

REACTIONS OF ATOMIC HYDROGEN IN WATER: SOLVENT AND ISOTOPE EFFECTS

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I. INTRODUCTION

It has been known for many years that hydrogen atoms can be easily created and studied in water using radiolytic techniques [1]. The use of CW EPR detection coupled with electron radiolysis proved extremely useful in estimating many reaction rates, and revealed the interesting phenomenon of chemically induced dynamic electron polarization (CIDEP). [2] In recent years, we have made use of pulsed EPR detection to make precision reaction rate measurements which avoid the complications of CIDEP. [3] Activation energies and H/D isotope effects measured in these studies [4-14] will be described below.

An interesting aspect of the hydrogen atom reactions is the effect of hydrophobic solvation. EPR evidence -- an almost gas-phase hyperfine coupling and extremely narrow linewidth -- is quite convincing to show that the H atom is just a minimally perturbed gas phase atom inside a small "bubble". In several systems we have found that the hydrophobic free energy of solvation dominates the solvent effect on reaction rates.

II. PROCEDURE

The basic apparatus used in these measurements is illustrated in figure 1. Pulses of 3 MeV electrons are produced with a van de Graaff accelerator and strike the aqueous sample in an EPR cavity. The de-oxygenated solutions are recirculated through the cell at a high rate to allow signal averaging at 120Hz repetition frequency. In general acidic solutions (pH=2) are used to convert solvated electrons to hydrogen atoms on a nanosecond timescale and increase the signal amplitude. A small amount of methanol (ca. 10^{-2} M) is typically added as well to scavenge hydroxyl radicals. However, a major advantage of this technique is the ability to work in neutral and alkaline solution when necessary.

Some typical data from the experiment is plotted in figure 2. Immediately following the 12-50ns electron pulse, a 25ns x-band microwave pulse is applied to the cavity. After approximately 120ns, the sensitive detection electronics are switched in, and a free induction decay from the hydrogen atom is detected as in figure 2. In general the microwave frequency is set to about 10MHz above or below the Larmor frequency for the H atom low field transition. The effective damping time constant for the free induction decay is given by

$$1/T_2(\text{eff}) = 1/T_2^0 + k_s[S] + \sum_i k_{\text{ex}}^i [R_i] \quad (1)$$

where $1/T_2$ is the natural dephasing rate and $\sum k_{\text{ex}} [R_i]$ is the effect of second order reaction and spin exchange. This latter term is not negligible, but roughly constant over the five microsecond timescale of the experiment. A plot of the dephasing rate vs. scavenger concentration [S] gives the scavenging rate constant k_s as intercept.

III. RESULTS

Table 1 summarizes a large (but not exhaustive) number of hydrogen atom rate constant measurements in terms of Arrhenius activation energies and pre-exponential factors. Some of the greatest surprises were reactions of H with the nitrate [10] and hydrazinium [9] ions and with the per-iodic acid molecule [6], which have quite large activation energies, but enormous pre-exponential factors. These ion reactions involve large solvent (hydrogen bond) reorganization on the way to the transition state, and the large entropy increase dominates the activation free energy. In the case of per-iodic acid, the hydrated H_5IO_6 species must lose two water molecules and rearrange to IO_3^- and hydroxyl radical product. The rearrangements involved in the hydrazinium ion and nitrate ion reactions are not so obvious, and deserve further study.

The hydrophobic nature of the H atom solvation was demonstrated convincingly in the study of its addition to benzene [14]. The activation energy in solution is similar to that in the gas phase, but the rate constant is some forty times faster. Using the assumptions of transition state theory, the solvent effect (ratio of rates in gas phase to those in aqueous phase) can be reduced to an expression involving only the solvation free energies of reactants and transition state. Then, assuming that the transition state solvation free energy is very nearly the same as that of benzene itself or cyclohexadiene (both known from solubility measurements), the rate enhancement in water reduces simply to

$$k_{aq}/k_{gas} = \exp\{(\Delta G_{hyd}(H)/RT)\} = L^{-1} \quad (2)$$

and L is just the Ostwald solubility parameter for the hydrogen atom. The size and polarizability of the H atom are very similar to the H_2 molecule, and using the solubility of H_2 as a model in this equation produces essentially quantitative agreement with the benzene reaction rate data. The reaction is accelerated by the collapse of the hydrophobic solvation sphere of the H atom, resulting in a "hydrophobic attraction" of the H and benzene.

Other comparisons with gas phase reaction rate data are typically limited by the quality of the gas phase data available. In the case of methanol, the activation energy is found to be ca. 6kJ/mole higher in the aqueous phase, and one should expect an order of magnitude slower reaction rate. Instead, the reaction rate is roughly the same as the gas phase by virtue of a larger pre-exponential factor. We have suggested that this larger pre-exponential might represent a "hydrophobic acceleration" effect similar to that found in the benzene case [4,11].

No doubt the strangest reactions investigated in this work are the reactions of H and D with iodide and bromide ions (giving HI- and HBr- product) [15]. At 3×10^8 and $2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for iodide and bromide respectively, the reactions have substantial free energy barriers, but the activation energies are zero or slightly negative! Measurements in H_2O/D_2O mixtures reveal a small isotope effect favoring D over H reaction. Other measurements have shown that the light Muonium atom (1/9 the mass of hydrogen) reacts about five times slower than H [7]. It is important to recall that our technique measures the rate of H atom dephasing, and so is not sensitive to any back reactions or equilibria which might occur: only the forward rate is measured. We have considered every alternative we can imagine, and conclude that the only barrier possible for these reactions consists of the water of the solvation shells. We postulate that the strongly hydrated small ions repel approach of the hydrophobic H atom. Molecular dynamics simulation of these systems has been initiated to explore the strange activation energy and isotope effects.

VII. CONCLUSIONS

The pulse radiolysis and EPR techniques described here have proven particularly useful for the study of hydrogen atom reactions in water. The hydrophobic hydrogen atom proves to be a unique probe for solvent and isotope effects in aqueous reactions.

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Table 1: Measured Arrhenius Parameters for H atom Reactions in Water

H reaction partner	$\log_{10}(A/M^{-1}s^{-1})$	E_a / (kJ/mole)
benzene:	12.34	19.1
alcohols:		
methanol	11.64	29.4
ethanol	11.53	24.1
ethanol-d ₅	12.03	31.9
2-propanol	11.86	22.0
2-propanol-d ₅	12.00	27.4
aldehydes:		
propionaldehyde	11.77	22.2
butyraldehyde	12.20	23.9
ketones:		
acetone	11.68	30.7
methyl ethyl ketone	11.25	22.3
diethyl ketone	11.30	21.0
methyl isopropyl ketone	10.96	17.2
methyl isobutyl ketone	11.24	21.2
cyclopentanone	11.15	19.7
iodo compounds:		
iodomethane	11.90	10.39
iodoethane	12.20	11.8
1-iodopropane	12.24	12.0
IO ₃ ⁻	11.96	27.46
HIO ₃	12.83	22.35
IO ₄ ⁻	13.30	36.55
H ₅ IO ₆	17.77	53.0
I ⁻	8.48	-1.0
peroxide and hydrazine:		
H ₂ O ₂	11.26	21.1
HO ₂ ⁻	13.65	25.6
D ₂ O ₂ (D atom reaction)	10.37	17.3
N ₂ H ₄	10.69	16.28
N ₂ H ₅ ⁺	16.95	61.38
nitrite and nitrate:		
NO ₂ ⁻	11.94	15.6
HNO ₂	12.36	21.5
NO ₃ ⁻	15.28	48.7

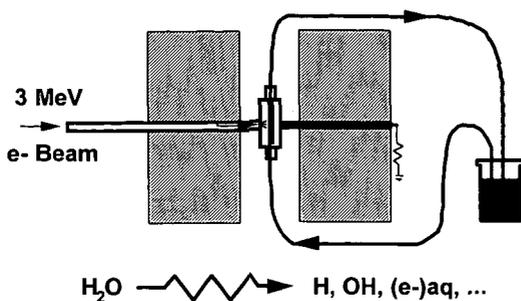


Figure 1. Typical experimental arrangement of the FID attenuation experiment. Temperature controlled aqueous sample is recirculated through a glass cell in the EPR cavity. H atoms are generated by in situ pulse radiolysis with 3 MeV electrons. Scavenger concentrations are changed by successive injections into the flow stream.

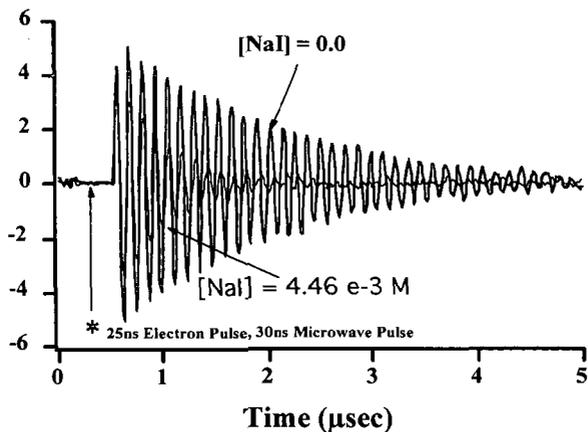


Figure 2. Free induction decay from the H atom low field EPR line. Addition of scavenger (in this example I-) shortens the damping time constant, and provides a pseudo-first order measurement of reaction rate.