

PRIMARY PROCESSES IN THE RADIATION CHEMISTRY OF WATER†

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Abstract—Insights into the primary processes of water radiation chemistry developed fairly recently are reviewed, with particular emphasis on time-resolved experiments performed at Argonne National Laboratory. Properties and reactivity of the three important species H atom, solvated electron, and "dry" or presolvated electron are reviewed first, followed by a discussion of the role of water excited states and the process of electron solvation. Finally, nonhomogeneous spur processes are discussed, including the role of spin-dependent radical chemistry and the initial distance distribution of the $(e^-)_{aq}$ ion.

INTRODUCTION

Primary processes of water radiation chemistry have been the object of considerable study for over 50 years (Hart and Anbar, 1970; Farhataziz and Rogers, 1987). Early experimenters were driven by the need to understand the biological effects of radiation. It was quickly realized that the "primary" processes were in fact fast chemical reactions of highly reactive transients created by radiation in the aqueous environment of biological molecules. The challenge was to identify the transient species, characterize their reactions, and measure their reaction rates.

Conclusions of many of the early studies disagreed considerably, leading to a great deal of controversy and confusion. Experimental results were not consistent with the existence of only H' and OH' radicals and many new chemical species were suggested. A major simplification of aqueous radiation chemistry came with the first observation of the hydrated electron (Hart and Boag, 1962), whose properties had been hypothesized for several years (Platzman, 1953; Stein, 1969). The solvated electron provided an explanation for many experimental facts, including the ionic strength dependence of reaction rates and apparently disparate product yields for what were thought to be H' reactions.

At this point it seemed quite straightforward to measure the "primary" yields of reactive transients formed by radiation. In principle, it would then be possible to calculate chemical product yields from the solution of kinetic equations using the primary yields as initial conditions. However different laboratories, using different concentrations of scavengers, failed to agree on what the "primary" yields had to be. Eventually it was realized that if the product of scavenger concentration and reaction rate were kept below about 10^7 s^{-1} ($k[S] \leq 10^7 \text{ s}^{-1}$), the yields meas-

ured in different laboratories and by different techniques converged to common values. These results, along with other accumulated evidence, finally demonstrated the importance of nonhomogeneous kinetics in determining the "primary" yields. The radiation causes several ionizations and/or excitations in a relatively small region, and the initial chemistry is dominated by recombination of ions and radicals created close together. This idea of initial chemistry in "spurs" was formalized in terms of the classical "diffusion kinetics" model, which requires knowledge of reaction rates, diffusion coefficients, and the "probability distribution of initial distances" for finding a given species at some distance from the spur origin. Schwarz showed that experimental "primary" chemical yields could be predicted quite accurately from one realization of this model (Schwarz, 1969). The mystery of primary processes appeared to be resolved.

In the early 1970s the time scale for kinetic measurements was pushed into the picosecond regime. Subnanosecond pulse radiolysis experiments (Jonah *et al.*, 1973, 1976; Wolff *et al.*, 1973) demonstrated that the decay kinetics of e_{aq}^- was not well predicted by the diffusion kinetics model of Schwarz (1969). Better agreement with experimental results was obtained using different initial distance distributions (Trumbore *et al.*, 1978) or by simulating electron energy loss mechanisms with Monte Carlo techniques (Turner *et al.*, 1983; Zaider *et al.*, 1983). Recently, new calculational techniques using stochastic rate laws have been proposed but have not been applied to a system of sufficient complexity to adequately model the radiation chemical system (Clifford *et al.*, 1982a, b; Green *et al.*, 1984). A completely satisfactory theory has yet to be developed. In addition, picosecond experiments have shown that sufficiently high solute concentrations can reduce the solvated electron yield by scavenging pre-solvated electrons. Much current research aims at understanding "pri-

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mary processes" which occur on the sub-picosecond time scale.

Review of the history of radiation chemistry shows that the operational definition of "primary processes" follows very closely the current technology for measuring events at short times. For our present purpose we will include as primary processes the (femtosecond) interaction of radiation with molecular dipoles to cause ionization and electronic excitation, the (sub-picosecond) relaxation of excited states and electron solvation processes, and the (nanosecond) inhomogeneous spur kinetics which by common agreement terminates at about 100 ns after an isolated ionization event. All reactions at later times can be treated by homogeneous kinetics.

The primary processes of the radiation chemistry of water have been studied because of their inherent scientific interest as well as the impact they have on many different fields. The competition between recombination of the ions and radicals formed by radiation and the reaction of these species with solutes determines the effect that radiation has on a chemical system. In the cooling systems of nuclear reactors, concentrations of reactive ions can be as high as 1 M. This means that reactions of the species created by ionizing radiation with such solutes will take place on the time scale of 0.01–1 ns. This time overlaps the spur recombination time and the amount of reaction depends on this competition.

Another example where the details of water radiation chemistry are important is in radiation biophysics. Reactions of the radiation-produced transients, particularly OH radicals, with DNA and proteins leads to biological damage (Ward, 1987). One of the important considerations of radiation biophysics is the change in the severity of biological damage as radiation quality changes, i.e. as a function of energy and mass of the ionizing particle. When irradiations are done with heavy particles, such as α -particles, carbon nuclei, etc. the density and spatial distribution of ionization changes. Without an understanding of the chemical physics in "simple" aqueous systems irradiated with electrons or X-rays where the ionization events are discrete, extrapolation to the more complex systems is impossible.

To develop a successful model for the radiation chemistry of water, we must (A) understand the chemical properties and reactions of the primary radiolysis products as a function of various factors such as temperature and ionic strength, (B) understand the initial events ($t < 10^{-12}$ s) of radiolysis sufficiently to predict initial yields and distributions of spur sizes and (C) have available a correct (and tractable) treatment of the spur kinetics which can bridge the gap between initial (ca 1 ps) and long-time ($t > 100$ ns) product yields. The knowledge required for (A) has been largely accumulated, although several problems remain, particularly in the understanding of solvated electron properties and reactions. A good deal has been learned about the initial

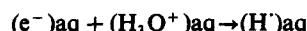
events of electron solvation by scavenging pre-solvated electrons with high concentrations of solute. The same cannot be said for the positive electron "hole" left behind, however, and virtually nothing is known for certain about the participation of water excited states in the initial events. Stochastic models of spur kinetics have now been developed which can treat reactions which are purely diffusion controlled (Clifford *et al.*, 1982a, b; Green *et al.*, 1984). However, even "diffusion controlled" radical recombination reactions are only partially controlled by diffusion because of the additional need to pair spins for singlet product formation. Thus, further development of these stochastic models is essential.

In this review we intend to discuss insights into the primary events which have been developed fairly recently, emphasizing some of the recent work at Argonne. The review will be divided into three sections. Section I will address recent advances in our knowledge of the properties and reactivity of three species of importance in aqueous radiation chemistry, the H atom, e_{aq}^- , and the "dry" or presolvated electron. Section II will emphasize some of the primary processes, including the role of excited states and recent advances in the electron solvation process. Section III will discuss the nonhomogeneous spur processes, including the role of spin-dependent chemistry and the initial distribution of the e_{aq}^- ion.

I. THE PROPERTIES AND REACTIONS OF IMPORTANT RADIOLYSIS PRODUCTS

(A) Atomic hydrogen

Atomic hydrogen has long been recognized as one of the major participants in water radiolysis (Farhataziz and Rogers, 1987; Draganic and Draganic, 1971). Prior to discovery of the solvated electron, it was assumed that H' and OH' were the only radical species which could possibly be formed in high yield (Draganic and Draganic, 1971). In radiolysis of H_2O vapor, both H' and OH' are indeed major products, formed by dissociation of H_2O excited states (Farhataziz and Rogers, 1987). In neutral water at room temperature, it is generally agreed that the yield of atomic hydrogen is ca 0.6 atoms/100 eV (at 1 ps), while solvated electrons are formed in much higher yield ($G \approx 4.8$ at 1 ps). Atomic hydrogen becomes the dominant reducing species in acid solution by virtue of the reaction:



Only through the application of magnetic resonance techniques in recent years, has sufficient evidence been accumulated to deduce the nature of the " $(\cdot)_{aq}$ " solvation sphere about hydrogen. Optical detection of atomic hydrogen in water radiolysis is a very difficult proposition, since the extinction coefficient for absorption is small and the absorption occurs in a wavelength region (ca 200 nm) where lamp intensities are low and virtually everything else

in solution also absorbs (Draganic and Draganic, 1971). In contrast, EPR detection of both H' and D' atoms is unambiguous because of the very large hyperfine splittings which separate the H' and D' resonance frequencies from overlap with any other free radicals. In addition, the spectra become intensely polarized by radical pair CIDEP and are therefore easily detected. Consequently, EPR is a natural choice for the measurement of hydrogen reaction rates in radiation chemistry (Bartels *et al.*, 1986; Beckert and Mehler, 1983; Eigen and Fessenden, 1971; Fessenden and Verma, 1977; Neta *et al.*, 1971).

Further important information is derived from a subfield of subatomic particle physics (Walker, 1981). The positive muon (μ^+) can be injected into most any material (including water) in a spin-polarized state. In a magnetic field, the muon spins precess at a Larmor frequency determined by their chemical environment. The muon undergoes radioactive decay (mean lifetime 2.2 μ s), emitting an energetic positron preferentially along the spin direction at the moment of decay. The positrons are measured as a function of time with a properly oriented detector, and the various muon spin Larmor frequencies appear as beat frequencies superimposed on the exponential radioactive decay. As it turns out, a significant fraction of the muons injected into water capture an electron from the solvent, forming the muonium atom: ($\mu^+ \dots e^-$). Although the mass of μ^+ is 0.11 times the mass of the proton, it is still 207 times the mass of the electron, and muonium (Mu) thus behaves chemically as a light isotope of hydrogen (Walker, 1981). Moreover, the muon spin rotation (μ SR) detection technique provides much the same information as NMR and EPR for μ -substituted chemical species.

The most important result derived from these magnetic resonance techniques is that hydrogen atoms in water exist in virtually the same ground state as in the gas phase. The *g* factors of H, D, and Mu in water are the same as in gas phase, and the hyperfine splittings are only slightly perturbed (Eigen and Fessenden, 1971; Percival *et al.*, 1976). In addition, the EPR linewidths are extremely narrow. Fessenden *et al.* (1981) report T_2 for H' at room temperature as $10.5 \pm 2 \mu$ s. This implies that proton exchange between H' and the surrounding solvent occurs infrequently, if at all. Since hydrogen possesses two hyperfine lines, the effect of exchange on the relaxation will be given by (Atherton, 1973)

$$(T_2)^{-1} = (T_2^0)^{-1} + \frac{1}{2}k_{ex}.$$

It follows that the maximum possible exchange rate is $k_{ex} \approx 2 \times 10^5 \text{ s}^{-1}$.

Reaction rates of muonium with various solutes can be measured by the μ SR technique if sufficiently high concentrations of solutes are used. Reaction rates can vary for 10^{-2} to 10^2 times the corresponding hydrogen reaction rates, depending on the nature of the reaction (Ng *et al.*, 1981; Walker, 1981). How-

ever, for reactions of muonium with rates greater than $10^{10} \text{ M}^{-1} \text{ s}^{-1}$, the analogous hydrogen reaction rate is always very nearly identical. This finding strongly suggests that there is essentially no kinetic isotope effect in the limit of diffusion-controlled reactions (Ng *et al.*, 1981). This, in turn, implies that the diffusion rates of hydrogen and muonium in water are similar—a surprising result given the factor of 9 difference in their masses (Walker, 1981).

Benderski *et al.* (1980) have reported room temperature diffusion coefficients of $7 \times 10^{-5} \text{ cm}^2/\text{s}$ for H' in H_2O and $5 \times 10^{-5} \text{ cm}^2/\text{s}$ for D' in D_2O . In agreement with the muonium work, they proposed that diffusion of atomic hydrogen in water is controlled by librations and rotations of the solvent molecules. Hence, diffusion in D_2O is slightly slower due to the greater diffusion in D_2O is slightly slower due to the greater mass of the solvent molecule, and in any given $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture, all atomic hydrogen isotopes should have virtually the same diffusion rates.

Klein and co-workers have constructed a computer model of the H' solvation sphere which seems to account for all the observations listed above (DeRaedt *et al.*, 1984; Tse and Klein, 1983). The water solvent was simulated with classical mechanics and a simple effective two-body potential. The Feynman path integral approach was used to treat the single quantum impurity (H or Mu) (DeRaedt *et al.*, 1984). The minimum energy of the system is found when the water molecules form a hydrogen bonded network around the hydrogen. The calculated radial distribution functions indicate a cavity (nearly the same for both isotopes) of about 3 Å radius. The average coordination number was found to be about 18 water molecules for H and 23 for muonium. Overall, the calculated structure is very similar to that of a rare gas atom in water (Tse and Klein, 1983), with the atomic species clathrated within a large solvent cavity.

This structure explains one other apparent anomaly which has been of concern at Argonne. The self-combination reaction of two hydrogen atoms proceeds at room temperature at a "diffusion controlled" rate, and generates readily observable EPR signals due to the CIDEP phenomenon (Bartels *et al.*, 1986). One expects that the reaction rate will be given by the Smoluchowski equation modified for spin dependent reactions:

$$k_{rxn} = \sigma s (4\pi RD);$$

where *R* is the "reaction distance", *D* is the sum of reactant diffusion coefficients, *s* is a statistical factor equal to 1/2 for identical reactants, and σ is a spin statistical factor (Lehni and Fischer, 1983; Saltiel and Atwater, 1988; Trifunac *et al.*, 1986). For reactions which form singlet products, only one in four random encounters should be effective, and $\sigma = 1/4$. The lowest (and possibly the best) reaction rate for the H + H reaction was measured by Pagsberg *et al.* (1969) as $k_{rxn} = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Using $D = 1.4 \times$

$10^{-5} \text{ cm}^2/\text{s}$ (Benderski *et al.*, 1980) and the appropriate values for σ and s , one deduces a reaction distance $R \approx 5 \text{ \AA}$. This number appears to be far too large, since the interatomic potential of H_2 at 5 \AA separation is much less than kT (Herring and Flicker, 1964), and there is no reason for reaction to be more probable than diffusion of the atoms apart. The reaction rate agrees perfectly with the computer calculations (De-Raedt *et al.*, 1984; Tse and Klein, 1983), however, from which the sum of two $(\text{H}')_{\text{eq}}$ radii is roughly 6 \AA . Presumably, once two atomic species are trapped in the same "cavity", the probability of reaction (of singlet pairs) is nearly unity.

(B) Hydrated electrons

Prior to its experimental observation, the hydrated electron was the subject of much theoretical speculation (Platzman, 1962; Stein, 1952). The speculation continued even after its experimental observation (Hart and Boag, 1962) and was coupled with efforts to develop a model which could explain the observed properties. Such theoretical efforts were and are important because they provide a conceptual framework of the hydrated electron. For example, is the electron associated with one water molecule or with many? How many water molecules are in close proximity? Does the electron move by hopping from one trap to another in the solution or does it move by moving the water molecules along with it? What sort of order does the electron create in these solutions? The answers to these questions determine how one thinks about the electron and its chemical properties.

The spectrum of the solvated electron, its mobility, partial molal volume, and reactivity have all been measured (Hart and Anbar, 1970). Unfortunately these measurements by themselves are insufficient to determine the structure of the hydrated electron. Theoretical input is needed to help interpret the results. Until recently only static models for the electron in a fluid had been solved, because the dynamics problem was intractable. These calculations have primarily tried to predict the optical absorption spectrum of the hydrated electron. The predicted spectra were narrower than those that are measured experimentally (Newton, 1975). This has led to questions about the basic model of the electron in a fluid. Should it really be considered as an electron in a cavity, or is the electron associated with a particular molecule?

Recently, new theoretical methods have been applied to the study of electrons in polar fluids (Parrinello and Rahman, 1984). These models make use of the formalism of the Feynman path integral (FPI) to directly include the dynamic structure of water. The results of these calculations have provided considerable insight into the hydrated electron "structure" (Jonah *et al.*, 1986; Schnitker and Rossky, 1987; Wallqvist *et al.*, 1987). Previous theoretical models had predicted that the lowest energy

structure arranges four or six water molecules around the electron in a symmetrical form (Newton, 1975). However, the FPI calculations do not predict a shell structure around the electron; there exist distances which are more probable than others but the increase in probability is not very large.

The FPI and the traditional molecular orbital quantum mechanical models predict very different alignments of the water molecules around the electron. The sophisticated MO calculations of Newton (1975) predicted that the molecular dipole of the water molecules points toward the electron while the FPI calculations predict that an O—H bond points toward the electron. This difference can be understood by considering the differing approximations. In the molecular orbital models, the system was defined as an electron, 4 water molecules, and a dielectric continuum. In such a model, no hydrogen bonding between the core water molecules and the surrounding medium is included. Thus the energy penalty for the absence of any hydrogen bond to the surrounding water molecules is not assessed. In the FPI approach, a large number of water molecules are used, and thus the presence or absence of hydrogen bonds affects the total energy calculated. If both hydrogens of a water molecule point towards the electron, neither hydrogen can form a hydrogen bond. If, however, only one points toward the electron, the second O—H bond can hydrogen bond with another water molecule. Thus the loss of energy that occurs without having both O—H bonds pointing toward the electron is more than compensated by the additional hydrogen bond.

Until recently the predictions of the FPI calculations have not been experimentally verifiable. Rossky and co-workers have simulated the optical absorption spectrum of the hydrated electron by carrying out a molecular dynamics FPI simulation of the electron in water (Schnitker *et al.*, 1988). The configuration of all the water molecules was saved at different "times" during the simulation. From a given configuration of water molecules, the potential energy for a point charge can be determined. The Schrödinger equation is solved for this potential to give the transition energy and transition strength for the "1s \rightarrow 2p" optical absorption. This process was repeated for the series of different water configurations that occurred in the molecular dynamics simulation. The spectrum was then determined from the summation of the transition energies and strengths. The predicted spectrum was broader than the experimentally determined spectrum and also was at higher energy. This is in contrast to the previous predictions of the electron spectrum which were narrower than the experimentally determined spectrum. Calculations performed at Argonne using a similar technique but a different potential energy lead to results which are similar to the experimental curves (Romero and Jonah, 1989). These results are seen in Fig. 1. The relevance of the FPI calculations are supported by the

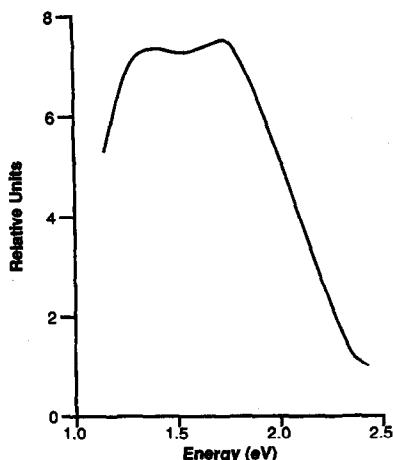


Fig. 1. The calculated spectrum using the Feynman Path Integral technique.

ability of two different simulations to give reasonable agreement to the experimental absorption spectrum and to make similar predictions as to the structure of the solvent around the hydrated electron.

The conclusions of these theoretical calculations are that the hydrated electron is not a charged species made up of an electron surrounded by 4 (or 6) water molecules but rather an amorphous, fluid structure. This means that energetics which are calculated based on rigid structures are questionable; the entropy of the system is highly important and there are many structures which contribute to the system.

(C) Dry electron reactions

A typical secondary electron will be formed initially with energy well above thermal energy. The route by which this energy is lost before solvation is difficult to determine because direct measurements are very difficult if not impossible. One of the few probes that exist is the measurement of reaction prior to solvation. Hunt and colleagues found that the initial (20 ps) yield of e_{aq}^- was reduced in the presence of scavengers (Lam and Hunt, 1975; Wolff *et al.*, 1970). Such reactions, often called dry electron reactions, can allow one to extract information about the importance of different energy states (Chernovitz and Jonah, 1988; Jonah *et al.*, 1977; Duplatre and Jonah, 1985; Lewis and Jonah, 1986). It has been found that the yield of solvated electrons remaining as a function of scavenger concentration can be described by the following equation:

$$\frac{G(c)}{G(0)} = \exp(-cQ_{37});$$

where c is the concentration of a scavenger, $G(c)$ is the yield of the solvated electron in the presence of a scavenger and $G(0)$ is the yield of the solvated electron in the absence of the scavenger.

In a recent study (Chernovitz and Jonah, 1989), the efficiencies of various presolvated electron scavengers, i.e. the Q_{37} values, in D_2O solution were found

Table 1. Measured values of Q_{37}

Scavenger	$Q_{37} (\text{M}^{-1})$ ($\text{H}_2\text{O}/\text{D}_2\text{O}$)
Acetone	0.7 ₁ /0.9 ₃
2,3-Butanedione	0.8 ₉ /0.8 ₅
Cd^{2+} (Perchlorate)	2.6 ₃ /2.7 ₈
Cu^{2+} (Perchlorate)	1.1 ₁ /0.80
$\text{Cr}_2\text{O}_7^{2-}$	8.3 ₃ /9.0 ₉
NO_3^-	2.3 ₆ /2.1 ₇
IO_4^-	7.1 ₄ /5.00
SeO_4^{2-}	2.3 ₃ /1.8 ₅

to be close to the previously reported values for H_2O (Jonah *et al.*, 1977; Duplatre and Jonah, 1985). These results are given in Table 1. Theoretical interpretation of new experimental data (discussed below) indicate that the distance the electron travels prior to thermalization is greater in D_2O than in H_2O . The similarity in the Q_{37} values, i.e. even with the increased thermalization distance for D_2O , decidedly suggest that the scavengers react with the electron in a localized state rather than with a more energetic subexcitation electron. This hypothesis is supported by the experimental data of Gauduel and co-workers (Migus *et al.*, 1987) who have used the recent advances in femtosecond laser pulse generation to directly observe an intermediate, localized electron state following the photolysis of liquid water (Jonah and Miller, 1977). This species absorbs light at 1250 nm, appears with a time constant of 110 fs, and relaxes in 240 fs to the hydrated state. Gauduel and colleagues (Gauduel, private communication) have recently observed that the rate of transfer of the absorption from the 1250 nm band to the 600 nm band of the electron is faster in the presence of dry electron scavengers. This signifies that the reaction of the scavengers with the localized electron is in competition with solvation.

II. PRIMARY EVENTS

(A) Participation of excited states

The role of H_2O excited states in the primary processes of liquid water radiation chemistry has long been debated (Draganic and Draganic, 1971; Farhataziz and Rogers, 1987), and unfortunately only a few new results can be cited in this review.

Chemical yields resulting from electron radiolysis of H_2O vapor have been analyzed by Willis and Boyd (1976) and the major processes together with their yields are indicated in Table 2. As has often been pointed out, the selection rules for excitation of molecules by energetic charged particles are the same

Table 2. Vapor phase radiolysis yields^a

Primary processes	G (process)
1. $\text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + e^-$	1.99
2. $\text{H}_2\text{O} \rightarrow \text{OH}^+ + \text{H} + e^-$	0.57
3. $\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH} + e^-$	0.67
4. $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}$	0.45
5. $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$	3.58

^aTaken from Willis and Boyd (1976).

as for optical excitation (Platzman, 1962). The lowest allowed transition in water is characterized by a continuum absorption (Herzberg, 1966). Excitation of this electronic surface results in immediate dissociation to give $H + OH$ (process 5 of Table 2). Higher transitions in the H_2O spectrum form Rydberg series converging to an ionization continuum at 12.6 eV. Vibrational structure can be resolved in these states, but the lines are strongly pre-dissociated. Within a few picoseconds, internal conversion to the lowest excited surface occurs, followed by immediate dissociation (Ashford *et al.*, 1984; Docker *et al.*, 1986). This explains the very large radiolysis yield for process 5 and the virtual absence of H_2O fluorescence. The ionic processes 1–3 result from excitation above the 12.6 eV ionization threshold (Tan *et al.*, 1978).

Comparison of the yields listed in Table 2 with the (30–100 ps) G values determined in liquid water raises the basic issue which must be resolved: why is the solvated electron yield ($G \geq 4.5$) so large (Jonah *et al.*, 1973; Sumiyoshi and Katayama, 1982), and why is the atomic hydrogen yield so small ($G \approx 0.6$) in the liquid? Bednar (1980, 1981, 1982) has estimated that virtually all of the oscillator strength associated with predissociated high Rydberg states in the vapor must be shifted from pre-dissociation to pre-ionization processes in order to account for the observed solvated electron yield. It seems clear that there are no H_2O excited states which persist much into the "chemical" time-scale ($t > 1$ ps). However, the relaxation dynamics of any excited states (excitons) which persist longer than one vibrational period may be important in determining the "initial distance distribution" which is the starting point for spur chemistry.

A promising approach to the study of this question appears to be the investigation of isotope effects in the initial yield of H^\cdot and D^\cdot in H_2O/D_2O mixtures. For any reaction involving the solvent molecules, one can define the relative isotope effect:

$$\alpha = \frac{(H/D)\text{product}}{(H/D)\text{water}}.$$

Measurements of this ratio were carried out some years ago for the atomic hydrogen formed in spurs of neutral and acidic water (Anbar and Meyerstein, 1968). It was found that formation of atomic hydrogen was strongly favored over atomic deuterium, especially in acid solution due to the $(H_3O^+)_\text{aq} + (e^-)_\text{aq}$ reaction in spurs. It was deduced that there must be an isotope effect in the H^\cdot, D^\cdot formation from excited state processes as well, characterized by $\alpha \leq 2.2$ in a 1:1 $H_2O:D_2O$ mixture (Anbar and Meyerstein, 1968).

Recent experiments at Argonne have begun to probe this isotope effect as a function of the water isotopic content (Bartels *et al.*, 1989). In strongly alkaline solution ($\text{pH} > 12$), fast neutralization of $(H_3O^+)_\text{aq}$ by $(OH^-)_\text{aq}$ prevents formation of atomic hydrogen in spur reactions. As explained in Section

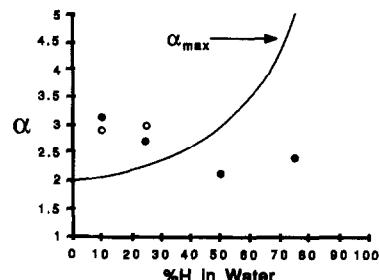


Fig. 2. Relative H/D isotope effect α vs proton content of a pH 13 water solution. (●), Argon saturated; (O) N_2O saturated. α_{max} is calculated assuming statistical excitation and unit quantum yield of dissociation for H_2 , D_2O and HDO . See text for details.

III, spin-dependent reactions of H^\cdot and D^\cdot in the spur give rise to CIDEP, allowing EPR detection of these species roughly 30–50 ns after a short radiolysis pulse (Bartels *et al.*, 1986). Assuming that the diffusion and reaction rates of H^\cdot and D^\cdot are identical in any given isotopic mixture (Section I), then the radical pair theory (Adrian, 1979) allows us to write (Bartels *et al.*, 1989):

$$S_H/S_D = \left(\frac{n_H}{n_D} \right) \cdot \left(\frac{3}{2} \right) \cdot \left(\frac{Q_H}{Q_D} \right)^{1/2} \approx 2.7 \cdot \left(\frac{n_H}{n_D} \right).$$

In this expression, S_H and S_D are the observed multiplet CIDEP signals, n_H and n_D are the actual numbers of H and D atoms, 3/2 accounts for the number of hyperfine lines, and the Q correspond to the difference in hyperfine energies between H or D and the solvated electron. The result of this calculation for several H_2O/D_2O mixtures containing 0.1 M NaOH are plotted in Fig. 2. The value of $\alpha = 2.1$ in a 1:1 H_2O/D_2O mixture is in excellent agreement with previous product yield measurements (Anbar and Meyerstein, 1968).

Due to the fast isotopic exchange in water, the mole fractions χ of H_2O , D_2O and HDO are given approximately by:

$$\begin{aligned} \chi(H_2O) &= f_H^2; \\ \chi(D_2O) &= f_D^2; \text{ and} \\ \chi(HDO) &= 2f_H f_D; \end{aligned}$$

where f_H is the mole fraction of proton and f_D is the mole fraction of deuteron in the water (Anbar and Meyerstein, 1968). Apart from a small blue shift of the D_2O spectrum, the energy loss functions of high energy electrons in H_2O and D_2O are virtually identical (Heller *et al.*, 1977) and in a mixture one can expect essentially statistical excitations of all three water species. One must consider four channels in the formation of H and D:

- (A) $H_2O^* \rightarrow H + OH$;
- (B) $D_2O^* \rightarrow D + OD$;
- (C) $HDO^* \rightarrow H + OD$;
- (D) $HDO^* \rightarrow D + OH$.

It is instructive to consider the maximum possible value of α in a given isotopic mixture *assuming* statistical excitation of the dissociating states. Presumably H and D are formed with unit quantum efficiency (as in the vapor) by dissociation of the lowest excited state. If all HDO* dissociated via channel C and none by channel D, then:

$$\alpha_{\max} = \frac{[\chi(\text{H}_2\text{O}) + \chi(\text{HDO})]/\chi(\text{D}_2\text{O})}{f_{\text{H}}/f_{\text{D}}}$$

This quantity is plotted in Fig. 2 along with the experimental values for α . It is clear from inspection of the figure that the dissociative state is *not* populated equally in all three isotopic molecules. In mixtures containing more D than H, $\alpha(\text{measured}) > \alpha_{\max}$. Even in the 1:1 and 3:1 H₂O/D₂O mixtures, the measured α values could only be obtained with unreasonably large branching ratios $k_{\text{C}}/k_{\text{D}} \approx 5-6$. It seems clear, therefore that the dissociative surface of O—H-containing molecules is somehow preferentially populated.

The greater yield of H atoms relative to D atoms can be explained by either a greater probability of the O—H bond to break or a greater probability for energy to localize in a molecule with an O—H bond. There is evidence which supports both hypotheses. The lifetimes of predissociated Rydberg states of H₂O vapor are typically several times shorter than those of corresponding states in D₂O (Ashfold *et al.*, 1984; Docker *et al.*, 1986). Presumably, this is due to the fact that O—H vibrations provide better promoting modes for the radiationless transitions. The same argument should hold in the liquid, where a competing process is autoionization and the formation of solvated electrons. The latter process would be favored in D₂O over internal conversion and dissociation. Alternatively, excited states (excitons) in the liquid can be postulated, and even though short-lived ($\tau \leq 1 \text{ ps}$), they could transfer excitation from one molecule to the next. The HDO and H₂O molecules would then act as shallow "traps" for this excitation energy, because their v_{∞} transitions are slightly red-shifted relative to D₂O (Ashfold *et al.*, 1984; Docker *et al.*, 1986; Heller *et al.*, 1977). Subsequent internal conversion would naturally favor dissociation of O—H bonds. Similar exciton trapping has actually been observed in isotopically mixed ice at low temperature (Judeikis *et al.*, 1962).

(B) Solvation

The mechanism of electron solvation has been a subject of much discussion, as summarized in a review paper by Kenney-Wallace and Jonah (1982). Some of the major questions are: does the electron create a trap for itself or does it solvate in a pre-existing trap within the liquid—a density fluctuation? Does the solvation process occur from the outside in or the inside out? That is, does the electron rearrange the water molecules near it, followed by water molecules further away? Or is the electron very

delocalized so it first polarizes the distant water molecules? This polarization then creates a potential well which starts to localize the electron. The localization will increase the charge density so that the molecules nearer the center of the electron charge distribution will be rearranged, and the process continues until the electron is totally solvated. One also would like to know if the longitudinal relaxation time is an appropriate measure for the solvation process. That is, is the appropriate parameter for solvation time the rotation time of the molecule in pure solution modified by terms for high fields and dielectric constants? How large a structure is needed in a polar fluid to solvate the electron? Are two molecules enough for solvation or four, or many more? The evidence cited in these discussions has come from measurements of the solvation time of the electron in alcohols, deduced from the growth of the solvated electron absorption e_{sol}^- in the visible, and the decay of an absorption in the near infra-red. This absorption change was assigned to the solvation process of the electron.

Until very recently it has not been possible to observe any growth in the absorption of the hydrated electron e_{aq}^- . However, in the last two years results at the Ecole Polytechnique (Gauduel *et al.*, 1987; Migué *et al.*, 1987) have displayed the time dependence for the absorption spectrum of the e_{aq}^- . These experiments resolved the growth of an absorption in the near infra-red with a time constant of approx. 110 fs. This absorption then decayed and the visible absorption of the solvated electron grew in with a time constant of about 240 fs. Previous measurements determined that the solvation time was less than 300 fs (Wiesenfeld and Ippen, 1980). The theoretical implications of these measurements have yet to be explored in detail. Further analysis of experiments with 100 fs time resolution will provide important insights into the solvation mechanism of the electron.

There have also been recent theoretical advances on the question of the role of preformed traps in electron solvation. Two of these studies have used a molecular dynamics simulation of water, albeit very different facets of such calculations. Schnitker *et al.* (1986) have explored the existence of preformed traps in water. A given configuration of water molecules that arose from their molecular dynamics calculation was searched for the existence of a low potential energy region, i.e. a preformed trap. They found that there always appeared to be at least one position in their simulated fluid where the potential was sufficiently low that the electron might be solvated. However they did not calculate whether an FPI simulation of the electron would indeed localize.

A different approach was used by Jonah *et al.* (1986). As was done by Schnitker and co-workers, a configuration of water molecules was created from a molecular dynamics simulation of pure water. However, instead of searching for a potential minimum, the water molecules were fixed in space and the FPI

representation of the electron was added to the system (see Section I). The quantum molecular dynamics of the system was followed to see if the representation of the electron would localize, presumably in a preformed trap. No localization was found for the small number of water systems that were studied.

Different conclusions can be inferred from these two calculations about the importance of preformed traps in the solvation of the electron. However Schnitker and co-workers (1986) did not show that the electron would indeed localize in their system while Jonah and co-workers did not show that the few configurations that they tried were "typical" and did contain low potential energy regions. Clearly both points need to be addressed in future studies.

III. SPUR PROCESSES

(A) Initial distribution

The nature of the initial spatial distribution of the ions and radicals produced by radiolysis is of central importance to the primary processes involved in the deposition of energy, in spur kinetics, and to the complete chemistry of the system. The initial distribution of the distance of the hydrated electron from the initial positive water ion depends upon the journey of the electron during the thermalization processes. The further the electron travels, the recombination reactions involving the ions and radicals created by the ionizing event(s) become less probable and the reactions of these ions and radicals with other components in the solutions become more likely.

Previously there have been no attempts to model the spur in D_2O . Recently however, experimental information about the initial distribution of the primary species e_{aq}^- and OH in spurs has been gathered and interpreted in terms of existing mathematical models (Chernovitz and Jonah, 1988). The radiation chemistry of D_2O corresponds very closely to that of H_2O ; however, there is sufficient difference between D_2O and H_2O , such as the vibrational frequencies and diffusion coefficients in these solvents, that an isotope study has provided new information about the distributions of primary radiolysis species.

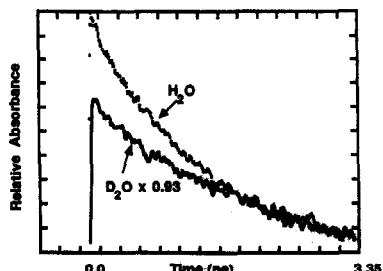


Fig. 3. Absorption of the solvated electron at 600 nm as a function of time in H_2O and D_2O . Note that the absorption in D_2O has been multiplied by 0.93 so that the curves correspond at 3 ns. These data do not mean that the initial absorption or yield of the electron is higher in H_2O than in D_2O .

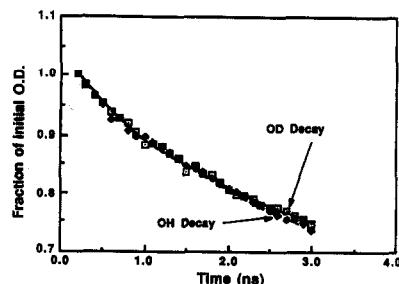


Fig. 4. Decay of the absorption of the OH (OD) radical at 281 nm.

The results shown in Fig. 3 indicate that there is a large difference between the rates of decay of the electron in H_2O and D_2O solutions at early times. A 10% decay of the electron takes 2.5 times longer in D_2O than in H_2O . These curves were normalized at 3 ns to show that there is a pronounced difference in decay rates only at early times. The results *do not* show a greater yield of the aqueous electron in H_2O . Previous studies (Hart and Anbar, 1970) of the reactions of the hydrated electron in D_2O with e_{aq}^- (D_2O), D, OD and D_2O^+ have found that the rate constants for these reactions differ by less than 20% compared to the rate constants for the corresponding reactions in H_2O . Therefore the difference in the kinetics cannot be due to a difference in the rate constants.

Recently the decay of the hydrated electron has been measured to 50 ns after the electron pulse in H_2O and D_2O and in 0.1 M NaOH and NaOD solutions (Jonah and Chernovitz, unpublished results). On this time scale no difference was observed between the decay in H_2O and D_2O after normalizing the curves with respect to each other. Figure 3 illustrates that the difference in the decay rates that occurs at very early times (0–2 ns) as seen via the picosecond experiments discussed above disappears at later times. As the time interval increases relative to the electron pulse, ions and radicals within the spur diffuse away from one another and the distribution is dominated by the diffusion process rather than the initial distribution. Thus, the H_2O and D_2O systems become increasingly similar at longer times.

The decays of the OD and OH radicals have been determined at 281 nm and are shown in Fig. 4 (Chernovitz and Jonah, 1989). There is virtually no difference between the two decay curves. From 200 ps to 3 ns, OD decays to a fraction 0.75 ± 0.06 of its initial absorbance, which is very close to the fraction 0.74 ± 0.06 for the OH radical. Since the initial spatial distribution for the hydroxyl radical is much tighter and, therefore, more concentrated than for the hydrated electron, the OD radical was found to decay more quickly than e_{aq}^- (D_2O). Similar results have been previously reported for OH and e_{aq}^- (Jonah and Miller, 1977).

The slower decay of the electron in D_2O has been

interpreted in terms of simple theoretical considerations. The kinetic energy of an electron in excess of the electronic excitation threshold of water is lost very rapidly, and most of the electron's travel occurs as a "subexcitation" electron. The subexcitation electron loses most of its energy to the vibrational modes of the solvent molecules. The most energetic vibrational mode of water is the O-H (O-D) antisymmetric stretch which has a frequency that is approximately $\sqrt{2}$ greater in H_2O than in D_2O . Therefore $\sqrt{2}$ more collisions are needed in D_2O than in H_2O to dissipate the excess energy of the electron, and the electron may be expected to travel a greater distance in D_2O compared to H_2O .

Since it is assumed that most of the energy is lost before the electron has traveled very far, the distribution of OH radicals is not expected to be markedly different from that of the OD radicals. Thus the H_2O and D_2O systems may be simulated assuming the electron distribution is broader in D_2O while the OH distribution remains unchanged for the D_2O environment.

A simple diffusion kinetic calculation was performed to see if these qualitative suggestions are consistent with the experimental results (Chernovitz and Jonah, 1988). This type of calculation is not expected to give quantitative results for reasons that are well-discussed in the literature (Clifford *et al.*, 1982a, b; Green *et al.*, 1984) but can be expected to correctly predict the trends that a change in distribution would give. The model that was selected for the radiolysis in H_2O was that formulated by Trumbore and co-workers (1978), because its predictions of the electron and OH decay in H_2O are in reasonable accord with the experimental data. This spur model assumes that all of the radiation-generated products are distributed in a Gaussian fashion except for the electron which is distributed in a spherical shell around the OH distribution.

The parameters for the H_2O system were precisely those of Trumbore. In line with the discussion above, the radius for the electron distribution was increased approx. 30% for D_2O while all the other parameters were left unchanged. The results of these calculations can be compared with our experimental results. As shown in Chernovitz and Jonah (1988), the change in decay of e_{aq}^- over the time range 0–3 ns is well described by the change in distribution although the actual decays are not precisely predicted by the calculation in either solvent. Similarly, the decay rate of e_{aq}^- at long times in the two solvents are predicted to be the same, in accord with the experimental results. The ratio of the yield of the electron in H_2O to that in D_2O at long times is in excellent agreement with the experimental results of Fielden and Hart (1968) (calculated ratio is 1.10 while the experimental value is 1.11). As discussed above, the decay of the OH radical is the same within experimental error as that of the OD radical. This experimental result is also predicted by the simple calculation and can be

attributed to the similarity of the OH and OD distributions in the two isotopic variants of water.

In summary, experimental measurements show that the change from H_2O to D_2O leads to a considerable change in the decay of e_{aq}^- on the time scale 0–3 ns but very little change for times greater than 3 ns. These results suggest that the distribution of the electron is broader in D_2O than in H_2O , which is consistent with simple energy loss considerations. Diffusion kinetic calculations show that a broader distribution of e_{aq}^- in D_2O than in H_2O will explain the experimental data.

(B) Spin dependent chemistry

Since most spur chemistry is free radical in nature, it is largely controlled by electron spin: to form a stable singlet product the spins must be properly paired (Saltiel and Atwater, 1988). Radiolysis of low dielectric liquids usually results in very fast recombination of most geminate radical ion pairs—fast due to the coulombic attraction, but also because the electron spins retain their singlet pairing even when separated (Brocklehurst, 1983, 1985). A number of very elegant magnetic resonance techniques have been devised to study these processes, based on conversion of the singlet spin configuration to triplet, thereby frustrating the recombination (Brocklehurst, 1985; Trifunac *et al.*, 1986). The lower recombination probability is typically detected as a reduction in yield of some product or recombination fluorescence.

In water, ion recombination is not nearly so fast due to the high dielectric constant. However, water also differs in that the spin coherence of geminate pairs decays very quickly. All geminate pairs include OH as one of the radicals, and OH is known to have an electron T_1 in the sub-nanosecond range (Verma and Fessenden, 1976). Thus, most free radical encounters in water spurs will occur with random spin orientations, and one can expect only 1/4 of the encounters to result in reaction (Saltiel and Atwater, 1988; Trifunac *et al.*, 1986).

Spin correlation effects in radiolysis spurs have been considered extensively by Brocklehurst (1982, 1983, 1985). In particular, Brocklehurst has worked out the spin dynamics for recombination in a spur consisting of two geminate H^\cdot , R^\cdot pairs and then applied the results to acidic water solutions (where $R^\cdot = OH^\cdot$). The specific prediction was made that the ortho/para content of H_2 and D_2 products should differ greatly from the thermal equilibrium ratio, and that HD formed in H_2O/D_2O mixtures would exhibit very large CIDNP polarizations (Brocklehurst, 1982). The latter prediction was tested at Argonne using proton NMR in D_2O solution with *ca* 1% H content, but no unusual CIDNP effects were discovered (Trifunac *et al.*, 1986). The CIDNP observed in HD was adequately explained in terms of the radical pair theory for random encounters.

It has already been noted that EPR is a natural choice for the study of hydrogen reactions in water

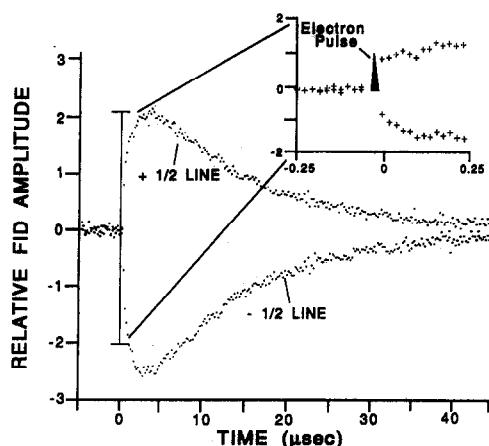


Fig. 5. H' atom signals observed in water ($\text{pH} = 1$) following a 5 nC radiolysis pulse. The low field line is seen in emission (negative signal) and the high field line exhibits enhanced absorption, characteristic of radical pair mechanism CIDEP. The inset illustrates that some polarization is generated during the radiolysis pulse in radiation spurs (Bartels *et al.*, 1986).

radiation chemistry. However, it is not at all obvious that magnetic resonance can be applied to the very old problem of aqueous spur chemistry, given the relatively slow time resolution (*ca* 10 ns) afforded by these methods. Observation of CIDNP in HD formed in spurs suggested that an "initial" or prompt H atom CIDEP signal should also be detectable by EPR. It must be emphasized that no prompt signal would be observable if spin-dependent reactions of H in spurs did not occur, since there is no reason to expect preferential formation of α and β electron spin states in the radiolysis and the normal T_1 relaxation of H' in water is many microseconds (Fessenden *et al.*, 1981). The "memory effect" of CIDEP and CIDNP is responsible for the presence of the signal from spurs and also gives an indication of the reaction mechanism.

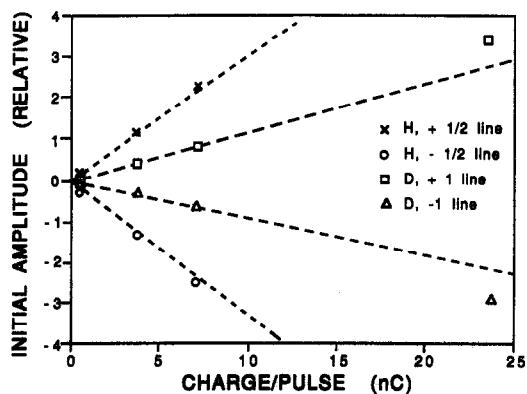


Fig. 6. Plot of relative initial signal amplitudes versus charge per pulse for the $+1/2$ and $-1/2$ lines of H' (in H_2O) and the $(+1)$ and (-1) lines of D' (in D_2O). The linear dependence for short pulses (< 25 ns, 7 nC) indicates that the initial signal arises from spur chemistry rather than from random encounters (F pairs) (Bartels *et al.*, 1986).

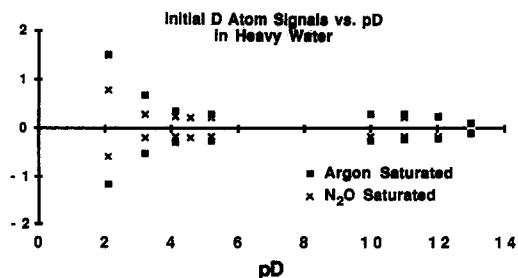


Fig. 7. Initial CIDEP signal from D' in D_2O radiolysis spurs. The low field line is in emission (negative signal) and high field line in absorption, characteristic of random (nonspin-correlated) encounter pairs.

The typical H atom kinetic signal in water is shown in Fig. 5, where we plot the signals observed from the $+1/2$ and $-1/2$ lines of H following radiolysis of the sample with a 5-ns, 0.7-nC electron pulse. The low-field ($+1/2$) line is observed in emission, and the high-field ($-1/2$) line exhibits enhanced absorption, as predicted by the (ST_0) radical pair mechanism (RPM) of CIDEP (Adrian, 1979). The initial signal ($t = 0$) corresponds to polarization of H atoms during the pulse, whereas the subsequent growth is due to RPM polarization from random encounters (F -pairs) of uncorrelated H atoms. In contrast to optical experiments where the number of species is measured as a function of time, the EPR experiment at early times counts the number of H atom *reactions*.

The problem facing us is the precise and unambiguous separation of the signal arising in spurs from the CIDEP subsequently generated in homogeneous solution. To take full advantage of the time resolution afforded by pulsed EPR techniques (Trifunac *et al.*, 1986), a 25-ns $\pi/2$ probe pulse is applied immediately (within 10 ns) after a short electron pulse, and the magnetic field is scanned. The amplitudes of these spectra are measured and plotted as a function of the charge in the radiolysis pulse as shown in Fig. 6. The amplitude of any signal from spurs should be linearly dependent on the dose, whereas CIDEP generated in homogeneous solution follows a second-order rate law. The initial signals plotted in Fig. 6 show a linear dependence on dose for pulses of 25 ns and shorter. At higher H' , D' concentrations (longer pulse

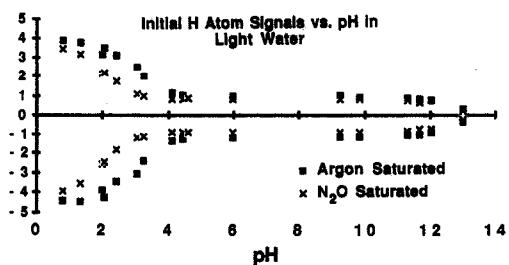


Fig. 8. Initial CIDEP signal from H' in H_2O radiolysis spurs. The low field line is in emission (negative signal) and high field line in absorption, characteristic of random (nonspin-correlated) encounter pairs.

lengths), RPM polarization via *F*-pairs becomes important during the electron pulse due to spur overlap, and the signal intensity is no longer a linear function of beam current. This is demonstrated by the failure of the 24-nC, 55-ns pulse data for D', to fall on the line extrapolated from shorter pulses.

This experiment has now been carried out for a wide range of pH (pD) conditions and in mixtures of varying H/D isotopic composition (Bartels *et al.*, 1989). Some results are plotted in Figs 7 and 8. The increased signal of both H' and D' in acid solution is certainly due to the fast conversion of the solvated electron to hydrogen via the reaction of $(H^+)_\text{aq}$ with $(e^-)_\text{aq}$. A small decrease (*ca* 10%) in signal amplitude can be detected between pH (pD) 10 and 12, which corresponds to the scavenging of $(H^+)_\text{aq}$ from the spur by OH⁻, thereby preventing any conversion of $(e^-)_\text{aq}$ to H'. Above pH 12, the reaction of H' and OH⁻ to give $(e^-)_\text{aq}$ is fast enough to interfere with the FID detection technique (resulting in signal attenuation), but the initial H' CIDEP appears not to change. Saturation of the solutions with N₂O causes attenuation of the initial signal in basic as well as acidic solutions. In acid, the reduction is easily explained in terms of the competition between $(H^+)_\text{aq}$ and N₂O for the solvated electrons. In neutral and basic solution, the loss of signal reveals the CIDEP mechanism: scavenging of $(e^-)_\text{aq}$ prevents some spin-dependent reactions of H' + $(e^-)_\text{aq}$, thereby reducing the signal.

Close inspection of Figs 7 and 8 reveals that the absolute amplitudes of the low and high field lines are not the same, which would be the case for pure ST, radical pair CIDEP (Adrian, 1979). The asymmetry increases with N₂O saturation in D₂O, but becomes less pronounced in H₂O. This additional information allows one to identify at least four different polarization mechanisms. A simple diffusion kinetics model has been used to reach a qualitative understanding of the phenomenon, but quantitative agreement with experiment is not at hand. We expect that CIDEP data of this type will serve as an excellent diagnostic for improved spur kinetic models in the future.

SUMMARY

In the last several years there have been very significant advances in the understanding of the primary processes in aqueous radiation chemistry. The structure of intermediates such as e⁻_{aq} and H have been clarified. The role of excited states and the migration of energy in water have been probed. New information about initial distributions of electrons and other primary species have come from measurements in H₂O and D₂O. Innovative experiments have provided information about the solvation processes in liquids. All of these advances have created a new vision of water radiolysis.

However, not all problems have been solved. For example, the isotope-dependence experiments pose as

many questions as they answer. The difference in initial distributions between normal and deuterated water that the electron decay measurements suggest must derive from the differing cross sections for low-energy electron scattering and energy loss. However, at present there is no method for simulating the experimental data. New calculational techniques may well be necessary.

Recent measurements also provide a new insight into old problems. The data from the EPR measurements in normal and deuterated water suggest a role for an excited water state. While such states have been often hypothesized, convincing evidence for their existence has been lacking. The EPR measurements should provide a new impetus to look at old data and to formulate new experiments to better understand the role of excited solvent molecules in radiolysis.

Theoretical measurements have given us contradictory views of the role of preformed traps in solvation. Further sub-picosecond experiments are necessary to provide differentiation between the multiple possibilities that are presently consistent with the experimental and theoretical facts.

Edwin J. Hart is fond of reminding us that he was told that the radiation chemistry of water was completely understood back in 1950 and that he was foolish for continuing to study it. Since that time the hydrated electron was discovered, spur chemistry was demonstrated and radiation chemistry was developed as a tool for the study of fast chemical processes. The advances in the last few years have shown that aqueous radiation chemistry continues to provide important new insights into reaction mechanisms, structure and dynamics in the liquid state.

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