

A Deuterium Perturbation upon Electron Transfer Kinetics

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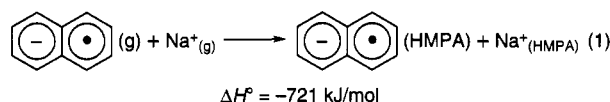
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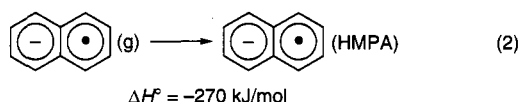
Abstract: ¹H-NMR and X-band EPR were used to study the second-order rate constant for the electron transfer reactions involving naphthalene (C₁₀H₈) and perdeuterated naphthalene (C₁₀D₈) in the absence of ion association. In hexamethylphosphoramide the second-order rate constant for the intermolecular electron transfer from C₁₀D₈^{•−} to C₁₀D₈ [(6.4 ± 0.2) × 10⁸ M^{−1} s^{−1}] is about 20% larger than it is for C₁₀H₈^{•−} + C₁₀H₈ = C₁₀H₈ + C₁₀H₈^{•−} (*k*_{H-H}/*k*_{D-D} = 0.80). This is explained in terms of Marcus theory and the known 0.012 Å bond shortening that takes place when H is replaced by D in C₁₀H₈ and an estimated 0.02 Å bond shortening when H is replaced by D in C₁₀H₈^{•−}. The rate constants for electron transfer from C₁₀D₈^{•−} to C₁₀H₈ [(9.8 ± 0.1) × 10⁸ M^{−1} s^{−1}] and from C₁₀H₈^{•−} to C₁₀D₈ [(3.5 ± 0.6) × 10⁸ M^{−1} s^{−1}] show that the electron transfer rates increase as the donor naphthalene is deuterated and the acceptor is protonated.

Introduction

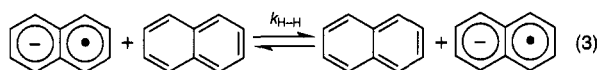
Hydrocarbon anion radicals in hexamethylphosphoramide (HMPA) are free of ion association, and the ion pair complex is surrounded by a tight solvation shell.¹ In fact, the calorimetric determined solvation enthalpy for the naphthalene anion radical plus the sodium cation in this solvent is 721 kJ/mol, reaction 1.² If we subtract the single ion heat of solvation of the sodium



cation in HMPA (−451 kJ/mol),³ we are left with the heat of solvation of the naphthalene anion radical (−270 kJ/mol), reaction 2.



As a consequence of the strong solvating power of HMPA, the electron exchange, reaction 3, proceeds without the exchange



of a cation.⁴ It has a rate constant of *k*_{H-H} = 5 × 10⁸ M^{−1} s^{−1} and an activation energy that reflects only energy of activation for the viscosity of the solvent.⁵ As a consequence of the need for solvent reorganization, there must be some energy expenditure to promote the activated complex during electron

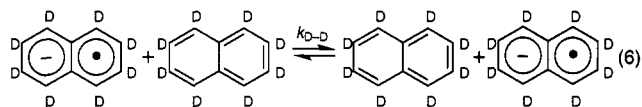
exchange, which is quantitatively accounted for in the theory developed by Marcus.⁶ The free energy of activation for this electron transfer is a function of the difference in the standard free energies of the exchanging species (Δ*G*°) and the solvent's reorganization parameter λ, eq 4. This expression reduces to Δ*G*° = λ/4 for reaction 3.

$$\Delta G^\ddagger = (1 + \Delta G^\circ)^2 \lambda / 4 \quad (4)$$

Since the work term is zero for an exchange involving an ion and a neutral molecule, λ is just a function of the two radii of the anion radical (*r*_{H^{•−}}) and neutral molecule (*r*_{H[•]}), where *r*_{H-H} is the distance separating the two ions in the encounter complex of reaction 3, and *D*_{opt} and *D*_{st} are the optical and static dielectric constants of HMPA (eq 5).⁶ Marcus theory has been shown to

$$\lambda_{\text{H-H}} = [1/2r_{\text{H}^\bullet} + 1/2r_{\text{H}^{\bullet-}} - 1/r_{\text{H-H}}](1/D_{\text{opt}} - 1/D_{\text{st}})e^2 \quad (5)$$

be unable to predict quantitative values for Δ*G*° of reaction 3.⁵ However, it still should be valuable in reflecting differences in free energies of activation due to slight alterations in the reacting species. If the reacting species is slightly perturbed, as in reaction 6, the new free energy of activation should reflect the



small isotopic perturbation in electron affinities in the two reorganization parameters, eq 7. The difference in the free

$$\Delta G^\ddagger_{\text{D-D}} - \Delta G^\ddagger_{\text{H-H}} = (\lambda_{\text{H-H}} - \lambda_{\text{D-D}})/4 = RT \ln (k_{\text{H-H}}/k_{\text{D-D}}) \quad (7)$$

energies of activation between reactions 3 and 6 should be reflected by the differences in the radii of the reactive species. Since *k* = (*k*_B*T*/*h*)*e*^{−Δ*G*°/*RT*}, where *k*_B is Boltzman's constant and *h* is plank's constant, the difference in the Δ*G*°'s can be expressed in terms of the ln of the ratio of *k*_{H-H} and *k*_{D-D}, eq 7. The energy expenditure needed to promote the activated complex during electron exchange is a consequence of solvent

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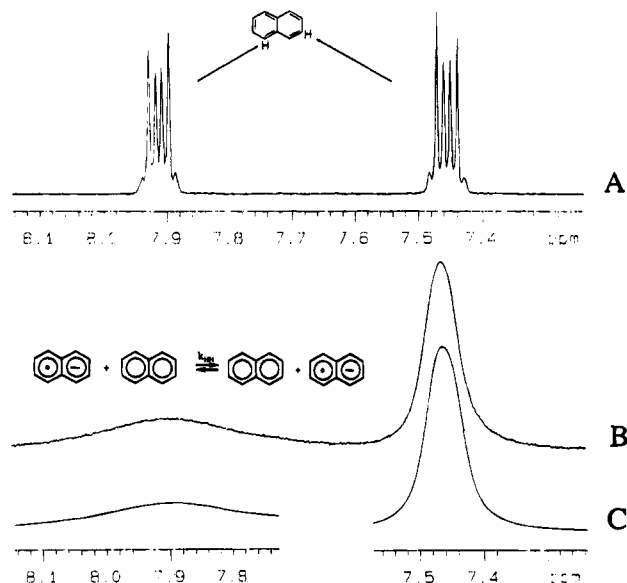
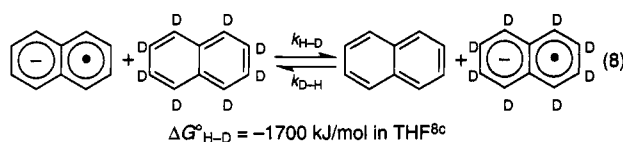


Figure 1. (A) 300-MHz ^1H -NMR spectrum of naphthalene (0.22 M) in HMPA ($T_{2,0} = 0.637$ s and $T_{2,0}^{\text{H-H}(\alpha)}/T_{2,0}^{\text{H-H}(\beta)} = 1.00$). (B) The spectrum of the same solution but with the naphthalene anion radical present. (C) A computer simulation generated using $T_2^{\text{H-H}(\alpha)}/T_2^{\text{H-H}(\beta)} = 6.46$. This corresponds to a rate constant for reaction 3 of $k_{\text{H-H}} = 5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

reorganization around the reacting species, hence it should be related to the effective radii of the neutral molecule and anion radical. Indeed, ab initio calculations, which are in agreement with EPR data, show that the C–D bond is shorter than the C–H bond by 0.01 Å in the pyrene anion radical system.⁷

Given that the relative solution electron affinities of perdeuterated hydrocarbon anion radicals are significantly smaller than those of their normal light analogues (e.g. reaction 8)⁸ and that



the kinetics of electron exchange reactions can be conveniently studied via NMR and EPR techniques,⁹ we were motivated to measure and compare the forward and reverse rate constants of reactions 3, 6, and 8 in the hope that these studies would lead to insight concerning the isotopic perturbation upon solvent reorganization.

Results

The ^1H -NMR spectrum at 298 K of a 0.35 M solution of naphthalene in a mixture of perdeuterated HMPA and HMPA (1:5) reveals the broadening of both the α and β patterns due to the rapid electron exchange (reaction 3, Figure 1). The signal for the α protons is broadened to a greater extent due a larger EPR coupling constant (spin density) for the α protons ($a_{\text{H}}^{(\alpha)} > a_{\text{H}}^{(\beta)}$ in G). Multiplying a_{H} by the gyromagnetic ratio

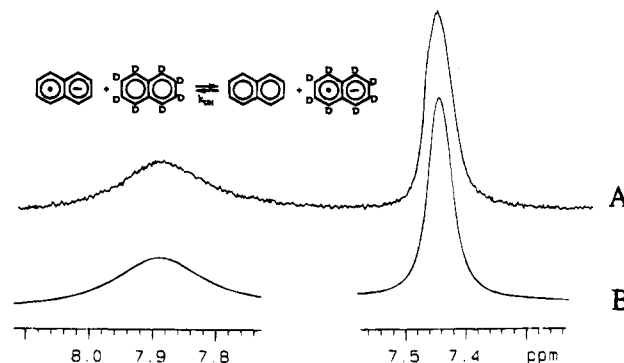


Figure 2. (A) 300-MHz ^1H -NMR spectrum of a naphthalene (0.18 M) and perdeuterated naphthalene (1.53 M) in HMPA in the presence of anion radical. (B) Computer simulation generated using $T_2^{\text{D-H}(\alpha)}/T_2^{\text{D-H}(\beta)} = 6.79$. This corresponds to $k_{\text{D-H}} = 9.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

converts it to $A_{\text{H}}^{(\alpha)}$ in radians/s. The rate constant for reaction 3 can be obtained from the line broadening of either the α or β signal with the use of Johnson's expression (e.g. eq 9).¹⁰

$$1/T_2^{\text{H-H}(\beta)} = k_{\text{H-H}}[\text{C}_{10}\text{H}_8^{\bullet-}]/\{1 + (4[\text{C}_{10}\text{H}_8]^2/A_{\text{H}}^{(\beta)^2})k_{\text{H-H}}^2\} \quad (9)$$

Fortunately, it has recently been shown that eq 9 can be successfully used in a rearranged form where the anion radical concentration need not be known, eq 10,¹¹ where $A_{\text{H}}^{(\alpha)}$ and $A_{\text{H}}^{(\beta)}$

$$k_{\text{H-H}} = \frac{\{A_{\text{H}}^{(\alpha)}/2[\text{C}_{10}\text{H}_8]\}[1 - T_2^{\text{H-H}(\beta)}/T_2^{\text{H-H}(\alpha)}]^{1/2}}{[T_2^{\text{H-H}(\beta)}/T_2^{\text{H-H}(\alpha)} - (A_{\text{H}}^{(\alpha)}/A_{\text{H}}^{(\beta)})^2]^{1/2}} \quad (10)$$

are 8.63×10^7 and 3.22×10^7 radians/s, and $T_2^{\text{H-H}(\alpha)}$ and $T_2^{\text{H-H}(\beta)}$ are the contributions to T_2 for the α and β protons due to the electron exchange ($1/T_2 = 1/T_2^{\text{H-H}(\beta)} + 1/T_{2,0}$). Computer simulation of the resulting spectrum from this experiment reveals $T_2^{\text{H-H}(\beta)}/T_2^{\text{H-H}(\alpha)} = 6.46$, which corresponds to a rate constant of $k_{\text{H-H}} = 5.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in agreement with the previously published EPR determined value⁴ and our own EPR measurements.

The rate constant for the electron transfer to naphthalene from perdeuterated naphthalene was obtained from a ^1H -NMR spectrum at 298 K of a 1.71 M solution of a 1:9 mixture of C_{10}H_8 and C_{10}D_8 and eq 11 (Figure 2). The large relative

$$k_{\text{D-H}} = \frac{\{A_{\text{H}}^{(\alpha)}/2[\text{C}_{10}\text{H}_8]\}[1 - T_2^{\text{D-H}(\beta)}/T_2^{\text{D-H}(\alpha)}]^{1/2}}{[T_2^{\text{D-H}(\beta)}/T_2^{\text{D-H}(\alpha)} - (A_{\text{H}}^{(\alpha)}/A_{\text{H}}^{(\beta)})^2]^{1/2}} \quad (11)$$

concentration of the isotopically heavy material ensures the majority of the electron transfers to C_{10}H_8 come from $\text{C}_{10}\text{D}_8^{\bullet-}$. From this experiment $T_2^{(\beta)}/T_2^{(\alpha)}$ was found to be 6.79. This corresponds to a rate constant of $9.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. However, we must correct for any contribution to this rate constant due to electron transfer from $\text{C}_{10}\text{H}_8^{\bullet-}$ to C_{10}H_8 , $k_{\text{obs}} = (0.90k_{\text{D-H}} + 0.10k_{\text{H-H}})$. This leads to a corrected rate constant of $9.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. From several such experiments $k_{\text{D-H}}$ is found to be $(9.8 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which means that electron transfer from the deuterated species is faster than from the protiated species by nearly a factor of 2.

The rate constant for the transfer of an electron from $\text{C}_{10}\text{H}_8^{\bullet-}$ to C_{10}D_8 ($k_{\text{H-D}}$) cannot be determined from ^1H -NMR measurements. However, the EPR spectrum of $\text{C}_{10}\text{H}_8^{\bullet-}$ extends well

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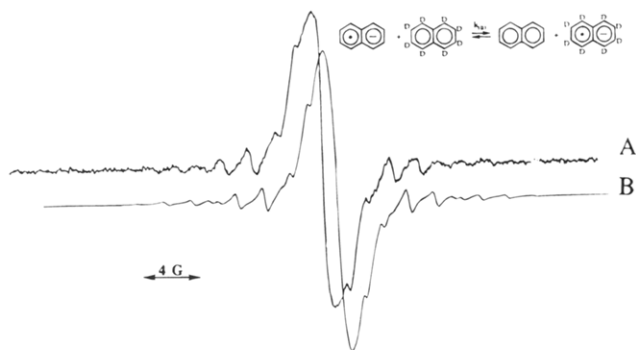


Figure 3. (A) X-band EPR spectrum of a mixture of the perdeuterated naphthalene (0.020) and naphthalene (0.002 M) anion radicals in HMPA. (B) A computer simulation generated using a rate constant for electron transfer (k_{H-D} , reaction 8) of $3.48 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

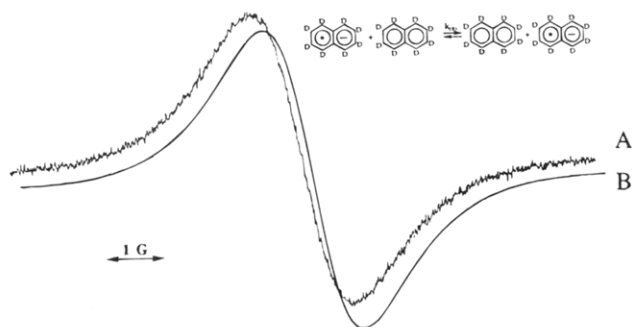


Figure 4. (A) X-band EPR spectrum of the perdeuterated naphthalene anion radical ($\text{C}_{10}\text{D}_8^{\bullet-}$) in HMPA in the presence of 0.028 M neutral C_{10}D_8 in the fast exchange region. (B) A computer simulation generated using a rate constant for electron transfer (k_{D-D} , reaction 6) of $6.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Table 1. Rate Constants for Electron Transfer at 298 K in HMPA

electron donor	electron acceptor	$k (\text{M}^{-1} \text{s}^{-1}) \times 10^{-8}$	method
$\text{C}_{10}\text{H}_8^{\bullet-}$	C_{10}H_8	5.1 ± 0.1	NMR and EPR
$\text{C}_{10}\text{H}_8^{\bullet-}$	C_{10}D_8	3.5 ± 0.1	EPR
$\text{C}_{10}\text{D}_8^{\bullet-}$	C_{10}H_8	9.8 ± 0.1	NMR
$\text{C}_{10}\text{D}_8^{\bullet-}$	C_{10}D_8	6.4 ± 0.2	EPR

beyond the spectral width for $\text{C}_{10}\text{D}_8^{\bullet-}$ allowing the determination of the line widths and hence the EPR T_2 's of $\text{C}_{10}\text{H}_8^{\bullet-}$ in the presence of large concentrations of C_{10}D_8 . A sample containing 91% C_{10}D_8 and 9% C_{10}H_8 reduced with a very deficient amount of sodium metal exhibits the simultaneous presence of both anion radicals upon EPR analysis. Due to the relatively high concentration of the perdeuterated material the spectrum for $\text{C}_{10}\text{D}_8^{\bullet-}$ is broadened into the fast exchange region due to reaction 6. The spectrum for $\text{C}_{10}\text{H}_8^{\bullet-}$ is in the slow exchange region and is broadened, for the most part, due to the electron transfer to C_{10}D_8 (forward direction of reaction 8). Computer simulation of this spectrum without a correction for line broadening due to electron transfer from $\text{C}_{10}\text{H}_8^{\bullet-}$ to C_{10}H_8 yields a rate constant of $3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Figure 3). Thus, the corrected k_{H-D} is $3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for this experiment. Three such experiments with k_{H-D} 's of 3.36×10^8 , 3.48×10^8 , and 3.48×10^8 average to a k_{H-D} of $(3.5 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

EPR proved to be ideal for the measurement of the rate constant for electron transfer from the perdeuterated naphthalene anion radical to perdeuterated naphthalene (Figure 4). Due to the small coupling constants and consequently the small spectral width, measurements were made in the fast exchange region.

The rate constant for reaction 8 is $(6.4 \pm 0.1) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1).

Discussion

The rate constant for the heavy-to-heavy system is 1.2 times larger than that for the light-to-light ($k_{H-H}/k_{D-D} = 0.80$). Subtracting eq 5 from an analogous expression for λ_{D-D} leads to eq 12. Since the electron transfer most likely takes place via

$$\lambda_{D-D} - \lambda_{H-H} = (1/D_{\text{opt}} - 1/D_{\text{st}})e^2[1/2r_{\text{H}^\circ} - 1/2r_{\text{D}^\circ} + 1/2r_{\text{H}^-} - 1/2r_{\text{D}^-} - 1/r_{\text{D-D}} + 1/r_{\text{H-H}}] \quad (12)$$

a face-to-face interaction (structure **I**), r_{D-D} is equal to r_{H-H} ,



allowing eq 12 to be simplified and rearranged to eq 13, where the reduced neutral radius is given by $\mu_0 = (r_{\text{D}^\circ} - r_{\text{H}^\circ})/r_{\text{H}^\circ}r_{\text{D}^\circ}$, and the reduced anion radical radius is $\mu_- = (r_{\text{D}^-} - r_{\text{H}^-})/r_{\text{H}^-}r_{\text{D}^-}$.

$$\lambda_{D-D} - \lambda_{H-H} = (1/D_{\text{opt}} - 1/D_{\text{st}})e^2[\mu_0/2 + \mu_-/2] \quad (13)$$

For naphthalene, X-ray crystallography reveals a reduction of the C-L (L = H or D) bond length from 1.085 (C-H) to 1.073 (C-D) Å;¹² thus μ_0 is -0.01031 . The numerical value for $(1/D_{\text{opt}} - 1/D_{\text{st}})e^2$ is 606 kJ Å/mol,¹³ and as a first approximation the 0.012 Å bond length reduction in neutral naphthalene is considered to be the same for the anion radical, in which case $\mu_0 = \mu_-$. This approximation leads to $\lambda_{D-D} - \lambda_{H-H} = -606 \text{ kJ Å/mol} \times 0.01031 \text{ Å} = -6.25 \text{ kJ/mol}$, and yields a theoretical value for k_{H-H}/k_{D-D} of $e^{(\lambda_{D-D} - \lambda_{H-H})/4RT} = e^{-6250/4RT} = 0.53$.

Using this approximation of Marcus theory, the theoretically predicted isotope effect upon the electron transfer rate is larger than that observed. The discrepancy probably involves one of the two assumptions involved in our application. It seems unlikely that r_{D-D} is different than r_{H-H} (structure **I**), but μ_0 and μ_- are not exactly identical. In fact, the addition of an electron destabilizes the deuterated species to a greater extent than it does the protiated species,⁸ so it is logical that $\mu_- > \mu_0$, and the 0.53 needs to be multiplied by a correction factor of $e^{606(\mu_- - \mu_0)/4RT}$. This attenuates the theoretical isotope effect, and for this term to bring the 0.53 up to 0.80, in agreement with experiment, $\mu_- - \mu_0$ needs to be about 0.0066 Å. This requires that replacement of a hydrogen with a deuterium in the anion radical reduces the bond length by nearly 0.02 Å, compared to a value of 0.012 Å for the neutral species.

X-ray data for the anion radicals of naphthalene are not available. However, such a reduction in bond length does seem plausible. The above calculation indicates that the total solvent reorganization energy is -5.25 kJ/mol . This very small perturbation in the anion radical (eight extra neutrons) decreases the solvent reorganization by 1.9% of the total solvation enthalpy, reaction 2.

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The analogous treatment of $k_{\text{H-D}}/k_{\text{D-H}}$ with eq 4, of course, leads to the fact that this ratio is simply the thermodynamic equilibrium constant. From Table 1, this value is 0.36, which is in agreement with the previously published value for K_{eq} for reaction 8 at 298 K.⁸ From Table 1, $k_{\text{D-H}} > k_{\text{D-D}} > k_{\text{H-H}} > k_{\text{H-D}}$, and these rate constants range from 3×10^8 to $10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Although Marcus theory does not yield quantitative agreement with the rate constants for electron transfer,⁵ it does seem to reasonably account for the perturbation upon the rate constants due to deuteration. Marcus theory does predict that $k_{\text{H-D}} = (k_{\text{D-D}}k_{\text{H-H}}K_{\text{eq}})^{1/2}$, and this has been pointed out in a previous preliminary communication concerning similar isotope effects in tetrahydrofuran where ion association exists.¹³ Our data (Table 1) fit this expression quite well.

Experimental Section

Prior to commencing our studies of reactions 5 and 8, EPR and NMR techniques were used to reproduce the known rate constant for reaction 3. In a typical experiment 1 mL of perdeuterated HMPA was mixed with 5 mL of perprotonated HMPA. A small chunk of potassium metal was added to this mixture and the apparatus was evacuated. After the blue color of the solvated electron appeared, the solvent mixture was distilled under high vacuum into a bulb containing 55 mG of naphthalene (C_{10}H_8). The resulting solution was touched to a freshly distilled sodium mirror until the faint green color of $\text{C}_{10}\text{H}_8^{\bullet-}$ was detected. A sample of this solution was poured into an attached NMR

or EPR sample tube, and the sample tube was subsequently sealed from the apparatus. Experimental values for the rate constants for reactions 6 and 8 were obtained in a similar manner, except that perdeuterated naphthalene (C_{10}D_8) or mixtures of C_{10}D_8 and C_{10}H_8 were used.

It should be noted that the anion radical of naphthalene is cleanly formed, is extremely stable, and does not contain EPR silent material that can interfere with the equilibria under consideration.¹⁴ Samples stored in our laboratory for over 5 years at room temperature still exhibit the original EPR signal for $\text{C}_{10}\text{H}_8^{\bullet-}$. However, this stability is not a necessary condition for the kinetic study, as both the EPR and NMR related formalisms are independent of anion radical concentration.

The NMR spectra were recorded on a Varian (Gemini) 300-MHz (^1H) NMR spectrometer. The NMR simulations were generated using version 5.1 of VNMR by Varian Associates. EPR measurements and simulations were carried out as previously described on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit.¹⁵

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