Magnetic Field Effects Observed upon Photolysis of Para-Substituted Diphenyl Disulfides in Micellar Solutions

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The recombination of pairs of para-substituted phenylthiyl radicals inside micellar supercages was studied by means of a nanosecond laser flash photolysis technique. Singlet and triplet pairs were formed by direct excitation and by triplet-sensitized photolysis of the corresponding disulfides, respectively. Magnetic field effects (MFEs) on the yield of escaped thiyl radicals were found for the triplet-sensitized photolysis of the *p*-amino compound. For the *p*-hydroxy-, *p*-methoxy-, and *p*-butoxy compounds, short-lived MFEs were observed but it is unlikely that they arise from the recombination of the thiyl radicals. No MFE was found on pairs of *p*-chloro-substituted and unsubstituted phenylthiyl radicals within experimental error. The absence of MFE is in this case explained by large spin-orbit coupling caused by orbital degeneracy. A stabilization mechanism of the (*p*-aminophenyl)-thiyl radicals lifts that degeneracy and reduces spin-orbit coupling. Variations of the MFE over the absorption spectrum were used to assign the MFEs to certain species in the reaction systems.

Introduction

Magnetic field effects (MFEs) on the reactions of radical pairs have hitherto been studied extensively.¹⁻³ They are mainly caused by the magnetic field dependence of the spin conversion rate between singlet and triplet pairs. These effects are closely related to magnetic isotope effects (MIEs), in that one of the mechanisms of MFEs is the hyperfine coupling mechanism (HFCM) determined by the magnitude of nuclear spins. On the basis of these MIEs, isotopes could be separated in a mass-independent way. Unfortunately, spin-orbit coupling (SOC) increases with increasing mass number and provides a fast, magnetic-fieldindependence mechanism of spin conversion of radical pairs, which can quench the MFEs and MIEs.⁴ On the other hand, we have started to study MFEs on heavy-atom-centered radicals and succeeded in finding the effects on the reactions of Si-, P-, S-, and Ge-centered radicals.⁵⁻⁸ These MFEs can be explained by a combination of the HFCM and relaxation mechanism (RM).9

Through preliminary work, we found MFEs on the recombination of (*p*-aminophenyl)thiyl radicals generated with triplet sensitization of the disulfide in a sodium dodecylsulfate micellar solution.¹⁰ Bohne et al. showed that an MFE for the reaction of a triplet pair of the phenylthiyl and benzophenone ketyl radicals is absent.¹¹ They suggest that the reason for this is that fast, magnetic-field-independent spin-rotational relaxation in unsubstituted phenylthiyl radicals occurs. Applying their rationale to the (*p*-aminophenyl)thiyl radicals, we find that no MFE should have been observed. Khudyakov et al.⁴ have also found that the rotational correlation times assumed by Bohne et al. were much shorter than those found experimentally for molecules of similar size. They therefore concluded that the cause for the absence of a MFE for the reaction of a triplet pair of the phenylthiyl and benzophenone ketyl radicals must still be determined.

In this paper, detailed information about the MFE for the recombination reaction of triplet (*p*-aminophenyl)thiyl radical pairs is given and the influence of substituent changes in parasubstituted phenylthiyl radicals is investigated. The striking changes of the MFE, as related to the nature of the substituent, have cast more light on the action of the SOC and the related spin-rotational relaxation as quenching mechanisms for MFEs. Emphasis is given to the assignment of the MFEs to certain species.

Experimental Section

Materials. Diphenyl disulfide (PDS), bis(p-chlorophenyl) disulfide (chloro-PDS), and bis(p-aminophenyl) disulfide (amino-PDS) were obtained commercially and recrystallized twice from a 3:1 (v/v) mixture of benzene and pentane. Bis(p-hydroxyphenyl) disulfide (hydroxy-PDS) was prepared by oxidation of the respective thiophenol by dimethyl sulfoxide¹² and purified in the same manner as the other compounds. Bis(p-methoxyphenyl) disulfide (methoxy-PDS) and bis(p-tert-butoxyphenyl) disulfide (t-butoxy-PDS) were prepared by the Williamson reaction¹³ between the corresponding alkyl bromides and disodium phenoxide obtained by treating hydroxy-PDS with sodium in ethanol. The obtained yellow oils are purified by chromatography on silica gel (Merck Silica gel 60) eluted with benzene/hexane (1:1, v/v). Each of the synthesized disulfides was identified by gas chromatography-mass spectrometry, and its purity was checked by high-pressure liquid chromatography. Xanthen-9-one (xanthone) was recrystallized from ethanol, and sodium dodecyl sulfate (SDS) from methanol/ethanol (1:1, v/v). Commercially available cetyl trimethylammonium chloride (CTAC) was used without further purification.

Laser Flash Photolysis. Laser flash photolysis experiments were performed at room temperature on an apparatus similar to one described elsewhere.¹⁴ The fourth (266 nm) and third (355 nm) harmonics of a Quanta-Ray GCR-11 Nd-YAG laser with a pulse width of 5 ns were used for direct excitation and triplet sensitization, respectively. Transient absorption was recorded by an HP54510A digitizing oscilloscope with a time resolution of 1 ns. Magnetic fields (B) were generated by a Mitsubishi 6MA-EM1275A electromagnet. The smallest magnetic field generated by a countercurrent for canceling the residual field was less than 0.2 mT. This magnetic field is hereafter designated as zero field. The concentrations of xanthone, SDS, and CTAC were 1.0×10^{-3} , 8.0×10^{-2} , and 1.13×10^{-1} mol dm⁻³, respectively. Disulfide concentrations were 5.0×10^{-4} or 1.0×10^{-3} mol dm⁻³, depending on the sample. All samples were dissolved in distilled water by sonication under a nitrogen atmosphere. The distilled water was previously nitrogen-bubbled for some hours in order to remove oxygen. All experiments were reproduced at least once.

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TABLE 1: Absorption Maxima (λ_{max}) and Rate Constants of Recombination (k_R) and Escape (k_{sec}) Obtained for Some Para-Substituted Thiyl Radicals in Micellar Solutions with Direct Excitation

para-group	λ_{max}/nm	solution	$k_{\rm R}/10^6 {\rm ~s^{-1}}$	$k_{\rm esc}/10^{6}~{ m s}^{-1}$
Н	450 ± 20	CTAC	22 ± 2	-
chloro	510 ± 10	CTAC	19 ± 2	
		SDS	50 ± 5	
methoxy	525 ± 10	CTAC	11.4 ± 2	
		SDS	25 ± 2	
tert-butoxy	525 ± 10	CTAC	9.5 ± 1.5	
hydroxy	520 ± 10	CTAC	7.7 ± 1.5	
amino	590 ± 20	CTAC	2.34 ± 0.2	1.56 ± 0.2
	350 ± 20			
		SDS	4.8 ± 0.2	5.2 ± 0.4

Simulations. Systems of kinetic equations were numerically integrated by fourth-order Runge–Kutta integration with adaptive step size.¹⁵ Parameter fits were performed by simplex minimization of the root mean square error between experimental and simulated traces.

Results and Discussion

Direct Excitation Laser Flash Photolysis. Transient optical absorption (TROA) signals were measured during the first 15 μ s after 266-nm laser excitation in the wavelength range of 300–700 nm for the SDS micellar solutions of amino-PDS, chloro-PDS, PDS, and methoxy-PDS. Similar measurements were performed for the CTAC micellar solutions of amino-PDS, *t*-butoxy-PDS, chloro-PDS, PDS, hydroxy-PDS, and methoxy-PDS. Disulfide concentrations were 5.0×10^{-4} mol dm⁻³ in these experiments.

For the amino-PDS in both SDS and CTAC micellar solutions the TROA spectrum of the (p-aminophenyl)thiyl radical was obtained. The two peaks at 350 and 580 nm were used to identify this radical, as in our previous paper.¹⁰ No significant time dependence of the TROA spectrum was observed in both solutions, at wavelengths below 600 nm. At higher wavelengths, we found some fast decaying absorbance which could be attributed to hydrated electrons. For all other disulfides, TROA spectra were time dependent, even between 350 and 600 nm. TROA spectra measured in the SDS solutions could be decomposed into spectra of three main components by fitting the sum of two exponentials and one second-order decay with fixed decay constants to the experimental data at each wavelength. For TROA spectra measured in the CTAC solutions, the same procedure for decomposition was used by replacing the second-order decay by a third exponential decay. Among these components, thiyl radicals were identified (cf. Table 1) by means of the spectra given in the literature.¹⁶⁻¹⁹ In the case of the (*p-tert*-butoxyphenyl)thiyl and the (p-hydroxyphenyl)thiyl radicals, the radicals were identified by comparing their spectra to the spectrum of the (p-methoxyphenyl)thiyl radical. The hydrated electron was identified as the component which decayed by a second-order process in SDS and by a first-order process in CTAC micellar solutions, in agreement with earlier observations.^{20,21} The third component has a much longer lifetime than the other ones. Its spectrum is significantly different from the one of the thiyl radicals. From the spectrum, this species could not be assigned.

The main reaction was in all cases sulfur-sulfur bond cleavage giving the thiyl radicals. No MFE for the decay of any of the thiyl radicals was found when direct excitation was used. Borisevich et al.²² observed that the bond cleavage is completed in less than 1 ps for PDS and amino-PDS. They suggested that bond cleavage occurs from a singlet state in the former disulfide and from a triplet state in the latter one. Although we found MFE for the decay of the (*p*-aminophenyl)thiyl radical obtained by triplet sensitization,¹⁰ no MFE was observed for the case of direct excitation. On the basis of this, we therefore suggest that the bond cleavage after direct excitation occurs from a singlet state for amino-PDS. Thus formation and decay of the thiyl radicals can be described by the following reactions:

$$\mathbf{R}-\mathbf{S}-\mathbf{S}-\mathbf{R} \xrightarrow{h\nu} {}^{1}\mathbf{R}-\mathbf{S}-\mathbf{S}-\mathbf{R}^{*} \xrightarrow{1} \overline{\mathbf{R}}-\mathbf{S}\cdot\cdot\mathbf{S}-\mathbf{R}$$
(1)

$${}^{1}\overline{R-S}\cdot S-R \xrightarrow{k_{R}} R-S-S-R \qquad (2)$$

$${}^{1}\overline{R-S}\cdot\cdot S-R \xrightarrow{k_{osc}} 2 R-S \cdot$$
 (3)

$$2 R - S \rightarrow R - S - S - R \tag{4}$$

Reaction 2 describes the recombination of the singlet spincorrelated radical pair with the rate constant $k_{\rm R}$, reaction 3 the escape of a radical from the micelle with the rate constant k_{esc} , and reaction 4 the recombination of escaped thiyl radicals in a second-order reaction with the rate constant k_{R2} . If we take into account that reaction 1 is complete in less than 1 ps, we can assume a given concentration c_0 of the spin-correlated radical pair at time zero (time after the laser pulse). Given this assumption, we can integrate the kinetic equations corresponding to reactions 1-4. The $k_{\rm R}$ and $k_{\rm esc}$ values given in Table 1 for (p-aminophenyl) thiyl radicals were obtained by fitting simulated decay curves to the experimental ones at 380 and 590 nm. No significant contribution of thiyl radicals to the absorbance after completion of the fast first-order decay (reaction 2) was found for any disulfide, with the exception of amino-PDS. This indicates that the escape rates (k_{esc}) are by at least 2 orders of magnitude lower than the recombination rates $(k_{\rm R})$ for the other disulfides.

Triplet-Sensitized Laser Flash Photolysis. In the case of tripletsensitized photolysis, a triplet sensitizer (TS) is excited and reaches its triplet state (${}^{3}TS^{*}$). If the triplet energy of the sensitizer is higher than that of the disulfide, energy transfer will take place to give a disulfide triplet. Since disulfide triplets are unstable,²³ this will result in sulfur-sulfur bond cleavage and the production of a triplet spin-correlated radical pair. The reactions can be described by the following equations:

$$TS \xrightarrow{n\nu}{\rightarrow} {}^{3}TS^{*}$$
 (5)

$${}^{3}TS^{*} + R - S - S - R \xrightarrow{k_{Q}} TS + {}^{3}\overline{R - S \cdot S - R}$$
 (6)

$${}^{3}\overline{R-S\cdots S-R} \xrightarrow{k_{SC}} {}^{1}\overline{R-S\cdots S-R}$$
 (7)

which would then be followed by reactions 2–4, given previously. For kinetic analysis it is impossible to separate the spin conversion (7), with rate constant k_{SC} , from the recombination of the singlet spin-correlated pair (2). Therefore it is appropriate to define a combined rate constant k_{RT} which includes both reactions. This approach has been widely used in earlier work.¹⁻³

It appears that no experimental data on the triplet energies of diphenyl disulfides are available in the literature. Maier et al. have, however, calculated electronically excited levels of PDS and amino-PDS by a quantum chemical approach.²³ Triplet energies taken from their work are 71.5 and 67.9 kcal mol⁻¹ for PDS and amino-PDS, respectively. Our experiments have shown that naphthalene triplets (triplet energy of 61 kcal mol⁻¹)²⁴ are not quenched by PDS, methoxy-PDS, and amino-PDS. On the other hand, xanthone triplets (triplet energy 74.2 kcal mol⁻¹)²⁵ are quenched by the diphenyl disulfides at rates which are about 1 order of magnitude lower than the encounter rate expected in CTAC micelles, as can be seen in Table 2. This indicates that triplet energies of the diphenyl disulfides are not much lower than that of xanthone in micellar solutions and thus at least as high as calculated by Maier et al.²³ This fact restricts the choice

TABLE 2: Quenching Rate Constants (k_0) of XanthoneTriplets with and without Addition of Disulfide

disulfide	c/10−3 M	micellar solvent	k _Q /10 ⁶ s ⁻¹
none		SDS	0.24 ± 0.05
none (k_{00})		CTAC	0.792 ± 0.025
unsubstituted	0.5	CTAC	1.36 ± 0.04
p-chloro	0.5	CTAC	1.80 ± 0.04
<i>p</i> -amino	0.5	CTAC	1.66 ± 0.04
p-amino	0.5	SDS	0.58 ± 0.04
<i>p</i> -methoxy	0.5	CTAC	1.48 ± 0.04
p-methoxy	1.0	CTAC	2.25 ± 0.06
<i>p</i> -hydroxy	1.0	CTAC	2.23 ± 0.06

of the triplet sensitizer considerably. Thus we used xanthone at an excitation wavelength of 355 nm despite some possible side reactions. Xanthone (X) was shown to abstract hydrogen to some extent from SDS surfactant molecules to form triplet radical pairs of the xanthone ketyl (XH) and alkyl (>CH) radicals.²⁶ We observed this reaction to an even higher extent in CTAC micellar solutions of xanthone. Recombination of the triplet pairs from the XH and >CH radicals is subject to MFEs itself.²⁶ Note that despite the higher encounter rate in the smaller SDS micelles, triplet quenching by amino-PDS is considerably slower in these micelles than in CTAC ones (cf. Table 2). This results in a much lower ratio between the rates of formation and recombination of thiyl radicals in SDS micelles and consequently in a much lower concentration of these radicals. Experiments with triplet sensitization were therefore performed in CTAC micellar solutions.

MFE on Triplet-Sensitized Laser Flash Photolysis. Triplet thiyl radical pairs need to be converted to singlet pairs according to reaction 7 before they can recombine. The rate of this process will depend on the magnetic field B, in the case where the fielddependent mechanisms of triplet-singlet transitions are more important than the field-independent ones. The dependence of the recombination rates on the magnetic field will be canceled if spin conversion is fast enough at all fields to equilibrate all states before re-encounter of the radical pair or if strong SOC allows for complete intersystem recombination of triplet pairs. If the magnetic-field-dependent recombination in the micellar supercage competes with radical escape from it, an MFE on the yield of escaped radicals is expected.

MFEs can be observed in laser flash photolysis as changes in the transient absorbance $(A(t,\lambda))$ as a function of the magnetic field. Here t is the time after excitation, and λ is the observation wavelength. Values of $A(t,\lambda)$ were obtained from the experimental time profiles by calculating the time average of A in the range from $t - \Delta t$ to $t + \Delta t$ in order to enhance the signal-to-noise ratio. The values of Δt were 0.1 μ s for $t = 1 \ \mu$ s and 0.5 μ s for $t = 9 \,\mu s$. For our further discussion, we define the relative MFE as $R = A(B,t,\lambda)/A(0 \text{ T},t,\lambda)$. The absolute MFE (ΔA) is then defined by $\Delta A = A(B,t,\lambda) - A(0 T,t,\lambda)$. Let us now consider the variations of the absolute MFE over the absorption spectrum, denoted as the MFE spectrum. This MFE spectrum is the difference between the TROA spectra observed at the magnetic field B and at zero field at a given time t after excitation. If the concentration of a species is increased (decreased) by the magnetic field, it will give rise to a positive (negative) MFE spectrum which has the same appearance as its absorption spectrum. The MFE spectrum is therefore a weighted sum of the absorption spectra of all species in the reaction system which are subject to MFE and can be used for the assignment of MFEs.

TROA time profiles after 355-nm laser excitation were measured in the wavelength region between 370 and 700 nm in the absence and the presence of a magnetic field of 0.1 T for the CTAC micellar solutions of PDS $(5.0 \times 10^{-4} \text{ and } 3 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$, chloro-PDS $(5.0 \times 10^{-4} \text{ and } 1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$, amino-PDS $(5.0 \times 10^{-4} \text{ mol} \text{ dm}^{-3})$, hydroxy-PDS $(1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$, and methoxy-PDS $(1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$ each with xanthone $(1.0 \times 10^{-3} \text{ mol} \text{ dm}^{-3})$ as a triplet sensitizer. An MFE was found for CTAC micellar solutions of xanthone in the wavelength range



Figure 1. MFE on the triplet-sensitized photolysis of bis(*p*-aminophenyl) disulfide in the CTAC micellar solution. (a, top) Transient optical absorbance (A) observed at 380 nm in the absence and presence of a magnetic field of 0.1 T and difference of both traces multiplied by 5. (b, bottom) Field dependence of the relative MFE (see text) observed at 380 nm 9 μ s after excitation. The error of each point is ± 0.02 . The inset shows MFE spectra observed at 0.1 T 1 μ s (open circles) and 9 μ s (filled squares) after excitation.

from 400 to 620 nm, but no MFE was found in the range from 370 and 400 nm within experimental error. The maximal MFE was observed at 520 nm, although the absorption of the xanthone ketyl radical is centered at 490 nm.²⁵ For these reasons the field dependence of the time profile was observed at 380 nm for amino-PDS. The other thiyl radicals do not absorb significantly outside the wavelength range where an MFE was observed for xanthone. Thus the field dependence of the time profile was observed at 510 nm for hydroxy-PDS, methoxy-PDS, and *t*-butoxy-PDS (1.0 × 10⁻³ mol dm⁻³). In this case the MFE was corrected for the contribution of the MFE caused by xanthone.

An MFE with time-dependent MFE spectrum was found for the xanthone triplet-sensitized photolysis of amino-PDS in the CTAC micellar solution. Absorbance curves observed at 380 nm in the absence and the presence of a magnetic field of 0.1 T, as well as the time dependence of the absolute MFE at that wavelength are shown in Figure 1a. The field dependence of the relative MFE and MFE spectra at two different times after excitation (inset) are shown in Figure 1b. MFEs with no significant time dependence of the MFE spectrum were found for hydroxy-PDS, methoxy-PDS, and t-butoxy-PDS. Those of hydroxy-PDS are shown in Figure 2. The largest of these effects was found for the hydroxy compound, while those for the methoxy and tert-butoxy compound are still significant even when the experimental error is taken into account. The MFE spectrum was also measured for the methoxy compound and is similar to that shown in Figure 2. If we add PDS or chloro-PDS to the CTAC solutions of xanthone, we observe formation of their thiyl radicals and some quenching of the xanthone MFE but no additional MFE

From the MFE spectrum of amino-PDS shown in Figure 1b, we can safely conclude that there are at least two MFEs each with a different time dependence in this system. A closer examination of the time dependence at different wavelengths



Figure 2. MFE on triplet-sensitized photolysis of bis(p-hydroxyphenyl) disulfide in the CTAC micellar solution. (a, top) Difference of transient optical absorbance observed at 510 nm between measurements at 0.1 T and zero field for the CTAC micellar solution of xanthone before and after addition of bis(p-hydroxyphenyl) disulfide. (b, middle) Time dependence of the absolute MFE on triplet-sensitized photolysis of bis(p-hydroxyphenyl) disulfide after correction for the contribution of the MFE for xanthone (see text). The solid curve was simulated under the assumption of recombination rates at zero field and 0.1 T of 4×10^6 and $3 \times 10^6 \text{ s}^{-1}$, respectively, to fit the experimental result (see text). (c, bottom) Field dependence of the relative MFE (see text) observed at 510 nm 1 μ s after excitation. The error of each point is ± 0.02 . The inset shows the MFE spectrum observed at 0.1 T 1 μ s after excitation (filled circles) and the absorption spectrom of (p-hydroxyphenyl)thiyl radicals (open circles).

reveals that the shorter living MFE is not completely quenched at 9 μ s, but that about 10% of its initial magnitude persists at that time. Furthermore, one finds that the decay of the long-lived MFE is much slower than that of the short-lived one. Thus we can obtain an approximate MFE spectrum for the short-lived MFE by subtracting the MFE spectrum at 9 μ s from that at 1 μ s, as shown in Figure 3a. The approximate MFE spectrum for the long-lived MFE may be obtained by subtracting 10% of the MFE spectrum at 1 μ s from the one at 9 μ s. This result is shown in Figure 3b (filled circles) together with the spectrum of the (*p*-aminophenyl)thiyl radical in the CTAC micellar solution found by direct excitation photolysis (open circles). The similarity of both spectra in Figure 3b strongly suggests that the long-lived



Figure 3. Separated MFE spectra at 0.1 T for the photolysis of bis(*p*-aminophenyl) disulfide in the CTAC micellar solution. (a, top) Shorter living MFE. (b, bottom) Longer living MFE (filled circles) and absorption spectrum of (*p*-aminophenyl) thiyl radicals (open circles).

MFE has to be assigned to the recombination of (*p*-aminophenyl)thiyl radicals. The remaining deviations may be caused by incomplete removal of the short-lived MFE, poor signal-to-noise ratio in the MFE spectra, and ground-state bleaching of xanthone below 400 nm.

The short-lived MFE cannot solely be attributed to the recombination of xanthone ketyl radicals and surfactant alkyl radicals since the alkyl radicals do not absorb in the given observation region and the absorption band of the xanthone ketyl radical at 490 nm is much narrower than the observed MFE spectrum. The shape of the observed MFE spectrum is also different from the MFE spectrum observed in solutions of xanthone in CTAC. Though the difference of the MFE spectra observed 1 and 9 μ s after excitation may include some contribution from the long-lived effect, this cannot account for all the additional absorption. On the other hand, it is well-known from the literature that xanthone triplets may be reduced by aromatic amines, either by hydrogen or by electron transfer.^{27,28} Triplet spin-correlated radical pairs or radical ion pairs are formed in these reactions, and recombination as well as electron back-transfer are expected to be subject to MFEs. Therefore, we suggest that the shortlived MFE is caused by one of these processes or even by a combination of the two. In order to determine the cause of these MFEs, a CIDEP study would be required. This is beyond the scope of this work.

The contribution of the short-lived MFE to the absolute MFE at a given observation wavelength of 380 nm at 9 μ s is less than 8%, a value which is below statistical error. The relative MFE is, however, downscaled by an additional magnetic-field-independent absorbance at this wavelength. One part of this absorbance is due to singlet-born thiyl radicals, since unlike the other disulfides amino-PDS does absorb significantly at the observation wavelength. The other component is due to an unknown long-lived xanthone transient.²⁵ Since it is not clear to which extent this transient is quenched by the addition of amino-PDS, we did not correct for the additional absorption. Therefore, the R(B) values given in Figure 1b are only a lower limit. The remaining systematic errors do not have any influence on the field dependence of R.

Photolysis of Para-Substituted Diphenyl Disulfides

The dependence of R on the magnetic field is shown in Figure 1b for the thiyl pair recombination in the CTAC micellar solution. The estimated statistical error of these R(B) values is ± 0.02 , the largest contribution being from small instabilities in the intensity of the excitation light. The reason for that is that the shape of the decay curve is very sensitive to the initial radical concentration because of the relative fast second-order decay of the escaped radicals. This complication was also the reason for the slightly different high-field behavior previously reported by us for the SDS solutions.¹⁰

The $B_{1/2}$ values, which are the fields for which half the saturation value of the MFE is reached, are about 10 ± 5 and 20 ± 5 mT in the SDS and CTAC micellar solutions, respectively. These values are larger than the values usually expected for a MFE caused by the HFCM only. Note that the structural information on (*p*-aminophenyl)thiyl discussed below indicates that only rather small hyperfine couplings to the hydrogen atoms are present. Hyperfine coupling to the sulfur atom can be neglected in this discusion because the natural abundance of the ³³S isotope with non-zero nuclear spin (I = 3/2) is only 0.75%, which is below the limit of observability. Even if we take into account ¹⁴N coupling, the $B_{1/2}$ values would hardly be expected to exceed 5 mT. On the other hand, the assumption of further contributions by the relaxation mechanism⁹ (RM) may explain the observed field dependence of *R*.

In the present study, the MFE on the reaction of two (p-aminophenyl)thiyl radicals was observed with the tripletsensitized excitation, but not with direct excitation. This may seem rather peculiar because any memory for singlet and triplet precursors should have been lost for the time scale of $0.1-1 \ \mu s$ at zero field due to spin-relaxation or coherent spin-motion and any MFE for triplet pairs would imply an MFE for singlet pairs with opposite sign.²⁹ Some asymmetry between MFEs of triplet pairs and singlet pairs may arise from the contribution of radical pairs having large absolute values for the electron-exchange integral (J).¹¹ Because the spin conversion between the singlet and triplet state is prevented in such pairs, two radicals in such a triplet radical pair cannot produce any singlet product after their re-encounter, but those in such a singlet radical pair can. Therefore, MFEs generated from singlet precursors should become smaller, in general, than those from triplet ones.

The time dependence of the absolute MFE on xanthone tripletsensitized photolysis of hydroxy-PDS $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ in the CTAC micellar solution is shown in Figure 2a, where the time dependence of the MFE for the reaction of xanthone in the same micellar solution is also shown. A system of kinetic equations can be established for reactions 2-7 by combining the reactions so as to make a new one with the rate constant $k_{\rm RT}$, as discussed earlier. The rate constants k_0 of the triplet quenching were obtained from an exponential fit of the decay of xanthone triplettriplet absorption at 600 nm and are given in Table 2. The rate constant for triplet quenching due to the disulfide only was calculated by subtraction of the rate constant k_{00} of triplet decay $(k_{00} = (0.792 \pm 0.025) \times 10^6 \text{ s}^{-1})$ found in the CTAC solution of xanthone without disulfide from the k_0 value given in Table $2 (k_0 = (2.23 \pm 0.06) \times 10^6 \text{ s}^{-1})$. Escape processes were neglected because these were found to occur at low rates in the direct excitation experiments. Formation of the xanthone triplets (3TS*) was assumed to be completed immediately after the laser pulse. Given these assumptions, decay traces for two different values of $k_{\rm RT}$ (at zero field and "high field") can be simulated. Their difference is the absolute MFE. A typical simulation result is shown in Figure 2b along with the experimental result. The experimental result was corrected for the contribution of xanthone MFE by subtracting out the absolute MFE measured in the same solution before the addition of the disulfide. In that correction it was assumed that the MFE due to the reaction of xanthone

with CTAC molecules, as shown in Figure 2a, is downscaled by a factor k_{Q0}/k_Q by the addition of hydroxy-PDS. The recombination rate constants (k_{RT}) at zero field and 0.1 T were found to be 4×10^6 and 3×10^6 sl⁻¹, respectively, by fitting the experimental trace. The deviation at longer times may be explained by the fact that the xanthone MFE, which is additionally quenched by cross-reactions, was overcorrected for. Comparison of the recombination rate constants with those for the singlet pairs of (*p*-hydroxyphenyl)thiyl radicals (cf. Table 1) shows that the time dependence would be consistent with the assignment of the MFE to the recombination of triplet pairs of these radicals. Note, however, that the kinetic equations themselves are the same for other reactions of triplet xanthone, which may be responsible for the MFE.

The MFE spectrum shown in the inset in Figure 2c is different from the absorption spectrum of the (p-hydroxyphenyl)thiyl radical, and the shape of the MFE spectrum is essentially time independent unless small time-dependent contributions of less than 10% are present. These contributions can be attributed to the unquenched part of the MFE of xanthone itself in the CTAC micellar solution. The time-independent part of the MFE spectrum cannot be explained by recombination of the thiyl radicals only. While MFE is found in the region where the thiyl radical does absorb, one could not easily explain the origin of the MFE at longer wavelengths. The unchanged time dependence of the MFEs in the region between 450 and 650 nm would even indicate that the entire MFE spectrum is caused by only one process. Thus it seems to be rather unlikely though not impossible that the significant part of the MFE is caused by the recombination of the thiyl radicals.

Hydrogen abstraction from the phenol groups of hydroxy-PDS by triplet xanthone cannot be ruled out from a chemical viewpoint. Therefore, we have measured the TROA spectrum of the phenoxy radical obtained by hydrogen abstraction from hydroxy-PDS by the triplet 9,10-anthraquinone. These triplets have an energy²⁴ of 62 kcal mol⁻¹, which is too low for triplet energy transfer to the disulfides. The TROA spectrum shows a broad and nearly featureless absorption, the intensity of which decreases with increasing wavelength from 350 to 540 nm. Such a spectrum is not found in the MFE spectrum of the xanthonesensitized photolysis of hydroxy-PDS. Thus, we assume that hydrogen abstraction from the phenoxy group is at best a minor reaction path, which cannot cause the observed MFE.

We cannot, however, exclude electron transfer from the disulfide to xanthone triplet. The reduction potential of triplet states is increased with respect to the ground-state potential by the triplet energy, and it was shown that a reduction potential of ~ 1.6 V is sufficient to generate radical cations from diaryl disulfides.³⁰ The MFE spectrum cannot exclude such photoinduced electron transfer as the process subject to the MFE, since significant MFE is observed in the region beyond 600 nm where the xanthone anion radical absorbs.³¹ On the other hand, the spectrum of the cation radical is unknown. The resolution of the MFE spectrum is not sufficient, however, for one to identify the process responsible for the MFE. The magnitude and field dependence of *R* observed 1 μ s after excitation is shown in Figure 2c. The magnetic field dependence excludes mechanisms other than HFCM and RM.

Structrure and g-Tensor of Phenylthiyl Radicals. The absence of MFE in the case of the unsubstituted and p-chloro-substituted compounds parallels the observations of Bohne et al., who could not find any magnetic field effect of the decay rate of a triplet pair of phenylthiyl and benzophenone ketyl radicals.¹¹ Despite the comments made by Khudyakov et al.⁴ on the rotational correlation times used in the explanation of Bohne et al.,¹¹ this should be reexamined, in particular since inconsistencies exist in the literature in terms of the g-tensor of phenylthiyl radicals.³²⁻³⁷ The spin-rotational relaxation time is calculated from³⁸

$$T_1^{-1} = T_2^{-1} = \frac{\delta g_x^2 + \delta g_y^2 + \delta g_z^2}{9 \tau_0}$$
(8)

with

$$\delta g_i = g_i - 2.002\ 319 \tag{9}$$

Bohne et al.¹¹ used the result obtained by Schmidt et al. for the g-tensor³² ($g_x = g_y = g_{\perp} = 2.003$; $g_z = g_{\parallel} = 2.017$) to calculate the relaxation times and were forced to assume that the rotational correlation time τ_0 was as short as ~ 10⁻¹³ s. Experimental values for organic radicals of similar size in SDS micelles are 10-11- 10^{-10} s.³⁹ Zandstra et al. on the other hand found $g_x = g_y = g_{\perp}$ = 1.9982 and $g_z = g_{\parallel} = 2.1246$, in agreement with quantum mechanical calculations.³³ Results similar to the ones of Schmidt et al. for phenylthiyl were found for phenylselenyl and benzylthiyl under similar conditions.³⁴ Benzylthiyl should, however, have a g-tensor similar to that for aliphatic thiyl radicals.^{40,41} The doubtless detection of phenylthiyl radicals in solution has also been proven to be difficult. Different isotropic g-values were published.³⁵⁻³⁷ McLauchlan et al. did not unequivocally assign the signals because large differences between relaxation times T_1 and T_2 could not easily be explained if the radicals were thivl ones. Furthermore, no additional evidence was found for the formation of larger oligomers.³⁷

While the reorganization energy of the phenoxy radical is -24.0 kcal mol⁻¹, that of the phenylthiyl radical is only -3.9 kcal mol⁻¹; i.e. the phenylthiyl radical is not largely stabilized by the interaction with the π -system of the benzene ring.⁴² From a theoretical viewpoint, therefore, one may expect that the *g*-tensor of phenylthiyl radicals are similar to those of aliphatic thiyl radicals.^{40,41} Among the published results, the one found by Zandstra et al.³³ is in agreement with this expectation. If this is the correct result, the explanation given by Bohne et al.¹¹ for the absence of MFE in their system can no longer depend on an unusually short rotational correlation time.

We have actually found low-field features similar to those of Zandstra et al.³³ in preliminary measurements of ESR spectra of UV-irradiated microcrystalline diphenyl disulfides and thiophenols at -160 °C.⁴³ Direct evidence which would enable one to assign the low-field features in the ESR spectra to the phenylthiyl radicals is, however, not so readily obtained. The *g*-value of these features depends on the substituent in the benzene ring. This would be readily explained for phenylthiyl radicals, since it was shown that para-substituents may stabilize them.⁴⁴ The last fact is supported by our observations of thiyl radical recombination rates in direct excitation photolysis of diphenyl disulfides (cf. Table 1) and by results reported in the literature on substituent dependencies of the reactivity of these radicals, which suggest changes in the electron density at the sulfur atom upon substitution.⁴⁵

If we go on with the assumption that faster spin-rotational relaxation explains the absence of any MFE on the unsubstituted and *p*-chloro-substituted phenylthiyl radical pairs, we should interpret the presence of an MFE in the case of (*p*-aminophenyl)thiyl by a change in the *g*-tensor. Borisevich et al. explained a spectral change during picosecond photolysis of amino-PDS and bis(*p*-*N*,*N*-dimethylaminophenyl) disulfide in polar solvents with the assumption of a twisted intramolecular charge transfer (TICT) in the respective radicals²²



The equilibrium depends on solvent polarity and is reached in time scales on the order of tens of picoseconds. From the absorption spectrum of (p-aminophenyl)thiyl in SDS and CTAC micellar solutions, we can conclude that the radical resides in these micelles at solubilization sites with a polarity similar to that of methanol.¹⁰ The equilibrium in methanol consists of 60% of the sulfur-centered structure and 40% of the nitrogen-centered TICT structure.²² This rapidly fluctuating equilibrium would certainly lift the p- π -orbital degeneracy which is responsible for the large g_r -main value. This would in turn decrease the spin-rotational relaxation time and re-establish the MFE. Note that, unlike the g-tensor, the rotational correlation time τ_0 is not largely dependent on substitution or structural changes.

Some electronic interactions of the substituent with the radical center are also expected in the cases of p-hydroxy-, p-methoxy-, and p-butoxyphenylthiyl radicals, though the effects may be lower than that for the TICT process in the (p-aminophenyl)thiyl radical. Unfortunately, neither the theoretical assumptions nor our experimental results for these compounds are precise enough to use the comparison as evidence for or against this hypothesis.

SOC, Spin-Rotational Relaxation, and MFE. The MFEs and MIEs of heavy-atom-centered radicals through the HFCM require hyperfine couplings with these heavy atoms. The hyperfine couplings are in turn dependent on the spin density at that atom. High spin density at a heavy atom will, however, increase the SOC, and this may more or less quench the MFEs and MIEs. Despite the TICT process in scheme 10, there is a significant spin density at the sulfur atom in the (p-aminophenyl)thiyl radical, as may be seen from the equilibrium constant for scheme 10 and proven by the reactivity of the radical. Thus, we can conclude that MFE on sulfur-centered radicals may exist despite SOC, as already found by Hayashi et al. for another case.⁵ On the other hand, SOC may be enhanced drastically by orbital degeneracies even in radicals centered at atoms of the second period as, for instance, in alkoxy radicals centered at the oxygen atom. This enhancement of the SOC by orbital degeneracy seems to be the reason why the unsubstituted phenylthiyl radical did not show MFE in the work of Bohne et al.¹¹ as well as in this paper. In this context we must also consider SOC-enhanced $T \rightarrow S$ interconversion in the contact state of the radical pair4 (intersystem recombination) as a possible source for quenching of the MFEs.

Since electron donor groups were found to stabilize phenylthiyl radicals, one would assume that they will also lift the orbital degeneracy to some extent, which would in turn reduce the SOC. This would partially reestablish the MFEs, for both spin-rotational relaxation and intersystem recombination, as reasons for their quenching. The delocalization of the unpaired electron caused by electron-donating substituents would also increase the hyperfine couplings to atoms other than sulfur as a source of MFE through HFCM and RM.

Conclusion

In this work, the MFEs on the recombination of triplet pairs of para-substituted phenylthiyl radicals in micellar supercages were investigated. No MFE could be detected within experimental error for the unsubstituted phenylthiyl and p-chloro-phenylthiyl radicals, while substitution by the p-amino group gave rise to MFE on the yield of escaped thiyl radicals. MFEs were found for the photolysis of hydroxy-PDS, methoxy-PDS, and t-butoxy-PDS, but it seems to be unlikely that they can be attributed to the recombination of thiyl radical pairs. Our results show that MFEs that occur for chemical reactions may be highly sensitive to the effects that substituents have on the electronic structure of the radicals involved.

The absence of any MFE for unsubstituted and p-chlorosubstituted phenylthiyl radicals may be attributed to faster spinrotational relaxation¹¹ and possibly to intersystem recombination because of strong SOC. Unlike other sulfur-centered radicals, these radicals are assumed to have very strong SOC because of orbital degeneracy. Mesomeric stabilization of the radical by

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electron donor groups as well as a TICT process in the (p-aminophenyl)thiyl radical are expected to lift the orbital degeneracy at least gradually and thus to reduce the SOC. This brings about changes in the g-tensor and reestablishes the MFEs for thivl radical recombination.

MFE spectra and their time dependence were introduced as a means of obtaining more information on the reactions which are subject to MFEs and were used in one case to assign a MFE to a certain process. The low resolution of optical absorption spectra limits the use of this approach. It may, however, be the only method which can be used in cases where CIDEP spectra cannot be recorded or are ambiguous.

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