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ARTICLES

Energy Requirements for Inverted CIDEP in Reactions between e_{aq}^- or Radical Anions and Phenoxyl Radicals

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Inverted (A/E) chemically induced dynamic electron polarization (CIDEP) is observed for random encounters of radical pairs such as the phenoxyl radical together with either e_{aq}^- or the radical anion of benzoate. A number of experiments have been carried out to clarify the relationship of the energetics of the reaction of oxidizing and reducing radicals to CIDEP behavior. Steady-state and time-resolved ESR experiments were carried out to determine the sense of F-pair CIDEP for a number of different radical pairs consisting of a phenoxyl radical together with one of a series of radical anions of para-substituted benzoates. Inverted polarization (A/E) was found for e_{aq}^- or the radical anions of benzoate and 4-methyl, 4-methoxy, and 4-carboxybenzoates in the presence of phenoxyl or 4-methylphenoxyl radicals. Other radical anions such as those of 4-formylbenzoate showed normal polarization. The pair consisting of e_{aq}^- with the *p*-benzosemiquinone radical anion also showed inverted polarization, but normal polarization was seen for all radical anions paired with the semiquinone radical anion. The corresponding excited-state energies of the reaction product (phenolate anion or hydroquinone dianion) were determined from the emission spectra, and the energies of the radical pairs were estimated from electrochemical experiments. The inverted CIDEP is clearly the result of a change in the normal energy ordering of the radical-pair states so that the triplet state is lower. The observations are discussed in terms of the electron-transfer reaction within the radical pairs using the approach presented by Kobori et al. (Kobori, Y.; Sekiguchi, S.; Akiyama, K.; Tero-Kubota, S. *J. Phys. Chem. A* **1999**, *103*, 5416. Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *J. Chem. Phys* **2000**, *113*, 465).

Introduction

Chemically induced dynamic electron polarization (CIDEP) is a process that leads to the observation of emission (E) or enhanced absorption (A) in ESR spectra. Two mechanisms are important: the triplet mechanism (TM) by which all ESR lines of each pair of radicals formed by the reaction of a triplet state are polarized in the same sense and the radical pair mechanism (RPM) that produces the multiplet effect by which the lines in the spectrum of each radical of a pair are polarized either E/A (low-field emission lines, high-field absorption lines) or A/E.[1−3] The important factors in determining the sense of RPM polarization are the initial spin multiplicity of the radical pair and the energy ordering of the singlet and triplet states of the radical pair for weak, but nonzero, electronic interaction within the pair. Thus, the RPM probes the electronic interaction between radicals in either geminate or random encounter pairs (the latter also known as F pairs). The most commonly observed spectra show intensities with an E/A pattern. This situation arises from F pairs because the pairs of singlet multiplicity react, leaving radicals from triplet pairs to provide the ESR response. Usually, the singlet state of the radical pair is of lower energy (exchange interaction, $J < 0$), and this leads to the low-field lines being in emission.

Several instances of inverted or unusual CIDEP have been reported that involve the hydrated electron, e_{aq}^-. Radiolysis experiments produced e_{aq}^- with the phenoxyl radical, the *p*-benzosemiquinone radical anion, or the carbonate radical anion ($CO_3^{\bullet -}$).[4,5] In each case, the *g* factor of e_{aq}^- (2.00043)[6] is lower than that of the other radical, so the ESR line of e_{aq}^- is above the center of the spectrum. In the cases mentioned,[4] the ESR of e_{aq}^- appears in emission and so is of the A/E type (the counter-radical having net absorption overall). A number of other counter-radicals ($SO_3^{\bullet -}$, $CO_2^{\bullet -}$, and several carbon-centered radicals) were studied[4] that had normal behavior (absorption for e_{aq}^-).[7] The two types of radicals (e_{aq}^- and phenoxyl, for example) are formed separately and are not initially correlated, so this behavior must be that of F pairs. The initial explanation[4] suggested that the triplet states of the encounter pairs (F pairs) reacted, leaving singlet pairs and that the energy ordering was normal (singlet lower). A subsequent study by Jeevarajan and Fessenden[8] involved the photolysis of the phenol anion (phenolate):

$$C_6H_5O^- \xrightarrow{h\nu} {}^1(C_6H_5O^-) \rightarrow C_6H_5O^{\bullet -} + e_{aq}^- \qquad (1)$$

Here, the intermediate singlet state may be vibrationally excited. The ESR line of e_{aq}^- was found to be in absorption for more than about 8 μs before it decayed to zero. The lines of the

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complementary phenoxyl radical showed an initial E/A pattern corresponding to their position relative to the position of the line of e_{aq}^-. Because the same radical species are involved in this photolysis experiment as in the radiolysis experiment, this polarization must represent the behavior of geminate pairs. The electronic interaction will be the same for any experiment, so the initial spin multiplicity of the photolytically produced pair must be opposite that of the F pairs in radiolysis. It was argued that the initial excited state in the photolysis experiment should be a singlet and that electron ejection is very fast, so the geminate radical pair must also be a singlet. Under that assumption, the observed inverted CIDEP predicts that the triplet state is of lower energy (S−T energy separation, $2J > 0$) during the development of CIDEP.

The multiplicity of the intermediate excited state and, therefore, that of the geminate radical pair play a vital role in the discussion to follow. A number of arguments based on various photochemical experiments can be given that support the singlet multiplicity of this initial radical pair. These include the rate of appearance of the e_{aq}^- optical absorption (probably faster than 10 ps[9]), the linearity of the amplitude of the ESR signal with the laser absorbed dose,[8] and several optical studies of the quantum yield and yield linearity of e_{aq}^- production under laser intensity conditions similar to those of the ESR experiments.[10]

These arguments seem quite convincing, but some doubt may remain in view of subsequent TRESR work.[11] This work involved the photolysis of tyrosinate with a quencher and concluded that, under their conditions, the excited state of the tyrosinate is a triplet and so J is negative. We have subsequently investigated the same photochemical system by optical absorption under the conditions of our ESR experiments and disagree with their interpretation that a triplet state is involved. A summary of those results will be given below.

A much stronger, elegant experimental demonstration of the geminate pair multiplicity in the photolysis of phenolate has been given by Bussandri and van Willigen.[12] Nitrate was used as a scavenger for e_{aq}^-, and the polarization was observed for the electron-scavenging product, $^\bullet NO_3^{2-}$. Because of the high reaction rate constant for $e_{aq}^- + NO_3^-$ and the relatively high concentration of nitrate, it was possible for $^\bullet NO_3^{2-}$ to replace e_{aq}^- in a time so short that much of the spin correlation of the geminate radical pairs was maintained. The polarization produced from the phenoxyl/$^\bullet NO_3^{2-}$ geminate radical pair (A/E) as well as that at longer times from the same pair in F-type encounters (E/A) could be both observed and compared. It is very unlikely that the F-pair reaction here produces other than the ground singlet states of the products, so the F-pair polarization represents that for triplet radical pairs. Correspondingly, the opposite polarization observed for geminate pairs shows that they must be singlets. The energy ordering for the e_{aq}^-/phenoxyl radical pair must then be triplet below singlet or $J > 0$ in agreement with Jeevarajan and Fessenden.[8] This conclusion will be accepted in all further discussion.

The study by Jeevarajan and Fessenden[8] also reported spin polarization from F pairs involving radical anions of some para-substituted benzoate anions with the phenoxyl radical in laser photolysis experiments. An inverted or A/E pattern was found in the case of the unsubstituted benzoate radical (di)anion with the phenoxyl radical, but the radical anion of 4-acetylbenzoate gave a normal E/A pattern. The most obvious difference is the reduction potential to form a radical anion; the value is less negative for the latter compound than in the case of benzoate. The radical pairs that show the inverse CIDEP effect all involve an oxidizing radical and a highly reducing one so that the reaction between the two radicals is highly exoergic. The difference in the reduction potentials of the two radicals gives the adiabatic energy (ΔG) of the back-electron-transfer reaction. A connection between the CIDEP behavior and the energetics seems clear, as noted previously.[4,8] The available energy may be sufficient to produce the reaction product in an electronic excited state. Alternatively, the proximity in energy of the excited state may affect the energy ordering of the radical pair states during the development of CIDEP.

The present study represents an attempt to investigate the relation between the radical pair energies and the phase of CIDEP systematically. Here we report the CIDEP observed for some series of radical pairs. Electrochemical measurements were conducted to determine the reduction potentials of the radicals. Optical emission spectra were measured to estimate the excited-state energies of the radical-pair back-reaction products. In the end, however, there will still be uncertainties in the energy values because of various unknown quantities in the determinations. It will be necessary to drop a fully quantitative correlation of energy with CIDEP behavior and to use the energy values to provide a more qualitative correlation. Although this is so, it is still instructive to consider the various issues involved.

The radical pairs consist of two types of radicals: one is a phenoxyl-type radical, and the other is a radical anion of a para-substituted benzoate. Various substituents were used to change the corresponding reduction potential of the radical anion. The oxidizing radicals were the phenoxyl radical itself,the 4-methylphenoxyl radical, and the *p*-benzosemiquinone radical anion. Changes to the phenoxyl radical have two effects—a change in the reduction potential as well as a change in the excited-state energies of the reaction product. The ESR experiments looked only at the ESR of the radical anions and not at the phenoxyl radicals because the shorter relaxation time of the phenoxyl radicals makes their study more difficult. Previous work[8] showed that the phenoxyl radical lines behaved as expected for a multiplet-type CIDEP.

Explanations alternative to the standard RPM for the observed CIDEP should be considered. Adrian[13] has discussed a situation in which the energy of a pair of radical ions is close to that of an excited state, so the reaction to produce a triplet product is possible. This explanation does not seem to apply here. (See the discussion below.) Other alternatives include that for radicals such as *tert*-butyl, where CIDEP evolving from E/A to A/E has been found.[14,15] These situations involve radicals that show large polarizations (because of a high radical concentration) and special structures that enhance electron−nuclear cross relaxation. This mechanism is not relevant in the present case because e_{aq}^- has no nuclear spin. Also, because the precursor is e_{aq}^-, no nuclear spin polarization is generated for the radical anions during the geminate process. Therefore, such an explanation does not seem very probable. A final alternative source of CIDEP involves the magnetic dipole−dipole interaction.[16,17] This is a rather weak interaction but would be relatively more important at larger radical−radical interaction distances. It produces the opposite sense of polarization for a given radical-pair spin multiplicity, and the dependence of ESR line intensities on the position in the spectrum is different for this case than for the exchange interaction. The analysis by Bussandri and van Willigen[12] of the spectrum of phenoxyl in the photolysis of phenolate clearly fits the square-root dependence of line intensity on line position expected from the normal CIDEP model. Thus, the polarization seen in this case is not likely to be the result of the dipole−dipole interaction.

Another possibility is the model developed by Kobori et al.[18,19] They recently conducted a systematic study on CIDEP for a number of geminate radical ion pairs produced by electron-transfer reactions between photolytically excited donor molecules and quencher molecules. The relationship of the polarization pattern to the energetics of the radical ion pairs was demonstrated. It was concluded that the radical ion pairs with a free energy of about 1.8 eV or higher relative to that of the parent molecules in their solvent had an energy ordering with the triplet state lower, but those with a lower energy had the singlet state lower. The origin of the excited states, either singlet or triplet, was clear because the photochemistry of the systems had been well investigated in independent studies.

Their primary innovation was to replace the exchange interaction in the normal RPM with the charge-transfer interaction in the radical pair that leads to the electron-transfer reaction. The radical−radical back reaction was interpreted in terms of Marcus theory including the reorganization energy. In their treatment, the radical-pair singlet and triplet states are degenerate in the absence of any interaction. This degeneracy is lifted through configuration interaction between the radical-pair state and the reaction product state at the equilibrium configuration of the radical pair. The strongest interaction will occur when the value of $-\Delta G$ for the back reaction is equal to the reorganization energy. The spin selectivity arises because (in almost every case) the energetics strongly favors the singlet product state. Whether this perturbation raises or lowers the energy of the radical-pair state depends on the energy ordering of the radical-pair state and the corresponding product state. The $S-T_0$ mixing that drives the CIDEP will then involve the S−T energy separation from this interaction and the magnetic interactions as usual.

It is convenient, therefore, to think of the location of the radical-pair energy level as being lowered by the reorganization energy.[20] When the reorganization energy equals the value of $-\Delta G$ for the reaction, the modified energy will be at the same level as the reaction product, and the reaction rate will be a maximum, as will the charge-transfer interaction between the product and radical-pair states. For a small $-\Delta G$, the (modified) energy of the radical-pair state will be below that of the ground-state product. The charge-transfer interaction then mixes the effective singlet radical-pair state with the ground state and lowers the singlet radical-pair state relative to the triplet radical-pair state. (The energy of the triplet ion-pair state is hardly affected because the triplet product state is much higher in energy. Kobori et al.[18] also studied the radical ion-pair systems where the excited triplet state of the parent molecule affects the radical-pair state energy.) The energy ordering of the radical-pair states then corresponds to the situation for $J < 0$, and normal CIDEP occurs. With a value of $-\Delta G$ that is larger than the reorganization energy, the modified radical-pair energy is still above that of the ground state, and the mixing raises the energy of the singlet radical-pair state. Therefore, the change from $J < 0$ to $J > 0$ corresponds approximately to a value of $-\Delta G$ near the reorganization energy. The treatment presented[19] includes the appropriate averaging over thermal energies and uses the stochastic Liouville equation to calculate the magnitude of CIDEP with the inclusion of diffusion and reaction.

Experimental Section

The steady-state photolysis ESR experiments were carried out in a manner similar to that of previous work[21] but with a Bruker ESP-300E spectrometer with an ESP 380-1010 microwave bridge. The light source was a HgXe high-pressure lamp with a filter solution to restrict the wavelength range to 250 to 300 nm. The direct-detection time-resolved ESR experiments were carried out as previously described[8,22,23] with a Lumonics HyperEx-400 excimer laser operating with XeCl (308 nm) at 25 Hz. The laser pulse length was about 20 ns, and the energy typically ranged from 60 to 90 mJ/pulse with a beam cross section of 0.9 cm^2. Time profiles of the ESR intensity were obtained by averaging responses from 200 to 1000 individual pulses. Both types of ESR experiments used a silica flat cell of 0.4-mm spacing and a flowing solution (flow rate about 10 cm^3/min). The solutions were bubbled with Ar or N_2 before adding the phenols to prevent oxidation. Bubbling of the solutions was continued during the measurements.

Optical emission spectra were taken with an SLM-AMINCO model 8100 spectrofluorimeter (version 1.00) using samples frozen at 77 K. The solutions were made with deoxygenated water in a separate container and were then put into the cell (3-mm inner-diameter suprasil tube) and further deoxygenated by freeze−pump−thaw cycles.

The optical transient absorption measurements were carried out with a Lambda-Physik COMPex 102 excimer laser operating with XeCl for 308-nm irradiation. The laser pulse was of about 20-ns duration, and the laser emission power was typically around 260 mJ/pulse. The laser power was attenuated to an appropriate level with Pyrex plates of various thicknesses. Typically, the laser power at the cell was adjusted to be in the range of 5 to 50 mJ/pulse. The laser power was measured with a Scientech 365 power and energy meter. The laser beam had a rectangular shape. A 1-kW high-pressure pulsed Xe lamp was used as a probe light. The probe light was focused toward the optical cell, and the cross section was ca. 2 mm in diameter at the cell. Three types of optical cells were used in the measurements. A flat quartz cell with a 2-mm optical path length was used for the determination of the second-order reaction rate constants. With this cell, the optical system was set up such that the excitation laser pulse was introduced somewhat collinearly with the probe light. The laser light was moderately focused with a cross section of around 15 mm^2. Another flat quartz cell with a 0.5-mm optical path length was used in some experiments. The other type of quartz cell was a square tube with a 5×5 mm^2 cross section. With this cell, the laser light path was at a right angle with respect to the probe light path. The probe light was refocused after the optical cell toward the monochromator, a Spex 270M. Cutoff filters were used for observations at longer wavelengths to eliminate the second-order output of the monochromator. The probe light at a particular wavelength was fed into a four-stage photomultiplier tube, Hamamatsu R928. The current from the photomultiplier was processed in a sample-and-hold circuit and amplified, and the transient signals were stored in a digital storage oscilloscope, a LeCroy 7200. The data were recorded with the same program as that used in pulse radiolysis experiments.[24] Pulse radiolysis experiments were made with an updated version of the equipment previously described.[24] The electrochemical measurements were made with a BAS-100 electrochemical analyzer using a glassy carbon working electrode, a saturated calomel reference electrode, and a platinum wire counterelectrode.

All of the solutions were prepared using water from a Millipore Milli-Q purification system with potassium hydroxide (for pH adjustment) from Fisher Scientific Co. Phenol was obtained from J. T. Baker Chemical Co., sodium benzoate, from Fisher Scientific Co., *p*-methoxy-benzoic acid, from K&K Laboratory Inc., and 4-nitrobenzoic acid, from Matheson Co.

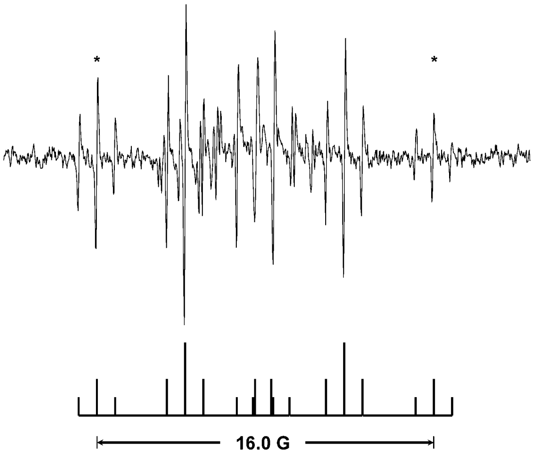

Figure 1. Steady-state ESR spectrum taken during the photolysis of 10 mM phenol and 2 mM benzoate at pH 13. High field is to the right. The lines are mainly those of the benzoate radical dianion and show a trend toward emission at high field. The simulation at the bottom has splittings of 7.57 (1H), 4.21 (2H), and 0.85 G (2H). The lines studied in time-resolved experiments are marked by an asterisk.

The other compounds were purchased from Aldrich Chemical Co. All chemicals were used as received without further purification.

Results

Steady-State ESR Experiments. e_{aq}^- is produced by reaction 1 and then reacts with various para-substituted benzoates to form radical anions.

$$e_{aq}^- + RC_6H_4CO_2^- \rightarrow [RC_6H_4CO_2^-]^{\bullet -} \qquad (2)$$

A random encounter (of differing species) then involves the radical pair $C_6H_5O^\bullet/[RC_6H_4CO_2^-]^{\bullet -}$. Alternative systems involve the 4-methylphenoxyl radical or the *p*-benzosemiquinone radical anion in place of the phenoxyl radical. The fact that e_{aq}^- can reduce the unsubstituted benzoate anion indicates that the corresponding reduction potential is less negative than that of e_{aq}^-, −2.87 V (vs NHE).[25−27] The substituents on the benzoate anions will change the corresponding reduction potentials.[28] Therefore, by varying the substituents, it is possible to see the effect of changes in the radical-pair energy on the ESR polarization pattern.

Steady-state photolysis ESR experiments were first done to screen the behavior of the various systems, and then time-resolved ESR experiments with laser photolysis were used to confirm the observations. Figure 1 shows the steady-state ESR spectrum of the radical anion of benzoate in the presence of phenoxyl radicals that are produced during the continuous photolysis of pH 13 solutions. Obviously, the low-field absorption lines are stronger than the high-field lines. This result is the same as that found previously.[8] Figure 2 shows a similar spectrum with 4-formylbenzoate and the phenolate anion, and the polarization behavior is opposite that with benzoate. The behaviors of the radical anions of *p*-toluate and 4-methoxybenzoate anions are similar to that of benzoate, and the behavior of 4-acetylbenzoate is similar to that of 4-formylbenzoate. No significant polarization was observed for radical anions from terephthalate and 4-cyanobenzoate. With the 4-nitrobenzoate radical anion, the line broadening caused by the nitrogen hyperfine anisotropy made the spectrum asymmetric in line amplitudes.[29,30] The polarization pattern of each of the radical anions was the same when the *p*-cresol anion replaced the phenolate anion as an electron source so that the radical pairs involved 4-methyl phenoxyl. Because the polarization is larger in laser photolysis experiments, the experiments were repeated using the time-resolved method to confirm the steady-state results and to determine the pattern in cases where the polarization was small.

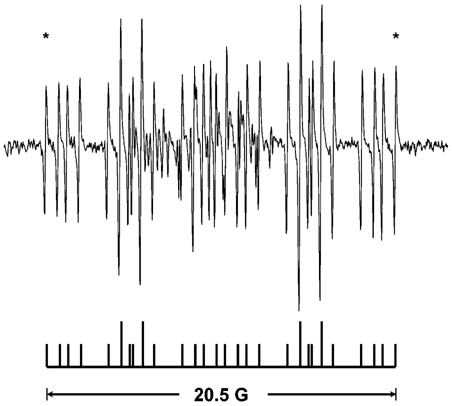

Figure 2. Steady-state ESR spectrum similar to that in Figure 1 but with phenol and 2 mM 4-formylbenzoate. The simulation for the radical anion at the bottom has splittings of 10.55, 4.35, 3.63, 1.23, and 0.73 G for one proton each.

Time-Resolved ESR Experiments. The results where the *p*-cresol anion was used as an electron source will be presented first. Time profiles for two symmetrically located ESR lines are shown in Figure 3a for the radical anion of benzoate and in Figure 3b for the radical anion of terephthalate. Each curve shows an initial enhanced absorption that is the result of the transfer of the spin-state populations of initially formed e_{aq}^- to the radical anion. (The ESR line of e_{aq}^- from the photolysis of *p*-cresolate at pH 13 is in enhanced absorption.[8]) It is evident for the benzoate radical anion that the low-field line remains absorptive but the high-field line changes into emission about 10 μs after the laser pulse. This change represents the relaxation of the initial spin populations and the production of polarization by bimolecular reaction. The A/E spectrum at longer times must be the result of F-pair CIDEP from radical re-encounters between the radical anion and 4-methylphenoxyl.[31] The A/E tendency in the steady-state spectrum of this system is in agreement with these curves at longer times. The difference between the time profiles of the low-field and high-field lines of the radical anion of terephthalate (Figure 3b) is small, but some A/E polarization can be seen. In this case, the steady-state spectra show no significant CIDEP and are also consistent with the time traces at longer times. The traces in Figure 4a and b show data for the radical anions of 4-formyl benzoate and 4-cyanobenzoate, respectively. These traces also show an absorption at short times for both lines, but then the spectrum changes to a clear E/A pattern. These results are also consistent with the steady-state experiments. Isophthalate (meta isomer) and phthalate (ortho isomer) were studied for comparison with terephthalate and showed A/E and E/A behavior, respectively. The polarization patterns are summarized in Table 1.

Experiments were also done with the hydroquinone dianion as an electron source to determine the effect of a larger change in the nature of the oxidizing radical. The benzosemiquinone anion is the counter-radical to e_{aq}^-. Parts a and b of Figure 5 show the ESR time profiles for the radical anions of benzoate and 4-formylbenzoate, respectively, in the presence of the *p*-benzosemiquinone radical anion. An initial absorptive signal for both lines is seen, followed by a difference that corresponds to a normal E/A pattern. All of the radical anions, including

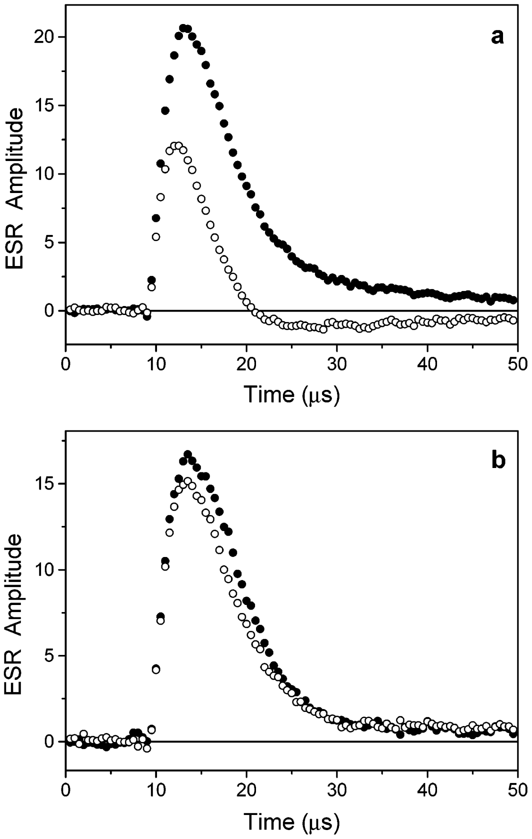

Figure 3. ESR time profiles in the laser photolysis of 10 mM *p*-cresol at pH 13 (a) with 2 mM benzoate and (b) with terephthalate. The behavior of symmetrically located lines in the spectra of the radical anions (such as those marked in Figure 1 or 2) is designated by solid circles (low field) and open circles (high field). Positive values represent absorption.

that of the unsubstituted benzoate, displayed a normal E/A pattern when paired with the benzosemiquinone ion.

Figure 6 shows time traces of the ESR signal for e_{aq}^- from the hydroquinone dianion in the absence of benzoates. An initial absorption is followed by decay to a weakly emissive signal that then decays to zero. The first curve (open points) was taken with very low microwave power (microwave magnetic field, $H_1 = 0.0057$ G) to avoid a contribution to the negative excursion from a Torrey oscillation. The absence of such an effect could be demonstrated by the second curve taken at 5 dB higher microwave power ($H_1 = 0.010$ G) that is of the same shape. As shown in the Figure, this trace can be essentially superimposed on that for the lower power with the appropriate scaling factor (1.78) for the change in H_1 taken into account. Extreme care was taken to avoid oxidizing the sample by oxygen or photolysis. A number of experimental variables such as the hydroquinone concentration, sample preparation, laser pulse energy, and sample flow rate were changed, but the form of the responses did not change significantly. The initial absorption is like that obtained with phenolate or *p*-cresolate and can be explained in a similar way as the geminate pair polarization of e_{aq}^-. (The ESR lines of the benzosemiquinone anion all showed an initial emissive polarization that was appropriate for lines of the second radical of the pair; all lines are at a lower field than that of e_{aq}^-.) The ESR signal should then evolve to an emissive signal as the initial magnetization relaxes and the effect of F-pair polarization takes over so that the situation becomes like that in radiolysis with hydroquinone.[4] This is exactly the behavior that is observed.

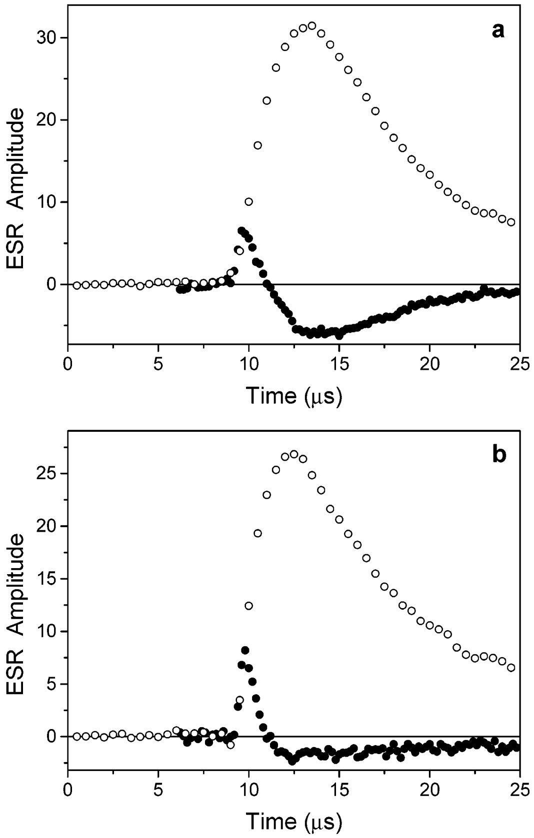

Figure 4. ESR time profiles of symmetrically located lines in the spectra of radical anions in the laser photolysis of 10 mM *p*-cresol at pH 13 (a) with 2 mM 4-formylbenzoate and (b) with 0.5 mM 4-cyanobenzoate, as in Figure 3.

TABLE 1: Electrochemical Behavior and CIDEP Patterns of Radical Anions of Substituted Benzoate Anions in Reaction with 4-Methylphenoxyl

substituent	peak potential[a] (V)	radical-pair energy (ΔG, eV)[b]	CIDEP
4-CH_3O−	≤ −2.1[c]	≥2.78	inverted
4-CH_3−	≤ −2.1[c]	≥2.78	inverted
none	≤ −2.1[c]	≥2.78	inverted
3- ^-O_2C−	(−1.83)[d]	2.51	inverted
4- ^-O_2C−	−1.69 (−1.69)[d]	2.37	inverted
2- ^-O_2C−	(−1.75)[d,e]	2.43	normal
4-NC−	−1.57	2.25	normal
4-$H_3C(=O)$−	−1.17	1.85	normal
4-HC(=O)−	−1.02	1.70	normal
4-O_2N−	−0.42	1.10	normal

[a] Volts relative to NHE, measured in water by differential pulse polarography in the presence of 0.2 M KOH. [b] Free energy of the pair comprising the 4-methylphenoxyl radical and the radical anion relative to that of 4-methylphenolate with the parent benzoate ion. On the basis of the reduction of acetone; see text. [d] Polarographic half-wave potentials.[38] [e] Corrected for the difference in the pH of the polarography (14) and that in the ESR experiment (13) because of the existence of a carboxyl-bridging proton in the phthalate radical anion even at pH 14.[68]

In contrast, the ESR time profile of e_{aq}^- produced from the photolysis of phenolate does not show an inversion of the polarization phase. The ESR signal for e_{aq}^- remains absorptive from the initial geminate-pair polarization and simply decays to zero without crossing to emission.[8] In the radiolysis experiments, an emissive ESR signal for e_{aq}^- has been observed in F pairs with the phenoxyl radical.[4] A number of factors could affect the time dependence of the spin polarization of e_{aq}^-, such

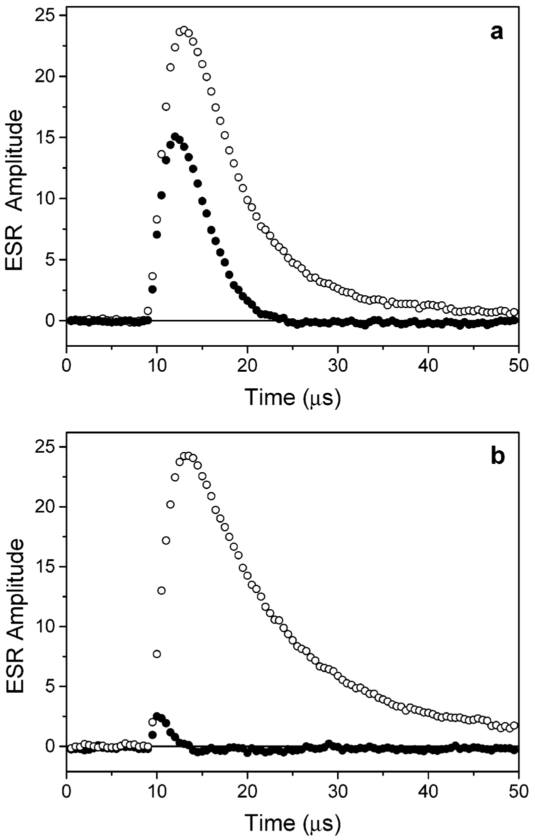

Figure 5. ESR time profiles of symmetrically located lines in the spectra of radical anions in the laser photolysis of 4 mM hydroquinone at pH 13 (a) with 2 mM benzoate and (b) with 0.5 mM 4-formylbenzoate, as in Figure 3.

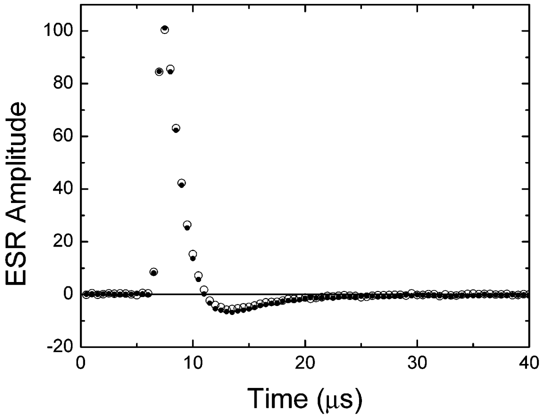

Figure 6. ESR time profiles for e_{aq}^- in the laser photolysis of 4 mM hydroquinone at pH 13. Two microwave power levels separated by 5 dB are represented. Open points are for microwave power corresponding to a microwave magnetic field of $H_1 = 0.0057$ G, and the solid points correspond to $H_1 = 0.01$ G. The data for the higher power are divided by the ratio of H_1 values, 1.78. The close superposition shows that the negative excursion is not a Torrey oscillation.

as the rates of relaxation of the signal (in enhanced absorption), the production of emissive F-pair polarization, Heisenberg spin exchange, and the chemical decay of e_{aq}^- by various reactions. The balance of these effects for the benzosemiquinone system must be different from that of phenolate. One difference between the two systems is the rate of the self-reaction of the counter-radical. The recombination reaction of the phenoxyl radical has quite a high rate constant ($2k = 2.6 \times 10^9$ M^{-1} s^{-1}),[32] but the *p*-benzosemiquinone radical anion is quite inert to self-reaction at high pH ($2k < 1 \times 10^6$ M^{-1} s^{-1}).[10] Thus, more random encounters take place for e_{aq}^- and the *p*-benzosemiquinone radical anion pairs to produce more A/E F-pair polarization.

Time-Resolved ESR Experiments: Singlet or Triplet? A clear demonstration of the singlet nature of the geminate radical pair, e_{aq}^-/phenoxyl, by Bussandri and van Willigen[12] has already been mentioned. We believe that the irradiation conditions in the current work are comparable. Nevertheless, it is useful to consider this question in more detail. A singlet origin is supported by a review of the photophysical behavior of phenol and phenolate.[33] For phenolate, the best evidence besides the rapid formation of e_{aq}^- is the complementary temperature dependences of the quantum yields for e_{aq}^- formation and fluorescence.[34] There is, of course, a question of whether these results at low light levels apply to laser irradiation.

The ESR results themselves[8] may provide evidence against a triplet precursor. The lines of the corresponding phenoxyl radical were initially in emission for lines at lower field than that of e_{aq}^- and in absorption for lines at higher field in the photolysis experiment. This pattern of CIDEP involves only RPM polarization. The absence of polarization from the TM is consistent with the formation of the radical pairs through a singlet state. However, TM polarization could be small depending on the selectivity of the intersystem crossing to the three individual triplet substates.

Because of the suggestion that the ejection of an electron from an excited phenolate anion[11] involves a triplet state, we conducted various experiments using transient optical absorption and laser photolysis. Solutions of *p*-cresolate at pH 13 were studied, and the transient spectra (from 320 to 740 nm) could be well reproduced by a superposition of the absorptions of equal concentrations of *p*-methylphenoxyl and e_{aq}^-. There is no optical absorption observed on our time scale (∼100 ns after the laser pulse) that can be ascribed to an electronically excited state of *p*-cresolate. The dose dependence of the yield of e_{aq}^- was investigated over a range of laser doses of about a factor of 40. To allow laser intensity conditions similar to those in the ESR experiment, an optical cell of 0.5-mm path length was used. Concentrations of *p*-cresolate were 5 and 50 mM at pH 13.[35] With 5 mM *p*-cresolate, the concentrations of e_{aq}^- (calculated from the known extinction coefficient) that were produced at 12 different doses varied from about 18 to 590 μM. A log−log plot of concentration against laser dose was quite linear, with a slope of 0.94. With 50 mM, the absorbance for e_{aq}^- at the lowest dose was about 2 times higher than with 5 mM because of a higher ground-state absorbance; the e_{aq}^- concentration at the highest dose was about the same as with 5 mM. There also was evidence of some nonlinearity in that the points tended toward a lower slope (downward curvature) at the higher doses. These curves strongly suggest that the production of e_{aq}^- from the phenolates is a monophotonic process. The range of e_{aq}^- concentrations clearly covers the range used in the ESR experiments.

In previous work,[11] the *trans*-2,4-hexadienoate anion was used as a triplet quencher. That work reported that no ESR lines were seen with 0.5 M quencher and 50 mM tyrosinate. (The pH was not stated, but some base was added.) When 0.5 M quencher is present in a pH 13 solution of *p*-cresolate, the transient optical spectrum shows a strong absorption peaking at about 360 nm that is attributable to the radical anion of the quencher. The rate constant of e_{aq}^- addition to the quencher is nearly 1×10^{10} M^{-1} s^{-1}. Clearly, no ESR line of e_{aq}^- should be observable on the ESR time scale in the presence of such a high quencher concentration. Also evident in the optical spectrum is a sharp shoulder at 405 nm that is clearly the absorption of the

4-methylphenoxyl radical. The reason for the absence, in the previous work, of any corresponding ESR lines of the phenoxyl radical from tyrosine is less clear. We note that the quencher does show a weak absorption tail past 300 nm such that at least 50% of the 308-nm laser light would be absorbed by the quencher in the absence of 50 mM tyrosine. Taken together, we believe that this evidence clearly does not support the conclusion that electron ejection from *p*-cresolate (or, in parallel, tyrosinate) involves a triplet state with a nanosecond lifetime under our conditions.

The results above show that electron ejection cannot be the result of a two-photon process through a normal triplet state. There is also the possibility that the initial excited singlet of phenolate undergoes picosecond intersystem crossing followed by electron ejection. This process would be linear in laser intensity. However, Bussandri and van Willigen's work[12] positively identifies a singlet state as the precursor to e_{aq}^-.

Excited-State Energies. A very important consideration in any discussion of the origin of the inverted polarization of e_{aq}^- with the phenoxyl radical is the energy of the pair of radicals (at a distance where electronic interaction is weak) relative to that of the excited states of the reaction product (phenolate anion). Therefore, an important part of this work is the determination of those energies by means of luminescence measurements on several of the systems of interest. Figure 7 illustrates the emission spectra of the phenolate anion, the *p*-cresol anion, and the hydroquinone dianion in frozen pH 13 aqueous solution at 77 K. The portion at the left in each case is fluorescence, and the peak at longer wavelengths is phosphorescence, as shown by the response to a rotating shutter. The fluorescence peak is in the expected relationship to the absorption spectrum, which is also shown. The emission of the phenolate anion is red-shifted compared to that of phenol at pH 7[36] and has less vibrational structure. The energies of the singlet excited states (0−0 transition) were taken from the crossover of the absorption and fluorescence and are presented in Table 1. The energy corresponding to the 0−0 transition of the triplet states was estimated by fitting a Gaussian curve (600-cm^{-1} width) to the structure on the spectrum for neutral phenol. This same curve was then used to estimate the shift of the 0−0 position from the onset. The energies so determined are also given in Table 2. These energies will be used to discuss the behavior in liquid aqueous solutions. Because the dielectric constants of water and ice are different, the excited-state energies may be somewhat different in liquid solution. It should be noted that the fluorescence from phenolate in water at room temperature can be seen.[33] We have also recorded such spectra with a peak at about 340 nm. The point corresponding to the 0−0 band of the emission (305 nm) is shifted by only about 5 nm from that at 300 nm for the frozen system. The corresponding energy difference is 0.07 eV. The effect of the phase and temperature change on the energy is therefore relatively small for the singlet state. The corresponding energy shift for the triplet state may be comparable.

Reduction Potentials of Radical Anions. To extend this discussion to the radical pairs involving radical anions rather than e_{aq}^-, it is necessary to know the corresponding reduction potentials. Only limited information is available because it is hard to measure precisely the reduction potentials of species that have large negative potentials and are highly reactive. For example, the value for the acetone ketyl anion in water has been determined to be −2.1 V on the basis of a comparison with the Tl system[26,37] (all values vs NHE). Polarographic measurements have been made for the three benzenedicarboxylates in water.[38] The half-wave potential for terephthalate was determined to be −1.69 V. Additional measurements were made here by differential pulse polarography for solutions of a number of the compounds in water. The half-wave potentials so determined

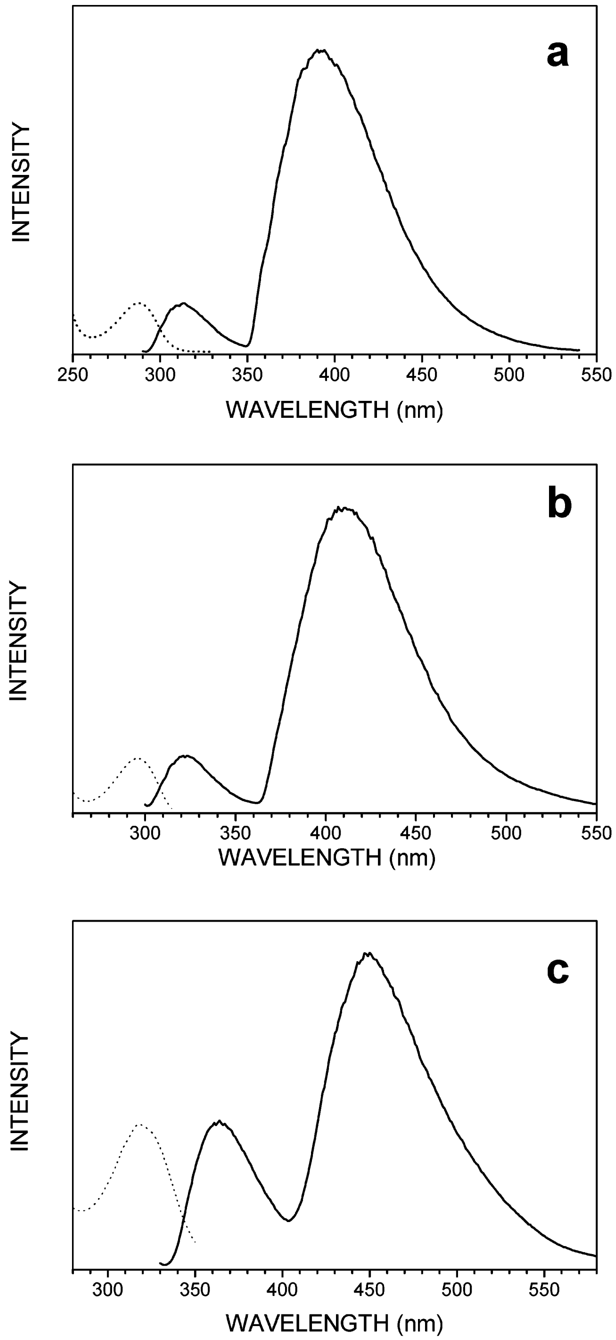

Figure 7. Emission spectra of pH 13 samples frozen at 77 K: (a) 1.3 × 10^{-4} M phenol in water, with excitation at 280 nm; (b) 1.5 × 10^{-4} M *p*-cresol, with excitation at 290 nm; (c) 1 × 10^{-4} M hydroquinone, with excitation at 320 nm. The dotted lines show the absorption.

TABLE 2: Estimated Energies (eV) of Excited States and Radical-Pair States

	excited singlet[a]	excited triplet[a]	corresponding radical pair[b] ($RO^\bullet/e_{aq}^-$)
phenol anion	4.13	3.45	3.66
p-cresol anion	4.03	3.32	3.55
hydroquinone dianion	3.61	2.99	2.89

[a] Energy from luminescence measurements. [b] Energy from reduction potentials.

are given in Table 1 along with the radical-pair energies (ΔG) and CIDEP behavior with 4-methylphenoxyl. The values in the first three rows for benzoate itself and with electron-donating substituents are based on the results below and may only be limits.

Some further idea of the value for benzoate can be obtained by comparison with acetone. An optical pulse radiolysis experiment involving solutions of benzoate and acetone at pH 13 was carried out by observing the longer-wavelength absorption of the benzoate radical (di)anion at 440 nm. It was found that this radical anion was formed but that it reacted with the acetone. Analyses of experiments with 2.2 and 4.9 mM acetone both gave second-order rate constants of about 9×10^6 M^{-1} s^{-1}. No evidence of a plateau level representing equilibrium between the radical dianion and acetone ketyl radical anion was seen. On this basis, the reduction potential of benzoate would appear to be at least as negative as that of acetone, −2.1 V. Methyl and methoxy groups seem not to have much calculated effect on the reduction potential,[28] and as para substituents on acetophenone, they make the potential 0.05 and 0.09 V more negative, respectively, in electrochemical experiments.[39] The methyl- and methoxy-substituted benzoates should have potentials at least as negative as the −2.1 V value entered in Table 1.

A further qualitative test of the values can be obtained by ESR experiments with acetone. The ESR spectrum of the radical anion of unsubstituted benzoate (like the spectrum in Figure 1) was obtained in the steady-state mode by using the *p*-cresol anion as an electron source. Adding a concentration of acetone equal to that of benzoate to the solution resulted in the disappearance of the radical anion of benzoate. This disappearance is not just the result of competition because the rate constants and concentrations are similar. This result is in accord with the pulse radiolysis observation. In contrast, the ESR spectra of the radical anions of 4-formyl-, 4-acetyl-, 4-cyano-, and 4-nitro-benzoate remain after the addition of a similar concentration of acetone in such an experiment. These results suggest that the reduction potentials of those benzoate anions are less negative than −2.1 V. The same conclusion can be reached for the radical anion of terephthalate from the fact that adding acetone did not remove the radical anion ESR. The stated potential of −1.69 V (in water) is in agreement with this argument. It is known that terephthalate is reduced by the acetone ketyl radical anion.[40]

Reaction Rate of e_{aq}^-. Because of the central role of the reaction of e_{aq}^- with the phenoxyl radical in the discussion of these results, it is important to know the rate constant. The rate constants for the reactions of a number of radicals with e_{aq}^- have been determined by means of optical absorption in conjunction with pulse radiolysis.[10] Only a brief presentation of the results will be given here. Water radiolysis produces mainly e_{aq}^- and $^\bullet$OH at comparable concentrations. Hydroxyl radicals were converted to $^\bullet N_3$ or $Br_2^{\bullet -}$ radicals, which subsequently oxidized phenolate or *p*-cresolate to produce phenoxyl or 4-methylphenoxyl radicals quantitatively. This measure was taken to avoid possible complications in the quantitative conversion of OH to the phenoxyl radicals (formation of longer-lived adducts). With azide, the solutions contained 10 mM sodium azide and 1 mM phenol at pH 11, where phenol is mainly dissociated. With bromide, the solution contained 0.1 M Br$^-$ and 8 mM phenol at pH 11. In each case, the phenoxyl radicals are produced rapidly (within 300 ns). The transient optical absorption was measured at 600 nm where only e_{aq}^- absorbs to a significant extent. The disappearance of e_{aq}^- occurs by reaction with itself, by bimolecular reaction with phenoxyl, and by reaction with phenolate, H_2O_2 from the radiation chemical spur, and impurities in the solution. The observed kinetic decay curves were fit to a kinetic model that included the 10 relevant reactions of primary radicals from water radiolysis and radical−radical reactions of e_{aq}^- with phenoxyl and of two phenoxyl radicals. The rate constants for the primary radical reactions and that for the self-reaction of the phenoxyl radical were taken from the literature. A first-order reaction of e_{aq}^- with unknown impurities (and phenolate) was also included, as was done by Elliot and Ouellette.[41] Decay curves were taken at two radiolysis doses, and the integrated numerical solutions to the kinetic differential equations were simultaneously fit to the two observations. A Marquardt procedure was used to optimize the rate constants for the reactions of e_{aq}^- with phenoxyl and the first-order reaction with impurities. This procedure was repeated for temperatures between about 5 and 70 °C.

The rate constants for both e_{aq}^- + phenoxyl and e_{aq}^- + 4-methylphenoxyl were found to be diffusion-controlled in that the activation energies (20 and 22 kJ mol^{-1}, respectively) from Arrhenius plots were close to 20 kJ mol^{-1}, as expected for the diffusion of e_{aq}^- in water. The rate constants so determined for 298 K were 1.1×10^{10} and 1.2×10^{10} M^{-1} s^{-1}, respectively. These values are quite large but can be compared with that for e_{aq}^- + nitrobenzene of 3.8×10^{10} M^{-1} s^{-1},[42] where there is no spin factor to consider. This reaction also has a large negative ΔG, and the reaction distance is expected to be similar. With a spin factor of 0.25 for a singlet reaction, this value would become 0.95×10^{10} M^{-1} s^{-1}. If much reaction to form triplet-state products were involved, then the rate constant for e_{aq}^- + phenoxyl should be considerably larger than the observed rate constant. The agreement between 0.95×10^{10} and 1.1×10^{10} shows that the reaction of e_{aq}^- + phenoxyl goes through a singlet pathway and is diffusion-controlled.

Discussion

Fundamental to this discussion is the idea that the energy ordering of the radical-pair states will be the same in all reencounters, independent of the origin of the pairs. The geminate CIDEP of e_{aq}^- in the photolysis of phenolate clearly produces absorptive ESR. The emissive ESR seen in radiolysis experiments with phenolate[4] is only the result of F-pair encounters. No geminate CIDEP of radiolytically produced e_{aq}^- occurs, presumably as a result of the very fast relaxation of $^\bullet$OH,[43] the partner of e_{aq}^-.

Implicit in the following discussion is the idea that the oxidizing and reducing radicals do undergo rapid cross reaction. In the cases that give A/E F-pair polarization, it is clear that those reactions must occur because there is no indication that the self-reaction of any of the radicals leads to polarization of that sort.

The electrochemical data can be used to determine the energy of the radical-pair state. The hydrated electron is a strong reducing agent with a reduction potential of −2.87 V. The reduction potential of the phenoxyl radical (phenoxyl radical/phenolate anion) is reported to be 0.79 V.[44] The difference in these values, 3.66 V, represents the adiabatic free-energy difference (−ΔG) between the radical pair and the reaction product, the phenolate anion. The same situation can be found for the other systems. Reduction potentials of 0.68 V for the 4-methylphenoxyl radical[44] and 0.02 V for the *p*-benzosemiquinone radical anion[45] give corresponding energy differences of 3.55 and 2.89 eV, respectively. Values determined in this

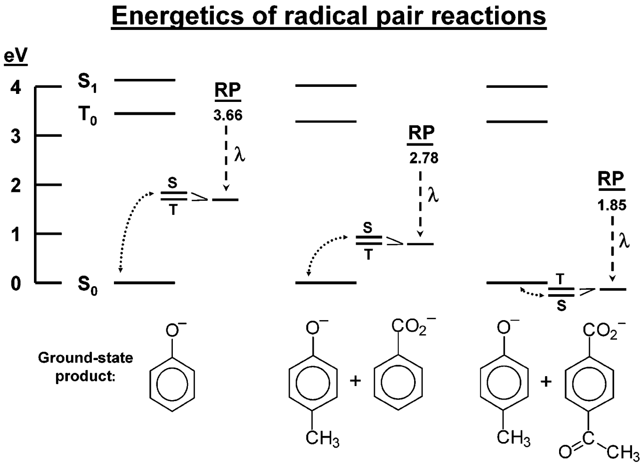

Figure 8. Diagram showing the relationship of the energy levels of the radical pairs e_{aq}^-/phenoxyl, benzoate radical anion/4-methylphenoxyl, and 4-acetobenzoate radical anion/4-methylphenoxyl with the ground state of the reaction product(s). The radical-pair energies have been reduced by a 2-eV reorganization energy (λ, vertical arrow) to show the most favored charge-transfer mixing (curved arrows) with the ground-state product.

way are listed in the last column of Table 2. Energy diagrams for radical pairs involving e_{aq}^- and several radical anions with phenoxyl or 4-methylphenoxyl are illustrated in Figure 8.

It is clear from Table 2 that the radical-pair state for the e_{aq}^-/phenoxyl radical pair lies high enough in energy to be close to the excited states, so that fact should be considered. On the basis of the values in Table 2, the radical-pair states are slightly above the triplet excited state (when e_{aq}^- is paired with the phenoxyl or 4-methylphenoxyl radicals). An analysis of the reaction rate, as discussed above, indicates that the main reaction path does not involve the triplet product state. That conclusion is consistent with Marcus theory in that such a reaction must involve a significant reorganization energy and therefore should not occur at a high rate with this small free-energy difference ($\Delta G \approx 0.2$ eV). All of the radical anions of benzoates have less negative reduction potentials than e_{aq}^-. Therefore, a reaction between a radical anion of a benzoates and a phenoxyl radical is even less likely to form an excited triplet state of the product. Thus, it is accepted in the following discussion that all of the cross reactions lead to singlet products and that the spin multiplicity of all of the F pairs is triplet.

In view of the apparent success of the model of Kobori et al.,[18,19] their approach, as described in the Introduction, will be explored for both the radical systems that produce inverted CIDEP and also for some that give normal CIDEP. Whether the charge-transfer interaction raises or lowers the energy of the radical-pair state depends on the energy ordering of the radical-pair state and the corresponding product state. The energy ordering can be determined with the free-energy difference of the radical cross reaction and the reorganization energy for the electron-transfer system. The consideration of reorganization energy is crucial because the energetics of the product state has to be evaluated at the equilibrium configuration of the radical-pair state.

As stated in the Introduction, inverted F-pair CIDEP has been observed for e_{aq}^- when paired with the phenoxyl radical, the benzosemiquinone radical anion, and $CO_3^{\bullet -}$ in the radiolysis experiment. However, normal CIDEP has been observed when the counter-radical was $SO_3^{\bullet -}$, $CO_2^{\bullet -}$, or $^{\bullet}CH_2C(OH)(CH_3)_2$. The energy ordering of the radical-pair singlet and triplet states in these radical pairs involving e_{aq}^- will be examined below.

A good model for the reaction of e_{aq}^- and the phenoxyl radical is that of e_{aq}^- and nitrobenzene.[46] The solvent reorganization energy for the reaction of e_{aq}^- with nitrobenzene has been estimated to be 1.6 to 1.9 eV at a reaction distance of 8.5 Å and 2.6 to 2.8 eV at long range.[46] For discussion, a value of 2 eV will be used.[47] The internal reorganization energy is also needed. The high rate constant for electron transfer between phenoxyl and phenolate[48] suggests that the value is not large, so the value will be taken as zero. In considering the relationship of the energy levels for the strongest interaction, one should compare the phenolate energy level with the energy of the radical pair as lowered by the reorganization energy (Figure 8). The radical-pair energy corresponds to the value at the equilibrium configuration. The phenolate ground state (singlet) is then about 1.7 eV below the (modified) radical-pair states. In addition, the phenolate triplet level is about 1.8 eV above the radical-pair states. The charge-transfer interaction in the first case will raise the singlet radical-pair state and in the second case will lower the triplet radical-pair state. Thus, the energy ordering of the states (triplet state lower) would produce CIDEP in the sense observed. The energies for *p*-cresolate are much the same, so the system should behave similarly.

The inverted polarization for the e_{aq}^-/*p*-benzosemiquinone radical anion pair and the $e_{aq}^-/CO_3^{\bullet -}$ pair can be explained in the same manner. It should be noted, however, that the internal reorganization energy for the *p*-benzosemiquinone radical anion/hydroquinone dianion couple and the $CO_3^{\bullet -}/CO_3^{2-}$ couple might be substantial. The self-exchange rate for the *p*-benzosemiquinone radical anion/hydroquinone dianion couple has been evaluated to be 2.6×10^4 M^{-1} s^{-1} from the Marcus cross relationship with another phenoxyl radical/phenolate anion couple.[49] This rate constant is significantly smaller than that for the phenoxyl radical/phenolate anion couple (2×10^8 M^{-1} s^{-1}).[48] Because the two redox systems have similar physical sizes, the solvent reorganization energies for the two couples should be about the same. The difference in the self-exchange rate is likely to be attributed to the different magnitude of the internal reorganization energy for the two couples. It may be relevant to note that transient resonance Raman measurements have revealed a major difference in the nature of the structural distortion between the two redox couples.[32,50−53] Although the C−O stretching mode is most enhanced for the phenoxyl radical, the C−C ring-stretching mode is most affected in the resonance Raman spectrum for the *p*-benzosemiquinone radical anion. The self-exchange rate for the $CO_3^{\bullet -}/CO_3^{2-}$ couple has been determined to be 0.4 M^{-1} s^{-1} from the Marcus cross relationship with a redox couple of an osmium complex.[54] This self-exchange rate is much slower than those for the $^{\bullet}OH/OH^-$ couple (3.2×10^2 M^{-1} s^{-1}) and the $^{\bullet}N_3/N_3$ couple (1.0×10^3 M^{-1} s^{-1}) determined in the same study.[54] The latter two couples are supposed to have little internal reorganization energy. A resonance Raman study has suggested that the carbonate radical anion has C_{2v} symmetry in aqueous solution.[55] This symmetry has also been proposed for $CO_3^{\bullet -}$ in ice by an ESR study.[56] Carbonate dianion has D_{3h} symmetry, and the difference in structure between $CO_3^{\bullet -}$ and CO_3^{2-} may indicate a rather large internal reorganization energy.

The free-energy change of the e_{aq}^- reaction with the *p*-benzosemiquinone radical anion is −2.90 eV. If the solvent reorganization energy is ∼2 eV, then around 0.9 eV of the internal reorganization energy from the *p*-benzosemiquinone radical anion/hydroquinone dianion couple would be required to match the total reorganization to the free-energy difference. Such a large magnitude of the internal reorganization energy is unlikely for this redox couple. Therefore, the modified energy of the e_{aq}^-/*p*-benzosemiquinone radical anion pair is most probably higher than that of the hydroquinone dianion ground state. This situation is just like that for e_{aq}^-/phenoxyl; the electronic interaction with the product ground state would raise the singlet energy of the radical pair, so inverted CIDEP would occur.

Although a relatively large internal reorganization energy may be involved in the $CO_3^{\bullet -}/CO_3^{2-}$ couple, the free-energy change for the e_{aq}^- reaction with $CO_3^{\bullet -}$ (reduction potential 1.59 V[57]) is very large in magnitude, −4.46 eV, and it is hard to imagine that the reorganization energy can match the magnitude of the free-energy change. Therefore, it is likely that the electronic interaction between the $e_{aq}^-/CO_3^{\bullet -}$ pair state and the ground state of CO_3^{2-} would bring about a lower triplet energy for the radical pair.

The radical pair of $SO_3^{\bullet -}$ (reduction potential 0.73 V[58,59]) with e_{aq}^- has almost the same free-energy change (−3.60 eV) as that for the e_{aq}^-/phenoxyl radical pair (−3.66 eV). However, the $e_{aq}^-/SO_3^{\bullet -}$ pair has an opposite CIDEP pattern from that for the e_{aq}^-/phenoxyl radical pair.[4] (The CIDEP is either close to zero or is absorptive for e_{aq}^-.)[7] The e_{aq}^- reaction with $SO_3^{\bullet -}$ proceeds in a diffusion-controlled manner with a spin factor of $^1/_4$, just like the e_{aq}^- reaction with the phenoxyl radical.[10] Thus, the energy ordering for the $e_{aq}^-/SO_3^{\bullet -}$ pair must be opposite ($J < 0$) that for the e_{aq}^-/phenoxyl radical pair ($J > 0$). The self-exchange rate for the $SO_3^{\bullet -}/SO_3^{2-}$ couple has been determined to be 4 M^{-1} s^{-1} from the Marcus cross relationship with a number of redox couples of metal complexes.[58,60] This small self-exchange rate implies a relatively large internal reorganization energy. In fact, the internal reorganization energy has been calculated to be 1.53 eV on the basis of the force constants and the optimum geometry for this redox couple.[58] Combined with the solvent reorganization energy, it seems possible that the energy of SO_3^{2-} becomes comparable to that of the $e_{aq}^-/SO_3^{\bullet -}$ pair (3.60 eV) at the equilibrium configuration of the radical pair. The observed CIDEP pattern signifies that the total reorganization energy is equal to or exceeds the free-energy change under this model of the CIDEP effect.

The $e_{aq}^-/CO_2^{\bullet -}$ and $e_{aq}^-/{}^\bullet CH_2C(OH)(CH_3)_2$ radical pairs show the same CIDEP pattern as that for the $e_{aq}^-/ SO_3^{\bullet -}$ pair.[4,7] Whereas $SO_3^{\bullet -}$ is an oxidizing radical, $CO_2^{\bullet -}$ and ${}^\bullet CH_2C(OH)(CH_3)_2$ are reducing radicals. The reduction potentials have been determined to be −1.28 and −0.57 V for $CO_2^{\bullet -}$ and ${}^\bullet CH_2C(OH)(CH_3)_2$, respectively, in polarographic measurements.[61] Thus, the free-energy changes for the e_{aq}^- reaction with $CO_2^{\bullet -}$ and ${}^\bullet CH_2C(OH)(CH_3)_2$ are −1.59 and −2.30 eV, respectively. In addition to the solvent reorganization energy, a relatively large internal reorganization energy is expected for the redox couples for the two radicals. The carbon dioxide radical anion is isoelectronic with ${}^\bullet NO_2$.[62] The couple ${}^\bullet NO_2/NO_2^-$ undergoes a large change in the bond angle.[63−65] The calculation has given an internal reorganization energy of 1.42 eV for this redox couple.[66] The internal reorganization energy is not known for the ${}^\bullet CH_2C(OH)(CH_3)_2$ couple with its reduced form, the carbanion. However, there should be a significant change in the bond angle for the radical center. Considering the relatively small free-energy changes and relatively large reorganization energies, the energies of the ground state of the products of the e_{aq}^- reaction with $CO_2^{\bullet -}$ and ${}^\bullet CH_2C(OH)(CH_3)_2$ are most likely higher than those of the corresponding radical-pair states at the equilibrium configuration of the radical pairs. The electronic interaction would lead to a singlet-state energy below that of the triplet for these radical pairs.

The behavior of radical pairs involving radical anions instead of e_{aq}^- should also be considered using this model. For radical pairs with the 4-methylphenoxyl radical, A/E polarization was observed in the radical anions of unsubstituted, 4-methyl-, methyl-, and 4-methoxy- benzoates and terephthalate (weakly). If the benzoate was substituted with a better accepting group (4-formyl, 4-acetyl, 4-cyano, or 4-nitro), then E/A polarization was found. Terephthalate seems to be very near the dividing line between the two behaviors. The corresponding energy of the radical pair in that case is 2.37 eV (as shown in Table 1) and is considerably below the 3.32-eV energy of the 4-methylphenolate triplet. Very similar behavior was found for radical pairs of the unsubstituted phenoxyl radical with the same radical anions. The predicted energetics is virtually the same as a result of slightly higher excited-state energies (Table 2) and a 0.1 V more positive reduction potential for the phenoxyl radical.

The phthalate isomers are also an interesting comparison. The isophthalate radical anion (meta isomer) gives A/E polarization, as shown in Table 1. Because there is no conjugation between structures with the excess electron on either one of the two carboxyl groups, the behavior should be like that of benzoate itself, as is observed. The polarographic data on this compound[38] (Table 1) give a reduction potential of −1.83 V, which is of a smaller magnitude than that of benzoate. Phthalate, however, has E/A behavior in time-resolved experiments. The pH-corrected reduction potential (Table 1) is slightly more negative than that of terephthalate instead of less negative but is close. Clearly, the dividing line between the two CIDEP behaviors is at about $-\Delta G = 2.4$ eV.

The energy of these radical pairs is not at all close to that for the triplet state of phenolate at 3.45 eV, so that relationship is probably not relevant. To fit the charge-transfer model, the reorganization energy would have to be close to this 2.4-eV level that divides the CIDEP behavior. No experiments were conducted to determine the reaction rate constants of the radical anions with phenoxyl, so no information is available on the reaction distances and consequently the solvent reorganization energy. A small value of the internal reorganization energy for phenoxyl on going to phenolate has been mentioned. There should also be an internal reorganization energy for the benzoate radical anion on going to benzoate, but the value is not clear and may not be large. Thus, it is not clear whether the reorganization energy could be as large as 2.4 eV. If it were, then the observed dependence on the reduction potential can be explained. The energy levels for radical pairs involving radical anions of benzoate and 4-acetobenzoate with 4-methyl phenoxyl are shown in Figure 8 with a reorganization energy of 2 eV. Inverted and normal CIDEP are predicted, respectively. As noted above, the dividing line between the two behaviors is not exactly predicted by the included value of the reorganization.

The final case is that of radical anions with the *p*-benzosemiquinone radical anion. The corresponding reduction potential of the radical on going to the hydroquinone dianion is 0.02 V,[45] so the radical-pair state with the benzoate radical dianion is about 2.1 eV above the nonradical products. When the reorganization energy is taken into account, the modified radical-pair state energy may be below the product ground state (hydroquinone dianion) in energy, so a normal CIDEP is observed.

In each of the cases considered, a relatively large reorganization energy must be invoked to explain the results. The value is uncertain, and some related systems seem to support smaller values. The case of electron exchange between the phenoxyl radical and the phenolate anion has been mentioned, and Meisel[67] has calculated a value of the total reorganization energy of about 0.8 eV for electron transfer in aqueous systems involving quinones with semiquinone anions. With this observation in mind, it can still be said that the model adopted to explain these observations works well, subject to the uncertainties in the reorganization energies. No satisfactory alternative explanation seems evident at this time.

Conclusions

A number of experiments were carried out to clarify the relationship of the energetics of the reaction of oxidizing and reducing radicals to the unusual CIDEP. The location of the excited states of the product species (phenolate, etc.) was determined from the emission spectra. Steady-state and time-resolved ESR experiments were carried out to determine the sense of F-pair CIDEP for a number of different radical pairs consisting of a phenoxyl radical together with either e_{aq}^- or one of a series of radical anions of para-substituted benzoates. Inverted polarization (A/E) was found for e_{aq}^- or the radical anions of benzoate and 4-methyl-, 4-methoxy, and 4-carboxybenzoates in the presence of phenoxyl or 4-methylphenoxyl radicals. Other radical anions such as those of 4-formylbenzoate showed normal polarization. The pair e_{aq}^- with the *p*-benzosemiquinone anion also showed inverted polarization, but normal polarization was seen for all radical anions paired with semiquinone. The geminate radical pair of e_{aq}^-/phenoxyl in the photolysis of phenolate has been shown to be a singlet by the work of Bussandri and van Willigen;[12] additional experiments carried out here support this conclusion and refute the suggestion of Clancy and Forbes[11] that a triplet state is involved. On this basis, the unusual polarization for geminate and F pairs is clearly the result of an inverted (triplet lower) energy ordering of the radical-pair states. The best explanation for this arrangement of the radical-pair states seems to be that based on the treatment by Kobori et al.,[18,19] which involves concepts of Marcus theory and invokes the charge-transfer interaction to shift the energies of the radical-pair states.

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References and Notes

(1) Adrian, F. J. *J. Chem. Phys.* **1971**, *54*, 3918.

(2) Monchick, L.; Adrian, F. J. *J. Chem. Phys.* **1978**, *68*, 4376.

(3) McLauchlan, K. A. In *Modern Pulsed and Continuous-Wave Electron Spin Resonance*; Kevan, L., Bowman, M. K., Eds.; Wiley & Sons: New York, 1990.

(4) Fessenden, R. W.; Verma, N. C. *J. Am. Chem. Soc.* **1976**, *98*, 243.

(5) Emission was also observed for e_{aq}^- in the presence of $^\bullet PO_3^{2-}$ and $H^\bullet PO_2^-$. Time-resolved ESR observations on $^\bullet PO_3^{2-}$ (Hornak, J. P. Ph.D. Disseration, University of Notre Dame, Notre Dame, IN, 1982) showed an E/A polarization during the initial ~10 μs when e_{aq}^- was present but not when it was absent. The emission for e_{aq}^- must be the net sum of the contrtibutions for encounters with $^\bullet PO_3^{2-}$ in the two ^{31}P nuclear spin states. Net emission suggests that ST_- polarization as well as ST_0 polarization is operative. The basic RPM polarization for this radical, and probably also $H^\bullet PO_2^-$, with e_{aq}^- is of the normal E/A sense. These cases will not be considered further here.

(6) Jeevarajan, A. S.; Fessenden, R. W. *J. Phys. Chem.* **1989**, *93*, 3511.

(7) The CIDEP seen for e_{aq}^- should be more carefully described. With an emissive ESR signal, there is no doubt that CIDEP is in play. For absorption, there can be either absorptive CIDEP or virtually none. The description given in ref 4 listed two absorptive ESR signal amplitudes for e_{aq}^-, in the presence of OH scavengers SO_3^{2-} and methanol and a higher amplitude for ethylene, formate, or *tert*-butyl alcohol. A careful study of the ESR signal of $SO_3^{\bullet -}$ with e_{aq}^- either present or not (N_2 or N_2O solution) shows evidence of very little or no CIDEP from interaction with e_{aq}^-. Also, the higher ampltude for e_{aq}^- in the second group implies, perhaps, an absorptive CIDEP. However, $CO_2^{\bullet -}$ is in this group, and its *g* factor is virtually the same as that of e_{aq}^- so little CIDEP is expected. In the absence of a detailed description (including all of the possible effects such as Heisenberg spin exchange) of the time profile of the ESR signal for e_{aq}^- in such experiments, it is hard to make a more definitive conclusion on an absorptive ESR signal.

(8) Jeevarajan, A. S.; Fessenden, R. W. *J. Phys. Chem.* **1992**, *96*, 1520.

(9) Mialocq, J. C.; Sutton, J.; Goujon, P. *J. Chem. Phys.* **1980**, *72*, 6338.

(10) Ichino, T. On the Mechanism of Unusual CIDEP. Ph.D. Disssertation, University of Notre Dame, Notre Dame, IN, 2001.

(11) Clancy, C. M. R.; Forbes, M. D. E. *Photochem. Photobiol.* **1999**, *69*, 16.

(12) Bussandri, A.; van Willigen, H. *J. Phys. Chem. A* **2001**, *105*, 4669.

(13) Adrian, F. J. *Rev. Chem. Intermed.* **1979**, *3*, 3.

(14) Jent, F.; Paul, H. *Chem. Phys. Lett.* **1989**, *160*, 632.

(15) Valyaev, V. I.; Molin, Y. N.; Sagdeev, R. Z.; Hore, P. J.; McLauchlan, K. A.; Simpson, N. J. K. *Mol. Phys.* **1988**, *63*, 891.

(16) Shushin, A. I. *Chem. Phys. Lett.* **1991**, *183*, 321.

(17) Shkrob, I. A. *Chem. Phys. Lett.* **1997**, *264*, 417.

(18) Kobori, Y.; Sekiguchi, S.; Akiyama, K.; Tero-Kubota, S. *J. Phys. Chem. A* **1999**, *103*, 5416.

(19) Kobori, Y.; Akiyama, K.; Tero-Kubota, S. *J. Chem. Phys* **2000**, *113*, 465.

(20) This energy shift is equivalent to raising the energy of the ground-state product by the reorganization energy.

(21) Davis, H. F.; McManus, H. J.; Fessenden, R. W. *J. Phys. Chem.* **1986**, *90*, 6400.

(22) Madden, K. P.; McManus, H. J. D.; Fessenden, R. W. *Rev. Sci. Instrum.* **1994**, *65*, 49.

(23) Hug, G. L.; Fessenden, R. W. *J. Phys. Chem. A* **2000**, *104*, 7021.

(24) Hug, G. L.; Wang, Y.; Schöneich, C.; Jiang, P.-Y.; Fessenden, R. W. *Radiat. Phys. Chem.* **1999**, *54*, 559.

(25) Hart, E. J.; Anbar, M. *The Hydrated Electron*; Wiley-Interscience: New York, 1970.

(26) Wardman, P. *J. Phys. Chem. Ref. Data* **1989**, *18*, 1637.

(27) See ref 31 of Han, P.; Bartels, D. M. *J. Phys. Chem.* **1990**, *94*, 7294−7299 for a comment on this value.

(28) Birch, A. J.; Hinde, A. L.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 3370.

(29) Kubozona, Y.; Aoyagi, M.; Ata, M.; Gondo, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3156.

(30) Kivelson, D. *J. Chem. Phys.* **1960**, *33*, 1094.

(31) There is no evidence that reactions between the radical anions themselves produce other than a normal E/A polarization. It is not possible to form only the radical anions, but mixtures with an OH adduct (hydroxycyclohexadienyl radical) can be made.

(32) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1984**, *81*, 113.

(33) Getoff, N. *Radiat. Phys. Chem.* **1989**, *34*, 711.

(34) Grabner, G.; Köhler, G.; Zechner, J.; Getoff, N. *J. Phys. Chem.* **1980**, *84*, 3000.

(35) Under the condition for 5 and 50 mM solutions, about 50 and 100% of incident photons were absorbed by phenolate, respectively. For the 50 mM solution, the initial radical concentration at high laser doses approaches 1 mM. The initial half-life of the radicals is about 100 ns under such a condition. The initial yield of the hydrated electron will be underestimated when extrapolation from the electron decay curve on a longer time scale to time zero is used.

(36) Sarkar, S. K.; Maiti, A.; Kastha, G. S. *Chem. Phys. Lett.* **1984**, *105*, 355.

(37) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409.

(38) Hall, M. E.; McNutt, R. C. *Anal. Chem.* **1960**, *32*, 1073.

(39) Wagner, P. J.; Truman, R. J.; Puchalski, A. E.; Wake, R. *J. Am. Chem. Soc.* **1986**, *108*, 7727.

(40) Qin, L.; Madden, K. P.; Schuler, R. H. *J. Phys. Chem.* **1988**, *92*, 3790.

(41) Elliot, A. J.; Ouellette, D. C. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 837.

(42) Maham, Y.; Freeman, G. R. *Can. J. Chem.* **1988**, *66*, 1706.

(43) Verma, N. C.; Fessenden, R. W. *J. Chem. Phys.* **1976**, *65*, 2139.

(44) Lind, J.; Shen, X.; Eriksen, T. E.; Merenyi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479.

(45) Ilan, Y. A.; Czapski, G.; Meisel, D. *Biochim. Biophys. Acta* **1976**, *430*, 209.

(46) Schmidt, K. H.; Han, P.; Bartels, D. M. *J. Phys. Chem.* **1995**, *99*, 10530.

(47) This value is from the standard continuum dielectric model. We note that there is a large hydration entropy for the hydrated electron (Han, P.; Bartels, D. M. *J. Phys. Chem.* **1991**, *95*, 5367−5370). Some of this

entropy may provide a contribution to the solvent reorganization energy in addition to that from the dielectric model for reactions involving the hydrated electron.

(48) Schuler, R. H.; Neta, P.; Zemel, H.; Fessenden, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 3825.

(49) Armstrong, D. A.; Sun, Q.; Schuler, R. H. *J. Phys. Chem.* **1996**, *100*, 9892.

(50) Tripathi, G. N. R. *J. Chem. Phys.* **1981**, *74*, 6044.

(51) Schuler, R. H.; Tripathi, G. N. R.; Prebenda, M. F.; Chipman, D. M. *J. Phys. Chem.* **1983**, *87*, 5357.

(52) Chipman, D. M.; Prebenda, M. F. *J. Phys. Chem.* **1986**, *90*, 5557.

(53) Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *100*, 5023.

(54) Schindler, S.; Castner, E. W., Jr.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1993**, *32*, 4200.

(55) Bisby, R. H.; Johnson, S. A.; Parker, A. W.; Tavender, S. M. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2069.

(56) Chantry, G. W.; Horsfield, A.; Morton, J. R.; Whiffen, D. H. *Mol. Phys.* **1962**, *5*, 589.

(57) Huie, R. E.; Clifton, C. L.; Neta, P. *Radiat. Phys. Chem.* **1991**, *38*, 477.

(58) Sarala, R.; Islam, M. A.; Rabin, S. B.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 1133.

(59) Das, T. N.; Huie, R. E.; Neta, P. *J. Phys. Chem. A* **1999**, *103*, 3581.

(60) Sarala, R.; Stanbury, D. M. *Inorg. Chem.* **1990**, *29*, 3456.

(61) Lilie, J.; Beck, G.; Henglein, A. *Ber. Bunsen-Ges. Phys. Chem.* **1971**, *75*, 458.

(62) Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, 1967.

(63) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: New York, 1984.

(64) Yu, D.; Rauk, A.; Armstrong, D. A. *J. Phys. Chem.* **1992**, *96*, 6031.

(65) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405.

(66) Stanbury, D. M.; Lednicky, L. A. *J. Am. Chem. Soc.* **1984**, *106*, 2847.

(67) Meisel, D. *Chem. Phys. Lett.* **1975**, *34*, 263.

(68) Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 620.