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Photo-CIDNP Investigation of the Deprotonation of Aminium Cations

Martin Goez* **and Ingo Sartorius**

Contribution from the Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Strasse 10, D-38106 Braunschweig, FRG

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Abstract: The photoreactions of triallylamine and triethylamine with a variety of triplet sensitizers containing carbonyl functions were studied in acetonitrile-d_3 by using pseudo-steady-state measurements of chemically induced dynamic nuclear polarization (CIDNP). These reactions are hydrogen abstractions formally, but they are known to proceed in two steps: electron transfer from the amine to the excited sensitizer, followed by deprotonation of the resulting aminium cation to give an α-aminoalkyl radical. From the CIDNP intensity patterns in the reaction products, we determined the intermediates (radical ion pairs or pairs of neutral radicals) that give rise to the observed polarizations. The products of free radicals were found to be identical regardless of their polarization patterns; hence, both types of intermediates lead to the same escape products. This is explained by two pathways for the deprotonation of an aminium cation. Within the cage, the proton is transferred to the sensitizer anion; outside the cage, it can be abstracted by the amine itself. Both processes yield free α-aminoalkyl radicals, which react further to the products, but in the former case the escaping radicals carry polarizations from the neutral pair, whereas in the latter their spin polarizations originate from the radical ion pair. The rate of the deprotonation within the cage relative to the cage lifetime (~nanoseconds) therefore determines the observed CIDNP patterns. The rate constant for deprotonation of aminium cations by the amine must be faster than the rate of degenerate electron exchange of these species (~1×10^8 L mol^{-1} s^{-1}, as found for similar compounds) but slower than diffusion control by about 1 order of magnitude. The free enthalpies for both reactions were estimated from experimental data (redox potentials and pK_a values) and from the heats of formation calculated by AM1. A correlation between the observed polarization patterns and the differences in the free enthalpies of the radical ion pair and the pair of neutral radicals was found, indicating that $\Delta G°$ of the in-cage proton transfer, from the aminium cation to the sensitizer radical anion, is a controlling factor of the investigated photoreactions. The deprotonation outside the cage, by the amine as a base, is fairly exergonic for the compounds studied. With these calculations, the different behavior of other amines (e.g., *N,N*-dimethylaniline) can be rationalized as well. With the sensitizer anthraquinone, these compounds undergo only reversible electron-transfer reactions, but their radical cations are not deprotonated in these experiments.

Tertiary aliphatic amines can act as quenchers of the excited states of suitable sensitizer molecules, such as carbonyl compounds.[1] If amines DH possessing protons at an α-carbon are employed, permanent photoproducts are formed by a pathway that formally represents a hydrogen abstraction,

$$\mathrm{DH} \xrightarrow{-\mathrm{H}^\cdot} \mathrm{D}^\cdot \rightarrow \text{products} \qquad (1)$$

leading to α-aminoalkyl radicals $\mathrm{D}^\cdot$ as intermediates, which stabilize by subsequent disproportionation or combination with the sensitizer. However, at least in polar solvents this hydrogen abstraction is known to proceed in two steps,[1,2]

$$\mathrm{DH} \xrightarrow{-e^-} \mathrm{DH}^{\cdot+} \xrightarrow{-\mathrm{H}^+} \mathrm{D}^\cdot \rightarrow \text{products} \qquad (2)$$

A primary electron transfer from DH to an excited sensitizer molecule produces an aminium cation $\mathrm{DH}^{\cdot+}$, which then undergoes deprotonation at C_α as a secondary reaction.

The deprotonation of aminium cations has received some interest recently.[2-11] Apart from direct kinetic investigations, for which experimental methods ranging from slow (stopped-flow[9]) to fast (pulse radiolysis[8,10]) and ultrafast (picosecond absorption spectroscopy[4]) techniques were employed, several product distribution studies[3,5,6,11] have been performed in order to obtain relative reactivities. Measurement of chemically induced dynamic nuclear polarization (CIDNP)[12-15] is another indirect method, which is, however, capable of yielding valuable mechanistic and kinetic information not easily obtained otherwise.

CIDNP denotes the occurrence of anomalous intensities (enhanced absorption or emission) of NMR spectral lines from the products of a chemical reaction that is carried out in a magnetic field. This effect is not due to changed transition probabilities but is caused by populations of the nuclear spin states that deviate from the equilibrium populations.

The radical pair mechanism[16,17] provides a qualitative as well as quantitative description of this phenomenon. According to this mechanism, nuclear spins are not flipped, but they are sorted

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[*] Author to whom correspondence should be addressed.

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(1) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141–161.

(2) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243–274.

(3) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1980**, *102*, 1751–1752.

(4) Shaefer, C. G.; Peters, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 7566–7567.

(5) Lewis, F. D.; Ho, T.-I.; Simpson, J. T. *J. Org. Chem.* **1981**, *46*, 1077–1082; *J. Am. Chem. Soc.* **1982**, *104*, 1924–1929.

(6) Lewis, F. D. *Acc. Chem. Res.* **1986**, *19*, 401–405.

(7) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879–4881.

(8) Das, S.; von Sonntag, C. *Z. Naturforsch.* **1986**, *41B*, 505–513.

(9) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646–8653.

(10) Werst, D. W.; Trifunac, A. D. *J. Phys. Chem.* **1991**, *95*, 1268–1274.

(11) Xu, W.; Mariano, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 1431–1432.

(12) Lepley, A. R.; Closs, G. L., Eds. *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973.

(13) Richard, C.; Granger, P. *Chemically Induced Dynamic Nuclear and Electron Polarizations—CIDNP and CIDEP*; Springer: Berlin, 1974.

(14) Muus, L. T.; Atkins, P. W.; McLauchlan, K. A.; Pedersen, J. B., Eds. *Chemically Induced Magnetic Polarization*; D. Reidel: Dordrecht, 1977.

(15) Salikhov, K. M.; Molin, Yu. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.

(16) Closs, G. L. *J. Am. Chem. Soc.* **1969**, *91*, 4552–4554.

(17) Kaptein, R.; Oosterhoff, L. J. *Chem. Phys. Lett.* **1969**, *4*, 195–197; 214–216.

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in intermediate electron spin correlated radical pairs. During a diffusive excursion of such a pair, intersystem crossing takes place with a rate that is modified by the spin states of its protons or other magnetic nuclei. Upon reencounter, the fate of the pair (recombination or separation) is determined by its electron spin multiplicity. By this interplay of nuclear spin selective and electron spin selective processes, the nuclear spins are distributed nonuniformly among the different types of reaction products (cage products or escape products), which leads to a population enhancement of certain spin states and a corresponding depletion of others.

As the spin polarizations are created during the short life of the correlated pairs (of the order of nanoseconds[15]) but are conserved in the reaction products for the spin-lattice relaxation time (typically a few seconds for protons), fast radical reactions can be studied by CIDNP in spite of the poor intrinsic time resolution of NMR. However, this experimental technique possesses another unique feature. Although only the reaction *products* are detected (and can be characterized quite well owing to the analytical potential of high-resolution NMR), the polarization intensities of different protons or other nuclei are strongly dependent on the hyperfine coupling constants of these nuclei in the radicals. Hence, the intensity patterns provide information about the spin density distribution, and thus the chemical constitution, of the *intermediates* as well.

In investigations of the sensitized photoreactions of tertiary amines, this particular aspect of CIDNP has already been put to use for the identification of the radical pairs giving rise to the nuclear spin polarizations observed.[18,19] In this way, it was possible not only to distinguish unambiguously between radical ion pairs and pairs of neutral radicals but also to show that the net hydrogen abstraction (eq 1) can proceed sequentially (eq 2) by oxidation of the amine to the cation DH$^{\bullet+}$ followed by deprotonation of DH$^{\bullet+}$.

In the present work, we focus on the deprotonation step. We vary the energetics of this reaction by employing different sensitizers as well as two amines and study the influence of these changes on the polarization patterns.

Experimental Section

Materials and Methods. Sensitizers and amines were obtained commercially in p.a. quality. They were further purified by double sublimation in vacuum and by double distillation under reduced pressure, respectively. The solvent was acetonitrile-d_3 (99.5%, Aldrich). It was dried over 3-Å molecular sieves. The sensitizer concentrations were chosen for an absorbance of the samples at the excitation wavelength of approximately 1.00; amine concentrations of 5×10^{-2} M were employed in most cases. The solutions were prepared and handled in an inert atmosphere to exclude moisture. Oxygen was removed by purging the samples with dry nitrogen.

CIDNP Measurements. The apparatus for the ^{1}H-CIDNP measurements consisted of a Bruker WM 250 NMR spectrometer equipped with a special probe[20] that allowed illumination of the samples from the side and a homemade pulse programmer. An excimer laser (EMG 101, Lambda Physik, XeCl, 308 nm) triggered by the pulse programmer was used as the light source. An energy of about 5 mJ per flash was absorbed in the samples, as determined actinometrically.

CIDNP measurements were performed under pseudo-steady-state conditions,[21] with 10 laser shots (repetition rate 60 Hz) per acquisition. Suppression of unchanging background magnetization was achieved with a pulse sequence (saturation pulse train-delay for partial relaxation-inversion pulse-illumination period-observation pulse) described in detail in a previous communication.[21] The coherence-transfer CIDNP experiments have also been reported elsewhere.[22]

Determination of Triplet Energies. Phosphorescence spectra were recorded in methanol/ethanol 1:4 or EPA at 77 K with a Perkin-Elmer MPF-44 photometer equipped with an Aminco Phosphoroscope C26. Triplet energies were obtained from the shoulders at maximum wavelength in the phosphorescence spectra.

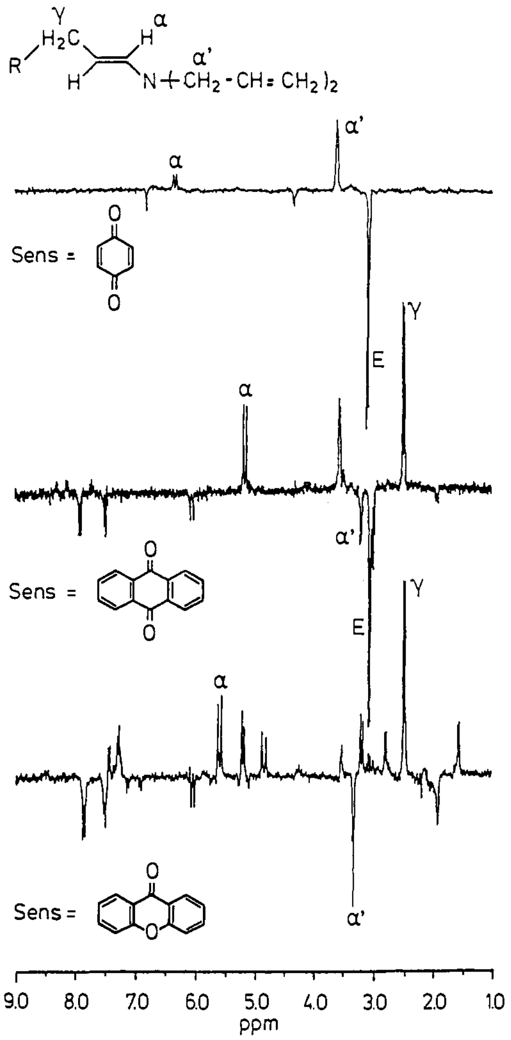

Figure 1. Background-free, pseudo-steady-state CIDNP spectra observed in the photoreaction of triallylamine with different sensitizers (top trace, benzoquinone; center trace, anthraquinone; bottom trace, xanthone) in acetonitrile-d_3. The structural formula of the respective sensitizer (Sens) is given below each spectrum. The CIDNP signals of the starting amine are labeled E. α, α', and γ denote the resonances of that combination product of the amine and the sensitizer which displays the most prominent polarizations, the assignment referring to the formula at the top of the figure (R is the sensitizer moiety).

Calculations. Semiempirical quantum mechanical calculations with the AM1 Hamiltonian[23] were carried out on an IBM 3090 with the program MOPAC 5.0 obtained from QCPE. Energies were computed with the half-electron method.[24]

Results

Sensitized Photoreactions of Triallylamine. In Figure 1 we show pseudo-steady-state CIDNP spectra observed in the photoreactions of triallylamine with three different carbonyl compounds as sensitizers. The structural formulas of these sensitizers are also displayed in the figure.

In previous communication,[22] we gave a complete assignment of all polarized product signals for the system anthraquinone/triallylamine (Figure 1, center trace). We sum up the salient features here, excluding the resonances with $\delta > 7.0$, as these stem from the protons of the sensitizer. The large emission signal at $\delta = 3.03$ is caused by the α-protons of the starting amine DH.

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(18) Roth, H. D.; Manion, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 6886-6888.
(19) Roth, H. D. In ref 14, pp 53-61.
(20) Goez, M. *Chem. Phys.* **1990**, *147*, 143-154.
(21) Goez, M. *Chem. Phys. Lett.* **1992**, *188*, 451-456.
(22) Goez, M. *J. Magn. Reson. Ser. A* **1993**, *102*, 144-150.
(23) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909.
(24) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953-1957.

DH$^{\cdot+}$	D
g = 2.0040	g = 2.0029
a_{H_α} = +1.90 mT	a_{H_α} = −1.07 mT
	a_{H_β} = +0.20 mT
	a_{H_γ} = −1.15 mT
	$a_{H_{\alpha'}}$ = +0.25 mT

Figure 2. Estimated hyperfine coupling constants and g-factors of the radical cation DH$^{\cdot+}$ [27] and the neutral radical D$^{\cdot}$ [28] derived from triallylamine. Only the hyperfine coupling constants of interest are included.

The β- and γ-protons of DH are unpolarized. Furthermore, six doublets occur that are due to metastable reaction products possessing lifetimes in the range of tens of seconds. Although these six doublets fall nicely into three groups of equal coupling constant J, each group containing two doublets, double resonance experiments show this apparent symmetry to be misleading: in this spectrum, no scalar coupling between any of the doublets with identical J exists, and all of the observed splittings are caused by unpolarized protons, which are undetectable in a conventional CIDNP experiment. However, the NMR transitions of these unpolarized nuclei can be made observable by means of coherence-transfer techniques. In this way, we were able to establish the topology of these spin systems.[22] The CIDNP signals were found to belong to two different combination products of triallylamine with anthraquinone. In both cases, the amine-based moiety constitutes a vinylamine of the formula displayed in Figure 1. Its α-, α'-, and γ-protons are strongly polarized, whereas the β-protons show no discernible polarization.

The spin density distributions and thus hyperfine coupling constants a are notably different (see Figure 2) for a triallylaminium radical cation DH$^{\cdot+}$ and its deprotonated form D$^{\cdot}$, an α-aminoallyl radical. In the neutral radical, the hyperfine coupling constants of the α-proton and the two γ-protons are both large, of practically equal magnitude, and negative,[25] whereas a_{H_β} is small and positive.[25,26] Besides, a nonzero (positive) hyperfine coupling constant is also expected for the four α'-protons. In contrast, AM1 calculations indicate that in the triallylaminium radical cation, only the six α-protons possess a significant, and positive, hyperfine coupling constant. By the radical pair mechanism, these different hyperfine coupling patterns in the intermediate radicals are translated into different intensity patterns of the CIDNP signals of the reaction products. For a particular chemical system, however, not all products need have the same radical pair as the source of their polarizations.

The relative polarization intensities in the two combination products of triallylamine with anthraquinone mirror the strength of the hyperfine coupling of the respective protons in an α-aminoallyl radical weighted with their number.[32] Thus, generation of these polarizations can only have taken place in a pair of neutral radicals. On the other hand, CIDNP of the regained starting amine DH must have originated in a radical ion pair, since only the α-protons of DH bear polarization.

A combination product of amine and sensitizer containing the same vinylamine substructure is also formed in the photoreaction of triallylamine with benzoquinone (Figure 1, top trace). The constitution of this product was again determined by coherence-transfer techniques. With this sensitizer, polarizations are found only for the α- and α'-protons of the vinylamine. This intensity pattern clearly reflects the spin density distribution in a triallylaminium radical cation and is not compatible with CIDNP generation in a pair of neutral radicals. As in the previous reaction, only the α-protons of the starting amine DH are polarized. Hence, in this system all the observed CIDNP signals can be traced to a radical ion pair.

With xanthone as the sensitizer, several reaction products displaying polarizations are found (Figure 1, bottom trace). The most prominent CIDNP signals are once more assigned to a combination product comprising an identical vinylamine fragment as in the foregoing examples and a xanthone-derived part. For the amine moiety of this product, the same CIDNP pattern as in the reaction sensitized by anthraquinone occurs, thus again pointing to a pair comprising the α-aminoallyl radical as the source of these polarizations. The CIDNP signals of the other reaction products are also consistent with this precursor, so all polarizations are due to neutral radical pairs. Interestingly, no polarizations are detected for the starting amine in this instance.

The formation of a combination product with a vinylamine substructure implies that linkage of sensitizer and amine takes place at the terminal position (i.e., C_γ) of the amine. As the spin density at C_γ is negligible in the triallylaminium radical cation DH$^{\cdot+}$, the α-aminoallyl radical D$^{\cdot}$ must be the precursor to this product, even if the observed polarizations are generated in a radical ion pair. On the other hand, it is somewhat surprising that no evidence for combination at C_α (which would lead to a $CH_2{=}CH{-}CH{<}$ fragment easily identifiable by the coherence-transfer methods[22] employed) exists, although in D$^{\cdot}$ the spin density at these two positions is practically the same. Obviously, steric control dominates, and the reaction occurs at the less crowded carbon atom.

Kaptein's rule[33] for a CIDNP net effect connects the polarization phase Γ_i of nucleus i ($\Gamma_i = +1$, enhanced absorption; $\Gamma_i = -1$, emission) with the sign of its hyperfine coupling constant, sgn a_i, the sign of the g-factor difference, sgn Δg, of the radicals constituting the pair, the precursor multiplicity (in this work we have either triplet- or, possibly, random-phase precursors, so μ

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(25) Carringtion, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row: New York, 1969; pp 91–93.

(26) Benn, R.; Hoffmann, E. G.; Lehmkuhl, H.; Nehl, H. *J. Organomet. Chem.* **1978**, *146*, 103–112.

(27) Our AM1 calculations gave negligible spin density at the β- and γ-protons of the triallylamine radical cation. The same result is found experimentally for the β-protons of the triethylamine radical cation.[18] Hence, we assume that the values of a_{H_α} are nearly identical for both of these radicals. By the same argument, the g-factors should also be approximately equal.

(28) For the α-, β-, and γ-protons of the neutral radical derived from triallylamine we take the values of the model compound Me(H)-NCH—CH═CH$_2$.[29] These hyperfine coupling constants remained practically unchanged if the methyl group at the nitrogen was replaced by H or a *tert*-butyl group.[29] The value of $a_{H_{\alpha'}}$ in our α-aminoallyl radical results from the data for the methyl protons of this model compound with the assumption of an averaged $\cos^2\theta$ dependence (Heller, H. C.; McConnell, H. M. *J. Chem. Phys.* **1960**, *32*, 1535–1539) of this hyperfine coupling constant for each α'-proton. The g-factor of the α-aminoallyl radical is expected to be lower than that of the α-aminoethyl radical (see Figure 4) because in the former case the spin density at the nitrogen atom is lower (a_N is 0.37–0.40 mT for the α-aminoallyl radicals of ref 29, compared to 0.518 mT for the α-aminoethyl radical[30] and 1.6 mT for the triethylaminium radical cation[31]). Assuming a linear relationship between g-factor and spin density at nitrogen (an analogous behavior is found for phenoxy radicals: Dixon, W. T.; Moghimi, M.; Murphy, D. *J. Chem. Soc., Faraday Trans. 2* **1974**, 1713–1720), we arrive at the value given in Figure 2.

(29) Griller, D.; Nonhebel, D. C.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1373–1379.

(30) McLauchlan, K. A.; Ritchie, A. J. D. *J. Chem. Soc., Perkin Trans. 2* **1984**, 275–279.

(31) Eastland, G. W.; Rao, D. N. R.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1551–1557.

(32) Although the hyperfine coupling constants for the α'- and β-protons in D$^{\cdot}$ are very similar (ratio 1.25:1), the resulting signals in the vinylamines are much stronger for the former protons owing to their greater number and the fact that they give rise to a doublet, whereas the signal from the β-proton is split into a triplet of doublets. The combined effect of all three factors should lead to peak heights differing by a factor of 10. This explains why no CIDNP signals from these protons are observable in the spectra of Figure 1.

(33) Kaptein, R. *J. Chem. Soc., Chem. Commun.* **1971**, 732–733. Equations 3 and 4 are only valid if cage recombination occurs predominantly from the singlet state of the correlated radical pair (Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6127–6128). This condition is fulfilled in our systems (see below).

$= +1$ in all cases), and the exit channel of the pair ($\epsilon = +1$, cage product; $\epsilon = -1$, escape product),

$$\Gamma_i = \operatorname{sgn} a_i \operatorname{sgn} \Delta g\, \mu\, \epsilon \tag{3}$$

The magnetic parameters of D$^\bullet$ and DH$^{\bullet+}$ have been compiled in Figure 2; the g-factors of the sensitizers are given in Table I. Except for the pair consisting of DH$^{\bullet+}$ and the xanthone radical anion—which need not be considered, since no CIDNP signals can be attributed to this pair—the g-factors of the triallylamine-based radicals DH$^{\bullet+}$ and D$^\bullet$ are lower than the g-factors of the associated sensitizer radical anions A$^{\bullet-}$ and the neutral sensitizer radicals AH$^\bullet$, respectively. For the systems investigated, enhanced absorption of H_α therefore indicates a cage product if the polarizations stem from a pair of neutral radicals or an escape product if CIDNP is created in a radical ion pair. Hence, it is evident from the given spectra that both cage recombination (see, for instance, the assigned products in the reactions sensitized by anthraquinone and xanthone, center and bottom traces of Figure 1) and secondary reactions of escaping radicals (e.g., in the case of the sensitizer benzoquinone, top trace of Figure 1) can lead to vinylamines.

For a given sensitizer, the vinylamines formed by these two pathways differ only by the structure of the sensitizer-derived part. With anthraquinone, for instance, the cage product was identified as 9-hydroxyanthrone substituted in the 9-position by the vinylamine fragment, whereas the escape product is probably a 2-substituted anthrahydroquinone.[22] The different connecting sites of the sensitizer moieties in these two classes of products are not surprising. Within the cage, an α-aminoallyl radical D$^\bullet$ reacts with a sensitizer radical, so the position of combination will be largely determined by the spin density distribution in the latter. In contrast, the escape products are most likely formed by attack of D$^\bullet$ on a ground-state sensitizer molecule, making the stability of the resulting radical an important factor.

Sensitized Photoreactions of Triethylamine. With this amine, a variation of the sensitizer also leads to changes in the polarization patterns. These can again be traced either to radical ions pairs or to pairs of neutral radicals. Two typical examples are shown in Figure 3. Also given in this figure are the structural formulas of the main products of this photoreaction and the assignments of their polarized NMR signals.

It is well known[18] that N,N-diethylvinylamine is formed in this reaction. This compound causes the characteristic multiplets[34] around 6.1 and 3.4 ppm. Moreover, polarized signals from the regenerated starting amine, as well as from a combination product of the amine and the sensitizer, are seen in Figure 3.

As in the previous instance, there are significant differences in the spin density distributions in the two intermediate radicals derived from triethylamine (Figure 4), which allows an unambiguous distinction, at which stage the observed polarizations are created.[18]

For a CIDNP net effect originating in a radical ion pair, notable polarizations will again occur only for protons adjacent to the nitrogen atom, because the hyperfine coupling constants a of the terminal protons are too small in the triethylaminium radical cation DH$^{\bullet+}$. As Figure 3 (top trace) shows, this is clearly found in the photoreaction of triethylamine with anthraquinone. We point out the different behavior of the same sensitizer in the reaction with triallylamine.

On the other hand, CIDNP stemming from a pair of neutral radicals will manifest itself by strong polarizations of opposite phase for the α- and β-protons of the reaction products, owing to the sign alteration (and almost equal magnitude) of a for the internal and terminal protons in the α-aminoethyl radical D$^\bullet$. This polarization pattern is observed in all products of the photoreaction of triethylamine with xanthone (Figure 3, center trace[37]).

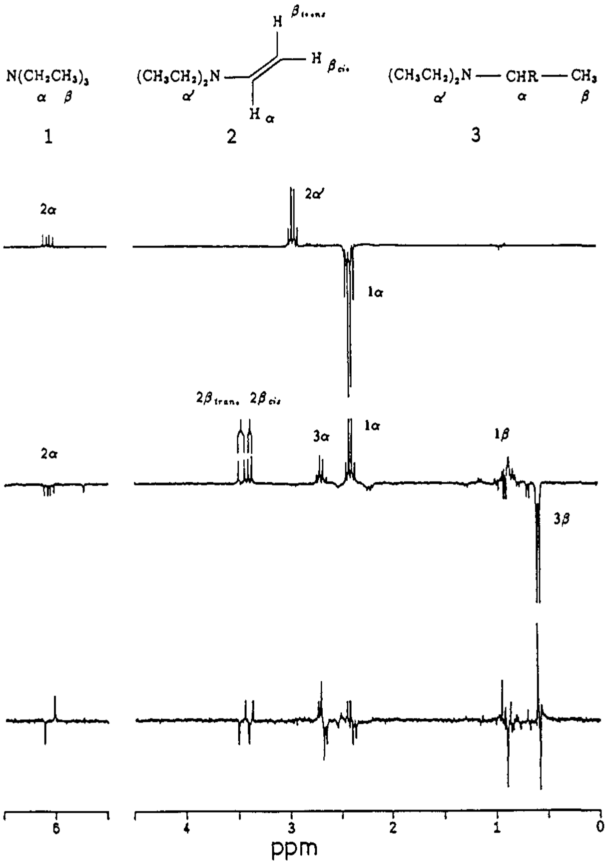

Figure 3. Background-free, pseudo-steady-state CIDNP spectra observed in the photoreaction of triethylamine with different sensitizers (top trace, anthraquinone; center trace, xanthone, CIDNP net effect; bottom trace, xanthone, CIDNP multiplet effect, amplitudes multiplied by 1.75 relative to the center trace) in acetonitrile-d_3. The structural formulas of the most important products bearing polarizations (1, regenerated starting material; 2, N,N-diethylvinylamine; 3, combination product of amine and sensitizer) are given at the top; R denotes the sensitizer moiety. The polarized resonances of these products are assigned in the spectra.

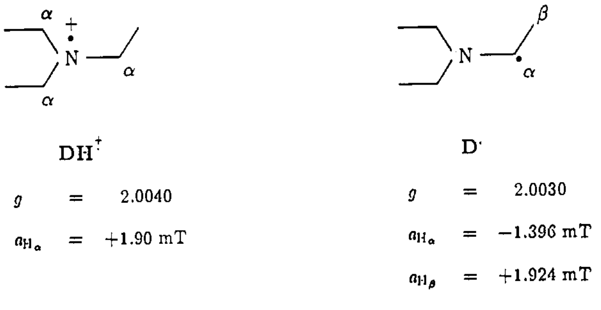

Figure 4. Magnetic parameters of the radical cation DH$^{\bullet+}$ [18,31,35] and the neutral radical D$^\bullet$ [18,30,36] derived from triethylamine. Only the proton hyperfine coupling constants possessing nonnegligible values are included.

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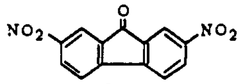
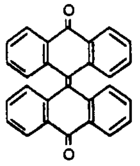
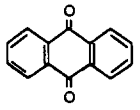
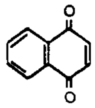
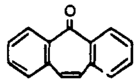
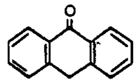
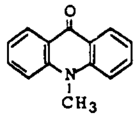
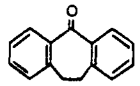
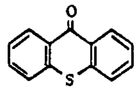
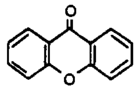
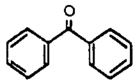
(34) The ABX spin system of this vinylamine gives rise to two doublets of doublets, so obviously $J_{AB} \approx 0$ Hz. Furthermore, we find $\delta_{H_\alpha} = 6.09$, $\delta_{H_{\beta cis}} = 3.41$, $\delta_{H_{\beta trans}} = 3.49$, ${}^3J_{cis} = 8.9$ Hz, ${}^3J_{trans} = 15.3$ Hz.

(35) The hyperfine coupling constant of 3.9 mT for the α-protons of the triethylaminium radical cation given in ref 18 is valid for the anisotropic case only (compare ref 31).

(36) The g-factor of the neutral radical of triethylamine given in ref 30 (2.003 32) is too high to be compatible with the observed polarization patterns in the photoreactions with benzophenones (see ref 18).

(37) However, the methylene protons of the regained amine DH are seen to be polarized more strongly in this spectrum than the methyl protons. This discrepancy with the intensity ratio expected from the hyperfine coupling constants in D$^\bullet$ (Figure 4) indicates an additional contribution of CIDNP originating from radical ion pairs for this particular product. (With the sensitizer xanthone, the product of Δg and a_{H_α} has the same sign for both types of radical pairs, so for the methylene protons the polarizations from these two precursors would add up.) A similar behavior was also observed in the system N,N-diethyl-p-toluidine/decadeuteriobenzophenone.[18] In our case, though, this intensity anomaly is at least partly explained by a superposition of the methylene signal with another polarized resonance from an escape product (compare the spectra).

Table I. Photoreaction of Triethylamine with Different Sensitizers in Acetonitrile-d_3[a]

sensitizer		$g(\mathrm{A}^{\bullet-})$	$g(\mathrm{AH}^{\bullet})$	E_T	$-\Phi$	$\Delta H_f(\mathrm{A})$	$\Delta H_f(\mathrm{AH}^{\cdot})$	$-\Delta G°_{\mathrm{dep}}$	CIDNP
2,7-dinitrofluorenone		>2.0040[b]	2.003 15[c]	235	0.64[d]	193	210	51	RIP
bisanthrone		>2.0040[b,e]	2.003 38[f]	259	1.14[g]	314	349	81	RIP
anthraquinone		2.004 43[h]	2.004 03[i,j]	261	0.94[k]	−25	−10	82	RIP
naphthoquinone		2.0048[l]	2.004 30[i,j]	240[m]	0.71[k]	−67	−74	82	RIP
benzoquinone		2.0047[n]	2.004 69[j,o]	221[p]	0.51[k]	−105	−135	85	RIP
dibenzosuberenone		2.0037[q]	2.003 15[c]	260	1.56[r]	168	210	115	RIP
anthrone		2.0037[q]	2.003 05[s]	300[t]	1.45[u]	62	90	118	RIP/NRP
N-methylacridinone		2.003 32[v]	2.003 20[s]	239	1.60[w]	132	168	125	RIP/NRP
dibenzosuberone		2.0037[q]	2.003 10[s]	274	1.55[u]	67	96	127	NRP
thioxanthone		2.0039[x]	2.003 85[s]	272[y]	1.66[z]	134	161	139	NRP
xanthone		2.0036[x]	2.003 45[s]	310[aa]	1.76[bb]	−28	5	143	NRP
benzophenone		2.0037[x]	2.003 15[s]	287[cc]	1.83[bb]	85	114	154	NRP

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[a] The table displays the name and structural formula of the respective sensitizer, the *g*-factors of its radicals $\mathrm{A}^{\bullet-}$ and $\mathrm{AH}^{\bullet}$, its triplet energy E_T (in kJ/mol), reduction potential Φ (half-wave potential in acetonitrile, V *vs* SCE, if not denoted otherwise), heats of formation (in kJ/mol) $\Delta H_f(\mathrm{A})$ and $\Delta H_f(\mathrm{A}^{\bullet})$ of the ground-state molecule and the neutral radical as computed by using the AM1 method, calculated free enthalpy $\Delta G°_{\mathrm{dep}}$ (in kJ/mol) for the deprotonation of $\mathrm{DH}^{\cdot+}$ by $\mathrm{A}^{\bullet-}$ (see Discussion), and source of the observed polarization pattern in the reaction product *N*,*N*-diethylvinylamine (RIP, radical ion pair; NRP, neutral radical pair). [b] From the phases of the CIDNP net effect. [c] Estimated to be very similar to $g(\mathrm{AH}^{\bullet})$ for benzophenone. [d] Half-wave potential in DMF (Empis, J. M. A.; Herold, B. J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 425–430). [e] See footnote 42. [f] Singer, L. S.; Lewis, I. C.; Richerzhagen, T.; Vincow, G. *J. Phys. Chem.* **1971**, *75*, 290–291. [g] This sensitizer displays a complex, multistage redox behavior. The potential given in the table is the indirectly evaluated formal potential for the reduction of the A-form of the sensitizer to the A-form of the radical anion (ref 44). [h] Sieiro, C.; Sanchez, A.; Crouigneau, P. *Spectrochim. Acta A* **1984**, *40*, 453–456. [i] Value for the 2-methyl derivative. [j] Adeleke, B. B.; Wan, J. K. S. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1799–1808. [k] Reference 67. [l] Alegria, A. E.; Fontanez, F.; Stevenson, G. R. *J. Phys. chem.* **1976**, *80*, 1113–1117. [m] Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2771–2775. [n] Maruyama, K.; Kato, H. *Mem. Fac. Sci., Kyoto Univ., Ser. Phys., Astrophys., Geophys. Chem.* **1985**, *36*, 463–480. [o] Value for the 2,6-di-*tert*-butyl derivative. [p] Beck, S. M.; Brus, L. E. *J. Am. Chem. Soc.* **1982**, *104*, 1103–1104. [q] Estimated to be very similar to $g(\mathrm{A}^{\bullet-})$ for benzophenone. [r] Value *vs* SCE calculated from the half-wave potential *vs* sodium calomel electrode (Diaz, A.; Parra, M.; Banuelos, R.; Contreras, R. *J. Org. Chem.* **1978**, *43*, 4461–4464). [s] Determined from the relative intensities of CIDNP net and multiplet effects (see text). [t] Alfimov, M. V.; Buden, N. Yu.; Glagolev, V. L.; Kuyumdzki, E. S.; Pomazan, Yu. V.; Shamshev, V. N. *Opt. Spectrosc.* **1977**, *42*, 267–270. [u] Calculated from the potential in DMF relative to that of dibenzosuberone (Kazakova, V. M.; Makarov, I. G.; Samokhvalova, A. I.; Ioffe, D. V. *Zh. Strukt. Chim.* **1974**, *15*, 227; *Chem. Abstr.* **1974**, *80*, 144947p; *Nov. Elektrokhim. Org. Soedin., Tezisy Dokl. Vses. Soveshch. Elektrokhim. Org. Soedin. 8th* **1973**; *Chem. Abstr.* **1975**, *78*, 82:16041t). [v] Janzen, E. G.; Pickett, J. B.; Happ, J. W.; DeAngelis, W. *J. Org. Chem.* **1970**, *35*, 88–95. However, in relation to the other compounds, this value seems to be too low. [w] Measured in this work. The value given by Timpe, H.-J.; Kronfeld, K.-P.; Lammel, U.; Fouassier, J.-P.; Lougnot, J. *J. Photochem. Photobiol. A* **1990**, *52*, 111–122 is 1.46 V, but these authors do not specify their reference electrode. [x] Aarons, L. J.; Adam, F. C. *Can. J. Chem.* **1972**, *50*, 1390–1400. [y] Dalton, J. C.; Montgomery, F. C. *J. Am. Chem. Soc.* **1974**, *96*, 6230–6232. [z] Yates, S. F.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 3349–3356. [aa] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753. [bb] Half-wave potential in DMF (Given, P. H.; Peover, M. E.; Schoen, J. *J. Chem. Soc.* **1958**, 2674–2679). [cc] Saltiel, J.; Curtis, H. C.; Metts, L.; Miley, J. W.; Winterle, J.; Wrighton, M. *J. Am. Chem. Soc.* **1970**, *92*, 410–411.

In this system, both CIDNP net and multiplet effects arise. One can separate these by acquiring two spectra using observation pulses with flip angles of 45° and 135°, respectively.[38] Addition of both spectra yields pure net effects (Figure 3, center trace), and subtraction yields pure multiplet effects (Figure 3, bottom trace). The multiplet phase Γ_{ij} ($\Gamma_{ij} = +1$, E/A multiplet, that is, emission to low field, enhanced absorption to high field; $\Gamma_{ij} = -1$, A/E multiplet) for two groups of coupled nuclei i and j with coupling constant J_{ij} is given by Kaptein's rule[33] for a CIDNP multiplet effect,

$$\Gamma_{ij} = \operatorname{sgn} a_i \operatorname{sgn} a_j \operatorname{sgn} J_{ij}\, \sigma_{ij}\, \mu\, \epsilon \qquad (4)$$

where σ_{ij} is +1 if the nuclei reside in the same radical of the pair (as in our intermediates) and −1 if they do not. With the known parameters of the radical $\mathrm{D}^\bullet$ and $^3J > 0$,[39] A/E multiplets indicate cage products (regenerated DH and combination product of amine and sensitizer) and E/A multiplets escape products (*N*,*N*-diethylvinylamine[40]). The same assignment of formation channels for these three products can be obtained from the phases of the CIDNP net effects as well (eq 3).

The polarization phases observed in the anthraquinone-sensitized reaction (Figure 3, top trace) show that *N*,*N*-diethylvinylamine is also an escape product in that system, as with the sensitizer xanthone. Regardless of the different CIDNP patterns occurring in these two cases, the neutral radical $\mathrm{D}^\bullet$ is the precursor to the vinylamine;[18] no mechanism is known that leads directly from $\mathrm{DH}^{\bullet+}$ to the latter compound without involving the α-aminoethyl radical as an intermediate. *N*,*N*-Diethylvinylamine may result from a disproportionation[2] of two free radicals $\mathrm{D}^\bullet$, though this seems to be less likely with the small radical concentrations present in our measurements, or it can be produced by a reaction of this species with a ground-state sensitizer molecule A,[1,41]

$$\mathrm{D}^\bullet + \mathrm{A} \rightarrow \mathrm{Et_2NCH{=}CH_2} + \mathrm{A}^{\bullet -} + \mathrm{H}^+ \qquad (5)$$

where the liberated proton may either be taken up by the sensitizer radical anion $\mathrm{A}^{\bullet-}$ to give a neutral radical $\mathrm{AH}^\bullet$ or be accepted by an assisting amine molecule. However, formation of *N*,*N*-diethylvinylamine is also possible within the cage, as transfer of a hydrogen atom from $\mathrm{D}^\bullet$ to $\mathrm{AH}^\bullet$ yields this product and an alcohol. CIDNP studies have furnished proof for this pathway, such as in the system triethylamine/4,4′-dimethylbenzophenone.[18]

To get more information about the mechanism of the investigated photoreaction, we performed CIDNP experiments with a variety of sensitizers A possessing carbonyl functions. Their names and chemical formulas are given in Table I. As a common structural feature, all but two of these sensitizers have benzophenone skeletons. Except for the parent compound, this skeleton is held fixed by the two aromatic rings linked in their ortho positions to form a central 5-, 6-, or 7-membered ring. The observed CIDNP phases prove that the photoreactions take place from a triplet state of the sensitizer, as expected for these carbonyl compounds.

In Table I, we further list the *g*-factors of $\mathrm{A}^{\bullet-}$ and $\mathrm{AH}^\bullet$. For the radical anions, most of them have been reported in the literature. The phases of the CIDNP net effects found with the sensitizers 2,7-dinitrofluorenone and bisanthrone unambiguously show that for these compounds the unavailable *g*-factor of $\mathrm{A}^{\bullet-}$ must be larger than the *g*-factor of $\mathrm{DH}^{\bullet+}$ (i.e., >2.0040), the reason for these high values obviously being substantial unpaired spin density on the nitro groups in the former radical and on the second oxygen atom in the latter.[42] In the case of the other compounds, for which $g(\mathrm{A}^{\bullet-})$ is unknown, we expect values very similar to those for the benzophenone ketyl. For $\mathrm{AH}^\bullet$, only a few *g*-factors have been published. However, as the relative amplitudes of net and multiplet effects (which may be separated by their flip angle dependence, as described above) are strongly dependent on Δg of the radical pair, $g(\mathrm{AH}^\bullet)$ can be obtained by a comparison of experimental and simulated CIDNP signal intensities. In this way,[45] we determined these quantities for six of the neutral sensitizer-based radicals. The *g*-factors of $\mathrm{AH}^\bullet$ derived from 2,7-dinitrofluorenone and dibenzosuberenone, which show no multiplet effect, should be almost identical to that of the neutral benzophenone radical, as in these species there is little unpaired spin density on the bridging atom or in the 2- and 7-positions of the aromatic rings.

The triplet energies $E_\mathrm{T}(\mathrm{A})$ and the reduction potentials $\Phi(\mathrm{A}/\mathrm{A}^{\bullet-})$ of the sensitizers have also been compiled in Table I. The oxidation potentials $\Phi(\mathrm{DH}^{\bullet+}/\mathrm{DH})$ of triethylamine and triallylamine are 0.96 and 1.21 V, respectively.[46] The heats of formation ΔH_f of A and of the neutral radicals $\mathrm{AH}^\bullet$ derived from the sensitizers have been computed by AM1 and are given in Table I, too. For triethylamine, the results of these calculations are $\Delta H_\mathrm{f}(\mathrm{DH}) = -65$ kJ/mol and $\Delta H_\mathrm{f}(\mathrm{D}^\bullet) = +22$ kJ/mol. For triallylamine, we have $\Delta H_\mathrm{f}(\mathrm{DH}) = +240$ kJ/mol and $\Delta H_\mathrm{f}(\mathrm{D}^\bullet) = +319$ kJ/mol. The energetics of the reactions will be considered in detail in the Discussion.

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(38) Hany, R.; Vollenweider, J.-K.; Fischer, H. *Chem. Phys.* **1986**, *120*, 169–175 and references therein.

(39) Reference 25, p 67.

(40) In the spectrum displaying pure multiplet effects (Figure 3, bottom trace), the inner two lines of the signal group from the α-proton of the *N*,*N*-diethylvinylamine are missing. The origin of this phenomenon is the adiabatic transition from the $\mathrm{A'X_3'}$ spin system of the α-aminoethyl radical to the ABX spin system of the vinylamine brought about by the removal of a β-proton from $\mathrm{D}^\bullet$. By this process the spin states $|m_s(\mathrm{A'})m_s(\mathrm{X_3'})\rangle$ are projected onto $|m_s(\mathrm{X})m_s(\mathrm{AB})\rangle$ such that $m_s(\mathrm{A'}) = m_s(\mathrm{X})$, $m_s(\mathrm{X_3'}) = m_s(\mathrm{AB}) \pm {}^1/_2$, and the populations of all sublevels for given $m_s(\mathrm{X})$ and $m_s(\mathrm{AB})$ are the same. Since a CIDNP multiplet effect leads to equal populations of spin states $|m_s(\mathrm{A'}){-}m_s(\mathrm{X_3'})\rangle$ and $|{-}m_s(\mathrm{A'}){-}m_s(\mathrm{X_3'})\rangle$ in the radicals, the populations of the spin states $|m_s(\mathrm{X})m_s(\mathrm{AB})\rangle$ and $|{-}m_s(\mathrm{X}){-}m_s(\mathrm{AB})\rangle$ in the product molecules are also equal. This implies that there is no population difference across those transitions of nucleus X for which $m_s(\mathrm{AB})$ is 0, and those lines drop from the spectrum. Due to the identical sublevel population, this holds regardless of whether the AB part of the vinylamine spin system is weakly coupled (as in our case) or strongly coupled. This effect might be potentially useful for the assignment of transitions of such spin systems in the CIDNP spectra.

(41) Hore, P. J.; McLauchlan, K. A. *Mol. Phys.* **1981**, *42*, 1009–1026.

(42) The *g*-factor inferred from the CIDNP experiments apparently contradicts the value of 2.0036 observed[43] for the radical anion of bisanthrone. However, this radical can exist in two forms. In our experiments, most likely the A-form is obtained by the photoinduced electron transfer. This species should resemble a semiquinone electronically, bearing substantial spin density on the second oxygen atom, and consequently should possess a semiquinone-like *g*-factor. The A-form is known to be transformed into the more stable B-form within microseconds,[44] but this is much slower than the radical pair lifetime. In that compound, the two anthrone moieties are twisted around the central double bond, so little conjugation between the two halves of the molecule is expected, and the *g*-factor should be similar to that of the radical anion of anthrone. Our CIDNP results thus provide additional evidence that the B-form of the bisanthrone radical anion gives rise to the EPR spectrum reported in ref 43.

(43) Mattar, S. M.; Sutherland, D. *J. Phys. Chem.* **1991**, *95*, 5129–5133.

(44) Neta, P.; Evans, D. H. *J. Am. Chem. Soc.* **1981**, *103*, 7041–7045.

(45) CIDNP intensities were computed with a refined reencounter model (Vollenweider, J. K.; Fischer, H. *Chem. Phys.* **1988**, *124*, 333–345). The calculations were based on the magnetic parameters of the α-aminoethyl radical given in Figure 4 and, additionally, $a_{^{14}\mathrm{N}} = 0.518$ mT and $a_{\mathrm{H}_{\alpha'}} = 0.254$ mT.[31] The hyperfine coupling constants of the radical derived from the sensitizer are too small to have a significant influence on the enhancement factors computed for the amine products. The diffusion coefficient *D* of $\mathrm{D}^\bullet$ was assumed to be equal to that of DH; for the latter a value of 2.85×10^{-5} cm^2 s^{-1} was estimated from the self-diffusion coefficient in neat triethylamine (Dudley, G. J.; Tyrrell, H. J. *J. Chem. Soc.*, *Faraday Trans. 1* **1973**, 2188–2199) with the Stokes–Einstein equation and the known viscosities of the amine (Dudley *et al.*, *loc. cit.*) and the solvent. The latter viscosity was taken to be identical to that of undeuterated acetonitrile (Grampp, G.; Jaenicke, W. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 335–340). *D* of $\mathrm{AH}^\bullet$ was approximated by the diffusion coefficient of anthraquinone in acetonitrile at room temperature (1.98×10^{-5} cm^2 s^{-1}, Howell, J. O.; Wightman, R. M. *Anal. Chem.* **1984**, *56*, 524–529). A reaction distance ρ of 7.5 Å was estimated from the results of the AM1 calculations and the van der Waals radii as described before (Goez, M. *Z. Phys. Chem. Neue Folge* **1990**, *169*, 133–145). Other parameters (length of diffusive displacement = 1.7 Å, $J_0 = 10^{13}$ rad/s, $r_\mathrm{ex} = 2\rho$, $r_0 = 1.25\rho$) were chosen as in ref 20. Electron spin relaxation in the free radicals was neglected. Although the uncertainties of several parameters (especially J_0 and r_ex) have a significant influence on the absolute values of the CIDNP intensities, the dependence of the relative magnitudes of net and multiplet effects on these quantities is only weak. The errors in Δg obtained by these calculations are estimated to be around ±0.000 05.

(46) Potentials relative to SCE calculated from the peak potentials in acetonitrile *vs* Ag/0.1 M $\mathrm{AgNO_3}$.[47]

(47) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970; pp 259–296.

As before, we utilized the characteristic polarization patterns observed in the photoproduct *N,N*-diethylvinylamine for the determination of whether CIDNP of this species stems from radical ion pairs or from pairs of neutral radicals. The results for the various sensitizers are listed in Table I. We concentrated on this particular compound for three reasons. First, its intensity patterns are unmistakable, and, moreover, the peaks fall into spectral regions devoid of other signals. Second, the product is independent of the sensitizer employed, so all conceivable assignment problems are eliminated. Third, in contrast to the combination products in the triallylamine system, *N,N*-diethylvinylamine is formed by the same pathway (escape) with all but one of our sensitizers.[48] Hence, a comparison of different reaction channels, which might lead to difficulties, can be avoided.

A variation of the amine concentration within the experimentally accessible range (about 5×10^{-3} to 5×10^{-1} M, where the lower limit was dictated by the high quantum yield of these reactions and the upper limit by the background suppression attainable with the pseudo-steady-state measurements), did not result in more than insignificant variations of (relative as well as absolute) CIDNP signal strengths.

CIDNP intensities depend on the magnetic parameters of the radical pairs involved. For the amines investigated, the hyperfine coupling constants of the protons used for discrimination of the possible intermediates (e.g., for the triallylamine systems, α-protons in $DH^{\bullet+}$ and γ-protons in $D^{\bullet}$) are of similar magnitude. However, the key quantity Δg may be substantially different for the two types of radical pairs, depending on the sensitizer. In principle, this could bring about changes in the CIDNP patterns not related in any way to changes in the reaction mechanism, namely if Δg were much more favorable with one sensitizer in the case of the radical ion pair than for the pair of neutral radicals, thus leading to dominating polarizations from the former pair, and the other way around with a second sensitizer.

To exclude this trivial explanation, we carried out extensive calculations of the nuclear spin polarizations.[49] The results indicate that for all systems studied, the CIDNP signal intensities from the respective two types of radical pairs should not differ by more than a factor of 4 at worst. The experimental effects are much larger than this, in most cases amounting to a 100% discrimination within the signal-to-noise ratio of our measurements. Moreover, there is no correlation between the calculated ratios of the CIDNP enhancement factors for both possible radical pairs and the source of the polarizations inferred from the spectra; the calculations, for instance, predict almost 4 times higher signal intensities from the neutral pairs for the system anthraquinone/triethylamine, but exclusive polarizations from radical ion pairs are found experimentally (Figure 3, top trace). Lastly, with the same combination of amine and sensitizer, we also observed such alterations in the polarization patterns if the solvent was varied.[50] The *g*-factors should have remained essentially constant in these measurements since we used aprotic solvents. Hence, we conclude that the described effects must be attributed to changes in the reaction mechanism.

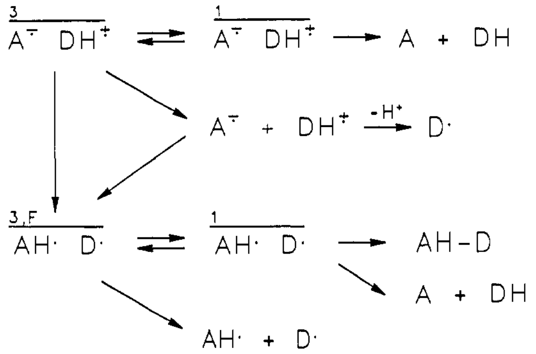

Figure 5. Reaction mechanism for the explanation of the polarization patterns observed in the triplet-sensitized photoreactions of tertiary aliphatic amines. A denotes the sensitizer, $A^{\bullet-}$ its radical anion, and $AH^{\bullet}$ its neutral radical. DH, $DH^{\bullet+}$, and $D^{\bullet}$ represent the amine, its radical cation, and its neutral radical, respectively. Correlated radical pairs are designed by bars, with the multiplicity given above (F means random phase precursors). The double arrows signify CIDNP generation by nuclear spin-selective intersystem crossing. Cage reaction of the pair of neutral radicals can recover the starting materials or lead to combination products AH–D of amine and sensitizer. Other types of products, either from the cage or formed by secondary reactions of the free radicals $D^{\bullet}$, have been omitted for clarity.

Discussion

Reaction Mechanism. It is well known[1] that the primary chemical step of the sensitized photoreaction of aliphatic amines is an electron-transfer process if this is energetically feasible. From the triplet energies $E_T(A)$ and reduction potentials $\Phi(A/A^{\bullet-})$ of the sensitizers (Table I) as well as the oxidation potentials $\Phi(DH^{\bullet+}/DH)$ of the amines,[46] the free enthalpy $\Delta G°_{ET}$ for quenching by electron transfer can be calculated by means of the Weller equation,[51]

$$\Delta G°_{ET} = F[\Phi(DH^{\bullet+}/DH) - \Phi(A/A^{\bullet-})] - E_T(A) \quad (6)$$

For all photosystems investigated, formation of radical ion pairs is found to be exergonic. Moreover, $\Delta G°_{ET}$ is strongly negative in most cases, so the quenching should be diffusion controlled. Back electron transfer to ^3A and DH is therefore not to be expected; back electron transfer to A and ^3DH is impossible, because the triplet energy of the amine is much higher[52] than $E_T(A)$.

An explanation of the different polarization patterns observed with different sensitizers is provided by the reaction mechanism shown in Figure 5. We start out with correlated radical ion pairs $\overline{A^{\bullet-}DH^{\bullet+}}$ in the triplet state, which are the primary result of the quenching process. We consider the following two limiting cases for the deprotonation of the aminium radical cations $DH^{\bullet+}$ contained in these pairs.

If proton transfer from $DH^{\bullet+}$ to $A^{\bullet-}$ is slow compared to the lifetime of the correlated radical ions pairs (~nanoseconds), then these pairs either can undergo back electron transfer to the ground-state reactants after intersystem crossing to the singlet manifold or must separate, yielding uncorrelated radical ions. The free aminium cations formed in this process carry the nuclear spin polarizations from their precursors, the radical ion pairs. Deprotonation of free $DH^{\bullet+}$ will most likely be effected by surplus amine, which is a base and present in fairly high concentrations (~5×10^{-2} M) in our experiments. As this deprotonation does not involve radical *pairs*, no CIDNP can be generated at this stage, and the polarizations from the ion pairs are simply transferred to the neutral radicals $D^{\bullet}$ and their subsequent products (coupling products with the sensitizer, or, additionally, *N,N*-diethylvinylamine in the triethylamine systems). This

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[48] From the phases of the CIDNP multiplet effect or by comparison of the phases of the net polarization that we observe for the vinylamine with the CIDNP phases of other products definitively formed in a cage reaction (e.g., starting amine), we can establish that in our systems the vinylamine is an escape product for all sensitizers except *N*-methylacridinone. At present, we have no explanation for the different behavior of this compound.

[49] These calculations were performed as described above.[45] For the diffusion coefficient of $A^{\bullet}$ derived from benzoquinone, the value of the parent compound in acetonitrile (2.2×10^{-5} cm^2 s^{-1}, Rüssel, C., private communication) was used. The diffusion coefficients of the remaining sensitizer-based neutral radicals were approximated by that of anthraquinone.[45] The Coulombic attraction of the radical ion pairs was taken into account[20] by multiplying the interdiffusion coefficients of $A^{\bullet}$ and $DH^{\bullet}$ with the Debye factor. It is estimated that the absolute CIDNP intensities obtained in this way are accurate to within a factor of 2.

[50] Goez, M.; Sartorius, I. Manuscript in preparation.

[51] Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834–839; *Isr. J. Chem.* **1970**, *8*, 259–271. The Coulombic term of the Weller equation can be neglected in the polar solvent acetonitrile (Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401–449).

[52] Muto, Y.; Nakato, Y.; Tsubomura, H. *Chem. Phys. Lett.* **1971**, *9*, 597–599.

limiting case is observed in the photoreactions of triallylamine with benzoquinone (Figure 1, top trace) and triethylamine with anthraquinone (Figure 3, top trace), for example.

At the other extreme, proton transfer from the aminium cations to the sensitizer radical anions occurs in a much shorter time than the cage life. In this case, all polarizations stem from the resulting pairs of neutral radicals $\overline{AH^\bullet D^\bullet}$. This limit is reached in the reactions of both amines with xanthone (Figure 1, bottom trace, and Figure 3, center trace[37]).

On the basis of the mechanism of Figure 5, it is obvious that for a given combination of sensitizer and amine, both radical ion pairs and pairs of neutral radicals yield identical escape products (e.g., *N*,*N*-diethylvinylamine in the photoreactions of triethylamine), because the species $D^\bullet$, which is the common precursor to these products, is formed directly in the latter case and by a deprotonation of $DH^{\bullet+}$ outside the cage in the former case.

The total absence of polarizations of the starting amine in the system triallylamine/anthraquinone is also easily rationalized with this mechanism. In contrast to the cage recombination of radical ion pairs, which is only possible by back electron transfer, more than one pathway exists for the cage reaction of neutral radical pairs. Apart from a hydrogen atom transfer regaining the educts, the formation of combination products AH–D of amine and sensitizer can also take place. For the systems investigated, these competing processes generally cause educt polarizations arising from neutral pairs to amount to much less than 100% of the total cage polarizations; for the triallylamine-based radical $D^\bullet$, the nearly equal spin densities at C_γ and C_α and the less demanding steric requirements for attack at the terminal positions decide this competition entirely in favor of the combination product AH–D.

In the photoreaction of triallylamine with anthraquinone (Figure 1, center trace), an intermediate situation is realized. Polarizations of the starting material can be traced to radical ion pairs, whereas product polarizations derive from pairs of neutral radicals. This behavior indicates that in these instances, the rates of back electron transfer within the cage and of the deprotonation of $DH^{\bullet+}$ by $A^{\bullet-}$ are of comparable magnitude. The latter reaction could also occur to some extent in *F*-pairs[53] (pairs formed by chance encounters of uncorrelated radical ions). Although the charge recombination is a very fast process, it is only possible from the singlet state of the radical ion pairs in our systems. As proton transfer within $\overline{A^{\bullet-}DH^{\bullet+}}$ is not subjected to this restriction, the competing reactions thus actually are the intersystem crossing of the radical ion pair and the deprotonation of the aminium cation by the sensitizer radical anion.

Chemical reactions proceeding via consecutive radical pairs may give rise to so-called "memory effects".[54] This term denotes spin polarizations that originate in the first radical pair but show up in the products of the second pair. Memory effects have been observed[55] with consecutive radical pairs resulting from radical fragmentations, radical rearrangements, and radical scavenging. In all those cases, transformation of the first radical pair into the second can occur at any time during the correlated life, hence also during a diffusive excursion. The in-cage proton transfer between $DH^{\bullet+}$ and $A^{\bullet-}$ provides an interesting example of such a transformation that can take place solely during an encounter of the two radicals. With our systems, memory effects are to be expected for the intermediate regime only. If proton transfer within the cage is slow compared to the lifetime of the correlated radical ion pairs, practically no pairs of neutral radicals are formed, and if the deprotonation of the aminium cation by the sensitizer radical anion is fast on the CIDNP time scale, the system spends too little time at the stage of the radical ion pair to permit a significant evolution of its density matrix. The superposition of polarizations stemming from radical ion pairs and from pairs of neutral radicals which is found in the reactions of triethylamine with anthrone and *N*-methylacridinone (see Table I) may well be caused to some extent by memory effects. However, on the basis of the existing data, we have not been able yet to discriminate between such effects and superpositions of polarizations from the two different escape pathways.

In chemical systems similar to ours, evidence for proton-transfer reactions involving free aminium cations has already been provided by the results of a CIDNP study of photosensitized amine oxidation in protic media.[56] Exchange of protons (or deuterons) between the amine and the solvent was observed in these measurements. Direct proof of a deprotonation of aminium cations by the parent amine as a base has been obtained from pulse radiolysis experiments of trimethylamine in aqueous solution,[8] The equilibrium

$$DH^{\bullet+} + DH \rightleftharpoons D^\bullet + DH_2^+ \qquad (7)$$

where DH_2^+ is the protonated form of the amine, was found to lie on the right-hand side of eq 7 ($K = 100$[57]).

The free enthalpy ΔG°_{PT} for this reaction can be estimated from the half-wave potential $\Phi(DH^{\bullet+}/DH)$ of trimethylamine in water (+0.76 V *vs* SCE[58]), which must be referred to NHE, the pK_a of the amine (9.80[59]), and the heats of formation ΔH_f of DH (−25 kJ/mol[60]) and $D^\bullet$ (+109 kJ/mol[61]),

$$\Delta G^\circ_{PT} = -F[\Phi(DH^{\bullet+}/DH) + 0.24\ V] - 2.303RTpK_a(DH_2^+) - \Delta H_f(DH) + \Delta H_f(D^\bullet) \qquad (8)$$

Equation 8 rests on three premises. First, we have taken the gas-phase entropies of DH and $D^\bullet$ to be identical, which is certainly an excellent approximation. Second, we have assumed that the free enthalpies of solvation of the compounds $DH^{\bullet+}$ and DH_2^+ are equal, which should be valid, since their molecular sizes and charge distributions are practically the same. Third, we have done likewise with the species DH and $D^\bullet$. That point may be arguable, because the ability of the lone pair at the nitrogen atom to undergo hydrogen bonding with the solvent will be lower in $D^\bullet$ than in DH, owing to the interaction with the singly occupied p-orbital at the α-carbon atom in the former compound. This should cause a better solvation of DH than of $D^\bullet$, thus making the free enthalpy of the proton-transfer reaction, eq 7, more positive in water. However, ΔG°_{PT} estimated with eq 8 (−19 kJ/mol) agrees very well with the experimental value obtained from K (−11 kJ/mol), considering the uncertainties of the parameters, so this effect is obviously quite small and can be neglected.

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(53) A referee has suggested that the inclusion of *F*-pairs might alter our mechanistic conclusions. However, for the pairs $\overline{DH^{\bullet+}A^{\bullet-}}$ the rate of proton transfer within the cage relative to the life of the correlated pair should not depend on the precursor multiplicity, since this process is not spin-forbidden. Hence, the reaction scheme of Figure 5 remains unchanged if *F*-pairs play a significant role. As both random phase precursors and triplet precursors show the same qualitative behavior,[33] one would not expect any changes of the CIDNP phases, i.e., of the polarization patterns, on which our discussion is based.

(54) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6262–6269.

(55) Kaptein, R. In ref 14, pp 257–266 and references therein.

(56) Gardini, G. P.; Bargon, J. *J. Chem. Soc., Chem. Commun.* **1980**, 757–758.

(57) From the kinetic data of ref 8 (Table I), an equilibrium constant k_{11}/k_{12} (for the rate constants we use the numbering of that work in the following) of 2700 is calculated for the proton transfer according to our eq 7 from the radical cation of trimethylamine to the parent compound (values given: $k_{11} = 7.3 \times 10^8$ L mol^{-1} s^{-1}, $k_{12} = 2.7 \times 10^5$ L mol^{-1} s^{-1}). However, this is incompatible with two other equilibrium constants in the same paper that have been measured directly (k_1/k_2 is the protonation constant of trimethylamine in water, $10^{9.76}$ M^{-1}, and k_{10}/k_9 is seen to be $10^{7.8}$ M^{-1} from Figure 2 of that work). Since the former equilibrium constant is certain and the latter appears to be quite reliable, we feel that the correct value of k_{11}/k_{12} should be nearly 100. Moreover, in ref 8, the rate constant k_{11} for the deprotonation of the trimethylaminium radical cation by trimethylamine seems to have been obtained from the experimentally determined quantity k_{12} with the (wrong) equilibrium constant k_{11}/k_{12}, so the value of k_{11} in Table I of that work should be replaced by $k_{11} = 2.7 \times 10^7$ L mol^{-1} s^{-1}.

(58) Masui, M.; Sayo, H.; Tsuda, Y. *J. Chem. Soc. B* **1968**, 973–976.

(59) Everett, D. H.; Wynne-Jones, W. F. K. *Proc. R. Soc. London* **1941**, *177A*, 499–516.

(60) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(61) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586–1587.

Applying this thermodynamic cycle to the tertiary aliphatic amines investigated in this work, we find much higher equilibrium constants for the deprotonation according to eq 7 than in the case of trimethylamine. The pK_a values in water for triethylamine and triallylamine are 10.67[62] and 8.31.[63] The oxidation potential *vs* SCE for the first compound is 0.69 V;[58] for triallylamine we estimate 0.85 V by assuming the potential difference between this amine and trimethylamine in aqueous solution to be identical to that in acetonitrile.[46] Finally, it is well known that primary alkyl radicals are less stable than secondary or allylic radicals. This additional stabilization of the radicals $D^\bullet$ derived from triethylamine and triallylamine relative to the neutral radical of trimethylamine is computed by AM1 to amount to 22 and 29 kJ/mol, respectively.[64] The low difference between the stabilization of these two compounds is probably due to the dominating interaction of the unpaired electron with the lone pair at the nitrogen atom, which is present in both these radicals. In this way, we arrive at equilibrium constants K of about 10^5 in the case of triethylamine and of about 10^7 for triallylamine.

Since the deprotonation reactions of eq 7 are simple charge shifts between molecules of the same size and involve neither charge separation nor charge recombination, their equilibrium constants should not be influenced significantly by the relative permittivity of the medium. On the other hand, the above-mentioned differential solvation of DH and $D^\bullet$, which leads to a stabilization of the former species in water, is absent in an aprotic solvent that is not capable of participating in hydrogen bonding with these reactants. Hence, if anything, the equilibria will be shifted slightly to the right in acetonitrile.

An interesting change in the reactivity of the aminium cations takes place if one alkyl group is replaced by an aromatic ring. We have extensively investigated the anthraquinone-sensitized photoreactions of *N*,*N*-dimethylaniline and its derivatives by time resolved CIDNP experiments.[20,65] In these cases, all polarizations can be traced to radical ion pairs, so with this particular sensitizer, no deprotonation occurs within the cage. On the other hand, no deprotonation of the free anilinium cations by the parent amine is observed either; these systems are photostable. This can be rationalized with the same calculations as above. The (nonreversible) oxidation potential of dimethylaniline in water[66] is only marginally lower than that of trimethylamine, but its protonation constant is much smaller (pK_a = 5.07[67]). As both neutral radicals are primary alkyl radicals, no stabilization is expected in this instance. (Actually, AM1 calculations predict a relative destabilization of the dimethylaniline-based neutral radical by about 20 kJ/mol.) The deprotonation equilibrium is thus expected to lie well to the left of eq 7; K is estimated to be less than 10^{-7}.

In these systems, the escaping radicals $DH^{\bullet+}$ carry exactly the opposite spin polarizations as the starting amine regained in the cage reaction. These free aminium cations take part in a degenerate electron exchange with surplus DH,

$$DH^{\bullet+} + DH \rightleftharpoons DH + DH^{\bullet+} \tag{9}$$

Although no net chemical change is associated with this process, the escape polarizations are transferred back to the educt DH by it, just as they are transferred to products in our systems by the deprotonation of $DH^{\bullet+}$ by the starting amine, eq 7, and the subsequent reactions of $D^\bullet$. The polarizations transferred by the self-exchange compensate the cage polarizations in DH, typically on a microsecond to submicrosecond time scale, depending on the concentration of DH. In the absence of nuclear spin relaxation in the radicals, this cancellation is complete, so CIDNP can only be observed in time-resolved measurements.

This degenerate electron exchange has been omitted from the reaction scheme of Figure 5 for clarity, but it will obviously take place in our photosystems as well and will destroy the polarizations from the radical ion pairs in the described manner. The fact that we do observe polarizations originating from pairs $\overline{A^{\bullet-}DH^{\bullet+}}$ in our products (e.g., Figure 4, top trace) therefore clearly indicates that the deprotonation is able to compete successfully with the self-exchange. Hence, the rate constants k_{dep} for the deprotonation of $DH^{\bullet+}$ by DH cannot be significantly smaller than the rate constants k_{ex} for the self-exchange between $DH^{\bullet+}$ and DH. Intuitively, one would assume an electron transfer to be faster than a proton transfer, owing to a larger intrinsic activation barrier in the latter type of reaction. However, one has to consider the different driving forces of these two processes: ΔG° is 0 for the self-exchange but strongly negative for the deprotonation according to eq 7 in the case of triethylamine or triallylamine.

We were able to determine k_{ex} for two tertiary aliphatic amines,[68] triisopropylamine and diazabicyclo[2.2.2]octane, in the same way as described in ref 20. These compounds behave exactly as *N*,*N*-dimethylaniline; their aminium cations are both stable toward deprotonation by DH in our experiments, the former for steric reasons (kinetic control) and the latter for electronic reasons.[68] The self-exchange rate constants are very similar, both around 1×10^8 L mol^{-1} s^{-1}, whereas the rate constant for the deprotonation of the trimethylaminium cation by trimethylamine in water is 2.77×10^7 L mol^{-1} s^{-1}.[8,57] As already stated, ΔG° is expected to be much more negative for the triethylamine and triallylamine systems in comparison to trimethylamine, so a value of k_{dep} higher than 1×10^8 L mol^{-1} s^{-1} does not seem unreasonable. On the other hand, an upper limit can be put on the rate of this reaction by noting that the polarizations from the radical ion pairs would be greatly reduced if the deprotonation of $DH^{\bullet+}$ by DH were so fast as to interfere with CIDNP generation by taking place to a large extent during the diffusive excursions of $\overline{A^{\bullet-}DH^{\bullet+}}$, that is, during the cage lifetime. The observation that significant polarizations stemming from radical ion pairs are measured (Figure 3, top trace), even if high amine concentrations (5×10^{-1} M) are used, thus excludes a deprotonation rate very much in excess of $\sim 2 \times 10^9$ L mol^{-1} s^{-1}.

Apart from this reservation, the independence of the CIDNP intensities on the concentration of DH is easily explained by the described mechanism. Under the experimental conditions, practically all the excited sensitizer molecules are quenched. It is obvious that the efficiency of proton transfer within the cage, from $DH^{\bullet+}$ to $A^{\bullet-}$, is not influenced by the concentration of the starting amine. On the other hand, the deprotonation of $DH^{\bullet+}$ by DH and the self-exchange between $DH^{\bullet+}$ and DH are competing reactions of the same species. As nuclear spin relaxation during the lifetime (<1 μs) of the radical cations can be neglected in these reactions, always the same fraction ζ, $\zeta = k_{ex}/(k_{ex} + k_{dep})$, of the cage polarization P_0, which is constant for a particular sensitizer/amine combination and constant starting concentrations of excited molecules, is compensated by the self-exchange, leaving educt polarizations of intensity $(1 - \zeta)P_0$. Exactly this fraction $k_{dep}/(k_{ex} + k_{dep}) = (1 - \zeta)$ of P_0 is also transferred to the deprotonated radicals $D^\bullet$ and, by their further reactions, to the products.

In principle, the two pathways for the deprotonation of $DH^{\bullet+}$, within the cage by $A^{\bullet-}$ or outside the cage by DH, could be separated by time-resolved CIDNP measurements ("flash

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(62) Fyfe, W. S. *J. Chem. Soc.* **1955**, 1347–1350.

(63) Girault-Vexlearschi, G. *Bull. Soc. Chim. Fr.* **1956**, 589–606.

(64) The absolute values of ΔH_f computed by AM1 for the small amines and their neutral radicals (trimethylamine, $\Delta H_{f,AM1}(DH) - \Delta H_{f,exp}(DH)$ = 17 kJ/mol and $\Delta H_{f,AM1}(D^\bullet) - \Delta H_{f,exp}(D^\bullet)$ = 8 kJ/mol) seem to be relatively reliable, as opposed to those for the large sensitizer molecules, where big discrepancies between $\Delta H_{f,AM1}(A)$ and $\Delta H_{f,exp}(A)$ occur (compare note 71). Relative errors within a series of amines should therefore be even smaller.

(65) Goez, M. *Z. Phys. Chem. Neue Folge* **1990**, *169*, 123–132.

(66) The half-peak potential *vs* SCE is 0.680 V (Galus, Z.; Adams, R. N. *J. Am. Chem. Soc.* **1962**, *84*, 2061–2065). However, in acetonitrile the oxidation potential of *N*,*N*-dimethylaniline is lower by some 0.3 V than that of trimethylamine.[47]

(67) Fickling, M. H.; Fischer, A.; Mann, B. R.; Packer, J.; Vaughan, J. *J. Am. Chem. Soc.* **1959**, *18*, 4226–4230.

(68) Goez, M.; Sartorius, I.; Frisch, I., manuscript in preparation.

CIDNP"[69,70]). To this end, one would have to vary the concentration of the starting amine and to monitor the time dependence of the polarizations in the diamagnetic products formed by subsequent reactions of the free 1-aminoalkyl radicals $D^\bullet$. However, with our chemical systems this did not prove feasible for kinetic reasons. The decay reactions of $D^\bullet$ are rather slow. Our time-resolved experiments showed that the buildup of the polarizations in the *N*,*N*-diethylvinylamine takes place on a millisecond time scale only. On the other hand, both formation processes for the radicals $D^\bullet$ are much faster. According to our estimation of k_{dep} given above, the deprotonation of free $DH^{\bullet+}$ by DH occurs on a time scale of microseconds, even with the lowest amine concentrations that may be employed in the pseudo-steady-state experiments, and formation of $D^\bullet$ by escape from the secondary cage $\overline{D^\bullet AH^\bullet}$ takes place on a nanosecond time scale. Thus, a discrimination between the two deprotonation channels by time-resolved CIDNP measurements is not possible in our systems, as it would require the decay of $D^\bullet$ to diamagnetic products to be faster by at least 2 orders of magnitude than found experimentally.

Sensitizer Dependence. Now we turn to the deprotonation of aminium cations within the cage, that is, to the deprotonation of $DH^{\bullet+}$ by $A^{\bullet-}$. The differences between the free enthalpies of the radical ion pair and of the pair of neutral radicals are a function of the sensitizer and the amine. We compute these quantities as follows.

AM1 calculations of the heats of formation for the parent compounds and the neutral radicals (see Table I) yield enthalpies of the neutral radical pairs relative to the ground-state molecules A and DH. We assume that $\Delta S°$ of the hydrogen-transfer reaction

$$D^\bullet + AH^\bullet \rightleftharpoons DH + A \qquad (10)$$

remains nearly constant if the sensitizer or the amine is varied. Moreover, this quantity is expected to be very small. The differences in the free enthalpies of solvation between the species $D^\bullet$ and DH or between $AH^\bullet$ and A, respectively, will also be quite small in an aprotic solvent. From the heats of formation, one should thus obtain good estimates of the free enthalpies $\Delta G°_{HT}$ for this reaction in our case. With $\Delta H_f(A)$ and $\Delta H_f(AH^\bullet)$ from Table I, we get fairly similar values of $\Delta G°_{HT}$ (−115 ± 15 kJ/mol) for most of these sensitizers. Significantly lower values result for naphthoquinone (−79 kJ/mol) and especially for benzoquinone (−56 kJ/mol).

Although the AM1 calculations do not seem to be very trustworthy for the carbonyl compounds investigated as far as absolute values of ΔH_f are concerned,[71] the computed differences between $\Delta H_f(A)$ and $\Delta H_f(AH^\bullet)$ are much more reliable. An independent test of these quantities is provided by noting that $\Delta H_f(A) - \Delta H_f(AH^\bullet)$ can also be obtained from experimentally accessible parameters, namely the reduction potential $\Phi(A/A^{\bullet-})$ of the sensitizer in water, which must be referred to NHE, and the pK_a of the neutral radical $AH^\bullet$,

$$\Delta H_f(A) - \Delta H_f(AH^\bullet) = -F[\Phi(A/A^{\bullet-}) + 0.24\ V] - 2.303RTpK_a(AH^\bullet) \qquad (11)$$

For the three quinones, the potentials[72] (−0.17, −0.37, and −0.62 V *vs* SCE) and pK_a values[73] (4,0, 4.1, and 5.3) lead to $\Delta H_f(A) - \Delta H_f(AH^\bullet)$ of −30, −9, and +7 kJ/mol. The agreement with the values obtained from the heats of formation computed by AM1 (−30, −7, and +15 kJ/mol, compare Table I) is surprisingly good considering the large errors of ΔH_f predicted by AM1 for the parent compounds.[71]

The free enthalpies $\Delta G°_{CR}$ for the charge recombination

$$DH^{\bullet+} + A^{\bullet-} \rightleftharpoons DH + A \qquad (12)$$

were determined from the oxidation potentials of the donor DH and the reduction potentials of the sensitizers A. Electrochemical oxidation of tertiary aliphatic amines in aprotic solvents is an irreversible process.[47] Hence, the measured peak potentials do not correspond to the half-wave potentials, causing the absolute values of $\Delta G°_{CR}$ computed from them to be unreliable. Nevertheless, a comparison of relative $\Delta G°_{CR}$ for the reactions of a particular amine with a series of sensitizers is obviously meaningful; since for the donors investigated the primary oxidation step is rate-determining in the cyclovoltammetric experiments,[47] it should, moreover, also be permissible to compare relative values of $\Delta G°_{CR}$ for the reactions of one sensitizer with different amines. We disregard the Coulombic interaction between $DH^{\bullet+}$ and $A^{\bullet-}$ in the contact ion pair, since we work in a polar solvent.[51] Besides, the molecular sizes of our sensitizers are very similar, excepting the two smaller quinones. In contrast to $\Delta G°_{HT}$, the values obtained for $\Delta G°_{CR}$ differ strongly for the molecules possessing a benzophenone substructure.

From $\Delta G°_{HT}$ and $\Delta G°_{CR}$ we calculate the free enthalpies $\Delta G°_{dep}$ of the deprotonation

$$DH^{\bullet+} + A^{\bullet-} \rightleftharpoons D^\bullet + AH^\bullet \qquad (13)$$

which have been compiled in Table I. A comparison with the experimentally observed CIDNP signals shows that there is a correlation between the polarization patterns and the free enthalpy of the deprotonation of $DH^{\bullet+}$ by $A^{\bullet-}$: in systems possessing strongly negative $\Delta G°_{dep}$, polarizations originate in pairs of neutral radicals, whereas in systems for which $\Delta G°_{dep}$ lies below a threshold value, polarizations stem from radical ion pairs. There is also a small intermediate regime of $\Delta G°_{dep}$, for which a superposition of polarizations from both types of radical pairs is found.

From this result, we conclude that the rate of the deprotonation of the aminium cations by the sensitizer radical anions increases with increasing driving force of this reaction. Owing to the competition between this proton transfer within the cage and the disintegration of the cage to free ions, the free enthalpy of this reaction, eq 13, therefore causes a selection of the deprotonation pathways for $DH^{\bullet+}$, as described in the preceding section.

Since $\Delta G°_{HT}$ is essentially constant for the series of sensitizers of similar size and structure employed in Table I, the energetics and kinetics of the deprotonation of the triethylaminium cation within the cage, and thus also the polarization patterns, are determined by the redox potentials of the sensitizer. This suggestion has already been put forward by Roth.[74]

Most of our observations with the donor triallylamine (see Figure 1) can also be explained by the influence of $\Delta G°_{dep}$. The peak potential for the oxidation of this amine in acetonitrile is higher by approximately 0.25 V than that of triethylamine.[47] In contrast to this, the computed differences in $\Delta G°_{HT}$ resulting from the stabilization of the α-aminoallyl radical $D^\bullet$ amount to

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[69] Schäublin, S.; Wokaun, A.; Ernst, R. R. *Chem. Phys.* **1976**, *14*, 285–293; *J. Magn. Reson.* **1977**, *27*, 273–302.

[70] Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1639–1641; *J. Am. Chem. Soc.* **1981**, *103*, 3586–3588.

[71] AM1 calculations of the heats of formation for molecules of this size appear to be relatively unreliable, and there seems to be a systematic error for cyclic carbonyl compounds with growing number of annelated benzene rings. Computed values of ΔH_f for benzoquinone, naphthoquinone, anthraquinone, and 1,2-benzanthracene-9,10-dione are too positive by 18, 44, 70, and 221 kJ/mol (Scano, P.; Thomson, C. *J. Comput. Chem.* **1991**, *12*, 172–174). These large deviations for unstrained closed-shell molecules in their electronic ground states would make us regard the heats of formation computed for the derived neutral radicals, and thus also the values obtained for $\Delta G°_{HT}$, with great scepticism if the estimations with eq 11 did not show that obviously an efficient compensation of errors occurs in the differences $\Delta H_f(A) - \Delta H_f(AH^\bullet)$, which enter the calculations of $\Delta G°_{HT}$ and $\Delta G°_{dep}$.

[72] Peover, M. E. *J. Chem. Soc.* **1962**, 4540–4549.

[73] Rao, P. S.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 2274–2276.

[74] Roth, H. D. In ref 14, pp 58–60. In that work, however, the examples given for nuclear spin polarizations originating from radical ion pairs and pairs of neutral radicals were triethylamine/benzoquinone and triethylamine/anthraquinone, respectively (both in acetonitrile). We were not able to reproduce these observations; we found polarizations only from radical ion pairs for *both* these systems (compare Figure 3, top trace). Also, with these sensitizers, the changes in $\Delta G°_{HT}$ and $\Delta G°_{CR}$ balance, so $\Delta G°_{dep}$ is very similar for the two of them.

only about 7 kJ/mol when compared to the value for the α-aminoethyl radical, as discussed above. Hence, for the same sensitizer, the calculations give values of $\Delta G°_{dep}$ that are more negative by 17 kJ/mol for triallylamine than for triethylamine. In accordance with this predicted higher driving force for the deprotonation within the cage, the radical anion of the sensitizer anthraquinone is seen to be capable of abstracting a proton faster from the radical cation of triallylamine (polarizations are observed from radical ion pairs as well as from pairs of neutral radicals, so the intermediate regime is realized; compare Figure 1, center trace) than from the radical cation of triethylamine (only polarizations from radical ion pairs are found; see Figure 3, top trace). The seeming discrepancy with the sensitizer benzoquinone, for which the calculated values of $\Delta G°_{dep}$ are identical to those for anthraquinone but which shows exclusive polarizations from radical ion pairs in the photoreaction with triallylamine (Figure 1, top trace), in our minds is due to the uncertainties of the AM1 computations of ΔH_f for molecules of different size.

For the system *N,N*-dimethylaniline/anthraquinone, the same calculations predict a free enthalpy $\Delta G°_{dep}$ of only –24 kJ/mol. It is thus not surprising that no deprotonation of $DH^{\bullet+}$ by $A^{\bullet-}$ within the lifetime of the cage is observed in this instance.

Finally, we can estimate the free enthalpy of the process

$$DH_2^+ + A^{\bullet-} \rightleftharpoons DH + AH^{\bullet} \qquad (14)$$

with the values of $\Delta G°_{dep}$ and of K for the deprotonation according to eq 7. This equilibrium lies well to the right; with all sensitizers investigated in this work, $\Delta G°$ of this reaction is found to be at least as negative as –29 kJ/mol for triethylamine and –40 kJ/mol for triallylamine. A proton that is abstracted from $DH^{\bullet+}$ outside the cage, by the amine as a base, will therefore react diffusion-controlled with a free molecule $A^{\bullet-}$. Moreover, proton transfer between DH_2^+ and DH should be rapid for small amines, so the chance of recombination of this proton with $A^{\bullet-}$ is exepcted to be quite large, owing to its high mobility. Thus, in effect, deprotonation within the cage and outside the cage ultimately lead to the same radicals $D^{\bullet}$ and $AH^{\bullet}$, the former process being direct and the latter being mediated by the amine, but with very different implications for CIDNP.

Conclusions

Two pathways have been identified for the deprotonation of aminium cations, which are key intermediates in the ketone-sensitized photoreactions of tertiary aliphatic amines. The observed polarization patterns allow a clear distinction between them. Proton transfer within the correlated radical ion pairs consisting of aminium cation and sensitizer radical anion competes with the escape of the radicals from the cage. The rate of this process is controlled by the difference $\Delta G°_{dep}$ of the free enthalpies of the radical ion pairs and the pairs of neutral radicals.

If $\Delta G°_{dep}$ is very large, the deprotonation is fast compared to the lifetime of the radical ion pairs, and nuclear spin polarizations are generated exclusively within the resulting pair of neutral radicals. On the other hand, if $\Delta G°_{dep}$ falls below a critical value, no significant deprotonation of the aminium cations by the sensitizer radical ions takes place within the cage. In this case, the escaping radical cations carry the nuclear spin polarizations from the radical ion pair. They can be deprotonated by surplus amine in a reaction that is exergonic for the compounds investigated, so these polarizations are simply transferred to the resulting α-aminoalkyl radicals. Since the subsequent reactions of escaping radicals leading to the products involve the α-aminoalkyl radical as a common intermediate in both cases, the same escape products are obtained, regardless of whether the spin polarizations derive from radical ion pairs or from pairs of neutral radicals.

Degenerate electron transfer between the aminium cations and the parent amine molecules is a reaction of the same species competing with the deprotonation outside the cage. The self-exchange rate constant constitutes a lower limit of the rate constant of the deprotonation, k_{dep}. An upper limit can be estimated, since a deprotonation that is fast compared to the lifetime of the correlated radical ion pairs would make their spin polarizations vanish. In this way, one obtains 1×10^8 L mol^{-1} s^{-1} $\lesssim k_{dep} \lesssim$ 2×10^9 L mol^{-1} s^{-1}.

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