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H ATOM PROBES OF RADIATION CHEMISTRY: SOLIDS AND LIQUIDS*

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Abstract:

Time-resolved pulsed electron paramagnetic resonance (EPR) was used to study formation and decay kinetics of spin-polarized mobile H atoms in radiolysis of "wet" fused silica containing ~1200 ppm of SiOH groups. Two reactions of H atoms can be distinguished: a slow component corresponding to scavenging of H atoms by metastable paramagnetic centers and a fast component which is ascribed to a reaction of a short-lived small polaron (intrinsic hole) with H atoms.

Introduction:

H atoms are ubiquitous in radiation chemistry. Radiolysis of most substances yield H atoms and studies of the mechanisms of their production are as old as the field of radiation chemistry. The problem is that study of products does not easily reveal the chemical mechanisms involved even with the clever use of isotopes.

Hydrogen has other very significant role as it serves to ameliorate defects in amorphous solids. It is commonly used to improve device materials like amorphous silicon, diamond films and amorphous silica. It appears that in amorphous silica the role of H atoms is significant in annealing radiation induced paramagnetic centers. This confers on the material the remarkable resistance to radiation damages so that both optical and mechanical properties of "wet" fused silica are excellent.

In liquids, the study of H• atoms in liquid methane, discovered chemically induced dynamic electron polarization CIDEP [Fessanden and Schuler, 1963]. H atoms react too quickly in other hydrocarbons so that they cannot be seen by time-resolved EPR. In aqueous solutions H atoms are easily seen and various studies of H atom reactions with many substrates were carried out in our group.

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We illustrate here studies of H atom dynamics. We discuss our recent work on H atoms in amorphous silica where pulse radiolysis was carried out at 180-530 K [Shkrob and Trifunac, 1997]. The study of liquids was illustrated by our on H(D) atoms in radiolysis of methane in several cryogenic fluids. This study examined methane (1-70 mol %) solution in liquid argon, krypton, xenon and nitrogen at 77-160 K. The H(D) atoms exhibited CIDEP. From the analysis of the polarization decay kinetics mechanistic insights about radiolytic pathways in such liquid solution can be obtained [Shkrob and Trifunac, 1995].

Time resolved EPR and the spin polarization in mobile H• atoms is an excellent way to probe chemistry in solids and in liquids. The mobile H atoms are observed by time-resolved pulsed EPR within 10^{-8} to 10^{-3}, after their creation in a radiolytic pulse. These H atoms exhibit non-thermal population of their electron spin states caused by CIDEP [McLauchlan, 1990]. There are two main pathways that give rise to CIDEP: (i) transfer of polarization from a short-lived triplet precursor to the product radicals or H-atoms (triplet mechanisms) and (ii) polarization due to spin correlation in a radical pair formed either by dissociation of a precursor or in a random encounter of radicals (radical pair mechanisms (RPM)). In the magnetic field on an X-band EPR spectrometer, only one of the triplet states of the radical pair, T_0, is close to the singlet state S. Hyperfine interactions (hfi) of electrons with nuclei induce rapid spin transitions between these two states. In close pairs, the electron spin exchange (J) between the radical partner enlarges the energy gap between S and T_0 states and slows the hfi-induced transition down. The so-called St_0 RPM originates in the interplay of hfi and spin exchange driven by modulation of J by diffusion [Monchick and Adrian, 1978]. The St_0 RPM polarized radicals, the high and low-field halves of the EPR spectra exhibit opposite polarization, either E/A (emission/absorption) or A/E, depending on the sign of J and the initial spin state of the radical pair. In the singlet born pairs the polarization is A/E if $J < 0$ and E/A if $J > 0$. The triplet born pairs and pairs formed by random radical encounters the polarization is opposite, i.e., E/A for $J < 0$, etc. The polarization formed in random encounters of radicals depends on spin sorting which is a consequence of a preferential reaction via singlet pair.

There are other interactions that can influence RPM polarization in radicals. One is due to the difference in g factors of radicals in the pair. Another is caused by hfi-induced transitions in the region of avoided crossing between the singlet (S) and the lowest triplet state (T_-) in radical pairs. This so-called ST_- RPM (for $J < 0$) would give an emissive contribution to the EPR lines of the polarized radicals.

There are subtle details which can trap the unwary, but careful examination of the polarization pattern and its time evaluation can provide insights into the reactions of radicals. Trapped H atoms were extensively studied by steady state EPR at low temperatures in amorphous SiO_2 [T. E. Tsai, et al., 1989; T. E. Tsai and D. L. Griscom, 1988; D. L. Griscom, 1985; N. Azuma, et al., 1986; M. Saeki, et al., 1984]. In a:SiO_2 the most likely precursor of the H atoms in the ≡SiOH group interacting with free triplet excitons [M. Stapelbroek, et al., 1979].

$$\equiv SiOH + {}^3exciton \rightarrow {}^3\{\equiv SiOH\} \rightarrow \equiv SiO\bullet + H\bullet \qquad (1)$$

If the spin lattice relaxation in the triplet is slower than the dissociation, the non-Boltzmann polarization of the triplet can be passed to the radicals (triplet mechanism).

Experimental:

The EPR spectra were obtained at 9 GHz using a pulsed microwave bridge with electron beams from a 3 MeV Van de Graaff accelerator. 5-100 nsec pulses and 60-720 Hz repetition rates were used with the average beam current of 3 μA. The time resolution of our experiment is ~ 10 nsec and the ring down time of the EPR cavity was 0.4-1 μsec. The suprasil samples were inserted in a sapphire jacket. Sapphire does not have the H-atom signal to interfere with the sample H-atom signal. In several studies of cryogenic liquids suprasil sample tubes were used. In such studies D atoms from CD_4 mixtures were examined in order to avoid any complications due to H atoms from suprasil sample tubes. Alternatively, H atoms were studied using sapphire sample tubes with CH_4 solution in cryogenic liquids.

Results and Discussion:

“wet” a:SiO_2

The observed EPR signals indicate the occurrence of CIDEP (Figure 1). Below 220 K at early times after the radiolytic pulse E/A+A pattern is observed (Figure 1 bottom). E/A polarization is due to ST_0 RPM, and suggests that H atoms have a triplet precursor that give rise to A contribution. At higher temperatures the pattern changes from E/A+A to E/A+E (Figure 1 from bottom to top). The most likely explanation for this emissive contribution to polarization is that at these higher temperatures ST_- mechanism becomes operative. Since this net emission is observed many microseconds after the radiolytic pulse, the explanation is that it is formed in random encounters of H atoms with spin centers, same as ST_0 polarization. Triplet polarization would contribute to the initial signal but would not contribute at later times.

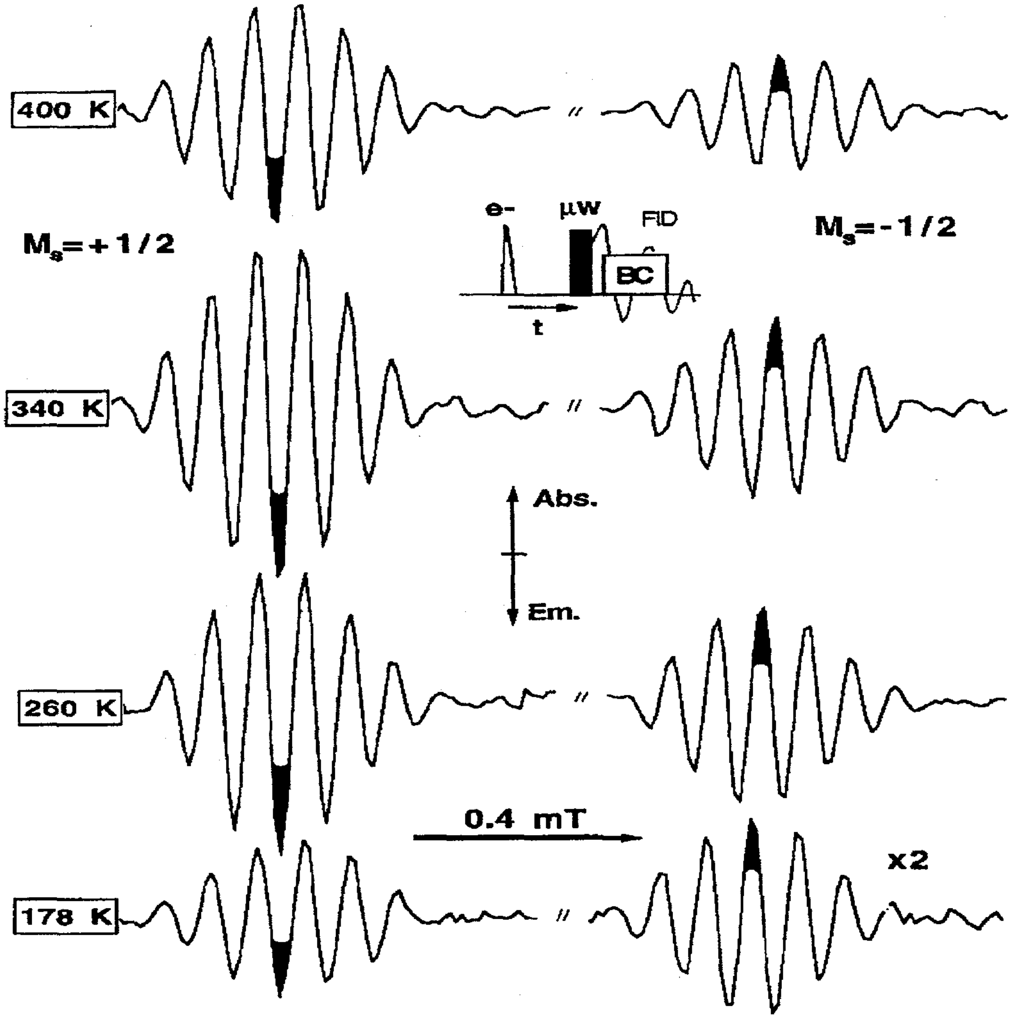

Figure 1. EPR spectra (9 GHz) of mobile H atoms in "wet" a-SiO_2 observed at t = 50 ns after the end of the 100 ns electron beam pulse (178 K to 400 K). The spectra are obtained by boxcar integration (BC) of free induction decay (FID) following the excitation of H atoms with 90° microwave pulses (≈ 30 ns wide). The oscillations in the field domain are due to transient nutation of the magnetization. The splitting between the $M_s = +1/2$ (low-field) and $M_s = -1/2$ (high-field) lines is 51.4 mT (these two lines were scanned individually). The exact field positions of the $M_s = \pm 1/2$ resonance are shown by shadows; these signals were used to acquire the EPR kinetics. As the temperature increases, the E/A + A polarization pattern transforms to the E/A + E pattern.

The emissive contribution to CIDEP can be separated from the E/A ST_0 polarization by subtracting the intensity of $M_s = 1/2$ (low field) line for the intensity of $M_s = - 1/2$ (high field) line. This difference ($S_-(+)$ signal is plotted as a function of temperature in Figure 2. There are fast and slow pseudo first order components (k_f and k_s). The activation energy of the slow component is 15-18 kJ/mol which is close to the activation energy of H atom diffusion determined by low temperature EPR.[4-6] Inversion recovery measurements of T_1 indicate $T_1^{-1} \approx 2\ k_s$ over the entire temperature range. This means that H atoms relax by electron spin exchange with metastable centers whose polarization is thermal. The factor 2 is expected since recombination occurs only in singlet encounters (1/4 of encounter are reactive), whereas the spin exchange occurs in every $\alpha\beta$ and $\beta\alpha$ encounter, i.e., in 1/2 of encounters.

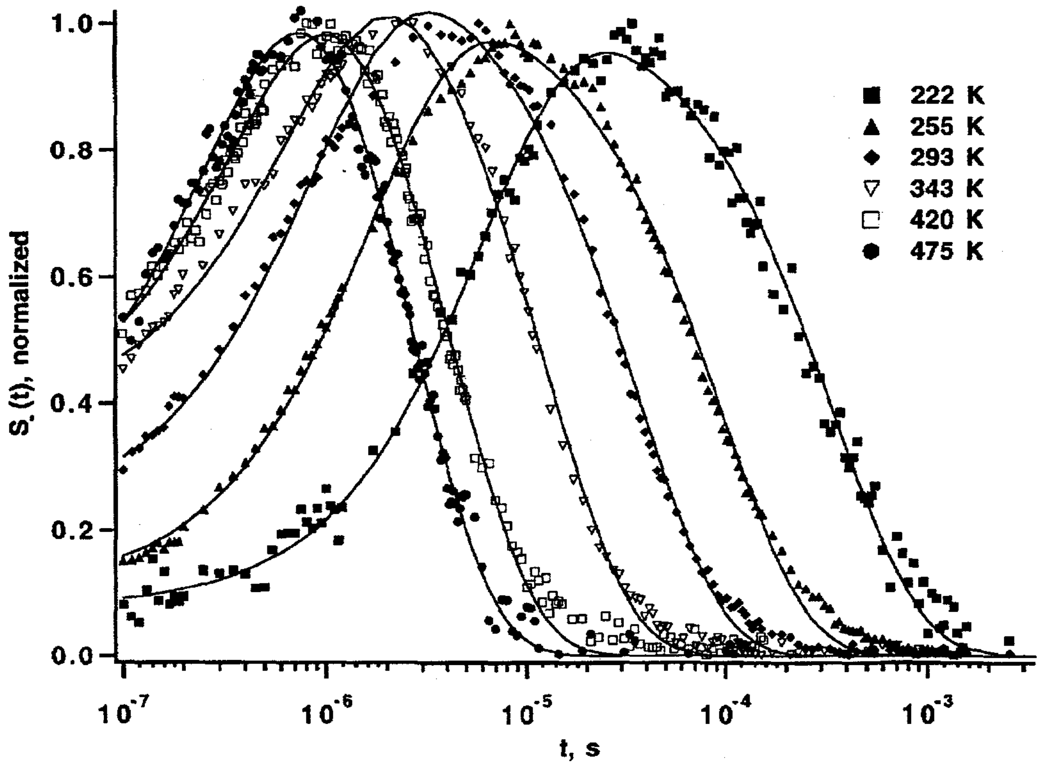

Figure 2. Normalized $S_-(t)$ kinetics as a function of temperature (55 ns electron pulse, FID detection). A pseudologarithmic sweep of delay time *t* was used to obtain these kinetics. The solid lines drawn through the points are biexponential fits, $S_-(t) = \exp(-k_s t]^{\beta})$ $\{A\text{-}B\exp(-k_f t]^{\beta})\}$ with $\beta = 1$. Using stretched exponential functions with $\beta \approx 0.8\text{-}0.9$ and corrections for the T_1 relaxation further improve the fit quality.

The fast formation component with the activation energy of 6-8 kJ/mol must involve some short-lived paramagnetic species.

Small polaron is the most likely candidate.

$$H\bullet + \equiv Si\text{-}O\bullet^{+} Si\equiv \rightarrow \equiv S\text{-}OH^{+}\text{-}Si\equiv$$

The fast decay of small polarons can occur via:

$$\equiv S\text{-}O\bullet^{+} S\equiv + \equiv Si\text{-}OH \rightarrow \equiv SiOH^{+} - Si\equiv + Si\text{-}O.$$

This was suggested as the main source of protons in MOS structures [Griscom, et al., 1988].

Conclusion:

The conclusions of this work are that at 180-530 K the H atoms in a-SiO_2 are not particularly mobile. At 300 K the diffusion coefficient of H atoms ~10^{-7} - 10^{-6} cm^2/s. H• atom reactions with small short-lived paramagnetic species suggests that short-lived polarons are involved. The fast decay of small polarons can be explained by the trapping by ≡Si-OH defects.

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