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Dependence of Molecular Hydrogen Formation in Water on Scavengers of the Precursor to the Hydrated Electron

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Molecular hydrogen yields have been measured in the γ radiolysis of aqueous solutions with a wide variety of scavengers of the hydrated electron and its precursors. A decrease in molecular hydrogen yield with increasing scavenging capacity of the hydrated electron is found with all solutes. Scavengers with particularly high rate coefficients for reaction with the precursors to the hydrated electron compared to the hydrated electron, such as selenate and to a lesser extent molybdate, show a more rapid decrease in hydrogen yields with increasing scavenging capacity than is observed with the other solutes. The yield of molecular hydrogen is better parametrized by the scavenging capacity for the precursors to the hydrated electron than by the scavenging capacity for the hydrated electron. Good scavengers of precursors to the hydrated electrons do not exhibit a "nonscavengable" hydrogen yield in the high scavenging capacity limit. These results suggest that the previously accepted "nonscavengable" yield of molecular hydrogen is due to precursors of the hydrated electron and it can be lowered with appropriate scavengers.

Introduction

Early studies on the radiolysis of water suggested a wide variety of precursors, and mechanisms, for the formation of the observed yield of molecular hydrogen.[1−15] Experiments using selected scavengers over a wide range of concentrations[16,17] and the use of a quantitative spur model for the radiation chemistry of water[18] strongly indicated that the following reactions are responsible for most of the formation of molecular hydrogen.

$$e_{aq}^{-} + e_{aq}^{-}\ (+2H_2O) \rightarrow H_2 + 2OH^{-} \qquad k_1 = 5.5 \times 10^{9}\ M^{-1}\ s^{-1} \quad (1)$$

$$e_{aq}^{-} + H\ (+H_2O) \rightarrow H_2 + OH^{-} \qquad k_2 = 2.5 \times 10^{9}\ M^{-1}\ s^{-1} \quad (2)$$

$$H + H \rightarrow H_2 \qquad k_3 = 7.8 \times 10^{9}\ M^{-1}\ s^{-1} \quad (3)$$

The rate coefficients are taken from the compilation of Buxton et al.[19] Further examination of the data[20] and the predictions of sophisticated Monte Carlo diffusion calculations[21] suggested that the above reactions may account for almost 70% of the observed yield of molecular hydrogen in the γ radiolysis of water. Even with this general success in describing the radiolysis of water and aqueous solutions, there has been no universally acceptable explanation for the mechanism responsible for the production of the remainder of the molecular hydrogen yield.

The yield of molecular hydrogen generally exhibits a steady decrease with increased scavenging capacity for the hydrated electron.[4,16,17,20,21] Here, scavenging capacity is defined as the product of the solute concentration and the rate coefficient for the scavenging reaction with the hydrated electron. Schwarz was the first to recognize that the yield of hydrogen was almost uniquely determined by the scavenging capacity of the solution for the hydrated electron in the low scavenging capacity regime.[4] He also observed that at very high scavenging capacity, the molecular hydrogen yield appeared to reach a limiting plateau of about 0.15 molecules/100 eV of energy absorbed. This limiting yield has been called the "nonscavengable" hydrogen yield, and it was believed to be due to some unknown unimolecular process in the decomposition of water. "Nonscavengable" hydrogen has been incorporated into virtually all models of the radiation chemistry of water since the pioneering work of Schwarz.[18]

Recent experiments on the scavenging of precursors to the hydrated electron have suggested that the use of selected scavengers can significantly alter the expected outcome.[22] These experiments clearly show that the yields of products found from the reduction of selenate, a good scavenger of precursors to the hydrated electron, are significantly higher than expected from reaction with the hydrated electron alone. Model calculations suggest that the radiation chemistry of selenate and other good scavengers of precursors to the hydrated electron can be understood and are predictable.[23] Since a wide variety of compounds have been examined as scavengers of precursors to the hydrated electrons,[24−27] this work was undertaken to examine their possible role in the formation of molecular hydrogen and to determine whether scavengers of the precursors to the hydrated electron can affect the yield of "nonscavengable" hydrogen.

The formation of molecular hydrogen has been examined in the γ radiolysis of water in the presence of the electron scavengers: SeO_4^{2-}, MoO_4^{2-}, $Cr_2O_7^{2-}$, NO_2^{-}, NO_3^{-}, Cd^{2+}, Cu^{2+}, and H_2O_2. Some of these scavengers, such as the selenate and molybdate anions, are known to scavenge precursors to the hydrated electron efficiently and the hydrated electron poorly.[27] The remaining scavengers react with both precursors and the hydrated electron with similar efficiencies. Therefore, it should

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be possible to distinguish between the effect of the scavenging of precursors to the hydrated electron and that of the scavenging of the hydrated electron.

Experimental Section

Hydrogen was measured using an inline gas chromatography technique. The experimental set up consisted of a well-regulated argon stream that continuously bubbled through a sample cell made from a 1 cm quartz cuvette. A four-way valve allowed the cell to be isolated from the argon stream during the course of the radiolysis. Opening the valve sent a surge of the volatile products to the chromatographic column, a 3 m silica gel at 22 °C, and they were observed with a thermal conductivity detector. A septum for the injection of calibration gases was placed upstream from the sample cell. The gas flow through the sample was 30 mL/min, and the volume of the sample was 4 mL.

The solutions were prepared with triply distilled water, and they consisted of 1 mM of KBr (to scavenge the OH radicals) with the electron scavengers at different concentrations. All the chemicals were from Aldrich, and they were used without further purification.

The irradiations were performed using a Shephard ^{60}Co γ source with a dose rate of 30.6 krad/min. The source was calibrated by observing the oxidation of ferrous ions in the Fricke dosimeter using the same sample cell and configuration as in gas analysis. The production of Fe^{3+} was determined spectrophotometrically at 304 nm and 25 °C with an extinction coefficient of 2194 M^{-1} cm^{-1} and 15.45 molecules/100 eV for the yield of Fe^{3+}.[28] The density of 0.8 N sulfuric acid was taken to be 1.025 g/cm^3.[2] The absorbed dose for each sample was corrected according to its electron density.

All the molecular yields were found to be linear with dose in the range of 150 krads to 1.4 Mrads. The results are reported for doses of 600 krads. The limit of the sensitivity of the measurement of hydrogen has been determined experimentally to be 1 μM. This value corresponds to a lower detectable limit of the hydrogen yield equal to $\Delta G(H_2) = 0.02$ molecules/100 eV in the case of a 20 min irradiation with a 4 mL sample (typical conditions). Calibrations with hydrogen were performed after each measurement, and the system was continuously monitored for air leaks and extraneous hydrogen outgassing. Total estimated errors in the hydrogen measurements are ±10%.

Results and Discussion

All of the experiments were performed with 1 mM KBr to remove the OH radicals that would otherwise react with the molecular hydrogen. The rate constant for OH and Br^- is 1.1×10^{10} M^{-1} s^{-1} while that for OH and H_2 is 4.2×10^7 M^{-1} s^{-1}. Only at concentrations of molecular hydrogen above a few tenths molar, an unlikely scenario in these circumstances, is interference from the OH radicals feasible. On the other hand, the OH radical lifetime is on the order of a few hundred nanoseconds, and its scavenging by Br^- will have no noticeable effect on the kinetics of the hydrated electron.

Figure 1 shows the molecular hydrogen radiation chemical yields, $G(H_2)$ expressed in molecules/100 eV of energy absorbed, determined in the presence of different concentrations of H_2O_2 and $Cr_2O_7^{2-}$. There is good agreement between the present results and those of other investigators.[4,8,16−18] The general trend of the data as a function of scavenger concentration is well-known and is easily explained in terms of the chemistry of the spurs produced by fast electrons.[18] Energy deposited by the radiation leads to a series of isolated clusters of reactive radical species, a spur, each characterized by a nonhomogeneous distribution of those species. Reactions 1−3, 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 among radical−radical reaction, diffusion, and scavenging. At very low scavenger concentrations, the nonhomogeneous spatial distributions of the reactants in the spur will be completely relaxed before scavenging occurs with those radicals that have escaped the spur reactions and are homogeneously distributed in the medium. It can be seen in Figure 1 that the escape yield of molecular hydrogen is about 0.45 molecules/100 eV.

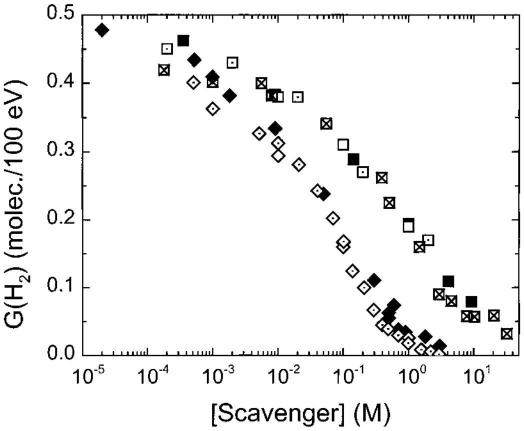

Figure 1. Molecular hydrogen formation as a function of the concentration of different solutes: (■) H_2O_2, (◆)$Cr_2O_7^{2-}$, this work; (□) H_2O_2, (◇) $Cr_2O_7^{2-}$, ref 16; (⊡) H_2O_2, ref 17; (cross in square) H_2O_2, ref 8; (dotted diamond) $Cr_2O_7^{2-}$, ref 7.

With increasing solute concentration, the chemistry within the spur is being probed at shorter times. The effective lifetime of the radical is inversely proportional to the scavenging capacity, and one does not expect the molecular hydrogen yield to be uniquely determined by the solute concentration. The molecular hydrogen yield exhibits a different concentration dependence for $Cr_2O_7^{2-}$ than for H_2O_2 because of the difference in the rate coefficients for H_2O_2 (1.1×10^{10} M^{-1} s^{-1}) and $Cr_2O_7^{2-}$ (2.9×10^{10} M^{-1} s^{-1}) reactions with the hydrated electron. The results presented suggest that the lower limit for the yield of molecular hydrogen is well below 0.15 molecules/100 eV, as previously accepted.[18]

Experiments with a variety of scavengers over a wide concentration range are required to gain more insight on the formation of molecular hydrogen. However, this approach necessarily requires knowledge of the rate coefficient for the hydrated electron scavenging reaction at high solute concentrations. Rate coefficients for reaction between ionic species can be very dependent on the concentration of neighboring ions, which may alter the long-range Coulombic fields, affect the diffusion of the reactive species, or change the viscosity of the medium.[29,30] Furthermore, high solute concentration will lead to a time-dependent change in the rate coefficients as the solute concentration gradient evolves.[31] Unfortunately, it is difficult to take these effects into account theoretically.

The rate coefficient for the reaction between the selenate anion and the hydrated electron was assumed to be constant for all concentrations following the results in ref 22. Table 1 gives a list of the solutes used here, the rate coefficients, and the observed molecular hydrogen yield. Unpublished results for molybdate also suggest that its rate coefficient for reaction with hydrated electrons is constant over the range of concentrations used here. It has been proposed that for large anions the diffusion-controlled rate coefficient gives a reaction radius larger

TABLE 1: Concentrations and Rate Coefficients of the Scavengers Used Here

scavenger concentration (M)	k_o (M^{-1} s^{-1})	k_{is}/k_o	k_j/k_{is}	$G(H_2)$ molecule/100 eV
$K_2Cr_2O_7$				
0.00002	2.9×10^{10}	1.000	1.001	0.478
0.00052		1.000	1.007	0.434
0.001		1.000	1.009	0.409
0.00183		1.000	1.012	0.382
0.009		1.000	1.027	0.334
0.05		1.000	1.064	0.238
0.1		1.000	1.091	0.166
0.3		1.000	1.157	0.111
0.5		1.000	1.203	0.059
0.6		1.000	1.222	0.074
0.7		1.000	1.240	0.038
0.9		1.000	1.272	0.035
1.8		1.000	1.385	0.028
3.0		1.000	1.497	0.014
$Cd(ClO_4)_2$				
0.000045	4.8×10^{10}	0.9771	1.013	0.462
0.001		0.9042	1.056	0.405
0.0229		0.7041	1.183	0.340
0.0865		0.5976	1.273	0.319
1.064		0.4507	1.571	0.273
H_2O_2				
0.000356	1.1×10^{10}	1.000	1.004	0.462
0.009		1.000	1.018	0.383
0.1435		1.000	1.070	0.289
1.0		1.000	1.175	0.194
4.1		1.000	1.307	0.109
9.225		1.000	1.396	0.079
Na_2SeO_4				
0.001	1.1×10^{9}	1.000	1.000	0.428
0.01		1.000	1.001	0.410
0.05		1.000	1.002	0.371
0.1		1.000	1.003	0.322
0.2		1.000	1.004	0.242
0.4		1.000	1.005	0.206
1.0		1.000	1.008	0.144
1.669		1.000	1.010	0.104
$Cu(ClO_4)_2$				
0.0000918	3.3×10^{10}	0.9678	1.014	0.461
0.00472		0.8219	1.078	0.370
0.1105		0.5793	1.213	0.290
1.05		0.4512	1.402	0.217
Na_2MoO_4				
0.00052	2.0×10^{9}	1.000	1.000	0.449
0.0025		1.000	1.001	0.423
0.01		1.000	1.002	0.381
0.027		1.000	1.003	0.362
0.04		1.000	1.003	0.341
0.1		1.000	1.005	0.288
0.2		1.000	1.007	0.251
0.3		1.000	1.008	0.227
0.4		1.000	1.010	0.222
0.7		1.000	1.013	0.191
1.05		1.000	1.016	0.170
2.0		1.000	1.022	0.128
$NaNO_3$				
0.000113	9.7×10^{9}	1.011	1.002	0.436
0.00113		1.034	1.006	0.460
0.00576		1.075	1.014	0.426
0.0112		1.103	1.020	0.387
0.0227		1.143	1.030	0.367
0.045		1.195	1.045	0.308
0.1		1.278	1.074	0.291
1.0		1.665	1.326	0.106
KNO_2				
0.0008	4.1×10^{9}	1.028	1.001	0.467
0.00824		1.089	1.005	0.397
0.0421		1.190	1.013	0.343
0.0927		1.269	1.020	0.331
1.0		1.665	1.092	0.202

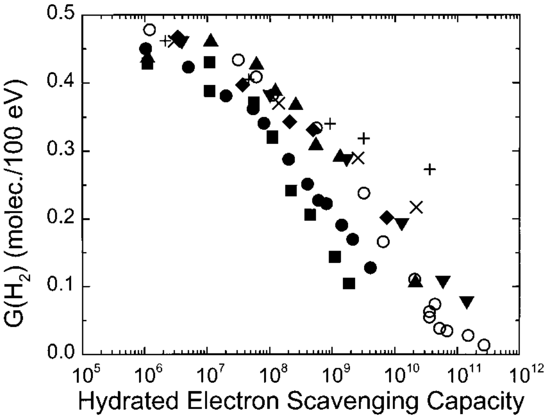

Figure 2. Molecular hydrogen yields as a function of the hydrated electron scavenging capacity: (■) SeO_4^{2-}, (●) MoO_4^{2-}, (▲) NO_3^-, (◆) NO_2^-, (▼) H_2O_2, (○) $Cr_2O_7^{2-}$, (+) Cu^{2+}, and (×) Cd^{2+}, this work.

than the expected physical radius because of tunneling.[31] Following this argument, it is expected that the rate coefficient for dichromate will be more or less invariant with concentration.

Rate coefficients for the reactions between the hydrated electron and the NO_2^-, NO_3^-, Cd^{2+}, Cu^{2+} ions were corrected for the ionic strength using the extended Bronsted–Bjerrium treatment as given by Davies's formula:[32]

$$\log \frac{k}{k_0} = 1.02 Z_A Z_B \left[\frac{\sqrt{\mu}}{(1 + \alpha \sqrt{\mu})}\right]$$

where Z_A and Z_B are the charges of the ions, k and k_0 are the rate coefficients at a given ionic strength μ and zero ionic strength, respectively, and $\alpha = 1$ for NO_2^- and NO_3^- ions and $\alpha = 2$ for Cd^{2+} and Cu^{2+} ions. The ionic strength is given by $0.5\,(C_A Z_A^2 + C_B Z_B^2)$, where C_A and C_B are the molarities of the cation and anion, respectively. A simple derivation of this equation can be found in ref 29, with fuller descriptions given in refs 30 and 32. The relative corrections for ionic strength effects to the standard rate coefficients are given in Table 1 as k_{is}/k_0. Comparisons of the above formalism with known ionic strength effects of rate coefficients give satisfactory results.

A further correction to the rate coefficient must be made to take into account the relaxation of the solute concentration gradients near the hydrated electron at very short times.[30,31] The formulation for this so-called "time-dependent" rate coefficient is well-known.[30] However, the use of this formalism in the present context requires a conversion from the time dependence to solute concentration dependence in order to properly present the data and to compare with model calculations. In this work, the approximation of Jonah and co-workers has been employed in which the half-life of the scavenging reaction is substituted into the time-dependent equation.[31] It is beyond the scope of the present work to examine the consequences of such a treatment in detail. However, preliminary calculations seem to support this approximation. The results are given with respect to the ionic strength corrected rate coefficient in Table 1 as k_j/k_{is}. Rate coefficients for each of the solutes are given by the product of the rate coefficient at zero ionic strength, k_0, the correction for ionic strength, k_{is}/k_0, and the "time dependence" correction, k_j/k_{is}. All values used here are given in Table 1.

Figure 2 shows the dependence of molecular hydrogen yields on the scavenging capacity for the hydrated electron of the various scavengers. The yields are virtually the same for all solutes and independent of solute concentration up to a scavenging capacity of about 10^8 s^{-1} where scavenging within the spur decreases the molecular hydrogen by more than 10%. Since the inverse of the scavenging capacity is approximately equal to the lifetime of the hydrated electron, the spur lifetime can be inferred to be about 100 ns, which is in excellent agreement with scavenging experiments on the H_2O_2 yields.[33] There is a decrease in molecular hydrogen yield with increasing scavenging capacity for hydrated electrons. However, the efficiencies of the scavengers toward the precursors to the hydrated electron are different for almost all of the solutes examined here. This variation manifests itself at the higher scavenging capacities by giving a variety of molecular hydrogen yields at a given hydrated electron scavenging capacity. The scavengers $Cr_2O_7^{2-}$, NO_2^-, NO_3^-, and H_2O_2 give somewhat similar hydrogen yields for the same scavenging capacities. A distinctly smaller molecular hydrogen yield for the same hydrated electron scavenging capacity is measured using selenate ion as electron scavenger. The molybdate anion also gives somewhat lower molecular hydrogen yields. The main characteristic is that for all scavengers, except for Cd^{2+} and Cu^{2+}, the $G(H_2)$ does not seem to reach a limiting value at high scavenger concentration and the molecular hydrogen yield is not uniquely determined by the scavenging capacity for the hydrated electron.

As seen in Figure 2, the selenate ion is the species that scavenges the molecular hydrogen the most efficiently. This result is consistent with previous pulse radiolysis results concerning the scavenging of the hydrated electrons.[22] The pulse radiolysis study compared selenate to the cadmium ion, and it was found that the selenate scavenges more electrons than the cadmium cation for the same hydrated electron scavenging capacity. This difference is attributed to the scavenging of a precursor to the hydrated electron. In this study, the electrons are the major species leading to the formation of molecular hydrogen (reactions 1 and 2). Scavenging their precursors will lead to a decrease of molecular hydrogen. The $G(H_2)$ values obtained with selenate ion seem to indicate that, whatever the mechanism of formation, it is possible to scavenge the molecular hydrogen without reaching any limiting yield. It is conceivable that with a further increase of the selenate ion, which is experimentally impossible because of the limited solubility (1.6 mol/dm^3), the molecular hydrogen yield would approach zero.

In the case of molybdate anion, the hydrogen yields are slightly lower than the yields obtained with other more common scavengers. It appears from the data that no limiting yield is predictable with concentrations up to 2 M. Molybdate anion is a good scavenger of the precursors to the hydrated electron, although the effect of this scavenger is less noticeable compared to the selenate ion because the rate coefficient for the hydrated electron is higher for MoO_4^{2-} than for SeO_4^{2-}. Therefore, the molybdate anion more closely resembles the behavior of other (conventional) hydrated electron scavengers, for which it is impossible to distinguish between the scavenging of the hydrated electron or its precursors.[23]

The $G(H_2)$ values measured in the presence of the $Cr_2O_7^{2-}$, NO_2^-, NO_3^-, Cd^{2+}, Cu^{2+} ions are higher than observed with SeO_4^{2-} because they are all good hydrated electron scavengers; that is, they all have high rate coefficients for the reaction with the hydrated electrons. This apparent contradiction can be easily clarified by comparing the concentrations needed to reach a given scavenging capacity for hydrated electrons. For a good hydrated electron scavenger (i.e., high rate coefficient) the concentration needed to reach a certain scavenging capacity will be much lower than for a less efficient hydrated electron scavenger (i.e., low rate coefficient) such as the selenate or the molybdate anions. A good hydrated electron scavenger will less efficiently scavenge the precursors to the hydrated electron than a bad one at the same hydrated electron scavenging capacity.

Copper and cadmium cations give higher hydrogen yields than anionic or neutral species, and there seems to be a plateau around $G(H_2) = 0.2$ molecules/100 eV. Higher hydrogen yields with cationic scavengers were also observed by Peled and Czapski.[16] Both of these cations should give the same results, since their respective rate coefficients toward the hydrated electron and its precursors are similar. However, Cd^0, which is formed by the oxidation/reduction reaction of two Cd^+ ions, readily reacts with nonoxidizing acids to give hydrogen and divalent ions.[34]

$$M^0 + H_2O \rightarrow H_2 + M^{2+} + 2OH^- \qquad (4)$$

This reaction creates an observable excess of molecular hydrogen at high solute concentrations.

The anions SeO_4^{2-}, MoO_4^{2-}, and $Cr_2O_7^{2-}$ would be expected to have the same ionic strength dependence, and yet they have very different effects on molecular hydrogen yields. On the other hand, the simple anions NO_2^- and NO_3^- have about the same effect on molecular hydrogen yield as the neutral H_2O_2. Although it is difficult to accurately predict ionic strength effects at high solute concentration, the formalisms used here seem to be adequate. The divergence of hydrogen yields with increasing scavenger capacity for the wide variety of solutes examined here indicates that ionic strength effects alone cannot account for the experimental observations.

The various solutes used here have widely different rate coefficients for the hydrated electron, with large variations in molecular hydrogen yields. However, all of the solutes are fairly efficient scavengers of the precursors to the hydrated electron, and it is natural to examine their contribution to the formation of molecular hydrogen. A dominant role of the precursors of the hydrated electron on the molecular hydrogen yield should be readily observable by its dependence on the scavenging capacity of the precursors to the hydrated electron. Experimental measurements have been made on the dependence of the fraction of the surviving hydrated electron, f, at a particular time as a function of the scavenging concentration, [S], using the empirical relationship $f = \exp(-[S]/C_{37})$. It is difficult to extract rate coefficients from this scavenging data because a simple Stern–Volmer approach is not valid over the entire concentration range. The most accurate manner in which to collate the data for the different scavengers is to use the concentration relative to the appropriate C_{37} values. However, this method does not give an indication of the time scale of hydrogen formation. It is beyond the scope of the present work to examine this problem in detail. For the purposes of the present work it is sufficient to estimate the rate coefficients associated with the observed C_{37} values following the procedure outlined in ref 23. The so-obtained rate coefficients for these reactions using the experimental C_{37} data of refs 24–26 are 2.19×10^{13} M^{-1} s^{-1} for SeO_4^{2-}, 1.46×10^{13} M^{-1} s^{-1} for MoO_4^{2-}, 7.9×10^{13} M^{-1} s^{-1} for $Cr_2O_7^{2-}$, 0.57×10^{13} M^{-1} s^{-1} for NO_2^-, 2.19×10^{13} M^{-1} s^{-1} for NO_3^-, 2.42×10^{13} M^{-1} s^{-1} for Cd^{2+}, 1.02×10^{13} M^{-1} s^{-1} for Cu^{2+}, and 6.33×10^{12} M^{-1} s^{-1} for H_2O_2. Figure 3 shows the yields of molecular hydrogen as a function of the scavenging capacity of the precursors to hydrated electron. Although some scatter is observed, there is a general coalescing of the data when presented in this manner. The yield of molecular hydrogen is much more defined relative to the scavenging capacity of the precursors to the hydrated electron than to the hydrated electron itself (see Figure 2). The agreement of the data with Cd^{2+} and Cu^{2+} is probably fortuitous because they produce extra hydrogen

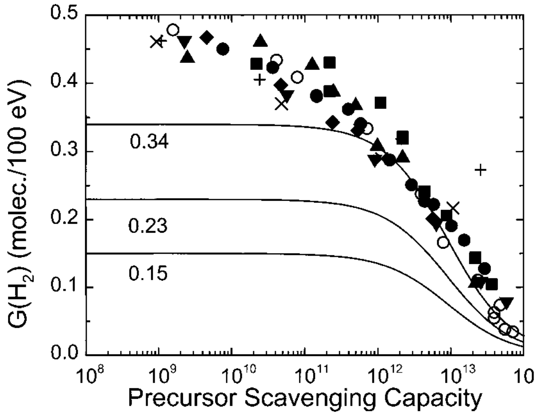

Figure 3. Molecular hydrogen yields as a function of the scavenging capacity of the precursor to the hydrated electron: (■) SeO_4^{2-}, (●) MoO_4^{2-}, (▲) NO_3^-, (◆) NO_2^-, (▼) H_2O_2, (○) $Cr_2O_7^{2-}$, (+) Cu^{2+}, and (×) Cd^{2+}, this work. The solid lines were obtained using eq I and $G_0(H_2)$ = 0.15, 0.23, and 0.34.

as discussed above. Experiments with these two solutes at higher concentrations, which is not possible because of solubility limits, would be expected to give considerably more molecular hydrogen than observed with the other solutes.

Efficient scavenging of the precursors to the hydrated electron can significantly lower the molecular hydrogen yield over that implied for scavenging of the hydrated electron alone. In addition, it is clear that good scavengers for precursors to the hydrated electron also inhibit "nonscavengable" molecular hydrogen formation. It is beyond the scope of the present work to determine the mechanism for "nonscavengable" molecular hydrogen formation, but several possible methods can be examined with respect to the present results for molecular hydrogen formation.

The strong dependence of the molecular hydrogen yield on the scavenging of a precursor to the hydrated electron may at first suggest that it is produced exclusively by reactions of the hydrated electron and hydrogen atoms as given by reactions 1−3. This scenario suggests that all precursors to the hydrated electron are eventually solvated. Efficient scavengers for its precursors would be expected to just deplete the yield of the hydrated electron. However, the yield of molecular hydrogen is about 0.3 molecule/100 eV at a scavenging capacity of 10^{12} s^{-1} for the precursors for the hydrated electrons (Figure 3). This value is half of the total molecular hydrogen produced and quite substantial. There would have to be a considerable amount of reaction of the hydrated electron within a few hundred femtoseconds for such a relatively high molecular hydrogen yield. Reaction of the hydrated electron with water occurs with a rate coefficient of 19 M^{-1} s^{-1}, so this reaction is definitely not a possibility. One of the fastest known reactions of the hydrated electron is with the hydrated proton ($k = 2.3 \times 10^{10}$ M^{-1} s^{-1}). Even this reaction would require hydrated proton concentrations of about 50 M to compete on these time scales (water is 55.6 M), which is impossible. Experimental measurements of the decay of the hydrated electron show that its yield is relatively constant to hundreds of picoseconds, which is 3 orders of magnitude too slow to account for the results observed here.[35] It appears that no known mechanism exists for producing molecular hydrogen from hydrated electrons on these time scales, and other processes must be responsible.

The rate coefficients for reaction of the precursor to the hydrated electron used here were estimated from measured C_{37} values as determined by observing the change in yield of the hydrated electron with added solutes. Therefore, it can be assumed that a common precursor is responsible for both molecular hydrogen and the hydrated electron. Rate coefficients were determined from the C_{37} values by assuming a simple competition scheme involving the immediate precursor to the hydrated electron with a formation time of 110 fs and a lifetime of 240 fs as measured in femtosecond studies.[36] However, this lifetime appears to be relatively long for the dependence of the molecular hydrogen yields observed here. Ultrafast transient absorption studies have suggested that the electrons pass through a p state that is the rate-determining step in the solvation process.[37] A simple competition calculation allows one to estimate both the time scale of the reaction and the magnitude of H_2 yield. The following equation can be used to predict the scavenging capacity dependence of that portion of the molecular hydrogen due to precursors to the hydrated electron.

$$G(H_2) = G_0(H_2)\frac{\tau^{-1}}{\tau^{-1} + k[S]} \qquad (I)$$

Here, τ is the lifetime of the precursor, k is the rate coefficient for the scavenging of the precursor by a solute at concentration [S], and $G_0(H_2)$ is the estimated yield of molecular hydrogen from this precursor. The curves in Figure 3 show the predicted results using $\tau = 110$ fs and $G_0(H_2)$ equal to 0.15, 0.23, or 0.34 molecules of H_2 per 100 eV. For this value of τ the necessary yield of H_2 is about 0.34 molecule per 100 eV or 75% of the total molecular hydrogen produced. Such a high value for the yield of H_2 produced in these processes leaves only about 0.1 molecule per 100 eV as the maximum to be formed through reactions 1−3.

Although it appears that a precursor to the hydrated electron is responsible for the formation of much of the total molecular hydrogen, the exact mechanism is not known. One possible source of molecular hydrogen is the dissociation of excited water molecules to give molecular hydrogen and O atoms. Excited water molecules may be formed directly by energy loss processes of the incident radiation or by geminate recombination of the electron with the molecular water cation. All of the scavengers used here could possibly quench excited water molecules. However, the near uniformity of the molecular hydrogen data with respect to the scavenging capacity of the precursors to the hydrated electron suggests that the rate coefficients for these reactions are extremely important in describing the overall process. The processes whereby excited water molecules produce molecular hydrogen do not lead to hydrated electrons. Only if the ratios of rate coefficients for the quenching of excited water molecules to that for scavenging precursors to the hydrated electron are the same for *all* of the solutes examined would one expect a coalescing of the molecular hydrogen data as observed in Figure 3. Some formation of directly excited water molecules is expected to occur in the radiolysis of water with γ rays, but this process does not appear to be a large source of molecular hydrogen.

A proposed mechanism for the production of molecular hydrogen involves the capture of precursors to the hydrated electron by water to give the molecular anion.[12,38,39] The water anion may decompose by giving a hydride anion that then produces molecular hydrogen.[40,41]

$$H_2O^- \rightarrow H^- + OH \qquad (5)$$

$$H^- + H_2O \rightarrow H_2 + OH^- \qquad (6)$$

Alternatively, the molecular water anion can decompose to give molecular hydrogen directly.[42,43]

$$H_2O^- \rightarrow H_2 + O^- \qquad (7)$$

The oxide anion has been observed in the gas phase, but experiments have not yet found it in the condensed phase.[40] On the other hand, the hydride anion and the formation of molecular hydrogen by hot electrons (>6 eV) have been observed in the water ices.[40,41] It is not known if either of these mechanisms could occur in liquid water, but both would be effected by efficient scavenging of the precursors to the hydrated electron.

Conclusions

The experimental results for selected scavengers at high concentration show that molecular hydrogen can be decreased to extremely low yields, if not completely scavenged. Its yield is reduced more efficiently using the selenate anion and, to a minor extent, molybdate anion as electron scavengers compared to other hydrated electron scavengers with increasing scavenging capacity for the hydrated electron. The difference is explained by the scavenging of a precursor to the hydrated electrons. A mechanism exists whereby this precursor to the hydrated electron can produce molecular hydrogen without the formation of a hydrated electron.

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