**REVIEW**

# Nuclear-Spin Polarization in Electron-Transfer Reactions of Amines

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This paper is dedicated to the memory of Professor *Hanns Fischer*, a pioneer in the chemistry and physics of free radicals, and in designing and adopting magnetic resonance and other physical techniques for their study

Chemically induced dynamic nuclear polarization (CIDNP) observed during electron transfer (ET) reactions of tertiary amines such as DABCO (**1**) or $Et_3N$ (**2**) with a wide range of electron acceptors support the involvement of amine radical-cations (*e.g.*, $\mathbf{1}^{\cdot+}$ or $\mathbf{2}^{\cdot+}$) as key intermediates. Radical ions such as $\mathbf{2}^{\cdot+}$ may be deprotonated, generating neutral aminoalkyl radicals (*e.g.*, $\mathbf{2}^{\cdot}$). When generated by reaction with an electron acceptor of energetically low triplet state such as naphthalene ($^1$Naph*), the resulting pair $\mathbf{2}^{\cdot+}$/Naph$^{\cdot-}$ reacts mostly by reverse electron transfer (RET) from triplet pairs populating the naphthalene triplet state.

**The Advent of Chemically Induced Dynamic Nuclear Polarization.** – In 1967, the journal *Zeitschrift für Naturforschung* published two papers from *Hanns Fischer*'s laboratory, describing unusual nuclear magnetic resonance (NMR) effects observed during the thermal decomposition of diaroyl peroxides [1]. Only two months later, *Ward* and *Lawler* reported related effects observed during rapid reactions of alkyllithium compounds with alkyl halides [2]. These publications introduced the phenomenon of chemically induced dynamic nuclear polarization (CIDNP) to the scientific community. In rapid succession, additional papers appeared reporting CIDNP effects during the thermal decomposition of dialkyl peroxides [3], various photoreactions [4–7], including reactions of photochemically generated carbenes [5] [7], molecular rearrangements [8], and radical-anion reactions [9].

Like many other chemists, we were fascinated by these effects and tried to design systems in which they might be observed to provide mechanistic information. We first studied photoinduced carbene reactions [7] and established that carbene singlet states undergo chlorine abstraction. While this work was in progress, *Closs* and coworkers [10], and *Kaptein* and *Oosterhoff* [11] demonstrated that CIDNP effects are induced in radical pairs; this theory could plausibly rationalize most or all then known effects.

At this time, we became interested in photoinduced electron transfer and applied CIDNP to such reactions. Interesting effects observed during the anthraquinone-sensitized cleavage of thymine dimers [12] encouraged us to pursue this research further. We chose photoreactions of carbonyl compounds with amines, which lead to reduction of the carbonyl group or quenching of the excited state without net chemical change as a promising target.

In this paper, we give an overview of the generation of amine radical cations by various sensitizers and discuss their deprotonation under different conditions.

**Principles of Chemically Induced Dynamic Nuclear Polarization.** – According to the radical-pair theory, enhanced NMR signals in emission or absorption may be induced in radical pairs. CIDNP Effects are induced as a consequence of two limiting principles: radical-pair reactions are electron-spin-dependent, and intersystem crossing (ISC) in such pairs is nuclear-spin-dependent. The interdependence of these processes causes divergent non-equilibrium populations of nuclear-spin levels for products formed by divergent pathways with different electron-spin restrictions [10][11][13].

The directions and intensities of the effects are governed by: the precursor spin multiplicity $\mu$; the $g$ factors ($\Delta g$) and hyperfine coupling constants (hfcc, $a$) of the radical intermediates; and the rates and reaction types ($\varepsilon$) by which the products are formed. Products arising from intermediates having nuclei with hfccs of different signs and magnitudes will display characteristic effects of different directions and amplitudes (polarization patterns) that reflect the hyperfine coupling (hfc) patterns of the intermediates and provide insight into their nature. The CIDNP method has revealed mechanistic insights into many reactions [13e,g,i] and structural information about many intermediates [14].

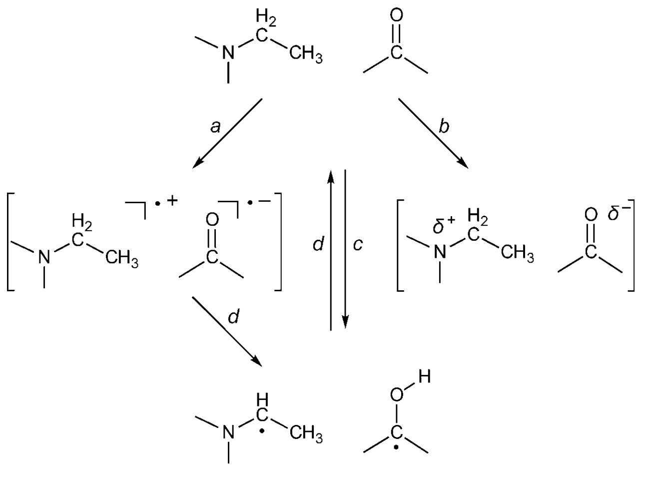
The interpretation of CIDNP patterns to derive structural features has some potential problems: an alternative (though rare) polarization mechanism may give misleading results [15]; polarizations may be distorted due to spin–lattice relaxation or cross-relaxation [16]. However, modern *Fourier*-transform (FT) methods can eliminate some or most of these artifacts [17]. Reactions proceeding *via* consecutive radical or radical-ion pairs with different magnetic properties ('pair substitution') may induce polarization reflecting the parameters of both pairs [18]. The CIDNP effects discussed in this paper are undoubtedly governed by the radical-pair mechanism [13].

**Photoreactions of Carbonyl Compounds with Amines.** – Photoexcited carbonyl compounds undergo fast reactions with amines, resulting in reduction of the C=O moiety or quenching of the C=O triplet state without net chemical change. In polar solvents, electron transfer from the amine to the carbonyl substrate (path *a*) is favored; non-polar solvents favor exciplex formation (path *b*) and/or hydrogen abstraction (path *c*) [19][20]. The neutral radicals produced by (net) hydrogen abstraction are necessary intermediates for most reaction products. However, they need not be formed in a single step; instead, they might arise by a two-step sequence: electron transfer (*a*, *Scheme 1*) followed by proton transfer (*d*).

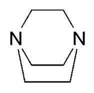
These insights were derived by traditional photochemical methods: product studies and their solvent dependence; probing the excited-state spin multiplicity with suitable quenchers; and fluorescence quenching to derive rate constants by *Stern–Vollmer* methodologies. These methods provide no structural information about the intermediates.

**CIDNP in Electron Transfer Reactions of Amines.** – The earliest CIDNP experiments, using tertiary bicyclic or aliphatic amines, *i.e.*, 1,4-diazabicyclo[2.2.2]octane (DABCO; **1**) and triethylamine (**2**), go back to the mid 1970s [21][22]. We used amines

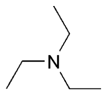
*Scheme 1*



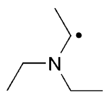
to quench the excited (triplet) states of aromatic carbonyl compounds in various solvents. Irradiation in an NMR probe showed two types of effects, CIDNP and line broadening, for the acceptor and/or the donor; we also noted significant solvent effects [21][22]. For example, the reaction of 4,4′-dimethylbenzophenone (**3a**) with DABCO (**1**) in MeCN resulted in strongly enhanced absorption (A) for the aromatic *ortho*-signals, and strong emission (E) for the Me signal; in contrast, irradiation in hexafluorobenzene produced only minor effects. When using the dichloro analogue **3b**, a somewhat better acceptor, strong CIDNP was observed in hexafluorobenzene, but line broadening in MeCN [21]; the signals of **1** were also broadened.



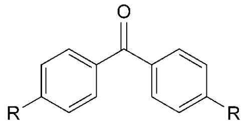
**1**



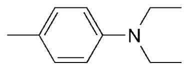
**2**



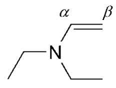
**2$^{\bullet}$**



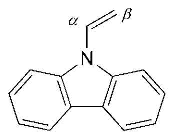
**3a** R = Me
**3b** R = Cl



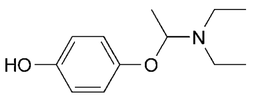
**4**



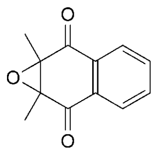
**5**



**6**



**7**



**8**

The above CIDNP effects are compatible with electron return in radical-ion pairs, initially of triplet multiplicity. The observed line broadening was ascribed to degenerate electron transfer between BP and BP$^{\bullet-}$ in the fast exchange limit [23]. No net hydrogen abstraction by $^3$BP$^{\bullet\bullet}$ from **1** or deprotonation of **1**$^{\bullet+}$ by BP$^{\bullet-}$ was observed.

The photoreactions of benzophenones (BPs) with $Et_3N$ (**2**) or with diethyl-*p*-toluidine (**4**) generated CIDNP effects induced in neutral radicals derived from the amines, particularly of diethyl(vinyl)amine (**5**), a product formed by net dehydrogenation of **2** [$\delta$(H) 6.1 (*dd*, $\alpha$-CH); 3.55, 3.4 (*d* each, $\beta$-$CH_2$); the upfield resonances of the two *doublets* (*d*) overlap at 90 MHz] [22]. Product **5** is of special interest, because the signals are unencumbered by other resonances (*Fig. 1*), offering a unique opportunity to probe by CIDNP the detailed mechanism leading to this product.

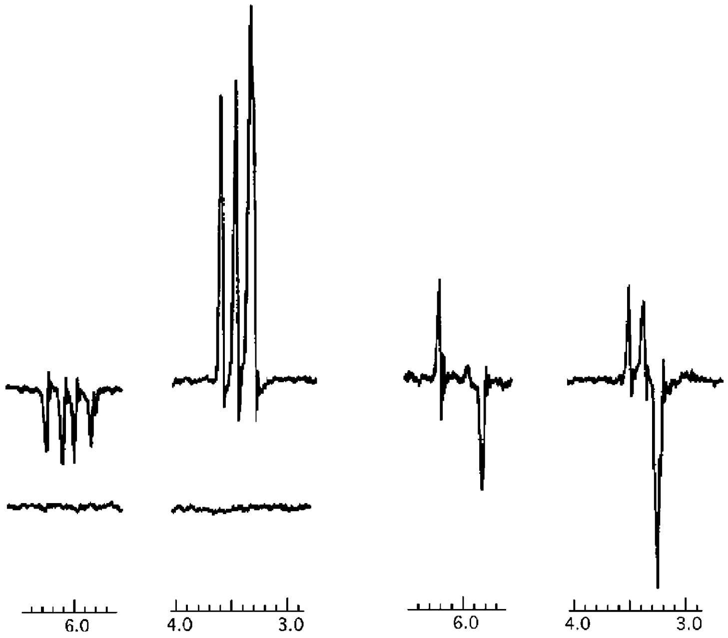


Fig. 1. *CIDNP Spectra of diethyl(vinyl)amine* (**5**) *induced during the reactions of triethylamine* (**2**) *with the benzophenones* **3b** (left) *or* **3a** (right) *in MeCN* [22]

The identity of the vinylamine **5** was confirmed by comparison with the spectrum of an authentic vinylamine, *N*-vinylcarbazole (**6**) [$\delta$(H) 7.3 (*dd*, $J = 22, 12$ Hz, $\alpha$-CH); 5.35, 4.95 (*d* each, $^3J = 22, 12$ Hz, $^2J < 1$ Hz)]. This donor exhibited strong polarization of the vinyl moiety during an ET reaction with 2,3,5,6-tetrachlorobenzoquinone (*Fig. 2*).

The interpretation of the observed CIDNP effects is based on the significantly different hfc patterns of the $Et_3N$ radical cation ($\mathbf{2}^{\cdot+}$) and the neutral 1-(diethylamino)ethyl radical ($\mathbf{2}^{\cdot}$). The amine radical cation $\mathbf{2}^{\cdot+}$ has appreciable $^1$H hfccs only adjacent to the N-atom ($a_\alpha = 37$ G, $a_\beta < 1$ G) [24], whereas the neutral radical $\mathbf{2}^{\cdot}$ has sizable hfccs of opposite signs for the $\alpha$- and $\beta$-H-atoms ($a_\alpha = -13.6$ G, $a_\beta = 19.6$ G) [25]. The opposite signs of the hfccs of the $\alpha$- and $\beta$-H-atoms reflect different coupling mechanisms for these nuclei (*Fig. 3*): $\pi,\sigma$-polarization ($a_\alpha < 0$) for $\alpha$-H *vs.* $\pi,\sigma$-delocalization (hyperconjugation; $a_\beta > 0$) for $\beta$-Me [26]. These species will, thus, generate different polarization patterns.

The polarizations observed with the benzophenones **3b** (emission for $\alpha$-H, absorption for $\beta$-H) and **3a** (absorption/emission for both $\alpha$- and $\beta$-H; see *Fig. 1*) reflect the hfc

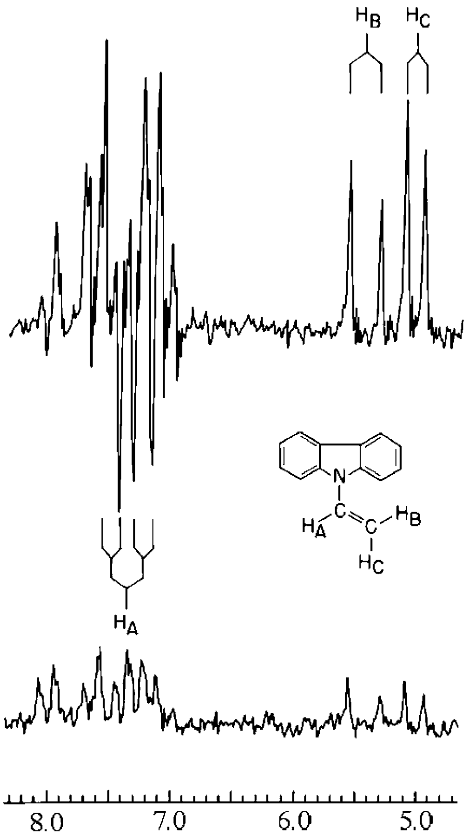


Fig. 2. *CIDNP Spectrum observed during irradiation of a MeCN solution containing a 1:1 mixture* (0.02M each) *of tetrachlorobenzoquinone and* N*-vinylcarbazole* (**6**)

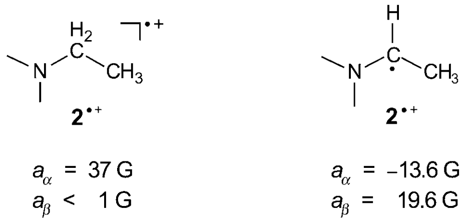


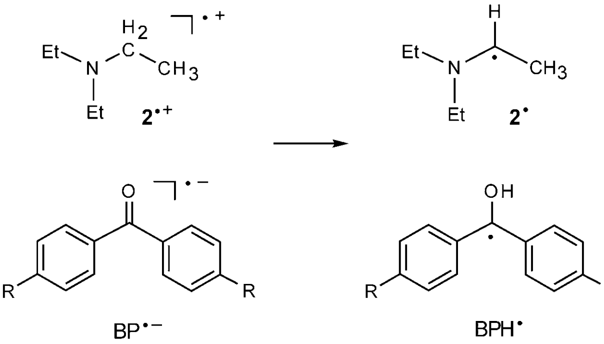
Fig. 3. *Hyperfine coupling constants* (*a*) *for the radical-ion* **2**$^{\cdot+}$ (left) *and the secondary radical* **2**$^{\cdot}$ (right) *of triethylamine*

pattern of the aminoalkyl radical **2**$^{\cdot}$. The signal directions support formation of **5** by intra-pair H-atom transfer (disproportionation) between the neutral radical **2**$^{\cdot}$ and the neutral benzophenone radical (BP$^{\cdot}$).

In the system BP/**4**, the vinylamine polarization (absorption/emission for both $\alpha$- and $\beta$-H) again reflects the hfc pattern of the neutral aminoalkyl radical; selective polarization for the $\alpha$-H-atoms of **4** (emission) supported the involvement of the corresponding radical ion **4**$^{\cdot+}$. In the system perfluorobenzophenone/**4**, line-broadening was observed for the $\alpha$-$CH_2$ and the aromatic *o*-H-nuclei of **4**, reflecting the involvement of $\mathbf{4}^{\cdot+}$ as an intermediate, which, in this experiment, was not deprotonated.

In summary, although our experiments were compatible with the involvement of a radical cation ($\mathbf{2}^{\cdot+}$), they did not provide any hard evidence that the neutral aminoalkyl radical $\mathbf{2}^{\cdot}$, the source of the vinylamine polarization in *Fig. 1*, was actually formed from $\mathbf{2}^{\cdot+}$ *via* $H^+$ transfer to $BP^{\cdot-}$ in the radical-ion pair (*Scheme 2*) [22].

*Scheme 2*



In an effort to find more-direct evidence for the putative involvement of radical ions and the deprotonation of $\mathbf{2}^{\cdot+}$, we chose two quinones, benzoquinone (BQ) and anthraquinone (AQ), as more-powerful electron acceptors. As shown in *Fig. 4,c*, irradiation of AQ/**2** in $CD_3CN$ generated (by then) unexceptional vinylamine polarization, analogous to those shown in *Fig. 1* (left). However, irradiation of BQ/**2** gave rise to *unusual* vinylamine polarization: in $CD_3CN$, both the $\alpha$- and $\beta$-H-atoms showed enhanced absorption (*Fig. 4,a*), whereas in ($D_6$)acetone only the $\beta$-H-atoms showed polarization (absorption; *Fig. 4,b*) [22].

To evaluate the potential mechanisms, we simulated the polarization patterns expected for diethyl(vinyl)amine (**5**), assuming a predominant involvement of $\mathbf{2}^{\cdot+}$ and $\mathbf{2}^{\cdot}$, respectively. The simulated CIDNP spectra are shown in *Fig. 5*. A comparison of the simulated patterns with the observed effects shows that the polarization induced with AQ (*Fig. 4,c*) is close to that expected for the pair $\mathbf{2}^{\cdot}$/AQH$^{\cdot}$. On the other hand, the effects resulting from the reaction of **2** with BQ in MeCN (*Fig. 4,a*) or acetone (*Fig. 4,b*) appear incompatible with either $\mathbf{2}^{\cdot+}$ or $\mathbf{2}^{\cdot}$: the terminal $\beta$-H-atoms show the enhanced absorption expected for $\mathbf{2}^{\cdot}$, but the polarization of the internal $\alpha$-H-atoms is incompatible with the exclusive involvement of either $\mathbf{2}^{\cdot+}$ (absorption; *Fig. 5*, left) or $\mathbf{2}^{\cdot}$ (emission; *Fig. 5*, right).

In addition to the vinylamine polarization (*e.g.*, **5**), the $\alpha$-H-atoms of **2** ($\delta$(H) 2.5) showed strong emission, whereas the signal of the $\beta$-H-atoms ($\delta$(H) 1.0) remained unchanged; the aromatic resonances ($\delta$(H) 6.7) of the reduced hydroquinone acceptor, $BQH_2$, appeared in emission; and the coupling product **7** (see chemical formulae above) of the aminoalkyl and semiquinone radicals showed enhanced absorption for the $\alpha$-H-nuclei ($\delta$(H) 3.1 (*q*)), unencumbered by other signals (see *Fig. 1*).

The polarization of the regenerated amine supports the view that the excited quinone, $^3BQ^*$, is quenched by ET from **2**. The strong emission observed for the $\alpha$-H-

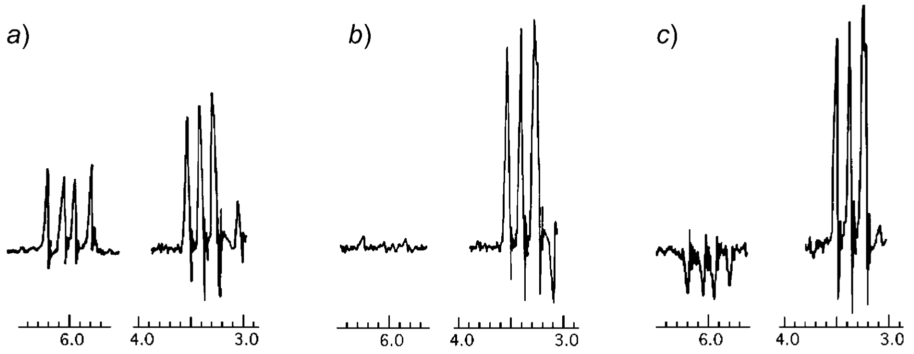


Fig. 4. *Alkene CIDNP spectra of diethyl(vinyl)amine* (**5**) *induced during the reactions of $Et_3N$* (**2**) *with benzoquinone* (BQ) *in either MeCN* (*a*) *or acetone* (*b*), *or of* **2** *with anthraquinone* (AQ) (*c*)

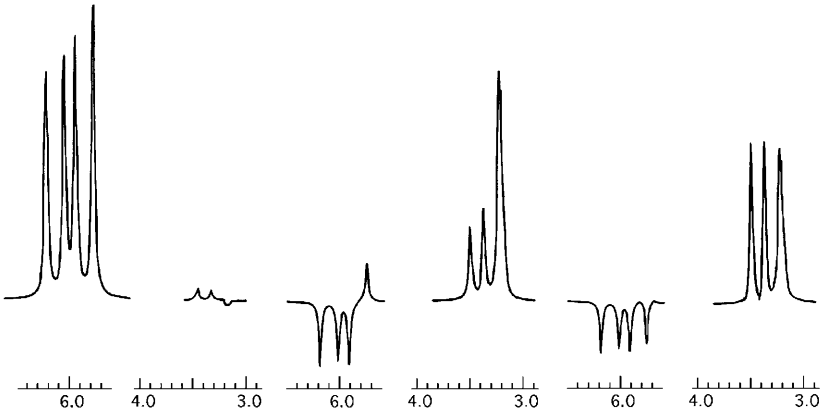


Fig. 5. *Simulated CIDNP spectra for the formation of the amine* **5** *from the ion pair* $\mathbf{2}^{\cdot +}$/ $BQ^{\cdot -}$ (left), or by disproportionation of neutral radicals, $\mathbf{2}^{\cdot}$ and **BQH**$^{\cdot}$ (center). An 'intranuclear-relaxed' spectrum is shown on the right.

nuclei of **2**, and the absence of polarization for the $\beta$-H-nuclei match with the hfc pattern of $\mathbf{2}^{\cdot +}$; the signal direction supports in-cage ($\varepsilon > 0$) RET from the semiquinone anion $BQ^{\cdot -}$ to $\mathbf{2}^{\cdot +}$ in a pair initially of triplet multiplicity ($\mu > 0$), with a hyperfine coupling constant $a_\alpha > 0$, and with $g(\mathbf{2}^{\cdot +}) < g(BQ^{\cdot -})$, *i.e.*, $\Delta g < 0$.

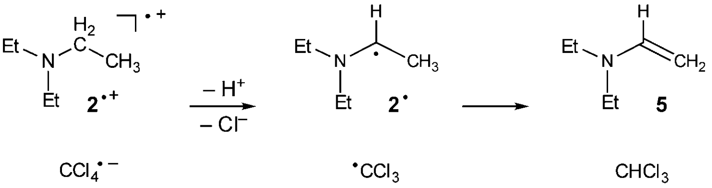
These results were mentioned briefly and selected spectroscopic features were illustrated in a review of ET-induced CIDNP effects written for the *NATO Advanced Study Institutes* [27]. We described the unusual vinylamine polarization as follows: '*The observed polarization patterns are incompatible with either the aminium radical ion or the aminoalkyl radical, but they may be interpreted as a superposition of effects originating in both species*'. [...] '*Since the product vinylamines cannot be formed from the radical ion pairs in a simple direct reaction, the polarization generated in a radical ion pair must be transferred to the product amines via the neutral aminoalkyl radical*'. The simple conclusion that $\mathbf{2}^{\cdot +}$ as well as $\mathbf{2}^{\cdot}$ contribute to the polarization of **5** has been confirmed.

The statements are compatible with two different mechanistic scenarios. First, the in-cage $H^+$ transfer from $\mathbf{2}^{\cdot +}$ to $BQ^{\cdot -}$ could occur at a rate allowing induction of polarization before as well as after intra-pair $H^+$ transfer; the polarization of two consecutive pairs (pair substitution) would be transferred to the vinylamine **5**. The concept of pair substitution had been demonstrated and modeled, at least for the case where one radical is exchanged/modified while the other remains unchanged [18]. The second scenario involves competing deprotonation mechanisms: *a*) vinylamine generated *via* rapid in-cage deprotonation followed by slower H-atom transfer would show the in-cage polarization due to radical $\mathbf{2}^{\cdot}$, analogous to the effects induced in the system BP/**2** [22]; *b*) vinylamine generated *via* radical ions escaping from the geminate pair and deprotonated by an adventitious base (or the reagent amine) would show the (escape) polarization due to the radical ion $\mathbf{2}^{\cdot +}$. Alas, our data and the experimental techniques available at the time did not allow us to differentiate between these two mechanisms. The competing deprotonation scheme could, in principle, be dissected by time-resolved CIDNP, but this technique had been demonstrated only one year earlier [28]. Accordingly, we did not pursue this system any further.

However, the allure of $Et_3N$ (**2**) as an electron donor, specifically the unique opportunity to probe by CIDNP the detailed mechanism leading to the vinylamine **5**, was not lost on other workers. Since our early experiments [21] [22] [27], at least 20 publications have appeared in which CIDNP induced in ET reactions of **2** are discussed. Beginning in 1980, laser-flash-spectroscopy studies were applied in these and related systems [29] [30]. In addition, more-traditional methods continued to be applied.

One of these contributions came from *Hanns Fischer*'s laboratory [31]. *Markaryan*, a visiting scientist, irradiated (340–380 nm) the weak charge-transfer (CT) complex between $Et_3N$ (**2**) and carbon tetrachloride ($CCl_4$) in either MeOH or MeCN (*Scheme 3*). This resulted in enhanced absorption for chloroform ($CHCl_3$) and for the terminal olefinic H-nuclei of **5**. The CIDNP effects are compatible with the singlet radical pair $^1[\mathbf{2}^{\cdot}/CCl_3^{\cdot}]$ formed from the radical-ion pair within nanoseconds. H-Atom transfer from the $\beta$-Me group to $CCl_3^{\cdot}$ accounts for the observed polarization (both types of polarized H-atoms originate in the methyl group of $\mathbf{2}^{\cdot}$). The line broadening of the $\alpha$-$CH_2$ *quadruplet* (*q*) of **2** was ascribed to the formation of the amine hydrochloride, and, indeed, the broadening could be eliminated by addition of base (NaOH).

*Scheme 3*



Later, *Markaryan* and co-workers further pursued related photoreactions of **2**, for example, with bromo(trichloro)methane ($BrCCl_3$) [32a] and hexachloroethane [32b]. These reactions showed analogous CIDNP effects for $CHCl_3$ and pentachloroethane, respectively. *Markaryan* invoked analogous mechanisms involving radical-ion pairs followed by pairs of neutral radicals. In some of these reactions, a conjugated paramagnetic polymer was identified as a secondary product. More recently, *Markaryan* and co-workers studied the laser-flash photolysis of the system BP/**2** in MeCN, and they observed absorption/emission polarization for the amine and for a recombination product of the ketyl and aminoalkyl radicals [33].

Following the work of *Fischer* and *Markaryan*, the group of the Japanese CIDNP pioneer *Kazuhiro Maruyama* used 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (=1a,7a-dimethyl-1a,7a-dihydronaphtho[2,3-*b*]oxirene-2,7-dione; **8**) as a sensitizer/acceptor [34]. The CIDNP signals observed in the reaction of this quinone derivative with **2** and dimethylaniline ($Me_2N-C_6H_5$) were interpreted as evidence for (net) H-atom abstraction in benzene and ET in both acetone and MeCN. The oxirane ring of **8** was reductively opened upon irradiation in the presence of **2**; with dimethylaniline in benzene, a cross-adduct was obtained.

Several groups studied additional aspects of tertiary-amine photooxidation with a range of acceptors, including acetylenic ketones [35], phthalimide derivatives [36], and a series of quinones, including anthraquinone [37][38], duroquinone [39], 2,6-dimethyl-1,4-benzoquinone, 2,6-di(*tert*-butyl)-1,4-benzoquinone, and 2,6-diphenyl-1,4-benzoquinone [40], or 2-chloro-5-methoxy-1,4-benzoquinone [41], utilizing a range of magnetic-resonance techniques. Most of the authors agree that the CIDNP effects are induced in radical-ion pairs as well as pairs of neutral radicals.

For example, *Tsentalovich et al.* studied the system AQ/**2** by time-resolved CIDNP and stimulated nuclear polarization, focusing on the influence of the solvent on the mechanism [37]. In $CD_3OD$, they observed a build-up of $H_2C=$ polarization for **5** on the microsecond scale; the observation that $CD_3OH$ was polarized was interpreted as evidence for deprotonation of $\mathbf{2}^{\bullet+}$ by $CD_3O^{\bullet}$, possibly generated by dedeuteration of $CD_3OD$ by $AQ^{\bullet-}$ [37]. Interestingly, the polarization of **5** in ($D_6$)benzene (emission for $\alpha$-H, absorption for $\beta$-H) was opposite to that observed in ($D_{12}$)cyclohexane (absorption for $\alpha$-H and emission for $\beta$-H).

In a way, this publication may have set the stage for the elegant and comprehensive study of the deprotonation of $\mathbf{2}^{\bullet+}$ by *Sartorius* and *Goez*, who applied pseudo-steady-state CIDNP measurements to systems involving a wide range of triplet sensitizers, including AQ [38]. These authors concluded that two parallel, *i.e.*, competing pathways exist for the deprotonation of aminium radical cations: either by the sensitizer radical anion ($AQ^{\bullet-}$) within the geminate pair or by the amine reagent (**2**) after escape from the cage. The fraction of vinylamine **5** generated within the cage carries polarization due to the radical $\mathbf{2}^{\bullet}$, whereas the fraction generated after cage escape reflects the hyperfine pattern of $\mathbf{2}^{\bullet+}$. The contributions of these processes to the CIDNP patterns are determined by the rate of in-cage deprotonation relative to the cage lifetime.

The authors derived the free enthalpies of the radical-ion pair (*e.g.*, $\mathbf{2}^{\bullet+}/AQ^{\bullet-}$) and the pair of neutral radicals (*e.g.*, $\mathbf{2}^{\bullet}/AQH^{\bullet}$) from redox potentials, p$K_a$ values, and calculated (AM1) heats of formation. A comparison of the pair energies led them to conclude that the free energy $\Delta G^0$ of in-cage $H^+$ transfer is a controlling factor of the investigated photoreactions [38a].

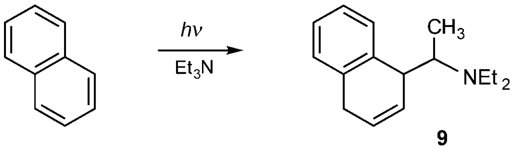
In a subsequent paper, the authors considered the solvent-polarity dependence of vinylamine polarization and established a marked threshold behavior: for values of $\Delta G^0$ more negative than $-125$ kJ/mol, $H^+$ transfer from the donor cation to the acceptor anion is faster than separation of the radical-ion pair; for $\Delta G^0$ values less negative than $-100$ kJ/mol, this reaction is too slow to compete with cage escape [38].

Finally, the authors quantitatively evaluated the polarization ratio $r$ of the $\alpha$- and $\beta$-H-nuclei of the vinylamine generated in reactions of **2** with AQ and 2,7-dinitrofluorenone (DNF) in a series of aprotic solvents. They developed a theory of pair substitution during encounters of the radicals, and derived an expression for the dependence of $r$ on $k_{\mathrm{dep}}$. This expression allows the extraction of $k_{\mathrm{dep}}$ from the observed polarization ratio. For the systems **2**/AQ and **2**/DNF, $k_{\mathrm{dep}}$ falls into the range of *ca.* $10^8$–$10^{10}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ [38c].

In a recent time-resolved FT-EPR study of the photoreduction of duroquinone by **2** in MeOH, *Lu* and *Beckert* noted that the signal intensity of $\mathbf{2}^{\bullet+}$ decreased with increasing concentration of **2**. They concluded that $\mathbf{2}^{\bullet+}$ is deprotonated by **2** [39], in accord with the results of *Goez* and *Sartorius* [38].

Several groups used $Et_3N$ (**2**) to quench excited singlet states of aromatic hydrocarbons such as naphthalene (Naph) [27] [42] [43], or stilbene (Stil) [44]. The CIDNP spectrum observed for the reaction of $^1$Naph* with **2** is dominated by strongly enhanced absorption for the $\alpha$-H-atoms of **2**. The signal direction is compatible with RET in triplet pairs, one of the many instances of this phenomenon [16a] [27] [42b] [45]. Because the RET falls into the inverted *Marcus* region [46], being governed by the 'energy-gap law' [47], deprotonation is largely suppressed. Very weak polarization for the $\beta$-H-atoms of **5** (absorption) and for the aminoalkyl $\alpha$-H-atoms of the resulting adduct **9** (emission; *Scheme 4*) suggests that deprotonation occurs to a limited extent (*Fig. 6*) [48]. *Kruppa et al.* reported that, in the reversible ET between **2** and Naph, the CIDNP intensity increases with increasing electron-exchange rate [43].

*Scheme 4*



**9**

*Klaukien* and *Lehnig* [44] studied the UV irradiation of (*E*)-stilbene (Stil) in the presence of $Et_3N$ (**2**). With this hydrocarbon/acceptor, the reaction takes a course different from that with Naph. The CIDNP effects observed for **5** are compatible with a mechanism initiated by electron transfer from **2** to excited singlet stilbene, $^1$Stil*. The resulting radical-ion pair, $\mathrm{Stil}^{\bullet-}/\mathbf{2}^{\bullet+}$ undergoes $H^+$ transfer (within *ca.* 30 ns), producing the neutral radicals $\mathrm{StilH}^{\bullet}/\mathbf{2}^{\bullet}$, in which the nuclear polarization is induced. In the reaction with Stil, as in the reaction with BP [22], the vinylamine **5** arises by disproportionation of the pair of neutral radicals [44]. In these experiments, no evidence for RET in triplet radical-ion pairs was observed.

Because of the potential involvement of RET in triplet radical-ion pairs, at least in the reactions with Naph or Stil as sensitizer/acceptors, we briefly review pertinent energetic features of the radical-ion pairs. The change in free energy $\Delta G$ for (forward) electron-transfer (ET) reactions is given by an empirical relation (*Eqn. 1*) [49], where $E_{\mathrm{T}}$ is the excited state energy, $E^0_{(\mathrm{D/D^+})}$ and $E^0_{(\mathrm{A^-/A})}$ are the one-electron redox potentials of

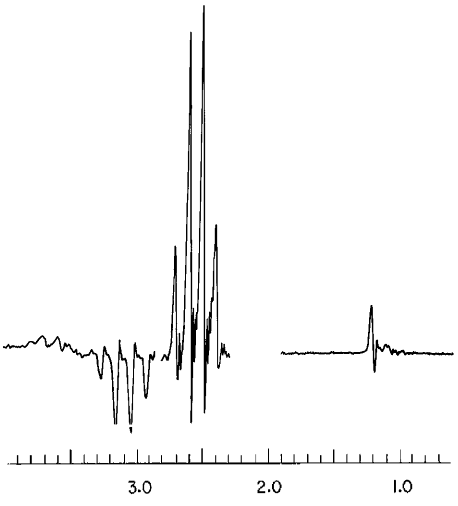


Fig. 6. *NMR spectra of a $CD_3CN$ solution containing naphthalene* (Naph) *and $Et_3N$* (**2**) (0.02M each) *during UV irradiation*. The spectrum shows enhanced absorption for the $CH_2$ signal of **2**, emission for the methine signal of the adduct **7** (see chemical formulae), and a very weak absorption for the terminal H-atoms of diethyl(vinyl)amine (**5**).

donor (D) and acceptor (A), respectively, and $e^2/\varepsilon a$ is a *Coulomb* term accounting for ion pairing. Combined, the terms $E_{0,0}$ and $E^0_{(A^-/A)}$ define the redox potential of the acceptor-excited state $*E^0_{(A^-/A)}$ according to *Eqn 2*, which provides a measure for its oxidative strength. Donors with oxidation potentials $E^0_{(D/D^+)} < *E^0_{(A^-/A)}$ can be expected to undergo electron transfer. The free energy of a radical-ion pair, $-\Delta G^0_{RP/G}$, relative to that of the reagent ground states (*Eqn. 3*) and the donor or acceptor triplet state (*Eqn. 4*), *i.e.*, $-\Delta G^0_{RP/T}$, must be considered, too. These quantities are measures for the reactivity of singlet and triplet radical-ion pairs, respectively, in RET reactions.

$$-\Delta G^0 = E_{0,0} - E^0_{(D/D^+)} + E^0_{(A^-/A)} - e^2/\varepsilon a \tag{1}$$

$$*E^0_{(A^-/A)} = -E_{0,0} + E^0_{(A^-/A)} \tag{2}$$

$$\Delta G^0_{RP/G} = E^0_{(D/D^+)} - E^0_{(A^-/A)} - e^2/\varepsilon a \tag{3}$$

$$\Delta G^0_{RP/T} = E^0_{(D/D^+)} - E^0_{(A^-/A)} - e^2/\varepsilon a + E^0_{(T)} \tag{4}$$

Because the oxidation potential of **2** is relatively low ($E^0_{(D/D^+)} = 0.62$ V *vs.* SCE) [50], and since the oxidative strength of the ketone and quinone excited states is significant1), the ET process from **2** to the singlet ($^1$Naph*, $^1$Stil*) or triplet ($^3$BP*, $^3$BQ*, $^3$AQ*) acceptors presented here is highly exergonic (*e.g.*, $\Delta G^0 = -1.8$ and $-0.9$ eV for BQ and AQ, resp.; *Table*). The highly favorable energetics for ET have been accepted as evidence that the photoreactions between the sensitizers/acceptors and $Et_3N$ (**2**) are initiated by ET from **2** to singlet or triplet acceptors, generating radical-

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1) BP: $E^0_{(T)} = 3.0$ eV, $E^0_{(A^-/A)} = -2.15$ V [52], $*E^0_{(A^-/A)} = 0.85$ eV; BQ: $E^0_{(T)} = 2.95$ eV [20], $E^0_{(A^-/A)} = -0.54$ V [51], $*E^0_{(A^-/A)} = 2.4$ eV; AQ: $E_{0,0} = 2.7$ eV [52], $E^0_{(A^-/A)} = -0.94$ V; $*E^0_{(A^-/A)} = 1.8$ eV [52].

ion pairs of singlet or triplet multiplicity, respectively. Similarly, return electron transfer (RET), regenerating the ground states, is highly exergonic ($-\Delta G^0_{\mathrm{RP/G}} > 0$) for all cases. In contrast, the reagent triplet states appear energetically inaccessible ($\Delta G^0_{\mathrm{RP/T}} > 0$), rendering RET from triplet pairs unlikely.

The radical anion Naph$^{\bullet-}$, formed in the reaction with $^1$Naph*, is a carbon-centered base; H$^+$ transfer from the C–H acid **2**$^{\bullet+}$ to the carbon-centered base Naph$^{\bullet-}$ apparently is less prominent (or favorable), in spite of its high pair energy (*Table*) and the high acidity of **2**$^{\bullet+}$.

Table. *Pertinent Energetics for Radical-Ion Pairs Generated by Electron Transfer* (ET) *from Triethylamine* (**2**) *to Selected Acceptors, and Return Electron Transfer* (RET) *from Singlet and Triplet Pairs.* For physical symbols, see text and *Eqns. 1–4.*

| Acceptor[a]) | $E_{0,0}$ [eV] | $E^0_{(\mathrm{T})}$ [eV] | $E^0_{(\mathrm{A^-/A})}$ [V] | $^*E^0_{(\mathrm{A^-/A})}$ [V] | $\Delta G^0$ [eV] | $\Delta G^0_{\mathrm{RP/G}}$ [eV] | $\Delta G^0_{\mathrm{RP/T}}$ [eV] |
|---|---|---|---|---|---|---|---|
| BP | | 3.0 | −2.15 | 0.85 | −0.15 | −2.75 | 0.25 |
| BQ | | 2.95 | −0.55 | 2.4 | −1.85 | −1.1 | |
| AQ | | 2.7 | −0.95 | 1.8 | −1.15 | −1.55 | |
| Naph | 3.95 | 2.65 | −2.5 | 1.45 | −0.85 | −2.15 | 0.5 |
| Stil | 3.9 | 2.2 | −1.9 | 2.0 | −1.4 | −2.5 | 0.3 |

[a]) BP, BQ, AQ, Naph, and Stil denote benzophenone, benzoquinone, anthraquinone, naphthalene, and (*E*)-stilbene, resp.

In closing, we note that the generation of amine radical-cations by a wide range of benzophenone [29] or quinone [30] acceptors have been studied by time-resolved optical spectroscopy, revealing several interesting facets of these reactions. Although the simple Et$_3$N radical **2**$^\bullet$ was not observed, an *N*-phenyl derivative has been identified spectroscopically [30b]. Similarly, the conjugate acid of at least one radical anion, that of 4,4′-dinitrostilbene, has been found to be different from that of the radical anion [30d]. However, these experiments provide no structural information. In contrast, the CIDNP experiments reviewed here provide unambiguous, though indirect, evidence for the successive involvement of **2**$^{\bullet+}$ and **2**$^\bullet$, illustrating unique mechanistic insights provided by the CIDNP technique originally introduced by *Hanns Fischer* and co-workers almost 40 years ago.

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