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CIDNP Determination of the Rate of In-Cage Deprotonation of the Triethylamine Radical Cation

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CIDNP (chemically induced dynamic nuclear polarization) effects in the sensitized photoreactions of triethylamine DH (sensitizers A, 9,10-anthraquinone and 2,7-dinitrofluorenone) are investigated in a series of aprotic solvents of widely varying relative permittivity ϵ, including mixtures of acetonitrile and chloroform. The dependence of the polarization pattern, that is, the relative polarization intensities of the olefinic α- and β-protons in the reaction product *N*,*N*-diethylvinylamine, on ϵ is studied quantitatively by evaluating the polarization ratio *r* of these protons. The factor responsible for the change of the polarization pattern is the rate, relative to the kinetic window of CIDNP, of in-cage deprotonation of the triethylamine radical cation by the sensitizer radical anion (rate constant k_{dep}), which converts the initially formed radical ion pair $\overline{A^{\bullet -}DH^{\bullet +}}$ into a neutral radical pair $\overline{AH^{\bullet}D^{\bullet}}$. A theory of pair substitution taking place solely during encounters of the radicals is presented. Based on this, an expression for the dependence of *r* on k_{dep} is derived, which in turn allows the extraction of k_{dep} from the experimentally observed polarization ratio. The accessible range of k_{dep} in these systems is from about 10^8 to about 10^{10} M^{-1} s^{-1}.

The radical cation $DH^{\bullet +}$ and the α-amino alkyl radical $D^{\bullet}$ of a tertiary aliphatic amine form a conjugate acid−base pair[1]

$$DH^{\bullet +} \rightleftharpoons D^{\bullet} + H^{+} \tag{1}$$

For the triethylamine radical cation, the pK_a value is 5.7, as estimated by a thermodynamic cycle.[2]

The deprotonation of $DH^{\bullet +}$ at carbon to give $D^{\bullet}$ is a key step in photochemical hydrogen abstractions from the amine DH by a sensitizer A, for example, a carbonyl compound.[3] Although such abstractions appear to be one-step processes when slow detection methods are used, the intermediacy of the radical cation

$$^{*}A + DH \rightarrow A^{\bullet -} + DH^{\bullet +} \rightarrow AH^{\bullet} + D^{\bullet} \tag{2}$$

is revealed when the time resolution of the detection system is increased.[4]

CIDNP[5] (chemically induced dynamic nuclear polarization) spectroscopy is a versatile tool for the investigation of reactions involving radicals. The CIDNP effect relies on the interplay of electron-spin selective chemical reactivity and nuclear-spin selective intersystem crossing in a magnetic field: Radical pairs are generated with the electron-spin multiplicity of their precursors, triplet for our sensitizers. The exchange interaction locks a pair in its multiplicity as long as the radicals reside near each other but becomes negligible once diffusion has separated them by a few molecular diameters. While the two radicals diffuse in this regime, their initially pure spin state evolves into a superposition state by differential precession of the uncoupled electron spins. The nuclear spins come into play through the hyperfine interaction, which causes the evolution rate to depend on the spin states of all nuclei in the two radicals. A diffusive excursion terminates if the two radicals reencounter. As they approach each other, the exchange interaction becomes effective once again and projects the superposition state onto singlet and triplet. A chemical reaction finally differentiates between these states, usually in the way that it is feasible for a singlet pair only, whereas a triplet pair has to separate again and repeat the process. Ultimately, a pair of initial multiplicity triplet has either undergone intersystem crossing and reacted to give a cage product of the two radicals or separated permanently, with the escaped radicals ending up by other termination reactions that do not involve the respective partner.

The participation of the nuclear spins in this process effects their sorting: Starting with triplet precursors, those nuclear spin states that increase the intersystem crossing rate are enriched in the cage products, and those that decrease it are enriched in the escape products. This is monitored by NMR spectroscopy, where the deviations from the equilibrium populations manifest themselves as anomalous line intensities.

Probably the most important feature of CIDNP is that the observables are generated at an intermediate stage of the reaction but detected in the final diamagnetic products. This has two implications. On one hand, the so-called polarization pattern,[6] the relative polarization intensities of the different nuclei in the products, reflects the distribution of hyperfine coupling constants in the radicals and is thus equivalent to the EPR spectrum of the intermediates; however, CIDNP is sensitive to faster processes than is EPR because the effect arises during the spin-correlated life of the radical pairs (nanosecond to subnanosecond). On the other hand, the polarizations can be regarded as labels that are attached at the paramagnetic stage; this makes it possible to trace secondary reactions of the radicals[5d] and even to distinguish between different reaction

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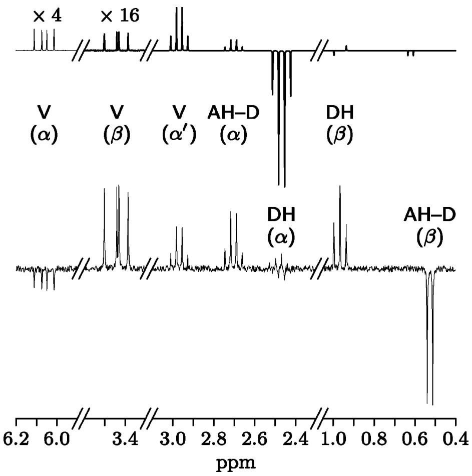
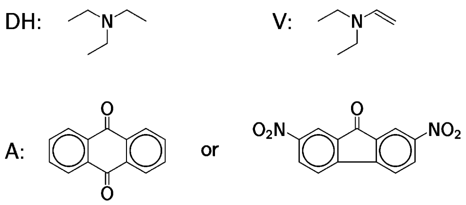


Figure 1. Background-free CIDNP signals in the photoreactions of triethylamine with the sensitizer 9,10-anthraquinone. Top trace, solvent acetonitrile (polarizations from radical ions only); bottom trace, solvent chloroform (polarizations from neutral radicals only). For an assignment of the resonances and further explanation, see text.

SCHEME 1



pathways that lead to the same product,[7] which the present work also exploits.

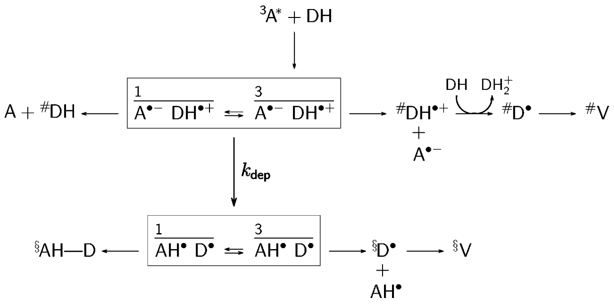
CIDNP spectroscopy has already been used to study several aspects of the sensitized hydrogen abstractions from triethylamine.[1,2,6,8,9] In this paper, we extend our previous semiquantitative investigations of the solvent dependence[9] and present a treatment that permits obtaining the rate constant of in-cage deprotonation from the change of the polarization pattern.

Results and Discussion

CIDNP Effects and Mechanism. The sensitized photoreactions of triethylamine are accompanied by characteristic ^{1}H-CIDNP effects that depend both on the sensitizer[2] and on the solvent.[8,9] The two limiting situations are displayed in Figure 1; in both cases, polarizations are found for the starting amine DH, a combination product of amine and sensitizer AH−D, and a secondary reaction product *N*,*N*-diethylvinylamine V. The chemical structures of DH, V, and the two sensitizers A studied in this work, 9,10-anthraquinone and 2,7-dinitrofluorenone, are shown in Scheme 1.

When carbonyl sensitizers A with reduction potentials more positive than about −1.2 V versus SCE (i.e., the two sensitizers investigated herein) are employed in a polar solvent,[2] CIDNP exclusively stems from amine radical cations $DH^{\bullet +}$ (top trace of Figure 1): Those protons of the products that were the α-protons in $DH^{\bullet +}$ are strongly polarized, and those that were the *β*-protons are very weakly polarized only, with the same polarization phase. This polarization pattern reflects the spin density distribution in $DH^{\bullet +}$.[6] In contrast, with carbonyl sensitizers that are more difficult to reduce[2] or generally, even with the above-mentioned two sensitizers, in a nonpolar solvent,[9] CIDNP can be exclusively traced back to α-amino alkyl radicals $D^{\bullet}$ (bottom trace of Figure 1): Both α- and *β*-protons are strongly polarized with opposite phases, and the α′-protons are polarized more weakly, with the same phase as the *β* protons, which corresponds to the characteristic distribution of hyperfine coupling constants in $D^{\bullet}$.[6]

SCHEME 2



Because CIDNP arises in radical pairs only, the described two patterns indicate that the polarizations are generated in radical ion pairs and in neutral radical pairs, respectively. The reaction mechanism shown in Scheme 2 explains the CIDNP effects. The two kinds of radical pairs have been enclosed in boxes; spin correlation is denoted by an overbar, with the spin multiplicity given above the bar. The polarization pattern resulting from radical ions is symbolized by a #-mark, and that resulting from neutral radicals by a §-mark.

The primary step is electron-transfer quenching of the sensitizer triplet ^{3}A by the amine to give spin-correlated radical ion pairs $^{3}\overline{A^{\bullet -}DH^{\bullet +}}$, where $A^{\bullet -}$ is the radical anion of the sensitizer. Because spin is conserved during chemical reactions, the pairs are exclusively formed in the triplet state.

Intersystem crossing driven by Zeeman and hyperfine interactions sorts the nuclear spins in the usual way during diffusive excursions of the radicals. Upon reencounter, pairs that have reached the singlet state can undergo reverse electron transfer to regenerate the starting materials; this transfers the characteristic polarization pattern of the amine radical cation to DH. For thermodynamic reasons, this pathway is not open for pairs that have remained in the triplet state. If the radicals constituting such a pair separate permanently, they remain as free radicals, for which $DH^{\bullet +}$ bears the same polarization pattern as the cage product DH but with all phases inverted.

The free radical cations are deprotonated by surplus starting amine[2] to give neutral radicals $D^{\bullet}$. The final product V is most likely formed by a disproportionation of two such radicals, one abstracting a hydrogen atom from the *β*-position of the other, although addition−elimination pathways involving a sensitizer molecule are also conceivable.[2] All these secondary reactions do not involve radical *pairs*, so they cannot generate new polarizations but simply transfer the polarization pattern present in free $DH^{\bullet +}$ to $D^{\bullet}$ and, ultimately, to V.

A third reaction possibility of the radical ion pairs $\overline{A^{\bullet -}DH^{\bullet +}}$ is in-cage proton transfer from the amine radical cation to the radical anion of the sensitizer. This step is equally feasible for singlet and triplet pairs and transforms a radical ion pair into a neutral radical pair $\overline{AH^{\bullet}D^{\bullet}}$ of the same spin multiplicity. Nuclear spin sorting during diffusive excursions of the neutral pairs then generates the polarization pattern characteristic for $D^{\bullet}$. This appears in the combination product AH−D, the formation of which is feasible in the singlet state only, and (with all phases inverted) in the free radicals $D^{\bullet}$, hence, ultimately in V.

CIDNP arises within a kinetic window[10] determined by the rate of intersystem crossing and that of permanent separation (escape) of the radicals forming a pair. The rate of in-cage

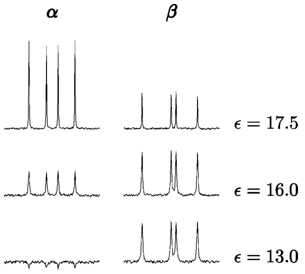


Figure 2. Polarizations of the olefinic α- and β-protons of the product V in the photoreactions of triethylamine with the sensitizer 9,10-anthraquinone in mixtures of acetonitrile and chloroform. Shown are the absolute CIDNP intensities for different relative permittivities ϵ of the medium.

deprotonation (rate constant k_{dep}), relative to that window, decides which polarization pattern is observed: If deprotonation is much slower than escape, no neutral radical pairs are formed at all, and all polarizations stem from the radical ion pairs (Figure 1, top). If, on the other hand, deprotonation is fast on the CIDNP time scale, the radical ion pairs are converted into neutral radical pairs before CIDNP can develop in the former, and all polarizations are generated in the neutral pairs (Figure 2, bottom). Finally, if the deprotonation falls within the kinetic window of CIDNP, a superposition of polarizations results.

In the following, we will show how k_{dep} can be obtained from the observed polarization patterns. For this, we concentrate on the product V, specifically its olefinic protons, for two reasons. First, their characteristic ABX resonances (H^{α} around 6.05 ppm, H^{β} around 3.45 ppm) fall in spectral regions completely free from other signals, allowing reliable integration without baseline problems even when they are very weak (compare Figure 1, top trace). Second, V is the only product in this system that is exclusively formed from free radicals (whereas, for instance, DH can result from disproportionation of free $D^{\bullet}$ as well as from reverse electron transfer of $^{1}\overline{A^{\bullet -}DH^{\bullet +}}$). The evaluation procedure mainly relies on the polarization *ratio* of the α- and β-protons of V, thus completely avoiding problems associated with measuring absolute CIDNP intensities.[11]

To change k_{dep}, we have to modify the thermodynamics of in-cage deprotonation. In previous studies, we used different sensitizers for this purpose,[2] which amounted to a yes/no decision between the polarization pattern of the radical ion and the neutral radical, and different aprotic solvents,[9] which allowed a rather coarse-grained sampling of the transition regime between these two extremes. In this work, we additionally use mixtures of acetonitrile and chloroform, by which we can smoothly vary the relative permittivity of the medium and thus fine-tune the free energy of in-cage deprotonation. As will be shown below, we found no evidence for preferential solvation in these systems.

Figure 2 displays examples of the signals of V in the transition regime between the two limiting cases shown in Figure 1. It is seen that slight changes of the relative solvent permittivity have a pronounced influence on the polarization ratio of the observed protons.

Theory of Pair Substitution upon Encounter. The transformation of radical pairs into other radical pairs on the CIDNP time scale is called pair substitution. Theoretical descriptions[12] only exist for pair substitution during diffusive excursions, that is, reactions of one of the radicals (such as fragmentations of rearrangements) without involvement of the other. The situation in the present chemical system is very different because the reaction is between the two radicals of the pair, and pair substitution can thus only occur during an encounter.

We treat the problem with the Freed–Pedersen reencounter formalism.[13] The density matrix $\underline{\rho}(t)$ of the first pair RP_1 (the radical ion pair in our example) is written as a vector with the components singlet population, triplet population, and phase correlation,

$$\underline{\rho}(t) = \begin{pmatrix} \rho_{SS} \\ \rho_{TT} \\ i(\rho_{TS} - \rho_{ST}) \end{pmatrix}(t) \qquad (3)$$

The fourth component of the density matrix, electron spin polarization $(\rho_{ST} + \rho_{TS})$, is omitted because for CIDNP it plays a negligible role only.

During a diffusive excursion, population difference and phase correlation are mixed. This evolution of $\underline{\rho}$ during an excursion is described by multiplication from the left with a mixing matrix $\underline{M}$,

$$\underline{M} = \begin{pmatrix} (p+c)/2 & (p-c)/2 & -s/2 \\ (p-c)/2 & (p+c)/2 & s/2 \\ s & -s & c \end{pmatrix} \qquad (4)$$

The quantities p, c, and s entering eq 4 are derived from the reencounter function $f(t,d|r_0)$, which is the probability density that a radical pair starting a diffusive excursion at interradical separation r_0 and time zero will reencounter at distance d and time between t and $t + dt$: p is the total probability of a first reencounter,

$$p = \int_0^{\infty} f(t,d|r_0)\,\mathrm{d}t \qquad (5)$$

and s and c are the Fourier sine and cosine transforms of $f(t,d|r_0)$ at the intersystem crossing frequency, which is determined by the magnetic parameters of the radicals. Numerical expressions are known both for neutral radical pairs[14] and for radical ion pairs[15] but will not be given here because they are unnecessary for the derivations that follow.

Upon reencounter, RP_1 will undergo two kinds of geminate reactions. The first yields nonradical products, and the second transforms RP_1 into another radical pair RP_2 (the neutral radical pair in our case). Each of these processes is modeled by multiplication of $\underline{\rho}$ from the left with a diagonal matrix, $\underline{\lambda}$ and $\underline{\kappa}$, respectively. Starting with an initial density matrix $\underline{\rho}_0$, and summing up the contributions of multiple reencounters in the usual way, one obtains for the total amount of geminate product F^* from RP_1, assuming that only singlet pairs can form nonradical products,

$$F^* = (1\ 0\ 0)\underline{\lambda}[\underline{E} - \underline{M}(\underline{E} - \underline{\lambda} - \underline{\kappa})]^{-1}\underline{\rho}_0 = (1\ 0\ 0)\underline{\lambda}\ \underline{X}\ \underline{\rho}_0 \qquad (6)$$

where $\underline{E}$ is the unit matrix and the exponent -1 denotes matrix inversion.

Let the density matrix of RP_1 at the ith encounter be $\underline{\rho}_i$. This encounter produces a certain amount of pairs RP_2 with density matrix $\underline{\rho}'_i$,

$$\underline{\rho}'_i = \underline{\kappa}\ \underline{\rho}_i \qquad (7)$$

which in turn undergo a series of diffusive excursions and reencounters. The evolution of $\underline{\rho}'$ during an excursion and the geminate reactions of RP_2 upon reencounter are described in the same way as for RP_1, using a mixing matrix $\underline{M}'$ and a reaction matrix $\underline{\lambda}'$. By summing up, one obtains for theamount of geminate product $F_i'^*$

$$F_i'^* = (1\ 0\ 0)\underline{\lambda}'[\underline{E} - \underline{M}'(\underline{E} - \underline{\lambda}')]^{-1}\underline{\rho}_i' = (1\ 0\ 0)\underline{\lambda}'\underline{X}'\underline{\rho}_i' \qquad (8)$$

A final summation over all encounters of RP_1 yields the total amount of geminate product F'^* formed from the initial density matrix via the reaction sequence $RP_1 \rightarrow RP_2$:

$$F'^* = (1\ 0\ 0)\underline{\lambda}'\underline{X}'\underline{\kappa}\ \underline{X}\ \underline{\rho}_0 \qquad (9)$$

The total yield G^* of free radicals from both types of radical pairs, which is detected in our experiments, is given by

$$G^* = 1 - (F^* + F'^*) \qquad (10)$$

In the following, we consider pure triplet precursors. As usual, we also assume that initially no phase correlation is present, so

$$\underline{\rho}_0 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad (11)$$

With this choice of $\underline{\rho}_0$, only a few of the elements of $\underline{X}$ and $\underline{X}'$ are important. We get

$$F^* = \underline{\lambda}_{11}\underline{X}_{12} \qquad (12)$$

$$F'^* = \underline{\lambda}'_{11}(\underline{\kappa}_{11}\underline{X}'_{11}\underline{X}_{12} + \underline{\kappa}_{22}\underline{X}'_{12}\underline{X}_{22} + \underline{\kappa}_{33}\underline{X}'_{13}\underline{X}_{32}) \qquad (13)$$

The three sum terms on the right-hand side of eq 13 describe transfer from RP_1 to RP_2 of singlet population, triplet population, and phase correlation, respectively.

In pair substitution during a diffusive excursion, all components of the density matrix are completely transferred from RP_1 to RP_2. The situation is very different for pair substitution at an encounter: not only are the probabilities for the transfer of populations unequal for singlet and triplet pairs but this discrepancy also results in a loss of phase correlation.

Upon encounter, a pair RP_1 in the singlet state will form diamagnetic products (in our example, undergo reverse electron transfer to regain the starting materials) with probability ${}^1\lambda$ and will be converted into RP_2 with probability ${}^1\kappa$. As usual, a reaction of the triplet state of RP_1 to give nonradical products is taken to be impossible, but pair substitution $RP_1 \rightarrow RP_2$ can occur with probability ${}^3\kappa$. Even though the rate constants of pair substitution (proton transfer from $DH^{\bullet+}$ to $A^{\bullet-}$ in our case) are spin independent, ${}^1\kappa$ and ${}^3\kappa$ necessarily differ (${}^1\kappa \ll {}^3\kappa$) because for the singlet state of RP_1 the existence of an efficient parallel reaction greatly decreases the probability of pair substitution.

Because the density matrix $\underline{\rho}$ must obey the relationship[16]

$$\mathrm{Tr}(\underline{\rho}^2) \leq [\mathrm{Tr}(\underline{\rho})]^2 \qquad (14)$$

where Tr denotes trace formation, the phase correlation remaining in RP_1 after the encounter cannot exceed the fraction $[(1 - {}^1\lambda - {}^1\kappa)(1 - {}^3\kappa)]^{1/2}$ of the phase correlation before the encounter. In the absence of pair substitution, this reduces to the known[5c] expression $\sqrt{1-\lambda}$, where λ is the geminate reaction probability of a singlet pair. Similarly, the maximum fraction of the phase correlation that can be transferred to RP_2 is equal to the geometric mean $[{}^1\kappa{}^3\kappa]^{1/2}$. If there is no imbalance of the reaction probabilities, as in pair substitution during diffusive excursions, the fractions of the populations and of the phase correlation transferred (or those remaining) are seen to become equal.

The probabilities ${}^1\lambda$, ${}^1\kappa$, and ${}^3\kappa$ are interdependent, and it is convenient to express them in terms of two independent quantities, the singlet reaction probability *in the absence of pair substitution* λ and the triplet reaction probability ${}^3\kappa$, which for simplicity we denote as κ. With the rate constants k_{dia}, k_{ps}, and k_{sep} of formation of diamagnetic products, pair substitution, and separation of the radicals, we have

$${}^1\lambda = \frac{k_{dia}}{k_{dia} + k_{ps} + k_{sep}} \qquad (15)$$

$${}^1\kappa = \frac{k_{ps}}{k_{dia} + k_{ps} + k_{sep}} \qquad (16)$$

$$\kappa = {}^3\kappa = \frac{k_{ps}}{k_{ps} + k_{sep}} \qquad (17)$$

$$\lambda = \frac{k_{dia}}{k_{dia} + k_{sep}} \qquad (18)$$

which can be rearranged to give

$${}^1\lambda = \lambda\frac{1 - \kappa}{1 - \kappa\lambda} \qquad (19)$$

$${}^1\kappa = \kappa\frac{1 - \lambda}{1 - \kappa\lambda} \qquad (20)$$

The matrices $\underline{\lambda}$ and $\underline{\kappa}$ are thus

$$\underline{\lambda} = \begin{pmatrix} \lambda\frac{1 - \kappa}{1 - \kappa\lambda} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 - \sqrt{\frac{1 - \lambda}{1 - \kappa\lambda}} \end{pmatrix} \qquad (21)$$

$$\underline{\kappa} = \begin{pmatrix} \kappa\frac{1 - \lambda}{1 - \kappa\lambda} & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & \kappa\sqrt{\frac{1 - \lambda}{1 - \kappa\lambda}} \end{pmatrix} \qquad (22)$$

Hence, the maximum phase correlation remaining in RP_1 and that being transferred to RP_2 are seen to be $\sqrt{(1-\lambda)/(1-\kappa\lambda)}$ times $(1 - \kappa)$ and times κ, respectively. The expression $\sqrt{(1-\lambda)/(1-\kappa\lambda)}$ decreases monotonically with increasing λ unless κ is unity; in the latter case, however, a significant buildup of phase correlation is unlikely because RP_1 will be transformed into RP_2 at the first encounter. The loss of phase correlation by the term $\sqrt{(1-\lambda)/(1-\kappa\lambda)}$ is expected to be significant because λ usually lies very near to unity. Therefore, it can be concluded that for pair substitution at encounters transfer of phase correlation from RP_1 to RP_2 should be negligible, in strong contrast to pair substitutions during diffusive excursions, where it gives rise to the so-called cooperative effects or memory effects.[12]

Apart from this loss of phase correlation by the chemical reactions of RP_1, the stochastic motion of the radicals within the exchange region also destroys phase correlation by randomizing it with electron spin polarization. Numerical simulations indicate that for radical ion pairs this occurs extremely rapidly.[17] For the further calculations we, therefore, assume that the strong-exchange case[5b] (complete loss of phase correlation upon encounter) holds and write the matrices $\underline{\lambda}$ and $\underline{\kappa}$ accordingly

$$\underline{\lambda} = \begin{pmatrix} \lambda\dfrac{1-\kappa}{1-\kappa\lambda} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \underline{\kappa} = \begin{pmatrix} \kappa\dfrac{1-\lambda}{1-\kappa\lambda} & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{23}$$

As it must for the strong-exchange case, the last term of eq 13, which describes phase correlation of the radical ion pairs being converted into polarization of the neutral radical pairs, becomes zero with this form of $\underline{\kappa}$. Further simplification is possible by assuming a reactivity of 1 for each singlet pair, that is, ${}^1\lambda + {}^1\kappa = (\kappa + \lambda - 2\kappa\lambda)/(1 - \kappa\lambda) = 1$ and $\underline{\lambda}'_{11} = 1$ (which results in $\underline{X}'_{11} = 1$), so

$$G^* = 1 - \underline{X}_{12} - \kappa\underline{X}'_{12}\underline{X}_{22} \tag{24}$$

$\underline{X}_{12}$ and $\underline{X}_{22}$ can now be written explicitly, using eqs 4 and 23 and carrying out the matrix inversion. The result is

$$G^* = \frac{1 - (1-\kappa)p + \kappa\underline{X}'_{12}}{1 - (1-\kappa)(p + c)/2} \tag{25}$$

The polarizations P that are detected are the differences of G^* for those pairs of nuclear spin states between which NMR transitions occur; for a CIDNP net effect, a description by a two-state model with two effective spin states is sufficient. Each such spin state is associated with an intersystem crossing frequency ν of the radical ion pair and another one for the neutral radical pair, which enter the quantities c and $\underline{X}'_{12}$, respectively. Under our conditions, that is, in solvents of low viscosity, an expansion of c and $\underline{X}'_{12}$ to first order in ν is permissible;[13c] in the denominator, the terms c can be replaced by p after the differences of G^* have been formed in this way. Finally, the limiting polarizations P_{∞,RP_1} and P_{∞,RP_2} are introduced by letting $\kappa \rightarrow 0$ (polarizations from RP_1 only) and $\kappa \rightarrow 1$ (exclusive polarizations from RP_2). The result no longer contains an explicit dependence on the magnetic parameters,

$$P = \frac{(1-\kappa)(1-p)P_{\infty,\mathrm{RP}_1} + \kappa P_{\infty,\mathrm{RP}_2}}{1 - (1-\kappa)p} \tag{26}$$

Derivation of the Solvent Dependence of the Polarization Pattern. The denominator of eq 26 cancels when the ratio of polarizations of the α- and β-protons in the vinylamine, $P(\alpha)/P(\beta)$, is formed,

$$P(\alpha)/P(\beta) = \frac{(1-\kappa)(1-p)P_{\infty,\mathrm{ri}}(\alpha) + \kappa P_{\infty,\mathrm{nr}}(\alpha)}{(1-\kappa)(1-p)P_{\infty,\mathrm{ri}}(\beta) + \kappa P_{\infty,\mathrm{nr}}(\beta)} \tag{27}$$

where the subscripts “ri” and “nr” denote the radical ion pair and the neutral radical pair. It is convenient to transform the absolute polarization ratio $P(\alpha)/P(\beta)$ to a relative polarization ratio r, which ranges from 0 to 1. This is effected by introducing the limiting polarization ratios at high and low ϵ (see Figure 1), $R_{\infty,\mathrm{ri}}$ and $R_{\infty,\mathrm{nr}}$.

$$r = \frac{P(\alpha)/P(\beta) - P_{\infty,\mathrm{nr}}(\alpha)/P_{\infty,\mathrm{nr}}(\beta)}{P_{\infty,\mathrm{ri}}(\alpha)/P_{\infty,\mathrm{ri}}(\beta) - P_{\infty,\mathrm{nr}}(\alpha)/P_{\infty,\mathrm{nr}}(\beta)} = \frac{P(\alpha)/P(\beta) - R_{\infty,\mathrm{nr}}}{R_{\infty,\mathrm{ri}} - R_{\infty,\mathrm{nr}}} \tag{28}$$

Inserting eq 28 into eq 27 and rearranging, one arrives at

$$1/r = 1 + \frac{\kappa}{1-\kappa} \cdot \frac{1}{1-p} \cdot Q \tag{29}$$

where Q is the ratio of limiting absolute polarizations from the neutral radical and the radical cation for the *same* proton (β); Q can be expressed by the analogous ratio for the α-proton as well:

$$Q = \frac{P_{\infty,\mathrm{nr}}(\beta)}{P_{\infty,\mathrm{ri}}(\beta)} = \frac{P_{\infty,\mathrm{nr}}(\alpha)}{P_{\infty,\mathrm{ri}}(\alpha)} \cdot \frac{R_{\infty,\mathrm{ri}}}{R_{\infty,\mathrm{nr}}} \tag{30}$$

Because intersystem crossing of the radical pairs can be neglected within the exchange region,[13] the probability κ is given by the competition of in-cage proton transfer (rate constant k_{dep}) and separation of the radicals (rate constant k_{sep}),

$$\kappa = \frac{k_{\mathrm{dep}}}{k_{\mathrm{dep}} + k_{\mathrm{sep}}} \tag{31}$$

From eqs 29 and 31, one thus finds that kinetic information about the deprotonation can be obtained from the relative polarization ratio according to

$$k_{\mathrm{dep}} = k_{\mathrm{sep}}(1-p) \cdot \frac{1}{Q} \cdot \left(\frac{1}{r} - 1\right) \tag{32}$$

For given starting distance r_0 and encounter distance d, the recombination probability p of a radical ion pair is

$$p = \frac{1 - \exp(r_c/r_0)}{1 - \exp(r_c/d)} \tag{33}$$

where the Onsager radius r_c,

$$r_c = \frac{z_1 z_2 e^2}{4\pi\epsilon_0 kT} \cdot \frac{1}{\epsilon} \tag{34}$$

is negative for oppositely charged ions, as in our case.

The rate constant k_{sep} refers to separation of the pair to r_0 because at that distance a new diffusive excursion starts. An expression for k_{sep} can be derived in the following way. First, the rate constant k_{rec} of a diffusion-controlled reaction of ions starting at distance r_0 is obtained by the usual[18] treatment. The result is

$$k_{\mathrm{rec}} = \frac{8RT}{3\eta} \cdot \frac{r_c/d}{\exp[r_c(1/d - 1/r_0)] - 1} \tag{35}$$

For $r_0 \rightarrow \infty$, eq 35 is seen to become the well-known Debye equation.[18] The equilibrium constant K for the reaction of the contact ion pair (separation d) to an ion pair separated by r_0

$$(A + B)_d \overset{K}{\rightleftharpoons} (A + B)_{r_0} \tag{36}$$

follows from the electrostatic interaction, assuming that entropy changes can be neglected and ΔH can be identified with ΔU,

$$K = \exp(-r_c/r_0) \tag{37}$$

From eqs 35 and 37, k_{sep} is found to be

$$k_{\mathrm{sep}} = \frac{8RT}{3\eta} \cdot \frac{r_c/d}{1 - \exp[-r_c(1/d - 1/r_0)]} \tag{38}$$

The unknown quantity r_0 conveniently drops out from the calculations because, as eq 32 shows, k_{dep} depends on the product $k_{\mathrm{sep}}(1-p)$,

$$k_{\mathrm{sep}}(1-p)=\frac{8RT}{3\eta}\cdot\frac{r_{\mathrm{c}}/d}{1-\exp(-r_{\mathrm{c}}/d)}=k_{\mathrm{diff}}\cdot\zeta(\epsilon) \quad (39)$$

where the solvent polarity enters through the known function $\zeta(\epsilon)$ and k_{diff} is the Smoluchowski rate constant for a diffusion controlled reaction of uncharged species.

Inserting eq 39 into eq 32 and rearranging, we obtain

$$r=\left[1+\frac{k_{\mathrm{dep}}}{k_{\mathrm{diff}}}\cdot Q\cdot\frac{1}{\zeta(\epsilon)}\right]^{-1} \quad (40)$$

The observable deprotonation rate constant k_{dep} is related to the true deprotonation rate constant k'_{dep} in the usual way,

$$k_{\mathrm{dep}}=\frac{k'_{\mathrm{dep}}k_{\mathrm{diff}}}{k'_{\mathrm{dep}}+k_{\mathrm{diff}}}=\frac{k'_{\mathrm{dep}}}{1+k'_{\mathrm{dep}}/k_{\mathrm{diff}}} \quad (41)$$

which transforms eq 40 into

$$r=\left[1+\frac{1}{1+k_{\mathrm{diff}}/k'_{\mathrm{dep}}}\cdot Q\cdot\frac{1}{\zeta(\epsilon)}\right]^{-1} \quad (42)$$

To describe the polarity dependence, we finally write the true deprotonation rate constant k'_{dep} as

$$k'_{\mathrm{dep}}=k'_{\mathrm{dep},\infty}\cdot\exp(+b/\epsilon) \quad (43)$$

with positive b, where $k'_{\mathrm{dep},\infty}$ is the limiting rate constant in a solvent of infinitely high polarity, that is, the lowest possible rate constant. Equation 43 presumes a linear free-energy relationship for the deprotonation. The polarity dependence of the polarization ratio follows from eqs 42 and 43,

$$r=\left[1+\frac{1}{1+a\exp(-b/\epsilon)}\cdot\frac{Q}{\zeta(\epsilon)}\right]^{-1} \quad (44)$$

where a,

$$a=\frac{k_{\mathrm{diff}}}{k'_{\mathrm{dep},\infty}} \quad (45)$$

b (eq 43), and Q (eq 30) are independent of the solvent polarity.

Evaluation of the Experimental Data. To reduce the number of fit parameters in eq 44, we determined the quantity Q independently. For this, absolute CIDNP intensities of different samples have to be compared. Any difference between these experiments in the intensity of the absorbed light will lead to a corresponding error in Q, so care was taken to minimize this effect; still, a significantly larger scatter of the data than in the case of the polarization ratio r is to be expected. Although it would be sufficient in principle to measure the absolute polarizations in a very polar and in a very nonpolar solvent, we performed a series of experiments in mixtures of acetonitrile and chloroform and fitted the results because this yields a better error estimate. From Figure 2, it is evident that Q lies near 1; we chose the α-proton for evaluation because its polarization changes more strongly with ϵ than does that of the β-protons.

The procedure adopted does not rely on the dependence of κ and p on ϵ: By inserting eq 31 into eq 32, κ can be expressed by Q and r. Inserting this result into eq 26 and using eq 30, one obtains the relationship between absolute polarization $P(\alpha)$ and polarization ratio r.

$$P(\alpha)=P_{\infty,\mathrm{nr}}(\alpha)+\frac{[P_{\infty,\mathrm{ri}}(\alpha)-P_{\infty,\mathrm{nr}}(\alpha)]r}{r+(1-r)\dfrac{P_{\infty,\mathrm{ri}}(\alpha)}{P_{\infty,\mathrm{nr}}(\alpha)}\cdot\dfrac{R_{\infty,\mathrm{nr}}}{R_{\infty,\mathrm{ri}}}} \quad (46)$$

As the limiting polarization ratio $R_{\infty,\mathrm{nr}}/R_{\infty,\mathrm{ri}}$ is known accurately, the ratio Q can be obtained by fitting eq 46 to the data, with r as the independent variable and the limiting polarizations as fit parameters. The results are displayed in Figure 3.

CIDNP enhancement factors are functions of the solvent viscosity η through their dependence on the interdiffusion coefficient D (they are approximately proportional to $\sqrt{\eta}$).[19] Because acetonitrile and chloroform possess very similar viscosities (0.39 and 0.43cP; both at 295K),[20] this changes Q by 5% only. We further stress that this correction is only necessary for the described method of obtaining Q because this involves, by necessity, measurements in different solvents. Once Q has been determined, no further correction has to be applied even though the variability of η is much larger in the series of solvents used because by definition Q refers to an infinitely polar and an infinitely nonpolar solvent of the same viscosity as the one actually employed. Likewise, no such correction is necessary for r: as D influences the enhancement factors for radical ion pairs and for pairs of neutral radicals in exactly the same way,[15] the effect of the solvent viscosity cancels when the ratios r are formed.

The values of Q with 9,10-anthraquinone and 2,7-dinitrofluorenone are quite similar (0.98 and 1.21); their difference, which is due to the different g-values of the radical anions of these two sensitizers, is not significant given the scatter of the data.

Figure 4 displays the dependence of the observed polarization ratio r on the solvent permittivity ϵ for our two sensitizers; fits of eq 44 to the data have also been included in the figure.

The fits are very well conditioned, because the fit parameters a and b influence r in quite different ways. This is best seen with the procedure used to obtain starting parameters for the nonlinear fit: Calculating the slope of the curves of eq 44 at $r = {}^{1}/_{2}$, inserting the definitions of r and $\zeta(\epsilon)$ and rearranging, one obtains

$$b=\epsilon_{1/2}\left[1+4\epsilon_{1/2}\left(\frac{\partial r}{\partial\epsilon}\right)_{\epsilon_{1/2}}+\frac{r_{\mathrm{c}}(\epsilon_{1/2})}{d}-\zeta(\epsilon_{1/2})\right]/[1-\zeta(\epsilon_{1/2})Q] \quad (47)$$

where $\epsilon_{1/2}$ is the relative permittivity at which r becomes ${}^{1}/_{2}$. The quantity b is thus solely determined by the slope at the midpoint of the curve and the midpoint position. The parameter a then follows from

$$a=\left[\frac{Q}{\zeta(\epsilon_{1/2})}-1\right]\exp\left(+\frac{b}{\epsilon_{1/2}}\right) \quad (48)$$

As Figure 4 shows, for both sensitizers the polarization ratios in the acetonitrile/chloroform mixtures fall on the same curve as those in pure aprotic solvents. From this, it can be concluded that preferential solvation does not play a role for the CIDNP effects in these systems.

Nuclear spin relaxation in the relatively long-lived free radicals distorts the CIDNP intensities in an escape product such as V; the loss of polarization is unequal for the α- and the β-protons because their relaxation rates differ. Our treatment takes this into account (compare eq 27) by expressing all polarization intensities relative to those in a very polar and those in a very nonpolar solvent, $P_{\infty,\mathrm{ri}}$ and $P_{\infty,\mathrm{nr}}$, which already contain

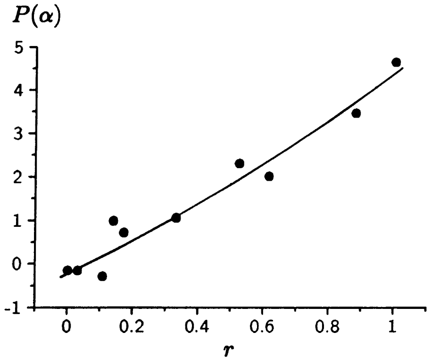


Figure 3. Absolute polarizations $P(\alpha)$ of the α proton of V as functions of the polarization ratio r, sensitizer 9,10-anthraquinone. The vertical scale is valid only for the acquisition parameters used in this particular set of experiments; these parameters were kept constant throughout the series.

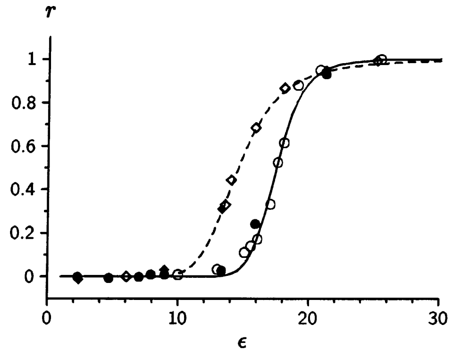


Figure 4. Polarization ratios r (eq 28) as functions of the relative permittivity ϵ of the reaction medium in pure solvents (filled symbols) and in mixtures of acetonitrile and chloroform (open symbols). Circles and solid line, sensitizer 9,10-anthraquinone; diamonds and short-dashed line, sensitizer 2,7-dinitrofluorenone. Pure solvents (ϵ):[21] benzene (2.27), toluene (2.38), chloroform (4.67), dimethoxyethane (7.00), 1,1,2,2-tetrachloroethane (7.90), dichloromethane (8.93), pyridine (13.00), cyclohexanone (16.20), acetone (21.00). The data for acetonitrile (35.94) and dimethyl sulfoxide (46.45) lie on the plateau value ($r = 1$) of the curves but fall outside the range of ϵ shown. Fit parameters for 9,10-anthraquinone, log $a = 8.480$, $b = 302.2$; for 2,7-dinitrofluorenone, log $a = 3.878$, $b = 84.82$.

the relaxation losses. Problems could only arise if the lifetimes of the free radicals $D^{\bullet+}$ and $D^{\bullet}$ were strongly solvent dependent. A dependence on the solvent polarity is not to be expected because neither deprotonation of $D^{\bullet+}$ by surplus amine nor disproportionation of $D^{\bullet}$ involves charge separation or a significant change of molecular size,

$$D^{\bullet+} + DH \rightleftharpoons D^{\bullet} + DH_2^{+} \qquad (49)$$

$$2D^{\bullet} \rightarrow DH + V \qquad (50)$$

and viscosity influences are seen to play no role, as Figure 4 shows: in the high-polarity regime, acetonitrile and dimethyl sulfoxide give the same ratio of polarizations, and in the low-polarity regime, the same holds for the pair dichloromethane and 1,1,2,2-tetrachloroethane; the viscosities of these solvents differ by a factor of 5 and 4, respectively. Hence, the relaxation losses should not influence our results.

The best-fit parameters a and b allow the calculation of k_{dep} according to

$$k_{\mathrm{dep}} = \frac{k_{\mathrm{diff}}}{1 + a\exp(-b/\epsilon)} \qquad (51)$$

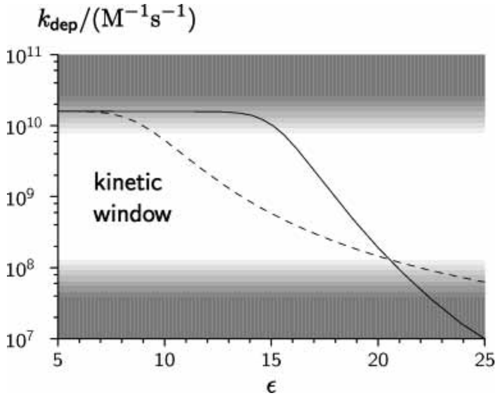


Figure 5. Polarity dependence of the deprotonation rate constants k_{dep}, as obtained from the CIDNP results. Solid line, sensitizer 9,10-anthraquinone; broken line, sensitizer 2,7-dinitrofluorenone. The shaded areas denote the approximate boundaries of the kinetic window of the CIDNP experiments.

With an average η of 0.41cP in the acetonitrile/chloroform mixtures, k_{diff} is estimated to be 1.6×10^{10} $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The results have been displayed in Figure 5. By comparison with Figure 4, the kinetic window of these experiments is seen to span approximately 2 orders of magnitude and to lie near to the diffusion-controlled limit.

We stress that in Figure 5 the continuous functions given by eq 51 have only been used for convenience; the CIDNP determination of k_{dep} can be performed point per point with eq 42 without relying on a specific model of the polarity dependence.

Finally, the deprotonation of the triethylamine radical cation by the sensitizer radical anion is seen to exhibit a much stronger polarity dependence with 9,10-anthraquinone than with 2,7-dinitrofluorenone. This observation is in line with electrochemical results: The reduction potential of 2,7-dinitrofluorenone was found to be a linear function of $1/\epsilon$ with a slope of 1.28 ± 0.08 V, both in pure solvents and in acetonitrile/chloroform mixtures. This is lower by a factor of 3.6 than that for 9,10-anthraquinone, for which we measured[9] a slope of 4.62 ± 0.04 V. The most probable reason is a more extensive delocalization caused by the nitro groups.

The results of this paper illustrate two of the features that make CIDNP spectroscopy unique: First, the inherent time scale of the CIDNP effect provides a kinetic window in a chemically very important range, that is, near diffusion control, against which the rates of radical pair transformations can be gauged. Second, simply by observing a reaction product, one can separate parallel pathways that lead to it and that even involve the same species (the radical cation $DH^{\bullet+}$ and the neutral radical $D^{\bullet}$ of the substrate), merely in different "contexts" (as part of a radical pair or as free radical), because the polarization pattern represents a frozen signature of a radical pair.

Experimental Section

Triethylamine was doubly distilled under nitrogen at reduced pressure and stored over 3 Å molecular sieve. The sensitizers were purified by repeated sublimation in high vacuum. All (perdeuterated) solvents were dried with the appropriate molecular sieve.

For the CIDNP measurements, the sensitizer concentrations were chosen to give an absorbance at the excitation wavelength of about 1 in a 5 mm NMR tube; the triethylamine concentrations were 5×10^{-2} M. The solutions were prepared under dry inert gas, deoxygenated by bubbling argon through them, and then sealed in the NMR tubes.

The CIDNP experiments were performed with a slightly modified Bruker WM-250 spectrometer and a 308 nm excimer laser.[9] The method employed, pseudo steady-state CIDNP measurements,[22] yields pure polarizations free from unchanging background signals.

CIDNP intensities (integrals) of the vinylamine signals were obtained from line fits of the characteristic multiplets of the ABX spin system. For the relative permittivities ϵ, the values of the undeuterated solvents or solvent mixtures[21] were used.

Redox potentials were determined with a Metrohm 506 polarograph in differential pulse mode; supporting electrolyte, 0.1 M tetrabutylammonium hexafluorophosphate; reference electrode, ferrocene/ferrocinium as inner standard.

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