Control of the Deprotonation Route of an Aminium Cation by the Solvent Polarity

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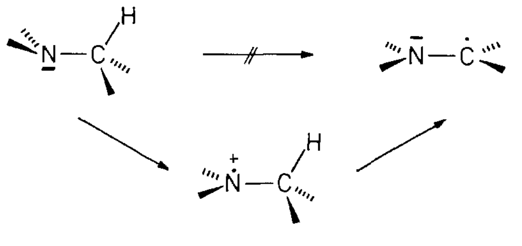
We have studied the photoreaction of triethylamine **DH** with the triplet sensitizer 9,10-anthraquinone in a series of aprotic solvents with relative permittivity ε_r varying between 2 and 50. The results are compared with those of an earlier investigation in which a series of triplet sensitizers in acetonitrile was used. All these reactions are two-step processes: an aminium cation **DH**$^{+\cdot}$ is formed by photoinduced electron transfer, and then deprotonated at C_α to give an α-aminoalkyl radical **D**$^\cdot$. The deprotonation of **DH**$^{+\cdot}$ can either occur within the cage, by the sensitizer radical anion, or outside the cage, by surplus amine. The final reaction products (e.g. *N,N*-diethylvinylamine) are independent of the deprotonation route. Nevertheless, a distinction between the two mechanistic alternatives is possible by using measurements of chemically induced dynamic nuclear polarization (CIDNP). This technique is sensitive to radical pairs only, and the different amine-based intermediates contained in the two possible kinds of radical pairs (radical-ion pairs for both deprotonation routes, and pairs of neutral radicals for in-cage deprotonation only) give rise to characteristically different signal patterns. The influence of solvent polarity as well as sensitizer oxidation potential E_{ox} on the deprotonation pathway (exclusive in-cage deprotonation at low values of ε_r, or high E_{ox}, and exclusive out-of-cage deprotonation at high ε_r, or low E_{ox}) can be quantitatively explained by the dependence of the in-cage deprotonation rate on the driving force $-\Delta G^0_{dep}$ of this process, which shows a marked threshold behavior. If ΔG^0_{dep} is more negative than -125 kJ/mol, proton transfer from **DH**$^{+\cdot}$ to the sensitizer radical anion is faster than separation of the primarily formed radical-ion pair, so the aminium cations are deprotonated within the cage. For ΔG^0_{dep} more positive than -100 kJ/mol, this reaction is too slow to compete with escape from the cage. By the latter process, free aminium cations are formed, which are then deprotonated outside the cage by surplus amine.

Aminium cations **DH**$^{+\cdot}$ are central intermediates in photosensitized hydrogen abstractions from tertiary aliphatic amines **DH**. It is well known[1] that these reactions are sequential (see Scheme 1). First, an electron is transferred from **DH** to an electronically excited molecule of the sensitizer **A**, if this is energetically feasible. The resulting aminium cation **DH**$^{+\cdot}$ is then deprotonated at C_α, which yields an aminoalkyl radical **D**$^\cdot$. Subsequent reactions of **D**$^\cdot$ finally lead to stable photoproducts.



DH DH$^{+\cdot}$ D$^\cdot$

As we recently reported[2], two alternative routes exist for the deprotonation of **DH**$^{+\cdot}$. The proton is either removed within the solvent cage, by the sensitizer radical anion **A**$^{-\cdot}$ formed by the primary electron transfer, or it is abstracted outside the cage, by surplus amine. In experiments with a series of sensitizers in acetonitrile, we found that for sterically unhindered amines the pathway taken is determined by a single parameter, the driving force $-\Delta G^0_{dep}$ of the in-cage deprotonation. In the present work, we vary the relative permittivity ε_r of the solvent to fine-tune ΔG^0_{dep}. As we will show, the deprotonation route may also be selected by these relatively weak perturbations. This can be explained quantitatively by the dependence of ΔG^0_{dep} on ε_r.

The two-step hydrogen abstraction must involve a radical-ion pair $\overline{\mathbf{DH^{+\cdot}A^{-\cdot}}}$[3] as a result of the primary electron transfer. If, and only if, the deprotonation of **DH**$^{+\cdot}$ occurs within the cage, we may in addition obtain a pair of neutral radicals $\overline{\mathbf{D^\cdot AH^\cdot}}$, where **AH**$^\cdot$ is the protonated form of **A**$^{-\cdot}$. Measurements of chemically induced dynamic nuclear polarizations[4,5] (CIDNP) allow a distinction between the two pairs[6,7] and thus the two deprotonation routes.

CIDNP manifests itself by the occurrence of anomalous line intensities (enhanced absorption or emission) in NMR spectra recorded during chemical reactions. This phenomenon is due to nonequilibrium populations of the nuclear spin states of the reaction products. CIDNP is caused by nuclear-spin-selective intersystem crossing in the intermediate radical pairs, which is induced by the interplay of Zeeman and hyperfine interactions. Hence, magnitudes and

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signs of the polarizations I_j of different protons j in the reaction products reflect the hyperfine coupling constants a_j of these protons in the radicals; in many cases, there is even a direct proportionality between a_j and I_j. As a_j in $\mathbf{DH}^{\cdot+}$ and $\mathbf{D}^{\cdot}$ differ strongly, polarizations originating in radical-ion pairs and polarizations stemming from pairs of neutral radicals lead to totally different CIDNP intensity patterns[6,7] of the product fragments derived from the amine moiety (Figure 1).

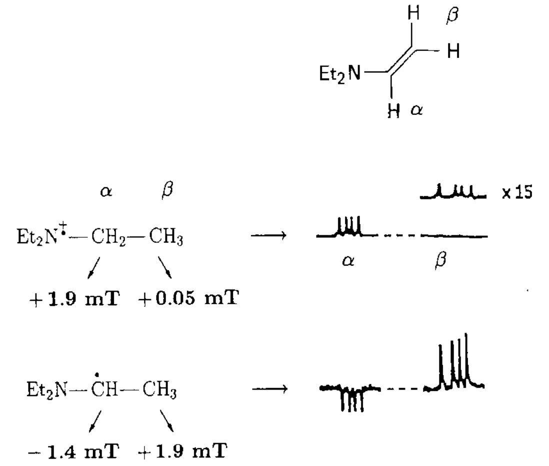
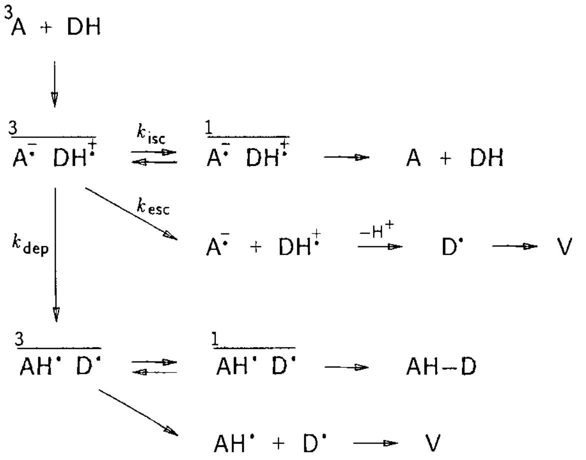


Figure 1. Left: hyperfine coupling constants[2,6] of the α and β protons in the two radicals $\mathbf{DH}^{\cdot+}$ and $\mathbf{D}^{\cdot}$ derived from triethylamine; right: typical polarization patterns for these protons in the product *N*,*N*-diethylvinylamine **V** ($\delta_{H_\alpha} = 6.09$; $\delta_{H_\beta} = 3.41$ and 3.49) observed in our experiments (top trace: solvent acetonitrile; bottom trace: solvent toluene)

Here we concentrate on the resonances of the olefinic α and β protons of a particular reaction product, *N*,*N*-diethylvinylamine **V**. Our measurements show that **V** is an escape product regardless of the deprotonation pathway[2]; its direct precursor is known[6,7] to be $\mathbf{D}^{\cdot}$ in both cases. The reaction mechanism of Scheme 2 explains the formation of **V** and the observed polarization patterns. The primary product of the quenching of an excited triplet sensitizer $^3\mathbf{A}$ by **DH** is a triplet ion pair $\overline{\mathbf{A}^{\cdot-}\mathbf{DH}^{\cdot+}}$. Neither back electron transfer to $^3\mathbf{A}$ + **DH** nor to **A** + $^3\mathbf{DH}$ is possible with our systems. Intersystem crossing (rate constant k_{isc}) under the influence of magnetic interactions leads to a singlet pair, for which back electron transfer to **A** + **DH** is spin-allowed. Proton transfer within $\overline{\mathbf{A}^{\cdot-}\mathbf{DH}^{\cdot+}}$, that is within the cage, may give a pair of neutral radicals $\overline{\mathbf{AH}^{\cdot}\mathbf{D}^{\cdot}}$ with rate constant k_{dep}. This process does not depend on the electron-spin multiplicity. After intersystem crossing of this second pair, combination products **AH−D** are formed in a cage reaction, not the starting compounds anymore. Separation of $\overline{\mathbf{AH}^{\cdot}\mathbf{D}^{\cdot}}$ yields free aminoalkyl radicals $\mathbf{D}^{\cdot}$, the precursors of **V**. With this pathway from $\mathbf{DH}^{\cdot+}$ to the vinylamine, the deprotonation of the aminium cation thus takes place within the cage. In contrast, escape (rate constant k_{esc}) from the primary cage $\overline{\mathbf{A}^{\cdot-}\mathbf{DH}^{\cdot+}}$ first leads to free radical cations $\mathbf{DH}^{\cdot+}$. These are then deprotonated by surplus amine, so $\mathbf{D}^{\cdot}$ is again obtained, and can react further to **V**. The equilibrium for this deprotonation of $\mathbf{DH}^{\cdot+}$ outside the cage lies far to the side of $\mathbf{D}^{\cdot}$ ($K > 10^5$); the equilibrium constant K is practically independent of the solvent[2].



The deprotonation route taken, and thus the polarization pattern observed, is determined by the product $k_{\text{dep}} \cdot \tau$ of the rate constant for in-cage proton transfer and the lifetime of the radical-ion pair. As usual, we take the probability of back electron transfer upon reencounter of a singlet pair to be essentially unity, so intersystem crossing from the singlet manifold back to the triplet manifold can be neglected. With the rate constant k_{esc} for the separation of the correlated radical-ion pairs, τ is thus given by $1/(k_{\text{dep}} + k_{\text{esc}} + k_{\text{isc}})$. For small k_{dep}, τ is of the order of nanoseconds[4,5]. If k_{dep} is very large, i.e. $k_{\text{dep}} \cdot \tau \approx 1$, the system spends too little time at the ionic stage for the development of polarizations, and CIDNP is generated solely in the resulting pairs of neutral radicals. If, on the other hand, k_{dep} is much smaller than $1/\tau$, disintegration of $\overline{\mathbf{A}^{\cdot-}\mathbf{DH}^{\cdot+}}$ yields free aminium cations bearing nuclear-spin polarizations from the radical-ion pairs. By the subsequent deprotonation of $\mathbf{DH}^{\cdot+}$ by the amine outside the cage these polarizations are simply transferred to $\mathbf{D}^{\cdot}$ and lastly **V**. New polarizations cannot result from these processes, since no radical *pairs* are involved.

In a previous study[2], we varied the free enthalpy ΔG^0_{dep} for the in-cage deprotonation of the radical cation of triethylamine by using triplet sensitizers of similar structure (carbonyl compounds possessing a benzophenone structural fragment) but different redox potentials. Qualitatively, we found a complete change of the polarization patterns within a narrow range of ΔG^0_{dep}. For a quantitative evaluation of such measurements, the ratio $2I_\alpha/I_\beta$ of the signal intensities of the olefinic α and β protons of **V** may be utilized. Use of a signal ratio obviates the necessity to measure absolute CIDNP intensities, which are often unreliable. For our systems, $2I_\alpha/I_\beta$ is about −0.6 if in-cage deprotonation of $\mathbf{DH}^{\cdot+}$ predominates, so that all polarizations stem from pairs of neutral radicals; for exclusive deprotonation outside the cage, i.e. origination of polarizations from radical-ion pairs only, this ratio amounts to +9.4.

In Figure 2, $2I_\alpha/I_\beta$ has been plotted as a function of ΔG^0_{dep} for the reaction of triethylamine with several sensitizers in acetonitrile. ΔG^0_{dep} was obtained[2] from the redox potentials of **DH** and **A** and the differences of ΔH_f of **DH** and $\mathbf{D}^{\cdot}$, as well as of **A** and $\mathbf{AH}^{\cdot}$, as calculated by AM1. The latter terms are essentially solvent-independent[2]. From Figure 2, it is evident that the probability of in-cage deprotonation is a strong function of the driving force of this reaction, showing a marked threshold behavior[8]. If $\Delta G^0_{\mathrm{dep}}$ is more negative than about -125 kJ/mol, one solely observes polarizations stemming from pairs of neutral radicals; obviously, $k_{\mathrm{dep}} \cdot \tau \approx 1$. In contrast, for $\Delta G^0_{\mathrm{dep}}$ more positive than approximately -105 kJ/mol, all CIDNP signals can be traced back to radical-ion pairs, so $k_{\mathrm{dep}} \ll 1/\tau$.

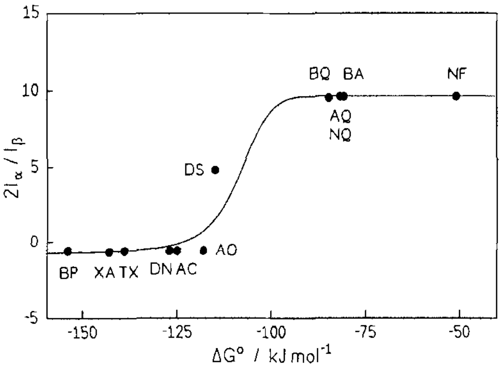


Figure 2. Photoreaction of triethylamine with different sensitizers in acetonitrile; the ratio $2I_\alpha/I_\beta$ of the CIDNP signals of the olefinic α and β protons in **V** is displayed as a function of the calculated free enthalpy of in-cage deprotonation $\Delta G^0_{\mathrm{dep}}$; the labels denote the sensitizers: BP: benzophenone, XA: xanthone, TX: thioxanthone, AC: *N*-methylacridinone, AO: anthrone, DS: dibenzosuberenone, BQ: benzoquinone, NQ: naphthoquinone, AQ: anthraquinone, BA: bisanthrone, NF: 2,7-dinitrofluorenone; the solid line is a global best fit to the data taking into account also the results of Figure 3

A variation of the sensitizer has two disadvantages. If commercially available compounds are to be used, $\Delta G^0_{\mathrm{dep}}$ may be spaced rather unevenly, as Figure 2 shows. Much more serious is that the *g* values of both $\mathbf{A}^{\cdot-}$ and $\mathbf{AH}^{\cdot}$ are altered. As a consequence, the intensities of all polarizations change, but in general not to the same degree for the pairs $\overline{\mathbf{DH}^{\cdot+}\mathbf{A}^{\cdot-}}$ and $\overline{\mathbf{D}^{\cdot}\mathbf{AH}^{\cdot}}$, and also in a nonlinear fashion. The influence of this effect on the ratio $2I_\alpha/I_\beta$ is obviously largest in the transition range of the curves according to Figure 2, because in that regime polarizations arising from both pairs are superimposed. In an extreme case, an unfavorable *g*-value difference could cause CIDNP from one of the two radical pairs to become vanishingly small, and may thus lead to wrong conclusions regarding the deprotonation pathway. In this work, we therefore utilized the solvent polarity to shift the redox potentials of one sensitizer/amine couple (**DH**: triethylamine; **A**: 9,10-anthraquinone), hence the free enthalpies of the radical-ion pairs. On the one hand, this allows variation of $\Delta G^0_{\mathrm{dep}}$ in smaller steps. On the other hand, the *g* values of the radicals are practically uninfluenced by the medium as long as aprotic solvents are employed. By excluding protic solvents one also avoids complications caused by participation of the solvent in the proton transfer between $\mathbf{DH}^{\cdot+}$ and $\mathbf{A}^{\cdot-}$. For sensitized amine photoreactions, the occurrence of different polarization patterns in different solvents was reported previously[6,9], but so far there has been no systematic investigation of their dependence on the solvent polarity.

Figure 3 shows the ratio $2I_\alpha/I_\beta$ as a function of the relative permittivity ε_r of the solvent. For low ε_r, the free enthalpy of the radical-ion pairs is high. All polarizations stem from pairs of neutral radicals, indicating that rapid proton transfer from $\mathbf{DH}^{\cdot+}$ to $\mathbf{A}^{\cdot-}$ occurs. If ε_r is high, the radical ion pairs are stabilized. In that instance only polarizations from $\overline{\mathbf{DH}^{\cdot+}\mathbf{A}^{\cdot-}}$ are observed so the deprotonation rate in the primary cage must be strongly decreased. For intermediate values of ε_r, a superposition of polarizations from both radical pairs is found.

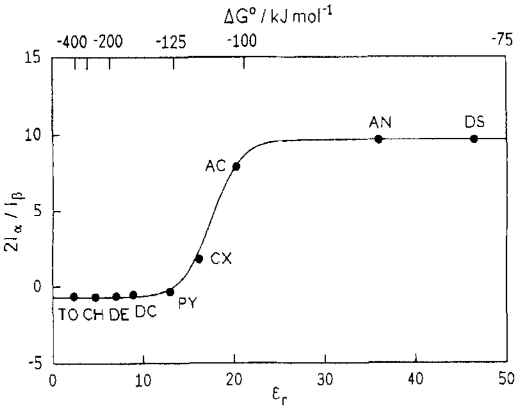


Figure 3. Photoreaction of triethylamine with anthraquinone in different solvents; the plot shows the ratio $2I_\alpha/I_\beta$ of the olefinic protons in **V** as a function of the relative permittivity ε_r of the solvent[10]; the scale at the top gives the calculated (see text) values of $\Delta G^0_{\mathrm{dep}}$; the labels denote the solvents: TO: toluene, CH: chloroform, DE-1,2-dimethoxyethane, DC: dichloromethane, PY: pyridine, CX: cyclohexanone, AC: acetone, AN: acetonitrile, DS: dimethyl sulfoxide; the solid line is a global best fit to the data taking into account also the results of Figure 2

By using a ratio of polarization intensities in the same product as a diagnostic criterion for the reaction pathway, the dependence of CIDNP-enhancement factors on the diffusion coefficients is largely eliminated. Consequently, we did not observe any effects attributable to the different viscosities η of our solvents, the variation in η amounting to a factor of about 7. In the case of the radical-ion pairs $\overline{\mathbf{A}^{\cdot-}\mathbf{DH}^{\cdot+}}$, on the other hand, changing the solvent permittivity directly influences the radical-pair dynamics and thus the generation of CIDNP. In a very unpolar solvent, the Coulombic attraction between the oppositely charged partners of such a pair greatly decreases the probability of diffusive separation, and CIDNP is suppressed. This behavior has been investigated[12] for the system triphenylamine/*trans*-stilbene, where solely electron-transfer reactions take place. However, in that study it was found experimentally that CIDNP is quenched only below $\varepsilon_r \approx 8$. Our theoretical calculations for the system triethylamine/anthraquinone also indicate that this effect can be disregarded for $\varepsilon_r > 10$. Hence, the change in the polarization patterns taking place in the range $13 < \varepsilon_r < 20$ cannot be explained by the pair dynamics but must be attributed to the variation of k_{dep} with $\Delta G^0_{\mathrm{dep}}$.

To estimate $\Delta G^0_{\mathrm{dep}}$, the reduction potential $E_{1/2}$ of the quinone was measured in the aprotic solvents used. The results are compiled in Table 1. We found that $E_{1/2}$ is well describable by a Born equation, $E_{1/2} = E_\infty - \mathrm{m}/\varepsilon_r$ (m = 4.62 V, $E_\infty = -0.792$ V, rms deviation 0.04 V). The oxidation potentials of triethylamine cannot be specified precisely, because aliphatic amines in aprotic solvents are irreversible redox systems[13]. However, the molecular radii of the amine and the quinone, as calculated from molar masses and densities[14], are very similar (3.8 and 3.9 Å). Their hydrodynamic radii are also expected to be comparable, because solvation numbers n of singly charged large ions in aprotic solvents are generally small ($n \lesssim 2$), and n is a little higher for cations than for anions[11], which should be partly compensated by the slightly smaller size of the aminium cation. Hence, $|m|$ should be very similar in both cases. A reasonable estimate of $\Delta G^0_{\mathrm{dep}}$ can thus be obtained by using twice the value of m and taking $\Delta G^0_{\mathrm{dep}}$ in acetonitrile as a reference. For the sensitizer anthraquinone, $\Delta G^0_{\mathrm{dep}}$ amounts to -82 kJ/mol in that solvent ($\varepsilon_r = 36.0$). With the above-mentioned threshold value of $\Delta G^0_{\mathrm{dep}}$, an increase of the driving force by 45 kJ/mol at maximum should thus be sufficient for the change of polarization patterns. As is evident from the equation for $E_{1/2}$, this can be effected by using pyridine as the solvent ($\varepsilon_r = 12.3$); Fig. 3 shows that this is indeed in accordance with the experimental observation.

Table 1. Reduction potential $-E_{1/2}$ of 9,10-anthraquinone in the aprotic solvents used in this work; the values of ε_r have been taken from ref.[11]

Solvent	ε_r	$-E_{1/2}$ [V] (versus SCE)
Toluene	2.38	[a]
Chloroform	4.67	1.764
1,2-Dimethoxyethane	7.00	1.500
Dichloromethane	8.93	1.317
Pyridine	12.30	1.134
Cyclohexanone	16.20	0.995
Acetone	20.56	0.970
Acetonitrile	35.94	0.938
Dimethyl sulfoxide	46.45	0.918

[a] Not measurable.

A global fit curve (hyperbolic tangent) taking into account the data sets of the measurements with different sensitizers as well as those in different solvents has been included in the two diagrams. From the good agreement with the experimental values, we conclude that a quantitative explanation of both sensitizer dependence and solvent dependence of CIDNP in these amine photoreactions is provided by a single key parameter, the free enthalpy of in-cage proton transfer $\Delta G^0_{\mathrm{dep}}$.

Experimental

Triethylamine and the sensitizers were obtained commercially in p.a. quality. For further purification, the amine was doubly distilled under N_2 at reduced pressure; the sensitizers were sublimed twice in vacuo. The solvents for the electrochemical measurements were of spectroscopic grade (Aldrich) and used as received. Perdeuterated solvents (minimum degree of deuteration 99.5%) were employed for all CIDNP experiments. Prior to use, they were dried over molecular sieves.

The concentration of triethylamine was 5×10^{-2} M in all CIDNP measurements. Sensitizer concentrations were chosen to give an absorbance of the samples of about 1.0 at the excitation wavelength. To exclude moisture, the samples were prepared in an inert atmosphere. Oxygen was removed by bubbling dry N_2 through the solutions. The NMR tubes were then sealed.

CIDNP experiments were carried out with a Bruker WM-250 NMR spectrometer equipped with a special probe allowing side-on illumination of the samples[15]. The timing of all experiments was provided by a homemade pulse programmer. For data acquisition and processing, the apparatus was interfaced to an 80486-based multitasking workstation equipped with a Keithley AD converter. An excimer laser (Lambda Physik EMG 101) operating at λ = 308 nm served 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[16]. Ten laser shots with a repetition rate of 60 Hz were used per acquisition. Background-free CIDNP spectra were recorded by means of a special pulse sequence described elsewhere[16].

Redox potentials were determined with a polarograph (Metrohm 506) operating in differential pulse mode. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. Ferrocene/ferrocinium was employed as inner standard. To facilitate comparison with earlier[2] measurements, the values obtained against this reference couple were recalculated versus SCE by using a constant shift of 0.39 V.

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