CIDNP Investigation of Radical Decay Pathways in the Sensitized Photolysis of Triphenylsulfonium Salts

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Abstract: The photodecomposition of triphenylsulfonium hexafluoroantimonate was studied by pseudo-steady-state and time-resolved CIDNP experiments, using naphthalene and 9,10-dimethylanthracene as (singlet) sensitizers. Key intermediates of these reactions are radical pairs consisting of the sensitizer radical cation $Sens^{\bullet+}$ and the phenyl radical $Ph^{\bullet}$, which are formed by photoinduced electron transfer followed by cleavage of the resulting neutral onium radical. The chemical fate of $Ph^{\bullet}$ is strongly influenced by the sensitizer. With 9,10-dimethylanthracene, in-cage hydrogen abstraction from the methyl groups of $Sens^{\bullet+}$ produces benzene and a carbocation that can function as a protic acid; free radicals $Ph^{\bullet}$ attack surplus sensitizer to give addition products. With naphthalene, geminate combination of the two radicals and in-cage oxidation of diphenyl sulfide (the by-product of cleavage of the onium radical) by $Sens^{\bullet+}$ are observed. In both systems, the solvent scavenges free $Ph^{\bullet}$, yielding monodeuteriobenzene. The rate constant of this reaction was determined to be 1.2×10^4 M^{-1} s^{-1} at 241 K. With 9,10-dimethylanthracene, the competition of sensitizer and solvent for the free radicals $Ph^{\bullet}$ was studied quantitatively by evaluating the lineshape of the superimposed CIDNP signals of undeuterated and monodeuterated benzene. By a simple kinetic model the dependence of the product distribution on temperature and sensitizer concentration could be described with a consistent set of parameters.

Introduction

The photoinduced decomposition of onium salts in the presence of hydrogen donors provides an efficient source of free radicals as well as of protic acids; therefore, initiator systems based on iodonium and sulfonium salts have found widespread application for both radical and cationic polymerizations, and also as light-sensitive depolymerization catalysts for lithographic processes.[1] Although in principle the onium salt itself can function as the light-absorbing component, its absorption properties will normally require short-wavelength light sources, which are too expensive for these technical processes. A possible solution is the incorporation of an additional chromophore into the molecule; however, the chemical modifications of the initiator must be compatible with other requirements (ground- and excited-state reactivities, solubilities, etc.). A much more flexible strategy is the use of a suitable photosensitizer, which induces onium salt decomposition by energy[2−4] or electron[4−13] transfer. By selecting an optimum combination of onium salt and sensitizer with respect to spectral and chemical properties,

such an initiator system can be tailored to the emission characteristics of commercial discharge lamps and the type of application.

In the case of photoinduced electron transfer sensitization the primary chemical step leads to a radical pair consisting of the radical cation of the sensitizer and a neutral radical derived from the onium compound. The latter cleaves on a time scale comparable with the pair life, so in-cage reactions of the resulting dia- and paramagnetic cleavage products with the radical cation compete with escape from the solvent cage.[7,8−11] Because these secondary reactions significantly influence the type and concentration of initiating species proper, a good understanding of their mechanisms and kinetics is a prerequisite for the design of onium-based initiator systems.

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Measurements of chemically induced dynamic nuclear polarizations (CIDNP)[14] belong to the most versatile tools for investigations of radical reactions in solution, especially such with complex mechanisms involving more than one type of intermediate, as in the present instance. The CIDNP phenomenon originates from nuclear spin sorting in the paramagnetic intermediates, usually radical pairs, and manifests itself as polarizations (i.e. nonequilibrium populations) of the nuclear spin states in the diamagnetic products, which lead to anomalous line intensities in NMR spectra recorded during the reaction. The polarization intensities and phases (absorption or emission) can be related to the magnetic parameters as well as the initial and final electron spin multiplicities of the intermediates. Two other unique features of CIDNP spectroscopy stem from the fact that generation and detection of the polarizations occur at different stages of the reaction. First, because generation of the polarizations is completed within the life of the radical pairs, CIDNP spectroscopy is sensitive to processes on a nanosecond or even subnanosecond time scale; yet it possesses the excellent spectral dispersion and analytical potential of high-resolution NMR detection. Second, the polarizations may be regarded as labels that are attached at the paramagnetic stage, and this "CIDNP labeling" often provides considerably more information on mechanisms and kinetics of subsequent reactions than does chemical labeling.[15]

Previous CIDNP studies of direct and sensitized photolysis of onium salts[4,7,13] have predominantly been concerned with mechanistic questions. In the present work, we also investigate kinetic aspects. By using time-resolved CIDNP experiments and studying the temperature and concentration dependence of the polarizations, kinetic and mechanistic data are obtained for several decay reactions of the onium-derived radicals.

Results and Discussion

Thermodynamics and Basic Reaction Pathways. The onium salt triphenylsulfonium hexafluoroantimonate (Ph_3S^+ SbF_6^-) was photosensitized by naphthalene (**Naph**) or dimethylanthracene (**Me_2An**). Relevant thermodynamic parameters of these two systems have been compiled in Table 1.

Ph_3S^+ cannot be excited at the wavelength used. As the data show, energy transfer from the excited sensitizer to the onium salt is feasible neither in the singlet nor in the triplet state. Electron transfer quenching of the excited sensitizer by the onium salt is exergonic in the singlet state but sufficiently endergonic to be disregarded in the triplet state. The primary chemical species resulting from the quenching process must thus be a spin-correlated radical pair of multiplicity singlet $^1\overline{Sens^{•+} Ph_3S^•}$ (RP1), where **Sens**$^{•+}$ is the radical cation of the sensitizer and $Ph_3S^•$ the neutral radical of the onium compound. For the sensitizer **Naph**, this quenching pathway has already been reported and corroborated experimentally.[4b,8] Because electron transfer in these systems does not involve charge separation but only charge shifts, no significant influence of the solvent polarity on the energetics of radical pair formation is to be expected. The fact that the nature and initial multiplicity of the radical pairs are established independently by the

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Table 1. Singlet and Triplet Energies of the Sensitizers **Sens** and the Onium Salt Ph_3S^+, Free Energies of the Radical Pairs, and Free Energies for the Oxidation of Diphenyl Sulfide Ph_2S (resulting from cleavage of the neutral onium radical) by **Sens**$^{•+}$ (All Values in kJ/mol)

	Sens =	
	Naph	**Me_2An**
$^1Ph_3S^{+•}$	>430[a]	
^{1}**Sens***	385[b]	309[c]
$^3Ph_3S^{+•}$	310[d]	
Sens$^{•+}$ $Ph_3S^•$	293[e−g]	229[e,f,h]
^{3}**Sens***	255[b]	169[c]
Sens$^{•+}$ + Ph_2S ⇌ **Sens** + $Ph_2S^{•+}$	−22[e,f,i]	+42[e,h,i]

[a] Estimated from the absorption spectrum (ref 1a). [b] Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401−449. [c] Kruppa, A. I.; Leshina, T. V.; Sagdeev, R. Z. *Chem. Phys. Lett.* **1985**, *121*, 386−389. [d] Reference 4c. [e] Calculated from the half-wave potentials $E_{1/2}$ in acetonitrile *vs* SCE. [f] $E_{1/2}$(**Naph**) = 1.54 V (Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970). [g] $E_{1/2}$(Ph_3S^+) = 1.5 V (value for the hexafluoroarsenate: Stasko, A.; Rapta, P.; Brezova, V.; Nuyken, O.; Vogel, R. *Tetrahedron* **1993**, *49*, 10917−10924). [h] $E_{1/2}$(**Me_2An**) = 0.87 V.[c] [i] $E_{1/2}$(Ph_2S) = 1.31 V (ref 8).

thermodynamic constraints is a prerequisite for unambiguous interpretation of the CIDNP data.

With both systems, in-cage back electron transfer of RP1, which regains the starting materials, is thermodynamically feasible in the singlet as well as in the triplet state; the triplet reaction, however, cannot yield $^3Ph_3S^{+*}$ but only ^{3}**Sens***. Fast cleavage of the onium radical $Ph_3S^•$ to give diphenyl sulfide (Ph_2S) and phenyl radicals ($Ph^•$) largely suppresses this back electron transfer and transforms RP 1 into a secondary radical pair **Sens**$^{•+}$ Ph_2S $Ph^•$ (RP2). While formation of RP2 is obviously independent of the sensitizer, its decay is not: As the data of Table 1 show, **Naph**$^{•+}$ is capable of oxidizing Ph_2S while **Me_2An**$^{•+}$ is not. On the other hand, $Me_2An^{•+}$ contains protons that are easily abstractable. The two sensitizers, therefore, differ in the cage reactions open to RP2.
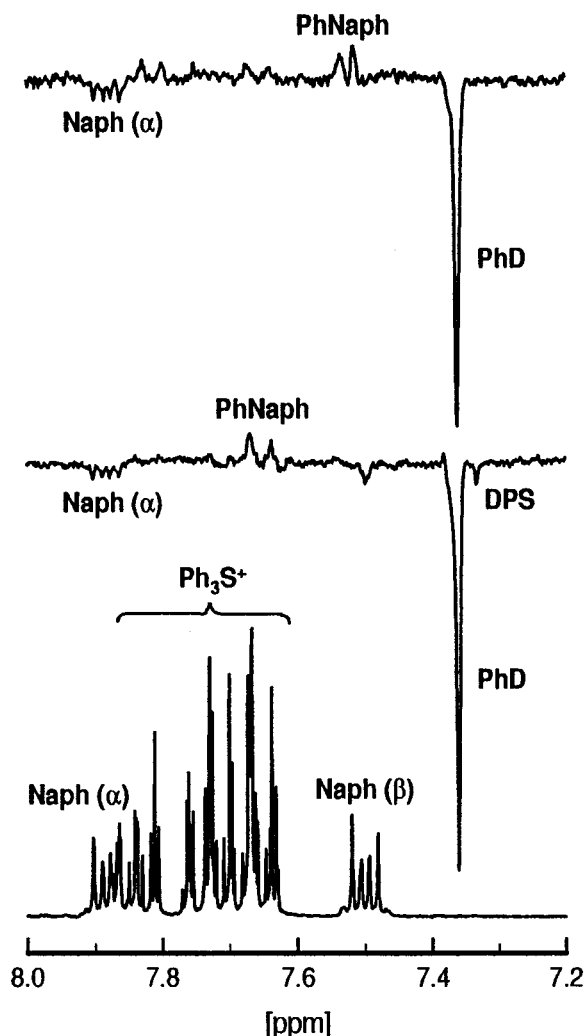
Naphthalene-Sensitized Photolysis. The photoreaction between Ph_3S^+ and **Naph** in acetonitrile has already been studied by CIDNP spectroscopy[4] as well as by other[8] methods. Figure 1 displays CIDNP spectra, obtained during irradiation of this photosystem, in acetonitrile (ϵ = 37.5) and in the nonpolar solvent dioxane (ϵ = 2.2). In agreement with the results in the literature,[4] the spectra are dominated by an intense emission peak of monodeuteriobenzene (**PhD**). Owing to the high sensitivity and strong background suppression (*cf.* Experimental Section) of the pseudo-steady-state CIDNP technique[16] employed in the present work, we were also able to observe other polarizations that in the previous CIDNP investigation were hidden by the equilibrium NMR signals of the starting compounds or the products. Most of these weaker polarizations could be assigned by comparison with the NMR spectra of authentic samples: naphthalene (emission for H$^\alpha$), 1-phenylnaphthalene (**PhNaph**, absorption for the phenyl protons), and diphenyl sulfide (**Ph_2S**, emission). Furthermore, the spectra of Figure 1 clearly show that the onium salt is not appreciably polarized.

Two factors account for the absence of polarizations in the starting compound Ph_3S^+. The first is the already mentioned rapid transformation of the initial radical pairs **Sens**$^{•+}$ $Ph_3S^•$ (RP1) into secondary pairs **Sens**$^{•+}$ Ph_2S $Ph^•$ (RP2). Ph_3S^+ can only be regained from RP1. The fast reaction RP1 → RP2 not only reduces the yield of this product but also decreases the

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Figure 1. : Photoreaction of 8.5×10^{-3} M **Naph** with 1.1×10^{-2} M **Ph$_3$S$^+$** in acetonitrile-d_3 (bottom and center) and dioxane-d_8 (top). The bottom trace shows the NMR spectrum before irradiation, the other traces the pseudo-steady-state CIDNP spectra (λ_{exc} 308 nm, 10 laser flashes per acquisition, 32 acquisitions per spectrum, room temperature). For the assignment of the resonances, see text.

efficiency of spin sorting in RP1 by shortening the life of that pair; for the latter reason, polarizations originating from RP1 are expected to be rather weak in any case. The second factor is that RP1 can undergo back electron transfer both in the singlet and the triplet state (Table 1), and the opposite spin polarizations from these two exit channels leading back to **Ph$_3$S$^+$** cancel.

The strong polarization of the product **PhD** must stem from RP2. It can be analyzed with Kaptein's rule,[17] which connects the polarization phase Γ_i of nucleus i in a product ($\Gamma_i = +1$, absorption; $\Gamma_i = -1$, emission) with the reaction pathway, i.e. the precursor multiplicity μ ($\mu = +1$, triplet; $\mu = -1$, singlet) and the exit channel ϵ ($\epsilon = +1$, product formation from singlet pairs; $\epsilon = -1$, from triplet pairs), and the magnetic parameters (a_i, hyperfine coupling constant of nucleus i; Δg, difference of the g values when the radical bearing nucleus i is counted first) of the radical pairs,

$$\Gamma_i = \mu \times \epsilon \times \text{sign}(a_i) \times \text{sign}(\Delta g) \qquad (1)$$

When radical pairs RP1 are transformed into other radical pairs RP2 on the time scale of the CIDNP effect ("pair

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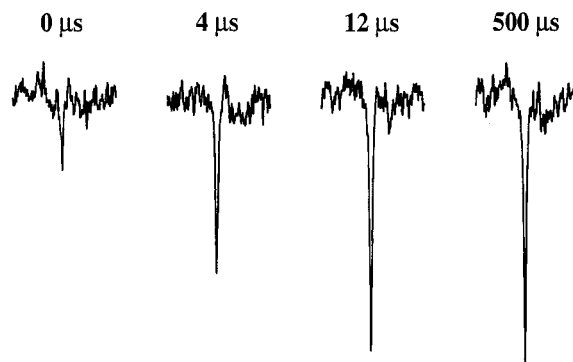
Figure 2. Time-resolved CIDNP spectra in the system **Naph/Ph$_3$S$^+$** at 241 K. Reactant concentrations are as in Figure 1. The signal of the product **PhD** is shown at different delays (given above the spectra) between laser flash and NMR sampling pulse (duration 2 μs).

substitution"), the resulting polarizations in the products of RP2 can be described as arising in a hypothetical pair possessing the precursor multiplicity of RP1, the exit channel of RP2, and magnetic parameters that are averages of those in each pair weighted with the respective lifetime.[18] The proton hyperfine coupling constants in the phenyl radical are positive;[19] their signs in the triphenylsulfinyl radical (**Ph$_3$S$^\bullet$**) are not known but most likely are also positive, by analogy with those in the corresponding radical derived from the iodonium[13] salt. The g value of **Ph$^\bullet$** ($g = 2.00227$)[20] is lower than that of **Naph$^{\bullet +}$** ($g = 2.0025$),[21] so Δg is negative for RP2 when the polarizations of the phenyl protons are being considered. Although Δg of RP1 probably has the opposite sign because the heavy atom in **Ph$_3$S$^\bullet$** will increase the g value of that radical, the averaged Δg is presumed to remain negative because in the present case the weight of RP1 in the superposition will be much smaller than that of RP2 owing to the short life of RP1. The observed emissive polarization of **PhD** is thus consistent with formation of this product via the triplet exit channel of RP2. This supports the natural assumption that **PhD** is an escape product, i.e. results from *free* radicals **Ph$^\bullet$**, which abstract deuterium from the solvent.

Independent evidence that **PhD** is an escape product is provided by time-resolved CIDNP experiments. With this technique,[22,23] the rate of appearance of the spin-polarized diamagnetic products is measured by starting the reaction with a flash and sampling the magnetization with a radiofrequency pulse after a variable delay. Cage reactions are completed within a few nanoseconds, which is below the time resolution of these experiments; in contrast, reactions of free radicals occur on a much slower time scale.

Figure 2 shows representative CIDNP signals of **PhD** at different delays between laser flash and acquisition pulse. To reduce the rate constants, the measurements were performed at low temperature. It is evident that the intensity of the **PhD** peak increases with time, and that it does not reach its constant maximum value until some ten microseconds after the flash.

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This immediately rules out a cage reaction and demonstrates unambiguously that **PhD** is a product of free radicals. Quantitative evaluation must take into account that the observed signal is a convolution of the true CIDNP magnetization with the envelope of the radiofrequency pulse,[24] which has a nonnegligible duration (2 μs) on the time scale of the reaction. This convolution is also the reason why the CIDNP intensity appears to differ from zero when the sampling pulse immediately follows the excitation pulse. When the deconvolution is performed, the CIDNP signal is seen to obey a pseudo-first-order rate law, as expected for deuterium abstraction from the solvent by free phenyl radicals. A bimolecular rate constant of 1.2×10^4 M^{-1} s^{-1} was obtained from our experimental data.

The absorptive phase of the corresponding protons in **PhNaph** indicates that this compound is formed via the singlet exit channel of RP2, i.e. presumably by a cage reaction of **Ph•** and **Naph•+**. This corroborates an earlier product study[8] of the same photosystem, in which formation of **PhNaph** was ascribed to in-cage combination of **Ph•** and **Naph•+** followed by elimination of H$^+$. In the high field of our NMR spectrometer, there is approximate proportionality between polarization intensities and hyperfine coupling constants weighted with the number of equivalent nuclei.[14] The hyperfine coupling constant of the α protons in **Naph•+** is about 40 % of that of the ortho protons in **Ph•** (the coupling constants of the other protons in these two radicals are significantly smaller and can be disregarded).[19,25] Taking into account that there are twice as many of the former protons but that one of these is lost by the deprotonation leading to **PhNaph**, the ratio of polarizations in the naphthalene and phenyl moieties of this product should be about 2/3. The most probable reason why no polarizations of the naphthyl protons of **PhNaph** are discernible in the CIDNP spectra of Figure 1 is that the NMR signal of these protons is a complex multiplet spread out over a large spectral region.

For back electron transfer of singlet pairs RP1 Kaptein's rule would predict an emissive polarization of the naphthalene α protons ($\Delta g < 0$, $a < 0$[25]), as is found in the spectra of Figure 1. An apparent dominance of the singlet exit channel would also not be at variance with the above-mentioned fact that for thermodynamic reasons back electron transfer of RP1 is possible also in the triplet state: CIDNP in a triplet product (such as ³**Naph***) is hidden during the triplet lifetime, and a large part of the polarizations is lost by nuclear spin relaxation in these paramagnetic species,[26] so even for equal probabilities of deactivation via the singlet and the triplet exit channels, the polarizations from the former prevail. However, because of the pair substitution RP1 → RP2 one would not expect RP1 to be an efficient source of CIDNP in the sensitizer **Naph**; most likely, the polarizations of this product also originate in RP2, as those of the other products **PhD** and **PhNaph**. From Kaptein's rule it then follows that **Naph** must be formed via the *triplet* exit channel of RP2 ($\Delta g > 0$). In the presence of a singlet-specific reaction such as the discussed geminate combination of **Naph•+** and **Ph•**, the triplet exit channel does not necessarily imply a reaction that occurs for triplet pairs only; it is sufficient that this reaction be independent of the electron spin state. As usual, this is provided by escape from the cage. In our case, electron exchange of the resulting free radicals **Naph•+** with surplus sensitizer molecules would then transfer their polarizations to **Naph**, where they can be observed; this mechanism is well known from other systems.[27] A second "escape reaction" for the system under study is in-cage oxidation of **Ph₂S** by **Naph•+** (see below), which regains **Naph** and is obviously independent of the electron spin multiplicity of RP2. While in principle a distinction between these alternatives would be possible on the basis of time-resolved CIDNP measurements, this is not feasible in our system because the optical absorption properties of **Naph** dictate the use of rather high sensitizer concentrations, which in turn increases the rate of the degenerate electron transfer between **Naph•+** and **Naph** so much as to exceed the time resolution of the method.

Another hitherto unobserved feature of the CIDNP spectrum in acetonitrile is the peak due to **Ph₂S**. Although quite weak, this signal is undoubtedly in emission. Generation of these polarizations in the radical pair **Naph Ph₂S•+ Ph•** (RP3) appears unlikely because of the absence of a suitable reaction leading back to **Ph₂S** (back electron transfer within the cage is endergonic, and electron exchange between free radicals **Ph₂S•+** and **Ph₂S** is too slow to compete with nuclear spin relaxation because **Ph₂S** is not present before the reaction), and because it is known that the final products of this oxidation are phenylthiobiphenyles.[8] However, if RP3 were the source of these polarizations, the exit channel to **Ph₂S** would have to be the triplet channel because the g value of **Ph₂S•+** (g = 2.0074)[4c] is higher than that of **Ph•** and the large hyperfine coupling constants in **Ph₂S•+** must be negative, by analogy with the radical cations of methoxybenzenes.[27b] A more straightforward pathway to **Ph₂S** with respect to chemical intuition is the spin-independent cleavage of **Ph₃S•**. In this case, the observed polarization phase requires a singlet exit channel ($\Delta g > 0$, $a > 0$, $\epsilon = -1$). This might point to a dominance of back electron transfer of triplet pairs RP1. An alternative explanation is a pair substitution effect: The nuclear spin state of the protons ultimately contained in **Ph₂S** affects the evolution of the electron spin state of RP1 only. However, after the transformation RP1 → RP2 the cleavage product **Ph₂S** is still contained in the cage, and the probability of its in-cage oxidation by **Naph•+** is fairly high. The latter reaction is spin-independent, which in RP2 unambiguously corresponds to a triplet exit channel. Hence, **Ph₂S** surviving in-cage oxidation leaves RP2 predominantly by the singlet exit channel, and is polarized accordingly.

As is evident from Figure 1, the solvent polarity has only a marginal influence on the polarizations. This is in agreement with our previous results[13] for the diphenylanthracene-sensitized photolysis of **Ph₃S+** and the corresponding iodonium salt. From the contrasting behavior of the iodonium compound—in acetonitrile, polarizations from the initial radical pair in addition to those from the secondary pair produced by elimination of iodobenzene; in a nonpolar solvent, only polarizations from the latter—it was concluded that cleavage of the neutral onium radical is faster in a nonpolar solvent, and intrinsically faster in the case of sulfonium. This increase of the rate of pair substitution RP1 → RP2 readily explains why the polarization of **Ph₂S** is no longer observed in a solvent of low polarity (Figure 1).

Dimethylanthracene-Sensitized Photolysis. Irradiation of a solution containing **Ph₃S+** and **Me₂An** in acetonitrile-d_3 leads to a strong signal of benzene in the CIDNP spectrum. The only other signals are some very weak multiplets at low field. However, in NMR spectra taken after irradiation no products
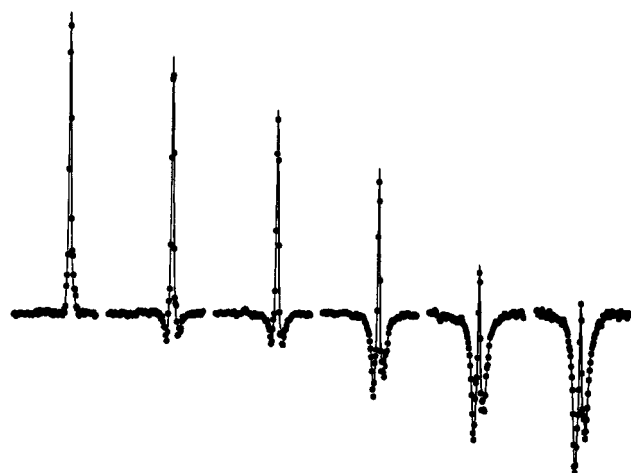
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238.9 K   252.1 K   257.7 K   275.0 K   292.5 K   306.6 K

Figure 3. CIDNP in the photoreaction of Ph_3S^+ (3.3×10^{-2} M) sensitized by Me_2An (4.4×10^{-3} M). Other experimental parameters are as in Figure 1. Shown are the benzene signals at different temperatures (given below the traces). The dots are the experimental data points, the solid line is the best fit with the model function $\mathcal{F}(\omega)$ of eq 4. For further explanation, see text.
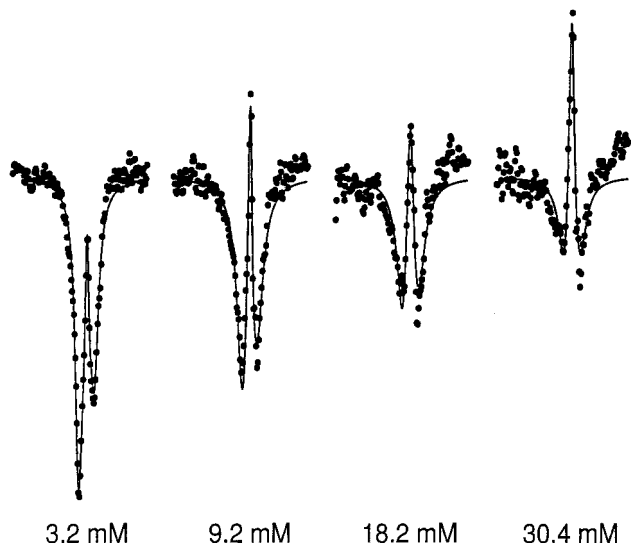
3.2 mM   9.2 mM   18.2 mM   30.4 mM

Figure 4. Dependence of the lineshape of the benzene signal on the sensitizer concentration (given below the traces) in the system Me_2An/Ph_3S^+ at room temperature. Other experimental parameters are as in Figure 3. Dots, experimental data; solid line, best fit of eq 4 to the data, as explained in the text.

corresponding to these transients were detectable, which prevented an assignment.

Interestingly, in this system the benzene signal was found to be a superposition of a broad emission signal S_D of **PhD** and a sharp absorption signal S_H of the undeuterated compound **PhH** (compare Figures 3 and 4). The ratio of these two contributions varies with temperature. While the temperature dependence of S_H is quite small, the signal of **PhD** decreases rapidly with decreasing temperature and becomes negligible at a few degrees above the melting point of the solvent used. The signal shape is also a function of the sensitizer concentration. Since the latter determines the optical density of the sample and, therefore, controls the sensitivity of the experiments, a variation was only possible within the interval 3×10^{-3} to 3×10^{-2} M. As Figure 4 shows, the **PhD** signal is favored by lowering the concentration of Me_2An.
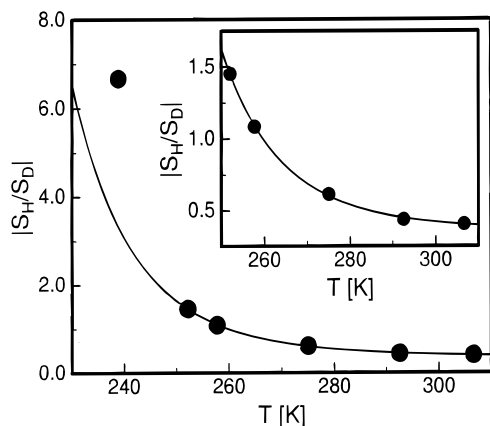
Because the g values of $Me_2An^{•+}$ and $Naph^{•+}$ cannot differ noticeably, Kaptein's rule predicts the same polarization phases for the products of the phenyl radical contained in RP2 as with the sensitizer naphthalene, emission for triplet products, and absorption for singlet ones. Hence, **PhD** must again be assigned to the triplet exit channel of RP2 whereas **PhH** must stem from singlet RP2. Quite obviously, the pathway to **PhD** is thus the same as in the preceding section, deuterium abstraction from the solvent by free $Ph^•$, while **PhH** is the product of hydrogen abstraction from the methyl groups of $Me_2An^{•+}$ by $Ph^•$ within the cage. That this in-cage reaction takes place in the singlet state only is very plausible when one considers the high triplet energy of benzene (353 kJ mol^{-1})[28] and the fact that the other product of this reaction is a carbocation, i.e. a species of relatively high energy already in its singlet ground state. Because the most likely deactivation pathway of this carbocation is loss of a proton from the remaining methyl group, the in-cage hydrogen abstraction leading to this intermediate (and to **PhH**) may well possess some importance for cationic photoinitiator systems.

As the influence of the sensitizer concentration on S_D shows, the observed lineshape effects are due to competitive scavenging of the free radicals $Ph^•$ by the solvent and by surplus sensitizer. This is corroborated by the fact that no comparable temperature and concentration dependence exists in the naphthalene system. The fact that scavenging by Me_2An can compete with scavenging by the solvent despite the disparity of concentrations (by a factor between 600 and 6000) must be due to the low rate constant of the latter reaction (see the time-resolved CIDNP results of the preceding section).

There are two conceivable mechanisms for scavenging of free $Ph^•$ by Me_2An. One is hydrogen abstraction at the methyl groups of Me_2An, the other is addition to give substituted cyclohexadienyl radicals. The first of these alternatives can be unambiguously excluded on the basis of the measurements of Figures 3 and 4: Owing to the spin-sorting mechanism of CIDNP, the opposite polarizations from the singlet and triplet exit channels are of exactly equal magnitude as long as nuclear spin relaxation in the free radicals can be neglected. That this condition holds for our systems is inferred from the fact that the limiting polarizations in the naphthalene-sensitized reaction show only a weak temperature dependence, which reflects the viscosity changes of the solvent. Hydrogen abstraction outside the cage would cancel a certain fraction of the polarization in **PhH** stemming from in-cage abstraction; since the free radicals $Ph^•$ consumed in this way are no longer available for scavenging by the solvent, the polarization transferred to **PhD** would decrease by exactly the same amount. The ratio S_H/S_D would thus remain constant when scavenging by the sensitizer is favored by the experimental conditions, which is contrary to observation. Addition of $Ph^•$ to Me_2An, on the other hand, decreases the polarization of **PhD** but leaves unchanged that of the cage product **PhH**, which is consistent with the experimental results. Hence, we conclude that scavenging of $Ph^•$ by Me_2An occurs by the addition mechanism. The fact that no CIDNP signals from products of this reaction route are found in the spectra is again attributed to a distribution of the polarizations over many lines and very likely also among several diamagnetic products, and to nuclear spin relaxation in the relatively long-lived cyclohexadienyl radicals.

For quantitative evaluation of Figures 3 and 4, the contributions of **PhH** and **PhD** to the observed signal must be separated.

(28) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

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Figure 5. Temperature dependence of the polarization ratio $|S_H/S_D|$. The circles display the values of $|S_H/S_D|$ obtained from eq 4, and the solid line is a best fit with eq 5. The inset shows the same data set on an enlarged vertical scale with the value at the lowest temperature omitted. For further explanation, see text.

The signal of **PhH** is describable simply by a Lorentzian line $\angle(\omega, \omega_0, T_2)$ with ω_0 and T_2 being the center frequency and the transverse relaxation time,

$$\angle(\omega, \omega_0, T_2) = \frac{T_2}{\pi}/[1 + T_2^2(\omega - \omega_0)^2] \qquad (2)$$

The CIDNP signal of **PhD** possesses a complex multiplet structure, which is not identical with that of the equilibrium ^{1}H-NMR signal of monodeuteriobenzene[29] because the different hyperfine coupling constants of the ortho, meta, and para protons in **Ph•** lead to different polarizations of these protons in the diamagnetic product. However, we found that the signal shape of **PhD** can be approximated very well by a sum $\mathcal{M}(\omega, \omega_0, T_2)$ of three Lorentzian lines of equal relaxation time T_2

$$\mathcal{M}(\omega, \omega_0, T_2) = c_{-1} \angle(\omega, \omega_0 - \Delta\omega, T_2) +$$
$$c_0 \angle(\omega, \omega_0, T_2) + c_{+1} \angle(\omega, \omega_0 + \Delta\omega, T_2) \quad (3)$$

Their relative line intensities c_i and the splitting $\Delta\omega$ were determined from the CIDNP signal of **PhD** observed in the naphthalene-sensitized photolysis. A least-squares fit followed by normalization gave

$$c_{-1} = 0.17, \quad c_0 = 0.54, \quad c_{+1} = 0.29;$$
$$\Delta\omega/(2\pi) = 0.59 \text{ Hz}$$

These parameters were used to approximate the shape of the composite benzene line in the CIDNP spectra by the model function $\mathcal{F}(\omega)$,

$$\mathcal{F}(\omega) = S_H \angle(\omega, \omega_{0,H}, T_{2,H}) + S_D \mathcal{M}(\omega, \omega_{0,D}, T_{2,D}) \quad (4)$$

Because the functions $\angle$ and $\mathcal{M}$ are normalized, the weights S_H and S_D are equal to the intensities of the two superimposed signals of **PhH** and **PhD**. For reasonable starting values, the least-squares fits of $\mathcal{F}$ to the data converged well and excellently reproduced the CIDNP signals (compare Figures 3 and 4). In Figures 5 and 6 the obtained ratios S_H/S_D are displayed as functions of the temperature and the sensitizer concentration.

These results can be interpreted with a simple model based on competitive scavenging of the free radicals **Ph•** by the solvent and by surplus **Me$_2$An**. Let $|\mu|$ denote the absolute value of the polarization generated in the radical pairs at a given temperature.

(29) Yonemitsu, T.; Kubo, K. *Chem. Lett.* **1981**, 1061−1062.
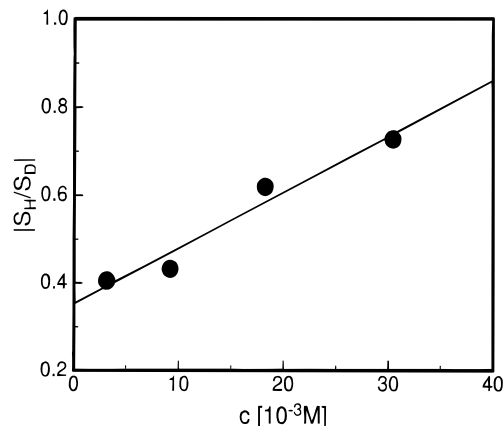
Figure 6. Dependence of the polarization ratio $|S_H/S_D|$ on the sensitizer concentration. Circles, experimental values (calculated with eq 4); solid line, linear regression according to eq 5. For further details, see text.

A fraction p of singlet radical pairs yields **PhH**, so the polarization of this product is $p \cdot \mu$. Neglecting relaxation (see above), the total polarization of all products from the triplet exit channel is $-\mu$. As shown, hydrogen abstraction from **Me$_2$-An•$^+$** by **Ph•** outside the cage decreases the polarizations from both channels by exactly the same factor, so any participation of this reaction is already contained in the value of μ. Because we have no evidence for other deactivation pathways of free radicals **Ph•** besides this combination reaction and the two scavenging reactions, we take the fraction of polarization transferred to **PhD** to be determined solely by the rate constants k_{add} and k_D of the two latter reactions. Assuming Arrhenius behavior with frequency factors k^0 and activation energies E_A we arrive at a three-parameter expression for the polarization ratio,

$$|S_H/S_D| = p \left[1 + B \frac{[\mathbf{Me_2An}]}{[\mathbf{CD_3CN}]} \exp\left(\frac{A}{RT}\right) \right] \qquad (5)$$
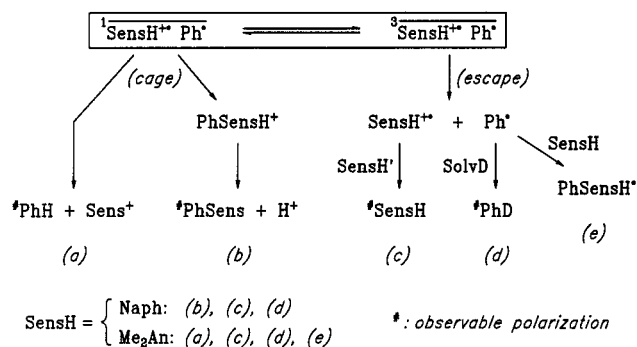
with

$$A = E_{A,D} - E_{A,add}$$

$$B = k_{add}^0/k_D^0$$

A least-squares fit of eq 5 to the observed temperature dependence of $|S_H/S_D|$ gave $A = (38 \pm 3)$ kJ/mol, $B = (0.2 \pm 0.2) \times 10^{-3}$, and $p = 0.36 \pm 0.02$. Figure 5 shows that the kinetic model reproduces the experimental data very well with the exception of the value at the lowest temperature, where the polarization of **PhD** is too weak for reliable determination (compare Figure 3). The model also correctly predicts a linear relationship between the polarization ratio $|S_H/S_D|$ and the sensitizer concentration, as seen in Figure 6. From the intercept of the regression line in that graph a value of 0.35 ± 0.03 is obtained for p. Using this value and the result for A from the preceding data set, B is calculated to be $(0.13 \pm 0.03) \times 10^{-3}$ from the regression. The consistency of the parameters determined from the temperature-dependent and the concentration-dependent experiments provide further evidence that the fate of the onium-derived radicals in this system is determined by the interplay of in-cage hydrogen abstraction and competitive scavenging of free **Ph•** by the solvent and surplus sensitizer.

Conclusions

Our results show that the sensitizer (naphthalene and 9,10-dimethylanthracene in this work) can exert a remarkable

Chart 1

$$SensH = \begin{cases} Naph: & (b),\ (c),\ (d) \\ Me_2An: & (a),\ (c),\ (d),\ (e) \end{cases} \qquad {}^{\sharp}: observable\ polarization$$

influence on the reaction steps that are important for the function of onium salts as polymerization initiators. Owing to their very similar energetic schemes, both systems studied behave identically as far as the pathways to radical pairs are concerned. However, the CIDNP spectra reveal that the deactivation pathways of the radicals differ considerably (see Chart 1). This can be attributed to the fact that the intermediate phenyl radical is able to abstract hydrogen from the radical cation of 9,10-dimethylanthracene but not from that of naphthalene. Because this reaction is only feasible in the singlet state of the radical pair, the distribution and the quantum yields of the cage products are determined to a high degree by the chemical reactivity of the sensitizer. In contrast, free phenyl radicals escaping from triplet pairs can either react with the solvent or be scavenged by surplus sensitizer. The respective quantum yields depend on temperature and sensitizer concentration.

These findings suggest a further selection criterion apart from spectral and thermodynamic properties for a tailor-made sensitizer/onium-salt combination. Regardless of the chemical reactivity of the sensitizer radical cation, electron-transfer sensitization from the triplet state should lead to a high concentration of free radicals, which is favorable for radical polymerizations; however, low sensitizer concentrations should be employed to favor scavenging of these radicals by the solvent (i.e. the monomer

in technical applications). Singlet sensitizers capable of donating a hydrogen atom after oxidation, on the other hand, largely suppress the formation of free radicals while producing a protic acid as a cage product; for cationic polymerizations with onium salts, they might, therefore, be better sensitizers intrinsically.

Experimental Section

The substrate triphenylsulfonium hexafluoroantimonate was prepared from the chloride by anion exchange and purified by precipitating it from a 2-propanol solution by adding heptane (50 % v/v). The sensitizers naphthalene and 9,10-dimethylanthracene were obtained commercially (>99%) and purified by sublimation. Sensitizer and quencher concentrations were chosen such that the optical density of the samples was about 1.0 at the excitation wavelength, and that the quenching quantum yields were at least 90%. The freshly prepared samples were deoxygenated by bubbling purified nitrogen through the solution and then immediately sealed.

The CIDNP experiments were performed on a Bruker WM-250 NMR spectrometer equipped with a home-made data acquisition system and pulser unit. An excimer laser (XeCl, $\lambda = 308$ nm) that was triggered by the pulse generator was used as the light source. An energy of about 5 mJ per pulse was absorbed in the samples, as determined actinometrically. Optical setup[30] and pulse sequences for the time-resolved[31] and pseudo-steady-state[16] CIDNP experiments have been described previously. Both these techniques completely eliminate the background signals and yield CIDNP signals that are undistorted by nuclear spin relaxation in the diamagnetic reaction products. Because 90° pulses were used for acquisition in the pseudo-steady-state measurements, all CIDNP effects observed were net effects. Owing to the small active volume, field homogeneity was not affected adversely by the optical parts inserted into the probe, and line widths down to 0.15 Hz could be reached in the CIDNP spectra by careful shimming.

(30) (a) Läufer, M.; Dreeskamp, H. *J. Magn. Reson.* **1984**, *60*, 357−365. (b) Goez, M. *Chem. Phys.* **1990**, *147*, 143−145.
(31) Goez, M. *Z. Phys. Chem. Neue Folge* **1990**, *169*, 123−132.