

Project 90107
Hazardous and Corrosive Gas Production in the Radiolysis of
Water/Organic Mixtures in Model TRU Waste
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RESULTS TO DATE: Scope. The radiation chemistry of aqueous systems containing chlorinated hydrocarbons is investigated using a multi-pronged approach employing ^{60}Co gamma ray and alpha particle irradiation experiments in conjunction with diffusion-kinetic modeling incorporating track structure simulations. The goal is to determine mechanisms, kinetics, and yields for the formation of potentially explosive gases and corrosive agents, such as H_2 and HCl , respectively, in the radiolysis of water-organic mixtures. The information obtained is of a fundamental nature, but the radiation chemical systems studied are found throughout the DOE portfolio and are important in radioactive waste remediation and management. Program Highlights. Radiation-induced production of H_2 and HCl from chlorinated hydrocarbons. ^{60}Co gamma-radiolysis experiments and stochastic kinetic modeling have been used to investigate the radiation-induced yield of H_2 and Cl^- from aqueous solutions of 1,2-dichloroethane (1,2-DCE) and 1,1-dichloroethane (1,1-DCE) over the concentration range 1-80 mM. In deoxygenated solution, the yield of H_2 from both 1,2-DCE and 1,1-DCE solutions decreases as the concentration of DCE is increased. The decrease in the H_2 yield shows that the reaction of H atom with DCE does not lead to the production of H_2 . This observation is unexpected and reflects the reverse of the effect seen in the gas phase, where the reaction of H atom with 1,2-DCE and 1,1-DCE leads to the production of H_2 . The yield of Cl^- from 1,2-DCE and 1,1-DCE solutions increases slightly from 2.8 ions/100eV to 3.6 over the concentration range 10-50 mM, demonstrating the increased competition of the DCE with intra-track processes. Comparison of the measured yields of Cl^- with the predictions of stochastic kinetic modeling shows that the reactions of eaq^- with 1,2-DCE and with 1,1-DCE are quantitative, and that the reaction of H atom with both DCEs leads to the production of Cl^- (and Haq^+). In aerated solution, the yield of Cl^- from 1,2-DCE and from 1,1-DCE solutions is very significantly higher ($\sim \times 3-4$) than from deoxygenated solution. Furthermore, the observed yield is both dose and dose rate dependent. The mechanisms for Cl^- production in aerated aqueous solutions of 1,2-DCE and of 1,1-DCE are currently under investigation. Rate coefficients for the reaction of eaq^- and $-\text{OH}$ with chlorinated hydrocarbons. There is considerable disagreement over the rate coefficients for the reaction of the primary radiation-produced reducing and oxidizing radicals from water, eaq^- and $-\text{OH}$ respectively, with 1,2-DCE and with 1,1-DCE. Electron pulse-radiolysis experiments monitoring the decay of eaq^- have been used to measure the rate coefficients: 1,2 DCE $\text{eaq}^- + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2^- + \text{Cl}^-$ $k_1 = 2.3 \times 10^9 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ 1,1 DCE $\text{eaq}^- + \text{CH}_3\text{Cl}-\text{CHCl}_2 \rightarrow \text{CH}_3-\text{CHCl}^- + \text{Cl}^-$ $k_2 = 3.5 \times 10^9 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ while competition kinetic experiments were employed to determine the rate coefficients: 1,2 DCE $-\text{OH} + \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl} \rightarrow \text{CH}_2\text{Cl}-\text{CHCl}^- + \text{H}_2\text{O}$ $k_3 = 1.8 \times 10^8 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ 1,1 DCE $-\text{OH} + \text{CH}_3\text{Cl}-\text{CHCl}_2 \rightarrow \text{CH}_3-\text{CCl}_2^- + \text{H}_2\text{O}$ $k_4 = 1.1 \times 10^8 \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ The values obtained are similar to those measured by Asmus and co-workers, but there is a significant discrepancy from the estimate of Getoff and co-workers for k_1 . Rate coefficient for the reaction of OH with thiocyanide ion. The rate coefficient for the reaction of the $-\text{OH}$ radical with a chlorinated hydrocarbon is obtained by a competition experiment, in which the change in the radiation-induced yield of $(\text{SCN})_2^{--}$ from an aqueous SCN^- solution is monitored on the addition of the hydrocarbon. The mechanism for the radiation-induced formation of $(\text{SCN})_2^{--}$ from a SCN^- is complex and involves a number of equilibria. Careful electron pulse radiolysis experiments have been performed and analyzed, employing the full, complex reaction mechanism, to re-evaluated the rate coefficient for the fundamental reaction $-\text{OH} + \text{SCN}^- \rightarrow \{\text{HOSCN}\}^{--}$ $k_5 = 1.4 \times 10^{10} \text{ dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ This reaction is central to the experimental determination of the rate coefficient of a solute with OH using the competition method. The value obtained for k_5 is about 30% higher than that generally employed, and this has a major effect on the measured values for k_3 and k_4 .

DELIVERABLES:

EMSP Sponsored Submissions in 2004

1. B. Milosavljevic & J. A. LaVerne, "Pulse Radiolysis of Aqueous Thiocyanate", J. Phys. Chem. A, submitted.

EMSP Sponsored Presentations in 2004

1.S. M. Pimblott, Invited Lecture, The Problem With Nuclear Waste, Forever Learning Institute, South Bend, IN 3rd November, 2004.

2.J. A. LaVerne, Invited Lecture, Hydrated Electron Yields in the Radiolysis of Water, Japanese Radiation Chemistry Society Meeting, Sapporo, Japan, 9th October 9, 2004.

3.S. M. Pimblott, Invited Lecture, Stochastic Analysis of Nonhomogeneous Dynamics in Ion Radiolysis, Gordon Conference on Radiation Chemistry, Colby College, ME, 20th June, 2004

4.B. Milosavljevic, Poster, Radiolysis of Aqueous Dichloroethane Solutions, Gordon Conference on Radiation Chemistry, Colby College, ME, 20-25th June, 2004.