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Photoionization of Phenothiazine: EPR Detection of Reactions of the Polarized Solvated Electron

Nicholas J. Turro,*,† **Igor V. Khudyakov**,†,‡ **and Hans van Willigen***,§

Contribution from the Departments of Chemistry, Columbia University, New York, New York 10027, and University of Massachusetts at Boston, Boston, Massachusetts 02125

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Abstract: Photoionization of phenothiazine (PTH) and reactions of the solvated electron with some electron acceptors were studied with steady state and time-resolved EPR and transient optical absorption techniques. Time-resolved EPR spectra from the phenothiazine cation radical ($PTH^{\bullet +}$) and hydrated electron (e_{aq}^-) formed in sodium 1-dodecylsulfate (SDS) micellar solution were observed in emission. By contrast, $PTH^{\bullet +}$ formed by photoionization of PTH in alcohols gives absorptive EPR signals. The spin polarization carried by the hydrated electron in SDS solutions can be transferred effectively to a stable nitroxyl free radical 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxyl ($N^{\bullet -}$) present in the bulk aqueous phase. EPR and flash photolysis measurements show that this electron spin polarization transfer process proceeds with a rate which is approximately five times faster than the chemical reaction between e_{aq}^- and $N^{\bullet -}$. The marked difference in rates is attributed to differences in spin-statistical factors and difference in reaction radii for spin exchange compared to reaction. In alcohol solutions of PTH and a nitroxyl stable radical (2,2,6,6-tetramethylpyperidin-1-oxyl, TEMPO), excitation of PTH also results in emissive polarization of the EPR spectrum of the stable radical. In this case the polarization is produced by the interaction between PTH triplets and TEMPO (doublet–triplet radical pair CIDEP). Trapping of e_{aq}^- produced by photoionization of PTH in SDS solution by electron acceptors such as acrylamide and chlorophenols yields free radicals whose formation was monitored with time-resolved EPR and flash photolysis.

Introduction

Photoionization is the first step in many light-driven reactions and, therefore, continues to be the subject of investigations concerned with mechanism and kinetics.[1,2] The solvated (hydrated) electron e_{sol}^- (e_{aq}^-) produced by the photoionization process can be detected by electron paramagnetic resonance (EPR) so that this technique has been found to be useful in studies of the e_{sol}^- generation step and of follow-up reactions involving this important chemical species.[3-9] Recent studies of photoionization of aromatics in microheterogeneous micellar solutions and homogeneous solutions with time-resolved (continuous wave) EPR (TREPR) have revealed a variety of Chemically Induced Dynamic Electron Polarization (CIDEP) effects. For instance, the TREPR spectrum of e_{sol}^- produced by photoionization of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in 2-propanol initially consists of a broad resonance peak with an emission/absorption (E/A) polarization pattern.[8] The E/A feature is attributed to the exchange interaction (J) between the unpaired electrons in the (spin-correlated) radical pair [$TMPD^{\bullet +}$, e_{sol}^-]. By contrast, Jeevarajan and Fessenden have found that e_{aq}^- generated by photoionization of phenols in basic aqueous solution gives rise to an absorptive CIDEP signal.[5] The spin polarization in this case is attributed to Radical Pair Mechanism (RPM) CIDEP. In both studies it is concluded that exchange interaction is positive ($J > 0$) in the geminate radical pairs (triplet lower than singlet) contrary to what is normally found. Finally, e_{aq}^- produced by photoionization of aromatic ketones in SDS micelles is found to give an emissively polarized TREPR signal.[6] In this case, the spin polarization is attributed to Triplet Mechanism (TM) CIDEP. From these earlier studies it can be concluded that time-resolved cw and pulsed EPR studies can be a valuable source of information on the photoionization process and media effects on the characteristics of the solvated electron. The present study in part is concerned with CIDEP effects observed in TREPR and FT-EPR spectra of the cation radical and e_{aq}^- (e_{sol}^-) produced by photoionization of phenothiazine (PTH) in aqueous micellar solutions and in alcohols. PTH has a well-documented photochemistry[10-13] and is a convenient source of e_{aq}^- and/or e_{sol}^-.

Electron spin polarization transfer (ESPT) from e_{aq}^- to a stable free radical added to the solution has been studied as well. The rate of ESPT is compared to the rate of the chemical reaction of e_{aq}^- with the stable free radical. The hydrated

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[†] Columbia University.

[‡] Present address: General Electric Silicones, Waterford, NY 12188.

[§] University of Massachusetts at Boston.

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electron is a powerful reducing agent which may be useful for degradation of organic pollutants, particularly halogenated phenols, in waste waters. Since photoionization of aromatics in SDS is an efficient process for formation of e_{aq}^-, it provides a convenient method for spectroscopic studies of the chemistry of organics in aqueous solution triggered by electron capture. We present results of TREPR and flash photolysis measurements of the reaction of e_{aq}^- with some electron acceptors.

Experimental Section

1. Instruments. A detailed description of the TREPR instrument is given elsewhere.[14] The instrument consists of a Bruker ER 100 D spectrometer, a PAR model 4402 digital boxcar integrator, a Quanta Ray DCR 2A Nd:YAG laser (third [355 nm] harmonic, 8 ns fwhm, typical laser energy 10−15 mJ/pulse at 20 Hz), and a Bruker broad band preamplifier with response time of 60 ns. Boxcar sampling gates were 100−500 ns. Typically, TREPR spectra were recorded with a sampling delay setting of 300 ns and 0.7 mW microwave power. The earliest time at which reliable data can be obtained is estimated to be *ca.* 200 ns after laser excitation; this time is considered as $t = 0$ in the cw TREPR data reported. TREPR measurements of the time dependence of the signal of e_{aq}^- were performed at fixed magnetic field by varying the sampling delay time of the boxcar integrator with a sampling window of 20 ns. Either the third harmonic (355 nm) of a Nd:YAG laser or the 308 nm light from a XeCl excimer laser (MPB Technologies AQX-150) fired at 5 Hz (fwhm ~ 15 ns, 10 mJ/pulse) was used. In some experiments the fourth harmonic (266 nm) of the same laser with similar fwhm and energy as well as 308 nm XeCl excimer laser pulses from a MPB Technologies excimer laser (AQX-150) fired at 5 Hz (fwhm ~ 15 ns, 10 mJ/pulse) was used. The experiments were run using a flow system with a flat quartz EPR cell (path length 0.5 mm). Flow rates typically were in the range of 2 to 5 mL/min.

FT-EPR measurements were performed with a Bruker ESR 300 pulsed EPR spectrometer (Columbia University) or a home-built spectrometer (UMB).[15] Lambda-Physik excimer lasers (308 nm, ~20 mJ/pulse, 10 Hz, fwhm ~ 15 ns) were used for sample excitation. Solutions were circulated through a flat quartz EPR cell (0.4 mm path length) and were purged with argon. Information on the time evolution of FT-EPR spectra was obtained by recording the FID of the transverse magnetization for a series of delay times (ranging from 10 ns to 5 μs) between laser excitation and microwave pulse. In most cases, the FID was the time average of a total of 40 acquisitions (10 per phase in the CYCLOPS phase-cycling routine).

For sample excitation, the nanosecond flash photolysis apparatus employed the Nd:YAG (third harmonic) or excimer laser systems used for the TREPR experiments. A pulsed Xenon lamp combined with an ISA H10 monochromator served as the monitoring system. Further details on the equipment are given elsewhere.[14] Typically, data acquired with 10−15 laser pulses were averaged to produce each experimental trace both in the kinetic experiments and in the acquisition of transient absorption spectra. Quartz cells having cross-sections of 1 × 1 cm were used. In measurements of the dependence of the optical density (OD) on excitation light intensity (I), the latter was varied by changing the laser power and/or by using neutral density filters. Intensities were determined with a power meter (Scientech 362). In OD *versus* I experiments, ODs were measured ~25 ns after the laser flash, the time at which the transient light absorption was found to reach a maximum.

Conventional steady state EPR spectra were measured with the Bruker ESR 300 spectrometer mentioned earlier.[16] The microwave power was ~2 mW and the 100 kHz field modulation amplitude was 0.1−0.5 G. Solutions in Pyrex EPR tubes were irradiated *in situ* with a 200 W Hg/Xe lamp.

Absorption spectra were taken with the HP 8452Win Diode-Array UV−vis spectroscopy system.

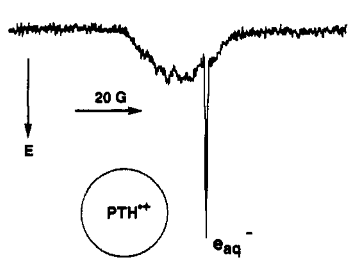
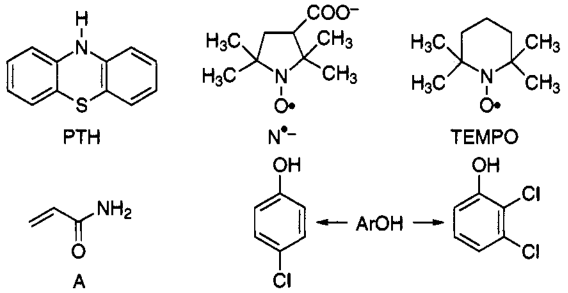


Figure 1. TREPR spectrum of PTH in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser. The circle around $PTH^{\bullet +}$ emphasizes that the radical cations reside in the micelles.

2. Reagents and Solutions. PTH (Fluka) was twice recrystallized from methanol and dried *in vacuo*. Stable nitroxyl free radicals 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxyl (denoted as $N^{\bullet -}$) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), both from Aldrich, were used as received. The structures of PTH, $N^{\bullet -}$, TEMPO, and some other reagents are given below:



In SDS solutions (pH 7−8) $N^{\bullet -}$ is present in the ionized form.[17] Acrylamide (A) from Aldrich was recrystallized twice from chloroform.[18a] 4-Chlorophenol (purity greater than 99%, Aldrich) was used as received and 2,3-dichlorophenol (City Chemical, NY) was purified by sublimation *in vacuo*. Both phenols are denoted as ArOH. Micellar solutions were prepared by dissolving sodium 1-dodecyl sulfate (SDS, Bio-Rad Laboratories) in deionized water or in a buffer solution (pH 8.0, Fisher). The concentration of micelles is estimated to be 1−5 mM assuming an aggregation number of ~64.[19] PTH does not dissolve significantly in water but millimolar concentrations are readily achieved in micellar solutions. For EPR experiments the PTH concentration was ~3.0 × 10^{-3} M, and for laser flash photolysis measurements the concentration was ~1.0 × 10^{-4} M. Micellar solutions were sonicated and filtered prior to use. PTH was dissolved in alcohols (methanol, 1-propanol, 1-butanol, all from Aldrich) in the same concentrations, i.e., 3.0 × 10^{-3} M for EPR and 1.0 × 10^{-4} M for laser flash photolysis experiments. No sonication was used in the preparation of micellar solutions of PTH and $N^{\bullet -}$, because this process appeared to promote oxidation of PTH by $N^{\bullet -}$. Instead, a micellar solution of PTH was mixed with a micellar solution of $N^{\bullet -}$ and gently stirred. Stock solutions of PTH were kept deoxygenated and in the dark to prevent oxidation. Experiments with $N^{\bullet -}$ were run not longer than ca. 10 min after preparation of solutions. Solutions were deoxygenated by prolonged Ar bubbling. All measurements were performed at room temperature.

Results

1. TREPR from SDS Solutions. Laser excitation (355 nm) of solutions of PTH in SDS produces the TREPR spectrum presented in Figure 1. Similar spectra are obtained by photoexcitation with 308- or 266-nm light. The spectrum is completely in net emission and is characterized by a broad resonance, with poorly resolved hyperfine (HF) structure, attributed to the radical cation produced by photoionization of

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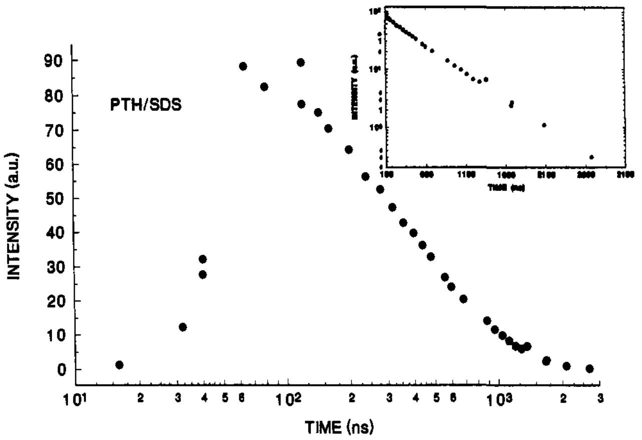

Figure 2. Time profile of the FT-EPR signal intensity of e_{aq}^- formed under flash photoexcitation of PTH in SDS micelles with the excimer laser. Inset: a semilogarithmic plot of the e_{aq}^- signal decay.

PTH and a narrow resonance due to e_{aq}^-. A *g*-value measurement using the *g*-value of TEMPO[20] (2.0059) as reference gives 2.0053 and 2.0005 for $PTH^{\bullet+}$ and e_{aq}^-, respectively. The values are in good agreement with literature data.[5,20,21] An increase in pH of the SDS solution by using the pH 8 buffer in sample preparation did not change the TREPR spectrum.

With FT-EPR, only the e_{aq}^- signal is observed. The contribution to the FID from the $PTH^{\bullet+}$ decays within the deadtime of the spectrometer because of the short T_2. Figure 2 displays a typical time profile of the intensity of the FT-EPR signal given by PTH/SDS samples. The maximum intensity is observed with a delay time of ~50 ns between laser pulse and microwave pulse. Signal growth is determined by the instrument response time. The decay is exponential (cf. inset Figure 2) and is found to depend on sample preparation. A sample prepared by solubilizing PTH in SDS solution by overnight sonication under an argon atmosphere gave a decay rate constant (k_d) of 1×10^6 s^{-1}. The decay rate of e_{aq}^- in a solution deoxygenated by passing argon over it for a couple of hours only was 2×10^6 s^{-1}. The time domain signal (FID) given by the hydrated electron was analyzed with the LPSVD method.[22] This is a least-squares fitting routine which simulates the FID in terms of a summation of a discrete number (in this case one) of damped sinusoids. Analysis shows that the FID decays exponentially with the rate constant (T_2^{-1}) that matches k_d, the rate of decay of the intensity of the FT-EPR (frequency domain) signal. Since T_2^{-1} defines the line width of the FT-EPR peak, it is concluded that this width is determined by the rate of signal decay.

2. Steady State cw EPR and Absorption Spectra. The mild oxidation of PTH in SDS micelles by air or by brief irradiation leads to the appearance of a purple colored solution due to the formation[23] of the radical cation $PTH^{\bullet+}$. The solutions give the EPR spectrum shown in Figure 3. The spectra shown in Figures 1 and 3 match that assigned in the literature[20,21] to $PTH^{\bullet+}$. Laser irradiation or prolonged lamp irradiation of SDS solutions of PTH leads to a blue colored solution, which does not show an EPR signal. The visible absorption spectrum of PTH and characteristic absorption bands of the purple and blue solutions are presented in Figure 4. $PTH^{\bullet+}$ participates in a number of reactions (deprotonation, radical−radical coupling and probably others[10,24,25]); a blue dimer (Figure 4c) is one of the main products of PTH (photo)oxidation.[25]

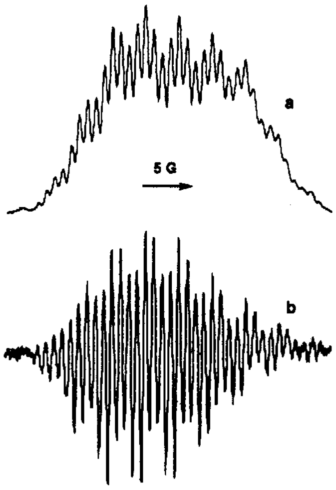

Figure 3. A cw EPR spectrum of the solution of PTH in SDS micelles under irradiation with a Hg/Xe lamp: (a) spectrum presented in the integrated form; (b) conventional (first derivative) presentation.

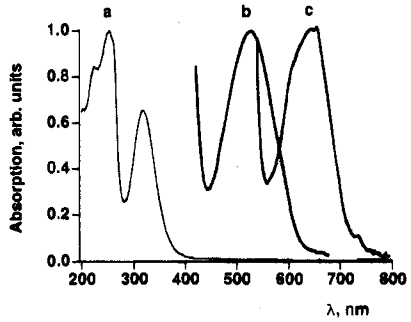

Figure 4. Absorption spectra of PTH in SDS micelles and products of PTH oxidation, see text: (a) the starting solution [the given absorption (OD) corresponds to the concentration of PTH of 1.5×10^{-5} M]; (b) purple product of mild oxidation; (c) blue product of oxidation.

Figure 5. TREPR spectrum of PTH in 1-propanol under flash photoexcitation with the third harmonic of a Nd:YAG laser recorded 700 ns after the laser pulse.

3. TREPR of PTH in Alcohols. A representative TREPR spectrum produced by pulsed laser excitation of PTH in alcohols is given in Figure 5. The spectrum is in net absorption and is markedly better resolved than that obtained in SDS solutions (cf. Figures 1 and 5). It closely matches the conventional EPR spectrum given by the stable radical obtained upon (photo)-oxidation of PTH, cf. Figure 3a. TREPR spectra do not show an e_{sol}^- resonance. Results of FT-EPR measurements are similar to those given by TREPR. Apparently the signal from e_{sol}^- in

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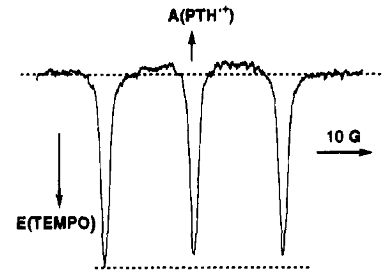

Figure 6. TREPR spectrum of PTH in 1-propanol under flash photoexcitation with the third harmonic of a Nd:YAG laser in the presence of TEMPO (3.0×10^{-3} M).

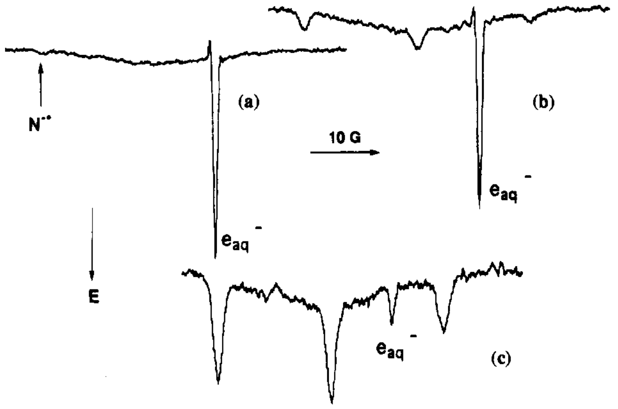

Figure 7. TREPR spectra of PTH in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser in the presence of different concentrations of $N^{•-}$: (a) 5.0×10^{-4} M; (b) 1.1×10^{-3} M; (c) 2.2×10^{-3} M. The arrow in part a shows the weak but reproducible component of polarized $N^{•-}$.

this case is weak and decays within the deadline of the pulse spectrometer. The FT-EPR spectrum from $PTH^{•+}$ shows a gradual increase in intensity with increasing delay time between laser excitation and microwave pulse during the first microsecond. This indicates that the cation radicals are born with little spin polarization.

Excitation of PTH in an alcohol solution containing TEMPO (5.0×10^{-4}–5×10^{-3} M) produces the TREPR depicted in Figure 6. The spectrum is dominated by the three emissively polarized resonances from the nitroxyl radical; in addition, a weak absorptive contribution due to the $PTH^{•+}$ can be discerned.

4. TREPR from SDS Solutions in the Presence of Electron Acceptors. The signal of e_{aq}^- was quenched by the addition of different electron acceptors, e.g., $N^{•-}$, A, and ArOH (Figures7–9). In the case of $N^{•-}$, TREPR shows emissively polarized resonances from the nitroxyl radical (cf. Figure 7).

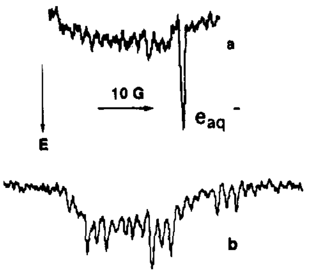

Figure 8. TREPR spectra of PTH in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser in the presence of A: (a) [A] = 2.8.10^{-3}; (b) [A] = 1.1×10^{-2} M.

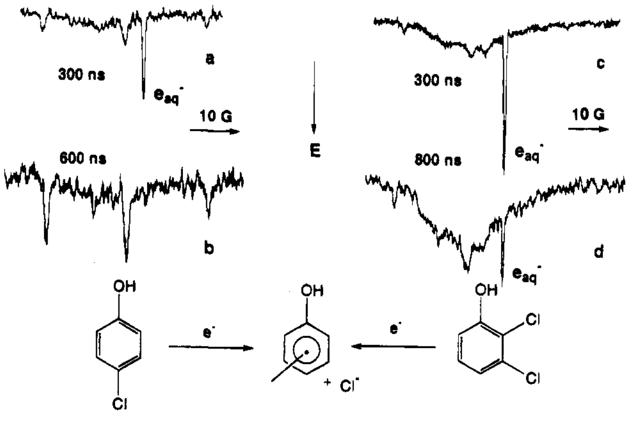

Figure 9. TREPR spectra of PTH in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser in the presence of 1.0×10^{-2} M ArOH at different times of detection of spectra: (a, b) 4-chlorophenol; (c, d) 2,3-dichlorophenol.

Addition of A to a PTH/SDS solution yielded the spectrum of a reduction product of A upon photoexcitation of PTH (cf. Figure 8). In the experiments with A and $N^{•-}$, a series of spectra were taken under comparable conditions except with a different concentration of A ($N^{•-}$). Concentrations ranged from 0–3.0×10^{-2} to 0–6.0×10^{-3} M for A and $N^{•-}$, respectively. Under conditions of $[A] \geq 2.5 \times 10^{-2}$ and $[N^{•-}] \geq 5 \times 10^{-3}$ M, the signal of e_{aq}^- is not observed and only signals of polarized products were observed. The intensities (I) of signals (at $t \sim 300$ ns) of e_{aq}^- as well as of components of polarized adducts $A^{•-}$ and $N^{•-}$ were determined under different concentrations of adducts within the range of concentrations given above.

In these TREPR experiments on the transfer of emissive polarization to stable nitroxyl radicals as well as in other similar experiments[32] we did not observe the turn to absorption ESR signal at a later stage of its observation.

5. Laser Flash Photolysis. Data from transient absorption measurements of PTH in SDS or alcohols are similar to those reported in the literature.[10,11] In particular, in SDS solutions the formation of the triplet $^3PTH^*$ ($\lambda_{max} \sim 460$ nm), the free radical $PTH^{•+}$ ($\lambda_{max} \sim 520$ nm), and e_{aq}^- (broad band with $\lambda_{max} \sim 720$ nm) is observed. The decay kinetics of the first two species were monitored at their absorption maxima. The decay of e_{aq}^- was monitored at 600 or 650 nm where the photomultiplier has higher sensitivity than at 720 nm. In general, the decay of the three transients did not conform to first- or second-order kinetics. The characteristic lifetime of e_{aq}^- under our experimental conditions was $\tau_{1/2} \geq 5\ \mu s$ in accordance with ref 10. As noted in these earlier investigations,[10] the photoioniza-

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(29) This paper does not claim to give the definitive answer regarding CIDEP generated under photoionization of PTH in alcohols. A Reviewer has advanced an interesting explanation for the absence of the RPM mechanism of CIDEP in the reaction. He suggested that "recombination" (electron transfer) occurs with equal ease into both singlet (S) and triplet (T) manifolds, which should lead to compensation of E/A and A/E patterns of RPM CIDEP and to the absence of RPM pattern in the observed CIDEP spectra. However, it is very improbable that electron transfer proceeds with equal probabilities into both S and T states because these states have different energies, and the $\Delta G°$ of reaction will be different. The rate constant of electron transfer depends upon $\Delta G°$, and fractions of RPs recombined into T and S states will be different. Moreover, it is very unlikely that recombination generating $^3PTH^*$ is energetically feasible. Thus, RP will recombine in either a S or T state (or in one state with a higher rate/probability than the other), and such a recombination will lead to the predominance of an A/E or an E/A pattern. Thus, the alternative offered by this Reviewer appears less probable than the explanation we suggest.

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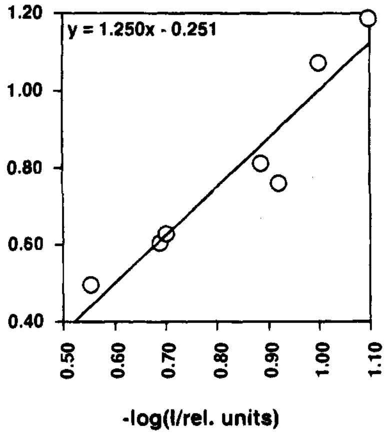

Figure 10. The dependence of the OD ascribed to $PTH^{\bullet+}$ at λ_{max} 520 nm upon laser power in the log–log coordinates. Data were obtained during photolysis of PHT solution in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser.

tion yield and the lifetime of transient species in alcohol solutions were found to be less than for PTH in micellar solution.

Transient absorption measurements were used to study quenching of e_{aq}^- by A and $N^{\bullet-}$. Addition of A or $N^{\bullet-}$ in the concentration of 10^{-4}–10^{-3} M to a micellar solution of PTH leads to a strong increase of e_{aq}^- decay. The decays are first order and measurement of the decay rate as a function of [A] and $[N^{\bullet-}]$ gave rate constants of the reactions

$$e_{aq}^- + A \xrightarrow{k_1} A^{\bullet-} \qquad (1)$$

$$e_{aq}^- + N^{\bullet-} \xrightarrow{k_2} \text{diamagnetic product(s)} \qquad (2)$$

$k_1 = (7.0 \pm 1.5) \times 10^9$ and $k_2 = (5 \pm 2) \times 10^9\ M^{-1}\ s^{-1}$ in SDS solution. The relatively large uncertainty in k_2 is due to the reaction of PTH with $N^{\bullet-}$ (*vide infra*).

Figures 10 and 11 show the dependence of $PTH^{\bullet+}$ and $^3PTH^*$ yields on laser intensity. Within experimental uncertainty the results were not affected by variation of [PTH] over a range from 5.0×10^{-5} to 2.5×10^{-4} M.

Discussion

1. CIDEP Effects. Photoionization of PTH in SDS micelles and alcohols can involve the following reaction steps:[10,11]

$$PTH + h\nu \rightarrow {}^1PTH^* \qquad (3)$$

$$^1PTH^* \rightarrow PTH^{\bullet+} + e_{sol}^-(e_{aq}^-) \qquad (4)$$

$$^1PTH^* \rightarrow {}^3PTH^* \qquad (5)$$

$$^3PTH^* + h\nu \rightarrow PTH^{\bullet+} + e_{sol}^-(e_{aq}^-) \qquad (6)$$

Flash photolysis studies[10,11] have shown that monophotonic ionization via the singlet excited state (reaction 4) is the major route of $e_{sol}^-(e_{aq}^-)$ formation in micellar solution and alcohols. However, a two-photon process involving an upper triplet state can play a role as well.[11] Our data on the laser dose dependence of the optical density of $[PTH^{\bullet+}]$ demonstrates that $[PTH^{\bullet+}] \sim I^{1.2}$ (cf. Figure 10). This indicates that a two-quanta process contributes only slightly to the formation of $PTH^{\bullet+}$ and e_{aq}^-. Furthermore, it is found that $[^3PTH^*] \sim I^{0.8}$ (cf. Figure 11) is consistent with some photoionization of $^3PTH^*$ according to reaction 6.

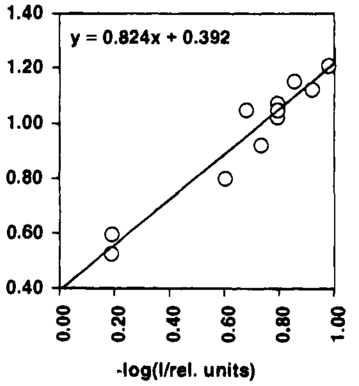

Figure 11. Dependence of the OD ascribed to $^3PTH^*$ at λ_{max} 460 nm upon laser power in the log–log coordinates. Data were obtained during photolysis of PHT solution in SDS micelles under flash photoexcitation with the third harmonic of a Nd:YAG laser.

$e_{sol}^-(e_{aq}^-)$ formation according to eqs 4 and 6 is fast compared to the time resolution of our spectroscopic measurements (ca. 50 ns). Hence, photoionization may be considered complete at the end of laser excitation of PTH. This accounts for the fact that FT-EPR signal growth for the PTH/SDS system (cf. Figure 2) is instrument limited. Photoionization via singlet or triplet excited states of PTH involves the $[PTH^{\bullet+}, e_{sol}^-(e_{aq}^-)]$ radical pair. Radical Pair Mechanism (RPM) CIDEP can give rise to a low-field absorption/high-field emission (A/E) or E/A pattern in time resolved EPR spectra of the separated radicals.[26] The finding that spectra generated by photoionization of PTH solubilized in SDS micelles are completely in net emission (cf. Figure 1) establishes that the RPM does not play an important role in this system. Development of RPM polarization requires that the radical pair survives for some nanoseconds. In view of the high reactivity of $e_{sol}^-(e_{aq}^-)$ and the nonpolar environment inside the micelle $[PTH^{\bullet+}, e_{sol}^-(e_{aq}^-)]$ is expected to be short lived. In fact, flash photolysis studies[27] of photoionization in micellar solutions indicate that the electron escapes to the bulk aqueous phase within picoseconds. The absence of observable RPM CIDEP, therefore, is not surprising.

The net emission spectrum given by PTH/SDS is consistent with spin polarization being carried over from $^3PTH^*$. If Triplet Mechanism (TM) CIDEP is strong and RPM CIDEP negligible, the triplet photoionization channel can make the dominant contribution to the observed signal even though it makes only a small contribution to the yield of e_{aq}^-. It is noted that the conditions are favorable for TM CIDEP in this system, because the spin–lattice relaxation time of $^3PTH^*$ is expected to be longer in micelles than in homogeneous solution as a result of the relatively high viscosity in the interior of the SDS micelles.[14,28]

For PTH in alcohols net absorptive TREPR and FT-EPR spectra are obtained (cf. Figure 5) with no sign of RPM CIDEP contribution. FT-EPR spectra generated by pulsed-laser excitation of PTH in 1-propanol show a complex pattern of HF lines that so far has not been analyzed in detail. However, the spectra show a gradual increase in intensity following laser excitation. Since, as far as the measurements are concerned, radical formation is instantaneous, the slow signal development is attributed to some sort of spin–lattice relaxation. Hence, we speculate that the radicals are born with less than the thermal equilibrium spin polarization and the RPM contribution apparently is negligible in alcohol solutions, see this section below. Contrary to what is found for PTH/SDS, the TM contribution must be very small as well. TM CIDEP is due to spin polarization transfer from $^3PTH^*$ to doublet radical products.[26] The magnitude of the effect depends, among other things, on the triplet spin–lattice relaxation time. It is expected that the T_1 gets smaller upon going from SDS to 1-propanol because of the reduction in viscosity. This can account for the sharply reduced TM effect found in homogeneous solution. Alternatively, it is possible that in alcohols the biphotonic triplet photoionization channel makes a negligible contribution. The finding that the yield of e_{sol}^- upon photoexcitation of PTH in methanol increases linearly with laser intensity[10] lends support to this interpretation.

We concluded that radical pair (RP) lifetimes in SDS are too short to generate significant RPM CIDEP. Surprisingly, no RPM was observed in alcohols as well. This conclusion stands in sharp contrast to findings in studies of other systems.[29] The lifetime of the RP given by the photolysis of TMPD in 2-propanol was reported to be 2.6 μs[30] and TREPR spectra were interpreted in terms of the presence of a long-lived spin-correlated radical pair.[8] On the other hand, TREPR spectra reported by Jeevarajan and Fessenden[5] show clear evidence of RPM CIDEP generated upon photoionization of phenols in basic aqueous solution suggesting a RP lifetime of the order of a nanosecond or so. The large variation in results is a good indication that radical pair lifetime and, more importantly, sign and magnitude of spin exchange interaction are strongly affected by changes in solvation of the ejected electron.

In their study of photoionization of aromatic carbonyls solubilized in SDS, Ishiwata et al.[6] find that the signal from e_{aq}^- has a lifetime of 0.7 μs. Our FT-EPR measurements of PTH/SDS give signal lifetimes of similar magnitude. The value is appreciably less than the estimated lifetime ($\sim$10 μs) and spin–lattice relaxation time ($T_1 \sim 5$ μs)[5] of e_{aq}^- so the question is what causes the first-order decay. Ishiwata et al.[6] attribute it to relaxation of the spin system. However, if their argument is correct one should be able to see the resonance turn from emission to (Boltzmann) absorption given sufficient signal to noise. FT-EPR measurements under a variety of conditions gave very strong signals with decay rates that depended strongly on sample preparation. Yet, we were never able to observe the expected signal phase change, so that we conclude that signal decay mainly reflects chemical decay. Given the dependence of decay rate on extent of deoxygenation of the micellar solutions (cf. Results, 1), it appears that molecular oxygen acts as a e_{aq}^- scavenger. High reactivity of molecular oxygen toward e_{eq}^- is well-documented in the literature.[2] Molecular oxygen should also lead to reduction of the signal lifetime ($T_2 = k_d^{-1}$, see Results, 1) due to acceleration of paramagnetic relaxation by the dipolar interaction between e_{aq}^- and O_2.[31] In fact, laser flash photolysis experiments which monitor kinetics of only chemical decay of e_{aq}^- and do not reflect the rate of paramagnetic relaxation of e_{aq}^- show a larger lifetime of this species than the lifetime of the FT-EPR signal, cf. Results, 5.

2. Electron Spin Polarization Transfer from e_{aq}^- to Acceptors in SDS Solutions. The signal of e_{aq}^- decreased upon addition of electron acceptors to the micellar solution at the same time that TREPR spectra of free radicals of acceptors appeared, cf. Result, 5. Electron Spin Polarization Transfer (ESPT) from primary radical to secondary radical is responsible for the observed spin polarization.[32]

In the present work we observed ESPT in the fast bimolecular reactions of $^{\#}e_{aq}^-$ with several acceptors (# denotes spin polarized). Negatively charged water-soluble spin trap $N^{\bullet-}$ is used to monitor $^{\#}e_{aq}^-$ in the aqueous phase of SDS micelles.[17] A, acrylamide, is water-soluble and is insoluble in hydrocarbons, so that it also resides in the aqueous phase. The chlorophenols (ArOH) probably are partitioned between aqueous and micellar phases. For relatively high [A] the TREPR spectrum ascribed to $A^{\bullet-}$ formed in reaction

$$^{\#}e_{aq} + A \xrightarrow{k_1'} {}^{\#}A^{\bullet-} \qquad (1')$$

1′ appeared (cf. Figure 8). A characteristic feature of the ESR spectrum of $A^{\bullet-}$ is the splitting due to the two β-protons (three components) with hyperfine coupling constant $a_{b\text{-}H} = 12.0$ G.[20,33]

Interaction of the stable nitroxyl free radical $N^{\bullet-}$ with $^{\#}e_{aq}^-$ can result in ESPT (eq 2′) or formation of a diamagnetic product(s) (eq 2).[32b,34]

$$^{\#}e_{aq}^- + N^{\bullet-} \xrightarrow{k_2'} e_{aq}^- + {}^{\#}N^{\bullet-} \qquad (2')$$

The TREPR spectrum of the nitroxyl radical shows three emissively polarized resonances (cf. Figure 7). With TREPR measurements only a change in the $N^{\bullet-}$ signal can be observed, so the signal (if there is one) is always in emission.[34]

ESPT is also observed in reactions of $^{\#}e_{aq}^-$ with ArOH:

$$^{\#}e_{aq}^- + \text{ArOH} \rightarrow \text{emissively polarized radicals} \qquad (7)$$

because both starting e_{aq}^- and reaction products are emissively polarized (Figure 9). However, the products of reaction 7 have not been identified and the reaction needs further study. Probably the first step initiated by electron capture is the formation of the (chloro)hydroxyphenyl radical as indicated in the reaction scheme in Figure 9.[35] However, the HF pattern of the observed spectra does not agree with literature data for the hydroxyphenyl radical.[20] Products of reactions of polarized hydroxyphenyl radicals may give the TREPR spectra shown in Figure 9. It is known that not only secondary but also tertiary polarized radicals can be observed.[32a]

To conclude this section we will consider CIDEP observed under photolysis of PTH in alcohols in the presence of TEMPO (Figure 6). The spectrum of TEMPO is found to be emissively polarized; by contrast, TREPR and FT-EPR spectra from $PTH^{\bullet+}$ produced by photoionization of PTH in alcohols show only absorption peaks (Figure 5). It is also noted that the signal from e_{sol}^- decays within the deadtime of the FT-EPR spectrometer suggesting that ESPT cannot be responsible for the emission signal in this case. Photoexcitation of PTH in homogeneous solutions leads primarily to $^3PTH^*$ formation and we attribute the polarization of the TEMPO spin system to the effect of the interaction between the doublet radical and $^3PTH^*$ (Radical Triplet Pair Mechanism, RTPM[36]):

$$^{3}\text{PTH}^* + \text{TEMPO} \rightarrow \text{PTH} + {}^{\#}\text{TEMPO} \qquad (8)$$

RTPM is very effective under interaction of triplet states with stable nitroxyl radicals.[16,36]

Radical $PTH^{\bullet+}$, being nonpolarized (see Discussion, 1, above), does not transfer polarization to TEMPO and the observed spectrum is the algebraic sum of the emissively polarized TEMPO and of the absorptive signal of $PTH^{\bullet+}$.[37]

3. Rates of ESPT from e_{aq}^- to A and $N^{\bullet-}$. We considered measuring experimentally the rate constant of the bimolecular

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(33) Gilbro, T. *J. Polym. Chem. B* **1973**, *11*, 309.

(34) Turro, N. J.; Khudyakov, I. V.; Dwyer, D. W. *J. Phys. Chem.* **1993**, *97*, 10530.

(35) Khudyakov, I. V.; Kuzmin, V. A. *Russ. Chem. Rev.* **1975**, *44*, 801.

(36) Blätter, C.; Paul, H. *Res. Chem. Intermed.* **1991**, *16*, 201.

(37) The emissive signal of the central component of #TEMPO looks smaller than the low-field component, which is not the CIDEP pattern of the only emissively polarized #TEMPO (cf. refs 16, 32b, and 34) due to the contribution of the absorptive signal of $PTH^{\bullet+}$.

reaction of electron spin polarization transfer, k_{ex}, between two species and comparing the value with the rate constant of the chemical reaction k_r between the two, under identical conditions. The two systems under consideration were e_{aq}^- and A, as well as e_{aq}^- and $N^{\bullet -}$. Obviously, in the first case the rate of ESPT should be the rate of the chemical reaction, $k_r = k_{ex}$ or $k_1 = k_{1'}$; in the second case, ESPT and the chemical reaction compete with each other and the relationship between k_r and k_{ex} or k_2 and k_2' is of special interest.

The rate constants of the chemical reactions in micellar solutions derived from transient absorption measurements were found to be $k_1 \sim 7 \times 10^9$ and $k_2 \sim 5 \times 10^9$ M^{-1} s^{-1} for A and $N^{\bullet -}$, respectively, cf. Results, 5. The values obtained are several times less than k_1 for aqueous solution[18] and reactions similar to reaction 2 between e_{aq}^- and some stable nitroxyls in aqueous solutions as well.[2d,e] Certain differences between the rate constants of reactions of hydrophilic reagents in different solvents (aqueous solution and aqueous *micellar* solution) are quite plausible due to "solvent effects", see refs 28 and 38.

Values of k_{ex} were determined with a Stern–Volmer analysis[1] of the quenching of the $^{\#}e_{aq}^-$ resonance and the appearance of signals of $A^{\bullet -}$ and $^{\#}N^{\bullet -}$ as a function of acceptor concentration, cf. Results 4. In the case of A the following equations apply:

$$I^0/I = 1 + K_{SV}[A] \tag{9a}$$

$$I^\infty/I = 1 + K_{SV}^{-1}[A]^{-1} \tag{9b}$$

Here K_{SV}, M^{-1}, is the Stern–Volmer constant; $K_{SV} = k_1/k_0 = k_{1'}/k_0$, where k_0, s^{-1}, is the rate of decay of the resonance in the absence of quenchers.[1] I^0 is the e_{aq}^- signal intensity in the absence of quencher. I^∞ is the intensity of the resonance given by the electron acceptor at high acceptor concentration when the signal of e_{aq}^- is completely quenched by A. The measurement of I^0/I vs [A] (eq 9a), and I^∞/I vs $[A]^{-1}$ (eq 9b), allowed us to obtain more accuracy in determining the value of K_{SV}.

Stern–Volmer analysis gave $k_{1'} = (6.0 \pm 1.5) \times 10^9$ M^{-1} s^{-1}. Thus the value of $k_{1'}$ coincides within experimental error with the k_1 value obtained with the transient absorption measurements (see Results, 5). This result demonstrates the validity of the Stern–Volmer treatment of ESPT data.

Consideration of two competitive reactions 2 and 2′ for the system with $N^{\bullet -}$ leads to eqs 9c and 9d:

$$I^0/I = 1 + (k_{ex} + k_r)[N^{\bullet -}]/k_0 \tag{9c}$$

$$I^\infty/I = 1 + k_0/(k_{ex}[N^{\bullet -}]) \tag{9d}$$

Analysis of I^∞/I vs $[N^{\bullet -}]^{-1}$ gave $k_{ex} = k_{2'} = (3.5 \pm 0.8) \times 10^{10}$ M^{-1} s^{-1}. The same $k_{2'}$ value, within experimental error, was obtained from the analysis of the quenching data for e_{aq}^- using eq 9c, substituting $k_r = k_2 \sim 5 \times 10^9$ M^{-1} s^{-1} (*vide infra*). Thus, the rate of ESPT is approximately five times larger than the rate of chemical reaction initiated by electron capture by $N^{\bullet -}$, or $k_{ex} > k_r$.

e_{aq}^- is a very reactive species, and most of its reactions with free radicals have high rate constants and are diffusion controlled.[2] The rate constant of diffusion-controlled reaction between free radicals is given by:[39,40]

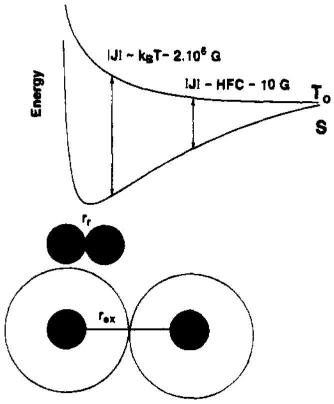

Figure 12. Schematic representation of the conditions required for chemical reaction and spin exchange, see text. Only terms *S* and T_0 are depicted.

$$k_r = \sigma_r k_{diff} = \sigma_r 4\pi r_r D \tag{10}$$

where s_r (=1/4) is the spin-statistical factor, k_{diff} is the rate constant, *D* is the mutual diffusion coefficient, and r_r is the reaction radius, equal to the sum of van der Waals radii of reagents.[41,42] The rate constant of the strong spin exchange between two radicals is given by:[40,44]

$$k_{ex} = \sigma_{ex} 4\pi r_{ex} D \tag{11}$$

Here s_{ex} (=1/2) is the spin-statistical factor, and r_{ex} is the radius of the strong spin exchange.[40,44] It has been proposed that, in order for a chemical reaction between two radicals to occur, the values of exchange interaction, depending upon the distance between radicals *J*(*r*), should be of the order of the thermal energy, or $|J(r_r)| \sim k_B T$, cf. Figure 12. On the other hand, for spin dephasing or ESPT between radicals to be effective, the *J*(*r*) should be of order of HF couplings of the radicals, cf. Figure 12. Since $k_B T \gg$ HF couplings, r_{ex} should be larger than r_r[40,45]

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(38) Study of this solvent effect is beyond the scope of the present work. Both reactions are probably diffusion controlled (see Discussion 3), and apparently the diffusion rates of ions (e_{aq}^- and $N^{\bullet -}$) are reduced by friction from the ionic atmosphere of studied aqueous solution of high ionic strength, cf. ref 2f. The effect of Coulomb repulsion in reactions of e_{aq}^- (reaction 2) is not significant, ref 2f.

(39) Burshtein, A. I.; Khudyakov, I. V.; Yakobson, B. I. *Prog. React. Kinet.* **1984**, *13*, 221.

(40) Bartels, D. M.; Lawler, R. G.; Trifunac, A. D. *Chem. Phys. Lett.* **1988**, *152*, 109.

(41) Reaction 3 is electron transfer; electron transfer between freely diffusion reagents in non-viscous solvent is a contact reaction, i.e., reaction occurring at the distance r_r; see e.g.: Burshtein, A. I.; Kapinus, E. I.; Kucherova, I. Yu.; Morozov, V. A. *J. Lumin.* **1989**, *43*, 291.

(42) The calculated average radius of e_{aq}^- equals 2.1–3.5 Å, depending upon the manner of estimating, see refs 2a, 2f, and 43.

(43) Jonah, C. D.; Romero, C.; Rahman, A. *Chem. Phys. Lett.* **1986**, *123*, 209.

(44) Molin, Yu. N.; Salikhov, K. M.; Zamaraev, K. I. *Spin Exchange*; Springer: Berlin, 1980.

(45) This conclusion cannot be considered to be well proven experimentally. In fact, the authors in ref 40 demonstrates that $r_{ex} > r_r$ for six self-reactions of radicals. It is not evident that all of the six reactions are diffusion controlled, see ref 40, meaning that the formal r_r calculated from eq 10 can be less than the sum of van der Waals radii of reagents, and the inequality of $r_{ex} > r_r$ would hold true due to the poor reactivity of the radicals. Moreover, let us consider the data in ref 46, where the sum of the rate constants of chemical reaction and the spin exchange between the radical anion of duroquinone and the stable nitroxyl free radical in benzene was measured ($k_r + k_{ex} = 6.6 \times 10^9$ M^{-1} s^{-1}), cf. ref 46. *This datum does not testify to the suggestion that* $r_{ex} > r_r$. Actually the diffusion rate constant for this solvent k_{diff} estimated according to the Debye formula to be $k_{diff} = 1.0 \times 10^{10}$ M^{-1} s^{-1}, with the Debye formula usually giving the lower estimation of k_{diff} (ref 39). The value of $0.75k_{diff} = 7.5 \times 10^9$ M^{-1} s^{-1} for benzene (see eqs 10 and 11) will give the lower estimation of $k_r + k_{ex}$, which happens to be even larger than the experimental value, see above. (It is probable that neither reaction is diffusion controlled, or the spin exchange is not strong, or any of these processes is characterized by a small steric factor, cf. refs 39 and 44.)

so that one expects $k_{ex} > k_r$ in good agreement with our experimental results.

The conjecture that $r_{ex} > r_r$ for reactions of e_{aq}^- seems to be quite logical if we note that e_{aq}^- has a diffuse structure and at room temperature the distribution of water molecules around the electron is rather smooth on the average.[2a,4,5,43] For such species of RP, one can expect a less steep decrease of $|J(r)|$ with the r increase compared to pairs of organic radicals, and a measurable difference between r_{ex} and r_r.

Conclusion

CIDEP under photoionization of phenothiazine in SDS micelles and in alcohols was observed for the first time. Strong emissive TREPR signals of the hydrated electron e_{aq}^- were detected. Electron Spin Polarization Transfer (ESPT) from e_{aq}^- to different electron acceptors (acrylamide, stable nitroxyl radicals, chlorophenols) was observed.

Rate constants of ESPT (k_{ex}) to acrylamide and a stable nitroxyl radical $N^{\bullet -}$ were measured in TREPR experiments. Rate constants of chemical reactions (k_r) between e_{aq}^- and acceptors mentioned above were measured with laser flash photolysis.

The values of k_{ex} and k_r for acrylamide coincide within experimental error. For the stable nitroxyl radical the value of k_{ex} is ca. five times larger than k_r. The difference in k_{ex} and k_r is in agreement with the theoretical prediction that ESPT takes place at larger distances than does a chemical reaction. An essential difference in k_{ex} and k_r can be expected especially for e_{aq}^- due to peculiarities of its electronic structure.

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(46) Bordat, P. P.; Tsvetkov, Yu. D. *Dokl. Akad. Nauk SSSR* **1984**, *278*, 900.