Frequency dependence of electron spin–lattice relaxation for semiquinones in alcohol solutions

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ABSTRACT

The spin–lattice relaxation rates at 293 K for three anionic semiquinones (2,5-di-t-butyl-1,4-benzosemiquinone, 2,6-di-t-butyl-1,4-benzosemiquinone, and 2,3,5,6-tetramethoxy-1,4-benzosemiquinone) were studied at up to 8 frequencies between 250 MHz and 34 GHz in ethanol or methanol solution containing high concentrations of OH^-. The relaxation rates are about a factor of 2 faster at lower frequencies than at 9 or 34 GHz. However, in perdeuterated alcohols the relaxation rates exhibit little frequency dependence, which demonstrates that the dominant frequency-dependent contribution to relaxation is modulation of dipolar interactions with solvent nuclei. The relaxation rates were modeled as the sum of two frequency-independent contributions (spin rotation and a local mode) and two frequency-dependent contributions (modulation of dipolar interaction with solvent nuclei and a much smaller contribution from modulation of g anisotropy). The correlation time for modulation of the interaction with solvent nuclei is longer than the tumbling correlation time of the semiquinone and is consistent with hydrogen bonding of the alcohol to the oxygen atoms of the semiquinones.

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1. Introduction

Semiquinones are ubiquitous in biology, from photosynthesis to environmental toxicology [1,2]. They are involved in many electron transfer reactions [3,4]. Semiquinones have been studied extensively by EPR [5], and their spin relaxation properties are important to understanding their EPR spectra. Semiquinones were selected for studies of mechanisms of electron spin relaxation because their g values are higher than for carbon-centered radicals, but their nuclear hyperfine couplings are smaller than for nitroxides.

Semiquinones were among the first species for which spin–lattice relaxation rates were measured directly by saturation recovery in fluid solution [6,7]. Semiquinone relaxation rates have been studied extensively at X-band as a function of temperature and viscosity [7–12]. In alcohol solutions relaxation rates could be fit with the relationship shown in Eq. (1) [7–11].

$$\frac{1}{T_1} = \frac{AT}{\eta} + Be^{-\Delta E/RT} \tag{1}$$

where η is the viscosity of the solution, ΔE was found to be about 1 kcal/mol ($\Delta E/R$ = 500 K), A and B were determined experimentally and depend both on semiquinone and on solvent [7–11].

There is general agreement that the term in Eq. (1) in T/η is due to spin rotation, which is usually written as in Eq. (2) [13,14].

$$\frac{1}{T_1^{SR}} = \frac{\sum_{i=1}^{3}(g_i - g_e)^2}{9\tau_R} \tag{2}$$

where $i = x,y,z$ and g_e is 2.0023.

The origin of the second term in Eq. (1) was not well understood and has been attributed to hindered rotation [7,11] and/or spin rotation [10]. A study at X- and Q-band of five semiquinones in glass-forming solvents between 25 and 295 K found that the dominant contributions to relaxation at 295 K were spin rotation and a local mode [15]. The energy for the local mode was 600 K, which is similar to the activation energy reported previously for the second contribution to semiquinone relaxation (Eq. (1)). The full expression for a local mode is given by Eq. (3) [16].

$$\frac{1}{T_1^{local}} = C_{local} \frac{e^{\Delta_{loc}/T}}{(e^{\Delta_{loc}/T} - 1)^2} \tag{3}$$

where Δ_{loc} is the energy of the local mode in Kelvin and C_{local} is determined experimentally. The local mode relaxation mechanism was initially proposed for defects in ionic lattices [16]. The temperature dependence of relaxation described by Eq. (3) has been observed for molecular species in glassy matrices, including organic radicals and transition metal complexes [17–19]. The magnitude of the contribution from the local mode is larger in soft matrices such

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as sucrose octaacetate than in harder ones such as sorbitol [18]. For a molecular species in a glass the local mode is interpreted as an intramolecular vibration that is impacted by interaction with the matrix. For nitroxides in highly viscous media [18,19] and for trityl radicals in water:glycerol [20] the local mode dominates relaxation in the glassy state below the glass transition temperature. There is no change in slope for a plot of $\log(1/T_1)$ vs. $\log(T)$ in the vicinity of the glass transition temperature, so it is proposed that the local mode relaxation mechanism persists in solution.

If $\Delta_{loc} \gg T$, Eq. (3) can be approximated as in Eq. (4), which has the same temperature dependence as the second term in Eq. (1).

$$\frac{1}{T_1^{local}} \sim C_{local} e^{-\Delta_{loc}/T} \tag{4}$$

These results indicate that the two dominant contributions to spin–lattice relaxation at X-band for semiquinones tumbling rapidly in solution are spin rotation and a local mode with an energy of 500–600 K. The contributions from these two relaxation mechanisms are independent of resonance frequency.

Studies of the frequency dependence of spin–lattice relaxation for carbon-centered trityl radicals [21] and nitrogen-centered nitroxide radicals [22–24] in fluid solution have demonstrated the significance of additional relaxation mechanisms. These frequency-dependent processes modulate anisotropic interactions – g anisotropy (Eq. (5)) [25,26], hyperfine (A_i) anisotropy (Eq. (7)) [25–27], dipolar coupling to solvent nuclei (Eq. (8)) [21], or involve a thermally-activated process (Eq. (9)) [23].

$$\frac{1}{T_1^g} = \frac{2}{5}\left(\frac{\mu_B \omega}{g\beta}\right)^2 \left\{\frac{(\Delta g)^2}{3} + (\delta g)^2\right\} J(\omega) \tag{5}$$

where $\Delta g = g_{zz} - 0.5(g_{xx} + g_{yy})$, $\delta g = 0.5(g_{xx} - g_{yy})$, μ_B is the electron Bohr magneton and $J(\omega)$ is the Bloembergen, Purcell, Pound (BPP) spectral density function (Eq. (6)).

$$J(\omega) = \frac{\tau_R}{1 + (\omega\tau_R)^2} \tag{6}$$

where τ_R is the tumbling correlation time of the semiquinone and ω is the resonance frequency.

$$\frac{1}{T_1^A} = \frac{2}{9}I(I+1)\sum_i (A_i - \overline{A})^2 J(\omega) \tag{7}$$

where A_i is a component of the nitroxide nitrogen hyperfine coupling in angular frequency units, $\overline{A}$ is the average nitrogen hyperfine, and I is the nitrogen nuclear spin.

$$\frac{1}{T_1^{solvent}} = C_{solvent} \frac{\tau_{solvent}}{1 + (\omega\tau_{solvent})^2} \tag{8}$$

where $\tau_{solvent}$ is the correlation time for motion of the solvent relative to the radical, and $C_{solvent}$ is a function of the dipolar interaction with solvent nuclei.

$$\frac{1}{T_1^{therm}} = C_{therm}\left(\frac{\omega}{\omega_{ref}}\right)\frac{\tau_{therm}}{1 + (\omega\tau_{therm})^2} \tag{9}$$

where $\tau_{therm} = \tau_c^0 \exp(E_a/RT)$, E_a is the activation energy, τ_c^0 is the pre-exponential factor, C_{therm} is the coefficient for the contribution of the thermally-activated process, and $\omega_{ref} = 9.5$ GHz. Variable temperature studies of semiquinone spin lattice relaxation did not find evidence of a thermally-activated process as described by Eq. (9) [7,15] so this contribution was not included in the models used in this paper.

To determine the extent to which frequency-dependent processes (Eqs. 5, 7, 8) contribute to the relaxation of semiquinones in alcohol solvents at 293 K, the three radicals shown in Fig. 1 were studied at frequencies between 250 MHz and 34 GHz.

2. Experimental

2.1. Semiquinone preparation

2,5-Di-t-butyl-1,4-benzosemiquinone (25DTBSQ) was prepared by mixing equal volumes of air-saturated ethanol solutions of 2,5-di-t-butyl hydroquinone (5 mM, Alfa Aesar, 98% purity) and KOH (5 mM) [28]. 2,6-Di-t-butyl-1,4-benzosemiquinone (26DTBSQ) was prepared from 2,6-di-t-butyl-1,4-benzoquinone (Aldrich, 98% purity) using the same procedure. 2,3,5,6-Tetramethoxy-1,4-benzosemiquinone (TMBSQ) was prepared by mixing a 2:1 volume ratio of 25 mM KOH and 5 mM tetraflouro-1,4-benzoquinone (Sigma–Aldrich, 97% purity) in methanol. Formation of the radicals was confirmed by X-band CW EPR [28]. Concentrations of the semiquinones were determined by comparison of the double integrals of the EPR spectra with double integrals of signals for 0.20 mM ^{15}N-CTPO (3-carbamoyl-2,2,5,5-tetramethyl-3-pyrroline-1-oxyl) in the same solvent. Concentrations were in the range of 0.2–0.5 mM. 1,4-Benzosemiquinones form adducts with, and react with, O_2 [29]. The EPR signals of the semiquinones in air-saturated solution are very broad and difficult to observe. Air-saturated solutions stored at 4 °C for up to 30 days produced well-resolved semiquinone EPR signals after deoxygenation. In deoxygenated sealed tubes the EPR signal decays within hours to days.

2.2. Oxygen removal

Samples were purged with N_2 to remove O_2. Relaxation time measurements were repeated, with continued N_2 purging, until no further increase in relaxation time constant was observed. At Q-band the samples were in Teflon tubes with 0.30 mm ID and 0.66 mm OD that were placed inside a 1.6 mm OD quartz capillary tube that was open at both ends. The Bruker cryostat was purged with N_2 throughout the measurements. At frequencies between 1 and 9 GHz samples were in 4 mm OD quartz tubes. The vapor space in the tube was initially purged vigorously with N_2, after which N_2 was gently bubbled into the solution through thin Teflon tubing. At X-band the resonator also was purged with N_2. At L-, S-, and X-band samples were purged continuously with N_2. At 600 MHz and 250 MHz 16 mm and 25 mm OD quartz tubes were used, respectively. The height of the solution in the tube was about 3 cm. To purge the large vapor space in these tubes the following protocol was developed: 15 min purging at the top of the tube, 15 min near the top, 15 min in the middle of the tube and 30 min gentle bubbling into the solution followed by constant gentle purging with N_2 at the top of the tube during the relaxation time measurements.

2.3. Relaxation times measurements

Spin–lattice relaxation times, T_1, were measured by inversion recovery at 250 MHz [30], 600 MHz [23], L-band (1.0, 1.5 GHz) [31], S-band (2.57, 3.0 GHz) [31], and X-band (9.5 GHz) [32] on locally designed spectrometers and at Q-band (34 GHz) on a Bruker E580 spectrometer. The experiments were performed at a resonator temperature of ~293 K. Multifit, a locally written program
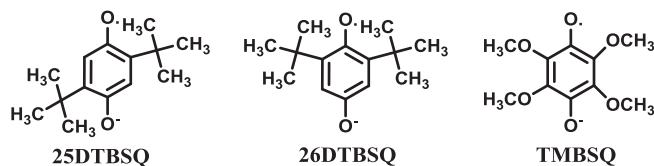

Fig. 1. Structures of the semiquinones studied.