

Precursor and Transient Species in Condensed Phase Radiolysis

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Program Scope

The final products of condensed phase radiolysis are largely governed by very early events (\leq picosecond) that occur immediately following the absorption of ionizing radiation. This program uses a multi-pronged approach employing heavy ion-, electron-, and gamma-radiolysis experiments in conjunction with stochastic kinetic modeling and electronic structure calculations to elucidate and interpret fundamental radiation chemical processes from their earliest stages. The specific goals are to characterize the precursor and transient species that are initially formed following absorption of high energy radiation in condensed systems, to determine the interactions of these species with their immediate environments, and to evaluate their effects on the mechanisms and kinetics of the various chemical reactions that dictate final product yields of radiolysis. Current focus is on aqueous solutions with some studies on other condensed phase systems, including hydrocarbons and related common heteroatomic solvents. The fundamental physical and chemical issues being addressed have direct applications to the underlying problems in design and operation of nuclear power plants, cleanup and management of radioactive wastes, nanotechnology, health physics, and other technological challenges of importance in the real world scenarios of significance to the mission of the Department of Energy.

Recent Progress

Scavenger studies clearly show that the precursors to the hydrated electron can lead to significant chemistry not normally associated with the hydrated electron.^{1,2} Molecular hydrogen previously designated as unscavengable is now known to be due to the precursor to the hydrated electron.³ These results gave a new appreciation to the role of extremely short lived transients on final product formation in the radiolysis of water. Techniques for the direct examination of these transients is not yet commonly available so the present experimental work depends on the indirect examination of stable products with varying concentrations of added scavengers for the transients.

Hydrogen peroxide is the main oxidizing molecular product ultimately produced in the gamma-radiolysis of water. The mechanism of hydrogen peroxide production has been examined⁴ by varying the concentrations of scavengers for OH radical and of scavengers for the precursor to the hydrated electron. Hydrogen peroxide yields were found to decrease toward zero with increasing concentration of OH radical scavenger in all solutions, indicating that essentially all hydrogen peroxide is formed by combination reactions of OH radicals that are produced in the initial radiolytic decomposition of water. In nitrate and selenate solutions the yields of hydrogen peroxide were found to be closely associated with the scavenging capacity of the precursor to the hydrated electron, suggesting that its reactions have a significant role in hydrogen peroxide formation.

Observed hydrogen peroxide yields at high nitrate concentrations coupled with stochastic diffusion-kinetic modeling calculations showed that the molecular cation of water, H_2O^+ , is the dominant precursor of the oxidizing species leading to hydrogen peroxide. Proton-transfer reactions of water molecular cations with neutral water molecules give 79% of the oxidizing species, whereas other reactions such as dissociative recombination reactions account for the rest. In radiolysis of selenate solutions a significant additional production of OH radicals was found due to the formation of $\text{O}^{\bullet-}$ and the scavenging of low-level excited water molecules.

A combined experiment with model approach is being used to examine the production of hydrated electrons and OH radicals in the heavy ion radiolysis of water. Scavenger capacity dependence studies give both the yields and temporal dependence of these main radical species in the radiolysis of water with protons, helium ions and carbon ions. Radical yields decrease with increasing particle linear energy transfer, LET, and the track reactions responsible for this decrease occur on very fast timescales (\leq nanosecond). Monte Carlo calculations are found to agree well with experiments in most cases. The track model clearly shows that the variation in radical yield more closely follows the density of reactive species in the track and not the LET. A major limitation of the model seems to be due to defining the correct spatial distribution of the hydrated electron and its precursor in heavy ion tracks.

Electronic excitation of small water clusters has been examined⁵ using high-level quantum chemical calculations. The lowest excited state energy of a central water molecule was found to be insensitive to stretching one of its OH bonds when the OH bond is hydrogen-bonded in an ice-like configuration to a neighboring water molecule. This result is in marked contrast to the behavior of the gas phase water monomer, where the lowest excited state is well known to be strictly dissociative along an OH stretching coordinate. The conclusions of this study may provide the basis for an explanation of the apparently long lifetime that has recently been experimentally inferred for excited water in irradiated thin ice films.⁶ Analogous calculations are now being initiated to address electronic excitation in model systems more directly relevant to liquid water.

Future Plans

Experimental studies are focusing on the production and reaction of hydrated electrons and OH radicals in the heavy ion radiolysis of water. The specific scavengers for each of these radical species are glycylglycine and formic acid, respectively. Agreement between experiment and model calculations at low scavenger concentrations is satisfactory, especially since effects due to track ends are very uncertain. Experimental energy dependences of product yields will be used to determine track segment yields, a quantity more accurately calculated. Neither of the scavenger systems is ideal for studies at high scavenging capacity and new solutes are being evaluated.

A particularly promising approach for examining the effects of track structure on transient species is to examine the variation in formation of the main stable product, H_2 in the case of hydrated electrons and H_2O_2 in the case of OH radicals. The production of these products with increasing scavenging capacity for precursors to the hydrated electron and OH radical gives considerable information on the yields and spatial distributions of these very short lived transients. Eventually, the role of the excited water

molecule will be examined for its role in the formation of oxidizing species such as the O atom.

The poorly understood energetics and fragmentation patterns of the molecular cation, H_2O^+ , in water will be studied with electronic structure methods. To model the situation in the liquid phase, small water clusters will be explicitly treated together with implicit solvation models that describe bulk effects by surrounding the clusters with dielectric continuum. All the available dissociation channels in low-lying states of the cation will be investigated, particularly focusing on the ultrafast deprotonation that produces OH and H_3O^+ . It has recently been shown² that about 70% of the total molecular hydrogen ultimately produced in the gamma radiolysis of water comes from some previously unrecognized ultrafast process. Possible explanations involving dissociative electron combination with H_2O^+ will be studied along with alternatives such as dissociative electron combination with H_3O^+ . The information obtained in these *ab initio* theoretical studies will guide stochastic simulations employing simulated fast electron and heavy ion track structures to study the ultra-fast reaction of the molecular cation of water with an adjacent water molecule to give H_3O^+ and OH radical, which is the dominant source of OH in liquid water radiolysis. There is no definitive observation of H_2O^+ in liquid water; however, there is evidence in photo-ionization studies suggesting a lifetime of < 100 fs.^{7,8} The rate coefficient of the proton transfer reaction in the gas phase suggests a lifetime of ~ 18 fs at the density of liquid water.⁹ Furthermore, theoretical calculations for the water dimer give a lifetime of 30-80 fs.¹⁰ Simulations will be made employing a range of lifetimes from 10–100 fs, and the results analyzed by comparison with the well-established scavenger kinetics of OH radical decay and H_2O_2 formation. Further calculations will consider scavenging of the molecular cation, looking at the ultra-fast formation of Br_2^- in concentrated Br^- solution and at the effect of concentrated nitrate solutions on the yield of H_2O_2 .

Not all the radiation induced reactive oxygen species are produced directly from H_2O^+ . A number of additional sources have been postulated, including formation of O^- (OH) by a dissociative electron attachment reaction, direct formation of excited singlet states of H_2O by the primary radiation particle, and singlet and triplet states of H_2O produced by low-energy electron interactions, as well as the dissociative electron recombination reaction of H_2O^+ with e^- in producing singlet and triplet excited states of water. Transition states and potential energy surfaces governing dissociative channels of low-lying excited states of neutral water, H_2O^* , will be calculated with electronic structure methods that model the situation in liquid to evaluate their possible importance in direct production of transient radiolytic species. Production of these reactive oxygen species will also be the objective of a series of stochastic diffusion-kinetic calculations investigating the roles of direct excitation and the dissociative electron recombination reaction in producing singlet and triplet excited states of water, and the nonhomogeneous chemistry of $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$ that have been postulated as the “extra” unobserved oxidizing species that is needed for material balance in kinetic and mechanistic models in high-LET water radiolysis. A final series of kinetic calculations will model the formation of HO_2 and O_2 in the high-LET radiolysis of aqueous Cu(II) – Fe(II) solutions, comparing predictions with available experimental data.

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