New Mechanism for H_2 Formation in Water

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The formation of H_2 in the radiolysis of liquid water is more closely associated with the nonhydrated electron or precursor to the hydrated electron than with the hydrated electron. Experiments with 5 MeV helium ions suggest that the principle mechanism for hydrogen formation is dissociative recombination of the water cation and the nonhydrated electron. The nonhydrated electron undergoing recombination does not appear to be in the lowest energy p-like state, but it probably has an excess energy of several eV. The second-order recombination processes is very sensitive to the type of ionizing radiation leading to the observed variation in hydrogen yields. Furthermore, the relative mobility of the reactants through heterogeneous interfaces may result in a substantial yield of molecular hydrogen in practical situations involving adsorbed water.

The radiolysis of water has been examined extensively in the past 50 years because of the rapid increase in the use of intense radiation sources in medicine and industry.[1,2] One of the fundamental products in the radiolytic decomposition of water is molecular hydrogen.[3] This radiolysis product is intricately associated with many high profile projects of interest to the public, including the maintenance and development of water-moderated nuclear reactors, long-term storage of transuranic waste materials containing adsorbed water, and management of high-level mixed waste storage tanks.[4,5] A variety of precursors to molecular hydrogen have been proposed, but only recently has it been shown that the nonhydrated electron plays a major role.[6] Here results with different types of radiation are used to show that the mechanism for molecular hydrogen formation probably involves a second-order dissociative recombination reaction of the nonhydrated electron with the water cation. As well as affecting some of the fundamental tenets of liquid water radiolysis, this realization has enormous implications in many applications involving nuclear materials.

Traditional models on the formation of molecular hydrogen in liquid water have postulated that the reactions of the hydrated electron were responsible for most (∼67%) of the formation of molecular hydrogen in irradiated water.[6−10] Energy deposited by the passage of ionizing radiation initially forms the parent water cation and a free electron with kinetic energy equivalent to the energy loss minus the associated binding energy. Femtosecond experiments have shown that the electron thermalizes and hydrates with a lifetime of about 240 fs,[11] and that the parent cation undergoes proton transfer to a neighbor medium molecule to give hydronium and the hydroxyl radical, $^{\bullet}OH$, with a lifetime of about 100 fs.[12] Because hydrogen atom yields are much smaller than hydrated electron yields, the majority of the molecular hydrogen was believed to be due to reaction 1.

$$e_{aq}^- + e_{aq}^- (+ 2H_2O) \rightarrow H_2 + 2OH^- \qquad 2k_1 = 1.1 \times 10^{10}\ M^{-1}\ s^{-1} \quad (1)$$

The rate coefficient was taken from the compilation of Buxton et al.[13] Although the hydrated electron can be examined in real time using spectroscopic techniques, molecular hydrogen can only be determined as a final radiolytic product using chromatography. Therefore, selected scavengers of the hydrated electron are added at different concentrations to examine the competition of a scavenging reaction,

$$e_{aq}^- + \text{solute} \rightarrow \text{product} \qquad (2)$$

with hydrogen formation by reaction 1. Nonhomogeneous diffusion kinetics has been very successful in describing the radiolysis of water and aqueous solutions, but it did not lead to an acceptable explanation for the mechanism responsible for the production of the observed molecular hydrogen yield.

Recently it has been determined that the molecular hydrogen yield more accurately follows the scavenging capacity of a precursor to the hydrated electron than the hydrated electron.[6] The scavenging capacity, s, is defined as the product of the solute concentration, [S], and the associated scavenging rate coefficient, k_s ($s = k_s[S]$). It is equivalent to the pseudo first-order rate coefficient and therefore independent of the type of solute. High solute concentrations or ionic strength effects on the rate coefficient are considered as in ref 6. The use of a scavenging capacity formalism implies a lifetime, $\tau = 1/(k_s[S])$, for the hydrated electron and its precursors. The concept of a lifetime is valid in this situation, but determination of the rate coefficient at very short times is problematic because reaction occurs faster than the diffusion limit. The rate coefficients used here were determined from C_{37} values using competition kinetics.[14] Although competition kinetics is prone to problems, especially at short times,[15] the rate coefficients used here give results consistent with Monte Carlo track calculations using IRT modeling. The lifetimes inferred from the present work may have some error in their absolute values, but they were determined in a consistent manner for all of the solutes, so relative comparisons are valid. Even absolute time scales are expected to be correct to within the order of magnitude.

Figure 1 shows the molecular hydrogen yield (G-values, in units of molecules of product formed per 100 eV of energy absorbed) as a function of the scavenging capacity for the

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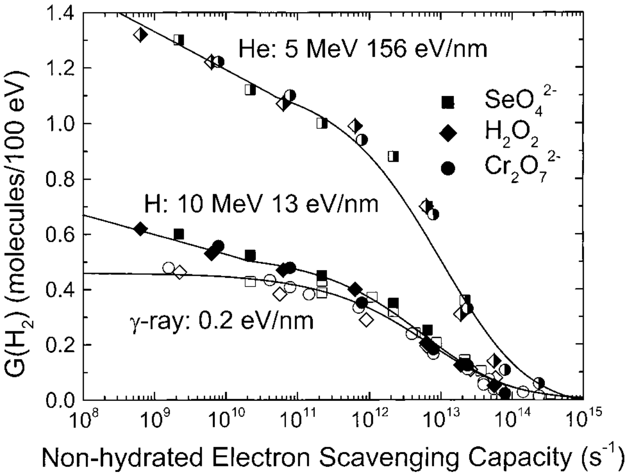


Figure 1. Molecular hydrogen yields as function of the scavenging capacity of the nonhydrated electron: (■) SeO_4^{2-}, (●) $Cr_2O_7^{2-}$, (◆) H_2O_2. The solid symbols are for 10 MeV protons and the half-filled symbols are for 5 MeV helium ions, this work. The open symbols are for γ-rays, ref 6.

γ-radiolysis of aqueous solutions of SeO_4^{2-}, $Cr_2O_7^{2-}$, and H_2O_2. Selenate is known to scavenge precursors to the hydrated electron very efficiently and the hydrated electron poorly, whereas the other scavengers react well with both precursors and the hydrated electron.[15] The general trend of the data as a function of scavenger concentration is well established and is easily explained in terms of the chemistry of the tracks produced by the γ-rays.[2] Energy deposited by the radiation leads to a series of clusters of reactive radical species, known as spurs. Reaction 1 and reactions pertinent to the other radicals occur within the spur as it spatially relaxes by diffusion. The addition of scavengers for the radical species leads to a competition between radical−radical reaction, radical diffusion, and radical scavenging. At very low scavenger concentrations, the nonhomogeneous spatial distributions of the reactants in the spur will be completely relaxed before scavenging occurs. It can be seen in Figure 1 that the escape yield of molecular hydrogen in γ-radiolysis is about 0.45 molecules/100 eV. The singularity of the hydrogen yield with respect to the nonhydrated electron scavenging capacity is a strong indication that a precursor to the hydrated electron is also responsible for much of the molecular hydrogen yield. This dependence on the scavenging capacity is unique to the nonhydrated electron, a similar singular dependence on the scavenging capacity of the hydrated electron is not found.[6] The consequences of this finding are substantial as discussed later. Unfortunately, the chemistry is on such a short time scale that it is difficult to directly probe for the responsible mechanism.

There have been a number of mechanisms proposed for hydrogen formation based on observations in the gas phase and in water ice. The dissociation of excited water molecules to give molecular hydrogen and O atoms has been observed in gas-phase photolysis.[16] Another proposed mechanism for the production of molecular hydrogen involves the capture of precursors to the hydrated electron by a water molecule to give a molecular anion.[17−19] The water anion may decompose by giving a hydride anion that produces molecular hydrogen by rapid reaction with a second water molecule,[20,21]

$$H_2O^{\bullet -} \rightarrow H^- + {}^{\bullet}OH \tag{3}$$

$$H^- + H_2O \rightarrow H_2 + OH^- \tag{4}$$

or it can decompose to give molecular hydrogen directly.[22,23]

$$H_2O^{\bullet -} \rightarrow H_2 + O^{\bullet -} \tag{5}$$

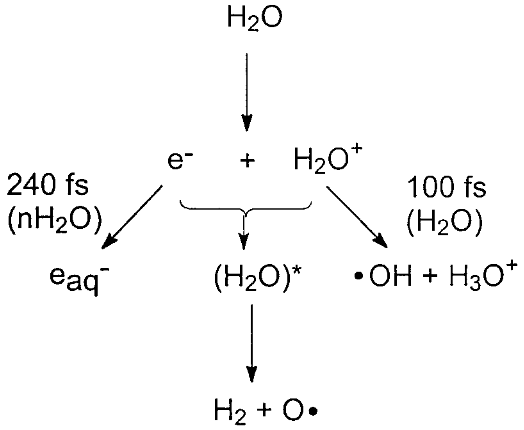
Some of the precursors involved in these mechanisms have been observed in the gas phase or in water ice, but not in the liquid.[20,21]

Heavy charged particles such as protons and helium ions have a much shorter mean free path between inelastic collisions with medium molecules than do γ-rays. The rate of energy loss by γ-rays is only about 0.2 eV/nm, whereas that for 10 MeV protons and 5 MeV helium ions are 13, and 156 eV/nm, respectively. Since the diameter of a water molecule is only about 0.3 nm, there can be several water ionizations in close proximity along the particle's path. The track of the energy deposition by charged heavy particles resembles a more columnar structure than is found with γ-rays.[2] With increasing rate of energy loss, the concentration of transient species in the track increases, thereby increasing the rate of second order reactions involving these transients. The rates of first order reactions, like that of radioactive decay, do not depend on the initial concentration of the reactants. Formation of molecular hydrogen by processes that are second order should be readily apparent in the radiolysis of water with heavy charged particles.

Hydrogen was measured using an inline gas chromatography technique with a thermal conductivity detector.[6] The heavy ion radiolysis was performed using the facilities of the Notre Dame Nuclear Structure Laboratory with techniques as reported elsewhere.[24] Figure 1 shows the yield of molecular hydrogen determined with 10 MeV protons and 5 MeV helium ions as functions of the scavenging capacity of the medium for the nonhydrated electron. It can be seen that hydrogen formation with protons and γ-rays is nearly the same from the initial passage of the radiation (scavenging capacity $\sim 10^{15}$ s^{-1}) until a few tenths of a nanosecond (scavenging capacity $\sim 10^{10}$ s^{-1}). At longer times the normal diffusion and reaction of reactive species occurs and the small increase in molecular hydrogen formation with protons over that with γ-rays is probably due to an increased amount of reaction 1 in the proton track. On the other hand, it can be seen that there is significant hydrogen formation even at the earliest times following the energy deposition in the helium ion track. These results clearly demonstrate that a second-order process is responsible for hydrogen formation. The process occurs on an extremely fast time scale and does not involve normal radical diffusion and reaction. Unimolecular processes such as the decay of excited states, water anion dissociation, and hydride anion reactions are first order and will not show the LET dependence shown in Figure 1 with helium ions. Clearly, most of the common explanations for the formation of molecular hydrogen in liquid water are not consistent with the observed experimental data.

The simplest second-order reaction that occurs on the fast time scales of molecular hydrogen formation in water radiolysis is dissociative recombination.[25] Molecular water cations and electrons that are formed in close proximity in the tracks of 5 MeV helium ions do not need to diffuse to each other, but rather they immediately react forming a charge coupled complex or some other type of excited state that decomposes to give molecular hydrogen. This process occurs in competition with hydration of the electron and with proton transfer by the water parent cation. Therefore, the model for the initial water decomposition seems to follow the mechanism on the next page.

The nature of the excited state, or even its existence, has not been determined. Obviously, as the dissociative recombination is in competition with hydration of the electron and the reaction



of the cation with water, it must be fast. Preliminary stochastic Monte Carlo diffusion kinetic calculations suggest a rate coefficient of ~4.3 × 10^{12} $M^{-1}s^{-1}$ for the processes leading to H_2. The nonhydrated electron involved in this process is short-lived and relatively energetic, so it is probably not associated with the p-like excited state.[26] The significant extent of dissociative recombination found in this work will require modification of many of the modern tenants of radiation chemistry. These modifications will have a major impact in a number of applications including those associated with nuclear materials.

One practical consequence due to the observations in Figure 1 involves estimation of the production of molecular hydrogen in heterogeneous systems. Such situations occur near the core elements or the walls of nuclear reactors and continue for the lifetime of the power plant. A similar example is found with water adsorbed on transuranic waste materials such as PuO_2.[4] These materials are intended to be stored for extremely long periods of time, and prediction of the effects of water radiolysis is extremely important. The main concern created by the present finding is due to the mobility of the nonhydrated electron and the hole created by the passage of the ionizing radiation. It is usually assumed that energy loss in the solid phase is "wasted" and not available for decomposition of water and radiation-induced chemistry. The amount of water decomposition would typically be determined using bulk water yields (low solute concentration yields) with that fraction of energy initially deposited in the water phase. It has been shown in the pulse radiolysis of aqueous suspensions of nanometer-sized silica that electrons formed in the particle readily migrate out into the bulk water.[27] The holes in silica apparently do not escape the particle, so molecular hydrogen formation in colloidal silica suspensions may only be due to the energy deposited in the liquid phase or due to reactions at the particle surface.[28] Migration of the holes may occur in other oxides of importance to the nuclear industry, and the net result would be more decomposition of water than would be predicted by simple dosimetry based on bulk densities of the materials. Clearly, studies need to determine the dependence of the mobility of the precursors to molecular hydrogen on the type of oxide, and the range or thickness of oxides over which these precursors may travel. There are many types of applications where the radiolysis of water at heterogeneous interfaces with high irradiation fields is important, but very little quantitative information is known.

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