different formation pathways. Mechanistic investigation of chromium(III) oxidation by peroxynitrite. Development of protocols for oxidative destruction of complexants and dissolution of chromium.