

Supporting Information for:

Neutron and Beta/Gamma Radiolysis of Water up to Supercritical Conditions. I. Beta/Gamma Yields for H₂, H[•] Atom, and Hydrated Electron[†]

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Cross-check Experiments

The HD yield at room temperature (Table 1) is very low compared to earlier measurements of H[•] atom yield, and we were not certain that a 0.02 *m* concentration of ethanol-*d*6 gives enough scavenging power ($5.4 \times 10^4 \text{ s}^{-1}$ at room temperature) to compete efficiently for H[•] atoms with other second order reactions or impurities. As a test we performed a series of experiments with 0.01 *m* (normal) ethanol aqueous solutions with $2.5 \times 10^{-3} \text{ m}$ N₂O. Figure S1 shows the radiation yields of H₂ in 0.01 *m* ethanol compared to the HD+H₂ yield in 0.02 *m* ethanol-*d*6. Both yields compare well from 100 °C up to 300 °C, justifying the small concentration of ethanol-*d*6 used for the H[•] atom yield determination.

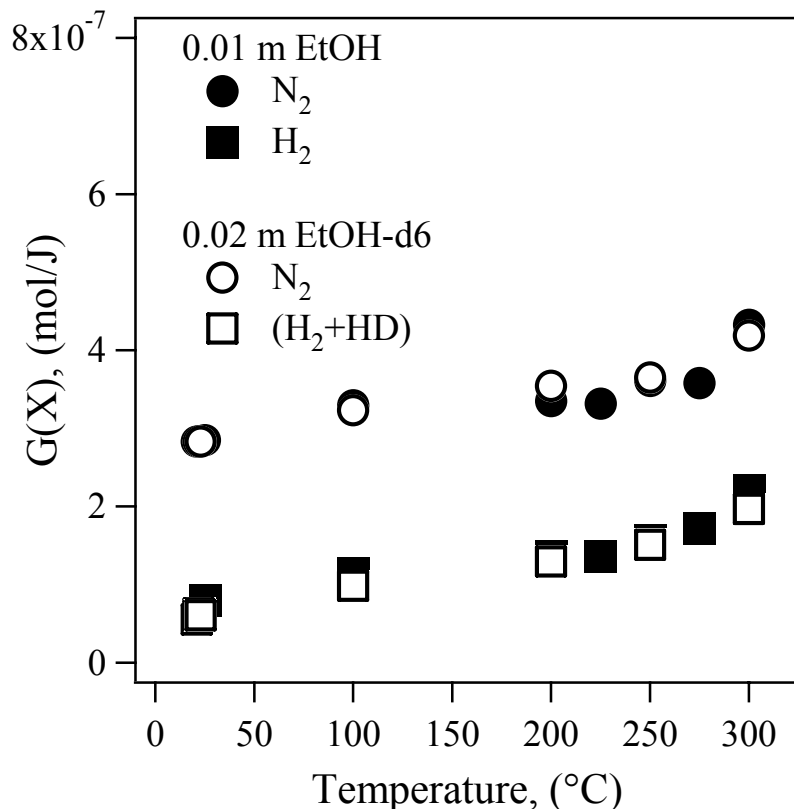


Figure S1. Comparison of isobaric (250 bar) temperature dependence of radiation yields of gaseous products formed during radiolysis of ethyl alcohol aqueous solutions in the presence of $2.5 \times 10^{-3} \text{ m}$ N_2O . Solid symbols 0.01 m ethanol; open symbols 0.02 m ethanol- d_6 .

The higher H_2 yields in ethanol- d_6 relative to phenol solutions at elevated temperature led us to ask what additional H_2 source could be present. Isotope exchange at the deuterio group in $\text{C}_2\text{D}_5\text{OD}$ in water is very fast already at room temperature, and therefore in all experiments the actual solute is $\text{C}_2\text{D}_5\text{OH}$. This alcohol hydroxyl group bears the only hydrogen available for abstraction by H-atoms that might contribute to the enhanced yield of H_2 . The abstraction of hydrogen from the hydroxyl group is considerably less efficient than abstraction of hydrogen from any aliphatic carbon atom in an alcohol. Assuming higher activation energy for reaction (14) than for other competing D-abstractions in reaction (11), one can expect that with increase of temperature reaction (14) will play a more important role.



To estimate the relative rate constant for reaction (14) we performed a competition experiment. Solutions of ethanol-*d*6 were mixed with phenol solutions, both containing $2.5 \times 10^{-3} \text{ } m \text{ } N_2O$. The added phenol scavenged H^\bullet atoms via reaction 6, thus



reducing the yields of both H_2 and HD. Assuming that we have not perturbed the scavengeable H^\bullet atom yield by an indirect mechanism, simple first order kinetics suggests the HD yield will follow equation (15), where $G_o(HD)$ is the HD yield in absence of phenol:

$$\frac{G_o(HD)}{G(HD)} = 1 + \frac{k_7[PhOH]}{k_{12}[EtOH_{d6}]} \quad (15)$$

The “excess” H_2 yield should follow a similar equation once the prompt “molecular” H_2 yield $G_m(H_2)$ is subtracted from the observed yield:

$$\frac{G_o(H_2) - G_m(H_2)}{G(H_2) - G_m(H_2)} = 1 + \frac{k_7[PhOH]}{k_{15}[EtOH_{d6}]} \quad (16)$$

We take the $G_m(H_2)$ value from the 0.01 *m* phenol scavenging experiment with no ethanol-*d*6 present. Figure S2 shows results of the experiment in the coordinates of equations (15) and (16). The ratio k_6/k_{11} is found to be 2.8 ± 0.1 , while k_6/k_{14} is 1.3 ± 0.3 . Consequently the ratio k_{14}/k_{11} at 380 °C is approximately 2.1. At room temperature the rate constant for reaction (14) is about ten times smaller than the total rate constant for deuterium abstraction from C_α and C_β (reaction 11). With these two points we can estimate a difference in Arrhenius activation energies $E_a(14) - E_a(11) = 13.8 \text{ kJ/mole}$. Thus above 300°C reaction (14) becomes very important in terms of the quantitative determination of radiolysis yield for the hydrogen.

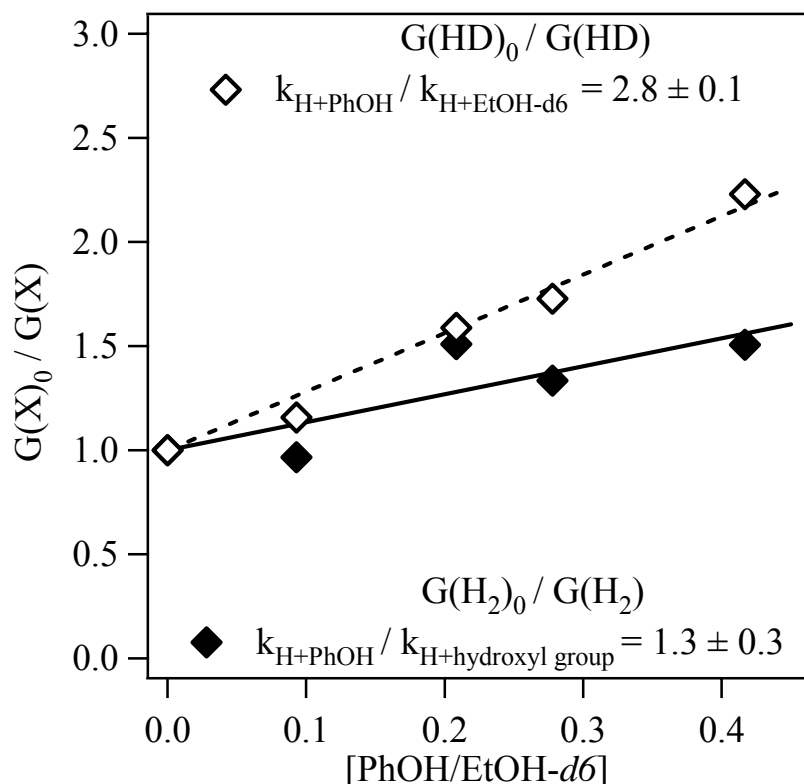


Figure S2. Competition study in deuterated ethanol/phenol mixture at 380 °C and 285 bar (density 0.52 kg/dm³) to demonstrate H₂ production from H[•] reaction with the EtOH-*d*6 OH group.

Realization that H[•] atoms could be extracted from ethanol-*d*6 led us to the question whether the H[•] atom can also abstract the phenol hydroxyl proton at higher temperatures. If so, then our molecular H₂ determination in phenol aqueous solutions is enhanced by additional hydrogen abstraction from the phenol hydroxyl group. To determine whether it occurs we used another aromatic scavenger -- nitrobenzene-- and performed product yield determination at 380 °C as a function of density. H[•] atoms and [•]OH radical are known to react with nitrobenzene by an addition similar to phenol, giving cyclohexadienyl and hydroxycyclohexadienyl radicals, respectively. However, as nitrobenzene has no alcoholic hydrogen to abstract there should not be any additional source of H₂. Figure S3 shows the comparison of phenol and nitrobenzene experimental results for H₂. There is not a large difference. At the lowest densities we obtained 15% less H₂ with nitrobenzene than with phenol. So perhaps a small amount of abstraction from phenol hydroxyl occurs under these conditions. But the difference might also be explained by substantially higher scavenging power of nitrobenzene for hydrated

electrons that disturbs spur chemistry and depresses formation of H₂ in recombination. This will have to be the subject of future experiments. For the moment we can take the phenol results as reasonably quantitative for the molecular H₂ yield.

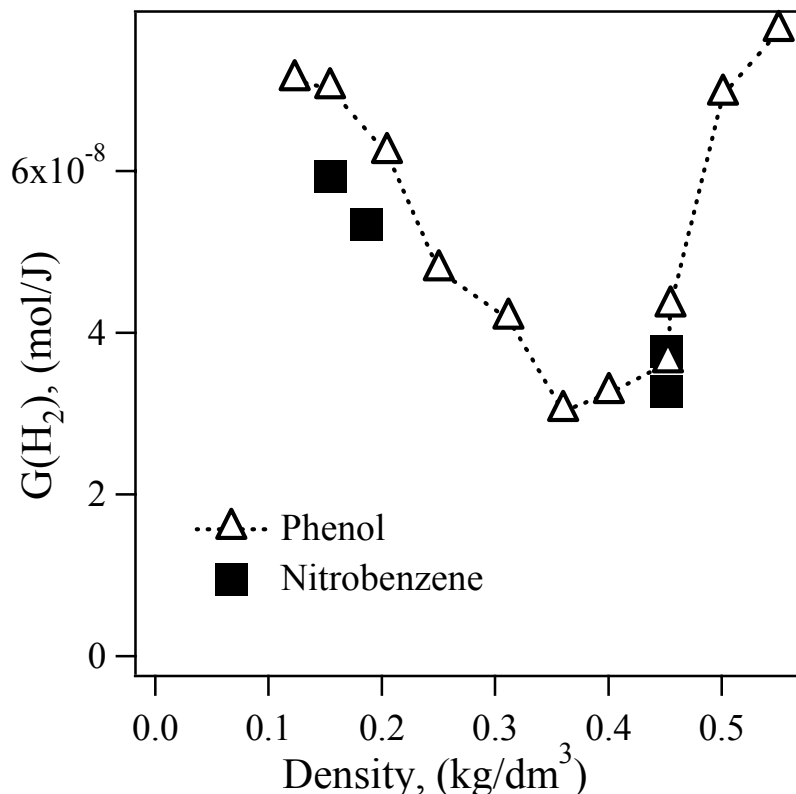


Figure S3. Comparison of H₂ yields determined for phenol and nitrobenzene solutions (both 0.01 *m*) in the presence of 2.5×10⁻³ *m* N₂O at 380 °C.

Further cross-checks on the validity of the HD and H₂ results with ethanol-*d*6 are indicated in Table S1. In particular we were concerned that N₂O might compete with the ethanol-*d*6 in scavenging the H[•] atom at elevated temperature, giving N₂ product rather



than the HD desired. As a first check, with the standard 0.02 *m* ethanol-*d*6 we increased the N₂O concentration an order of magnitude to 2.3×10⁻² *m*. A second check in supercritical conditions at 380 °C involved reducing the ethanol-*d*6 concentration a factor of ten to 0.002 *m*, and then also increasing the concentration N₂O an order of magnitude. Assuming simple first order competition, we obtain an estimate for the relative magnitude of *k*₄ and *k*₁₁. The tests indicate that with our “standard” concentrations of

N₂O and ethanol-*d*6, the N₂O scavenges less than 4 % of the H[•] atoms at any temperature, with the largest effect at room temperature.

Table S1. Data for cross-check of H atom scavenging by EtOH-*d*6 vs. N₂O.

| Temperature (°C) | Density (kg/dm ³) | [N ₂ O] (mol/kg) | [EtOH- <i>d</i> 6] (mol/kg) | G(H ₂) × 10 ⁻⁷ (mol/J) | G(HD) × 10 ⁻⁷ (mol/J) | k ₄ /k ₁₁ estimate |
|---------------------|----------------------------------|--------------------------------|--------------------------------|--|-------------------------------------|---|
| 20 | 1.00 | 0.0023 | 0.02 | 0.428 | 0.159 | 0.47 |
| | | 0.023 | 0.02 | 0.375 | 0.101 | |
| 100 | 0.970 | 0.0023 | 0.02 | 0.489 | 0.542 | 0.31 |
| | | 0.023 | 0.02 | 0.365 | 0.390 | |
| 200 | 0.881 | 0.0023 | 0.02 | 0.542 | 0.832 | 0.30 |
| | | 0.023 | 0.02 | 0.498 | 0.605 | |
| 350 | 0.625 | 0.0023 | 0.02 | 1.04 | 1.77 | 0.22 |
| | | 0.023 | 0.02 | 0.761 | 1.38 | |
| 350 | 0.625 | 0.0023 | 0.002 | 1.29 | 0.896 | 0.12 |
| | | 0.023 | 0.002 | 0.983 | 0.430 | |
| 380 | 0.190 | 0.0023 | 0.002 | 3.55 | 1.51 | 0.075 |
| | | 0.023 | 0.002 | 2.25 | 0.881 | |
| 380 | 0.461 | 0.0023 | 0.002 | 1.97 | 1.04 | 0.062 |
| | | 0.023 | 0.002 | 1.33 | 0.650 | |
| 380 | 0.532 | 0.0023 | 0.002 | 2.11 | 1.24 | 0.089 |
| | | 0.023 | 0.002 | 1.42 | 0.674 | |