CIDNP Effects of Sensitized Photochemical Dediazoniation of Arene Diazonium Salts
Manipulating CIDNP Intensities by the Experimental Conditions

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13C and 15N photo-CIDNP effects were determined for the reversible electron transfer from pyrene to arene diazonium salts on excitation of the charge transfer band at 360 nm. The diazonium salts being the products of back electron transfer ("cage products") show enhanced absorption for 15C(1) and the 15N-enriched diazonium group, whereas the escape products, ArH or N2, respectively, yield emission signals. It was shown that the intensities of the CIDNP effects depend on the rates of intersystem crossing ki sce within the geminate radical pair, i.e. on the magnetic nucleus used as a probe of the CIDNP effect. Using 1H, 13C or 15N the time domain of observation can be manipulated in the ranges of 90–100 ns, 15–20 ns and 3–5 ns, respectively. Furthermore, the CIDNP intensities depend on the proper balance of the rate of electron back transfer, ke, and the rate kp of formation of the escape product. Since ke increases with increasing energy of the geminate radical pair, this balance and therefore the CIDNP intensities vary according to the substituent present and the electron donor used.

1. Introduction

The Chemically Induced Dynamic Nuclear Polarization (CIDNP) is an excellent method to confirm fast reversible electron transfer reactions which have a special importance in photochemistry. Polarizations of nuclear spins are possible, if during a chemical reaction two radicals are formed in one and the same elementary process. The majority of the cases observed until now can be explained by the radical pair theory [1]. According to this the CIDNP effects of electron transfer reactions can be illustrated by the following simple model:

Scheme 1

A + D: \( \overset{1}{A} \rightleftharpoons \overset{3}{D} + \overset{5}{D} \)

Educts

(Educts)* (Products)*

"Cage Products" (CP) "Escape Products" (EP)

* Reprint requests to Prof. Dr. H. G. O. Becker.
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The geminate radical pair, which is formed by electron transfer e.g. in the singlet multiplicity, switches over into the corresponding triplet radical pair by intersystem crossing ki sce (or vice versa). Nuclear spin polarization of educts and/or products (symbolized in Scheme 1 by an asterisk) arises from the common action of two effects:

a) The rate of the intersystem crossing reaction

ki sce depends on the difference of g-values of the radicals A and D and on the hyperfine coupling constants of the interaction between the odd electrons and the magnetic nuclei under consideration, cf. eq. (1).

b) The stabilization reactions of the radicals pairs

The rates of these reactions depend on the relative orientation of the electron spins in the geminate radical pairs. The singlet radical pair can react back to the educts (ke) in a spin-allowed and therefore fast reaction. Compared with this, the stabilization reaction (kp) forming products is usually only of minor importance. In the geminate triplet radical pair the reverse electron transfer is spin-forbidden.
and therefore a relatively slow reaction. Thus the mutual separation ($k_p$) of the radicals dominates and the reaction products are formed from free radicals which are no longer correlated.

In summa an interconverting electron spin system results having two exit channels $k_e$ and $k_p$. Because the intersystem crossing rate $k_{isc}$ and therefore the time-dependent phase relation of the electron spins within the geminate radical pair depend on interacting nuclear spins, the radical pairs are so to say sorted into the appropriate exit channel according to their nuclear spins. Thus, the reaction products are being formed with a non-BOLTZMANN distribution of nuclear spins. A distribution of the nuclear spins corresponding to the thermal equilibrium is restored slowly (during several seconds) by spin-lattice relaxation. In the NMR spectrum enhanced absorption signals of educts and emission signals of products or vice versa are accordingly observed. A maximum intensity of these CIDNP signals can be expected if $k_{isc} \approx k_e \approx k_p$. Thus, it should be possible to manipulate the intensity of CIDNP signals by the experimental conditions which determine these $k$-values. Consequently, the dependences (1)-(3) have to be taken into consideration:

$$
k_{isc} = \frac{1}{\tau_{isc}} = \frac{2 \beta_c}{h} (\Delta g B_o + \sum_{j} a_{ij} m_j - \sum_{k} a_{2k} m_k)
$$

(1)

$$
k_e = f(\Delta G^+) = f(E_{radical\ pair}) = f(\text{substituents})
$$

(2)

$$
k_p = f(k_{dir}) = f(\text{viscosity of the medium})
$$

(3)

The present paper deals with influences of $k_{isc}$ and $k_e$ on CIDNP intensities. Effects of solvent viscosity will be published elsewhere.

2. Results and Discussion

The reaction studied is formulated in Scheme 2. During the photochemical electron transfer from pyrene to arene diazonium salts CIDNP signals were observed. In the $^1H$-CIDNP spectra the protons in 3-position of the aromatic ring showed enhanced absorption as did $C(1)$ in the $^{13}C$-CIDNP spectra, whereas the complementary emission signals were observed for the same nuclei in the dediazoniation products $Ar-H$ [2]. Special attention was paid to the CIDNP signals of the educts because they provide conclusive evidence of a reversible electron transfer reaction. The results from a series of reactions are shown in Table I which also contains the previous results [2].

The $^1H$-CIDNP signals have relatively low intensities whereas the $^{13}C$-CIDNP effects are strong. However, even with the more sensitive $^{13}C$-CIDNP technique we failed to detect a CIDNP signal in the 4-N,N-dimethylaminobenzene diazonium salt/pyrene system. With 4-nitrobenzene diazonium salt which represents the other extreme of the reaction series studied, only a very weak CIDNP signal was registered. A further increase in intensity was anticipated for $^{15}N$ as a nuclear magnetic probe because $^{15}N$-enriched diazonium salts $Ar^{15}N^{15}N^+$ were used. Furthermore, the transferred electron should reside with high probability on the $^{15}N$ atoms of the aryldiazo radicals $Ar-N=N$, formed, because they are $\sigma$-radicals with no marked delocalization of spin density into the aromatic ring. In fact, very intensive CIDNP signals were observed as shown in Fig. 1 for the example of pyrene/4-cyanobenzene diazonium salt (diazonium group with 96% $^{15}N$).

Whereas by means of the $^1H$-or $^{13}C$-CIDNP techniques only the secondarily formed escape products $Ar-H$ are registered, the $^{15}N$-technique allows the observation of the primary dediazoniation product $^{15}N_2$. 

![Scheme 2](image-url)
Allowing for the negative gyromagnetic ratio of $^{15}$N and using the corresponding modified KAPTEIN rule [3] with the parameters in [2] it can be deduced from the experimental results that the electron transfer starts from the excited singlet state. This is in full accordance with the results of $^1$H-and $^{13}$C-CIDNP experiments [2].

The $^{15}$N-CIDNP variant is in the present case even more sensitive than the $^{13}$C-variant. Thus, clear CIDNP signals were also obtained for the 4-nitro-

**Table 1. $^1$H, $^{13}$C and $^{15}$N photo-CIDNP effects of 4-substituted arene diazonium tetrafluoroborates in acetonitrile (saturated solutions, in the case of $^1$H-experiments 0.1 M) in the presence of pyrene (0.1 M) at $\lambda > 310$ nm (high pressure Hg lamp, 500 W). CP = cage product, EP = escape product. + indicates enhanced absorption, — indicates emission; the strength of the effects is symbolized by e.g. (+), +, ++, ++++. 0 indicates no CIDNP effect observed. Position of effects H(3), H(o) etc. as indicated in Scheme 2.**

<table>
<thead>
<tr>
<th>4-X</th>
<th>$E_{CP}$</th>
<th>$^1$H-CIDNP</th>
<th>$^{13}$C-CIDNP</th>
<th>$^{15}$N-CIDNP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CP (H(3))</td>
<td>EP (H(0))</td>
<td>CP (C(1))</td>
</tr>
<tr>
<td>NMe₂</td>
<td>1.30</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.00</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>OMe</td>
<td>1.04</td>
<td>+</td>
<td>—</td>
<td>++</td>
</tr>
<tr>
<td>Me</td>
<td>0.95</td>
<td>+</td>
<td>—</td>
<td>++</td>
</tr>
<tr>
<td>F</td>
<td>0.90</td>
<td>+</td>
<td>—</td>
<td>+++</td>
</tr>
<tr>
<td>Cl</td>
<td>0.85</td>
<td>+</td>
<td>—</td>
<td>+++</td>
</tr>
<tr>
<td>Br</td>
<td>0.82</td>
<td>+</td>
<td>—</td>
<td>+++ +</td>
</tr>
<tr>
<td>I</td>
<td>0.82</td>
<td>+</td>
<td>—</td>
<td>+++ +</td>
</tr>
</tbody>
</table>

a) Energy of the radical pair in eV according to eq. (5); b rubrene instead of pyrene, irradiation at $\lambda > 500$ nm; c no signal observed, cf. the discussion in the text; d in the case of Ar$^{15}$N₂+ besides the netto effect results a doublet (A/E); e besides the netto effect a doublet (A/E) is observed.

**Fig. 1. 9.12 MHz $^{15}$N—($^1$H)—PFT—NMR spectra of 4-cyanobenzene diazonium tetrafluoroborat,$^{15}$N(a), $^{15}$N(β), and pyrene in acetonitrile. Saturated solution, standard: CH₃$^{15}$NO₂, lock: CD₃NO₂.**

a) 100 scans, each 15 s duration; b) 50 scans, each 15 s duration, after repetitive irradiation (6 s duration) and a time lag before accumulation of 0.2 s.

Hg—High-pressure lamp, 500 W, with filter BG 24 of VEB Jenaer Glaswerke Schott & Gen.
benzene diazonium salt/pyrene system, whilst the 4,N,N-dimethylaminobenzene diazonium salt/pyrene system gave at least a weak emission signal for \(^{15}\text{N}_2\), cf. Table I.

The photochemical reaction of the diazonium salts in the absence of pyrene in dioxane (an n-electron donor) proceeded with violent evolution of nitrogen, but CIDNP effects were not observed. This indicates a thermal chain reaction during which, apart from the relatively unimportant starting reaction, no geminate radical pairs are formed which are a precondition for CIDNP effects.

As stated above, intensive CIDNP signals can be expected if the rates of the competing reactions \(k_{e^-}\) and \(k_p\) are similar. \(k_{e^-}\) is without doubt a very fast reaction. It is therefore to be expected that the intensity of the CIDNP signals increase if one proceeds within the reaction series (Table I) from N,N-dimethylaminobenzene diazonium salt, because \(k_p\) of the transient 4,N,N-dimethylamino phenyldiazo radical has a value of only \(2 \times 10^6\) s\(^{-1}\), but for the 4-nitrophyenyldiazo radical \(k_p = 5 \times 10^7\) s\(^{-1}\) [4].

It could then even become possible that \(k_{e^-}\) and \(k_p\) are no longer the two exit channels but \(k_{e^-}\) and \(k_p'\) (cf. Scheme 2), and that the 4-nitrophényldiazo radical cleaves off nitrogen within the life time of the geminate radical pair. Such a “pair substitution mechanism” has been found in other cases, cf. [5]. This mechanism can in the present case be excluded. If aryl radicals arise in the polarization-forming step, the escape products Ar-H should be formed with \(^1\text{H}-\)polarization in meta positions to the substituent X because the hyperfine coupling constants in aryl radicals vary in the order \(13\text{C} < 1\text{H} < 15\text{N}\), respectively.

According to these values, in the case of 4-nitrobenzene diazonium salt the corresponding aryldiazo radical \((t_{1/2} \approx 14\text{ ns})\) has suffered extensive dediazonation before a \(^1\text{H}(3)\)-polarization can be built up. Under the influence of the \(^{15}\text{N}(a)\) nuclear spin, however, a high phase difference arises during the short life time of the aryldiazo radical, so that CIDNP effects are possible. In fact, \(^{15}\text{N}\)-CIDNP effects were found even with the short-lived aryldiazo radicals containing strong electron attracting substituents, cf. Table I. Useful results can be achieved using \(^{13}\text{C}\) nuclei which lead also to fast interchange of the electron spin system.

These results show that the ISC conversion rates can be influenced experimentally by selecting as a probe the suitable magnetic nucleus, i.e. the “internal clock” can be adjusted to different time domains. According to eq. (2) the CIDNP intensities are also influenced by the energy \(E_{\text{Pr}}\) of the geminate radical pairs, i.e. by the substituents in the diazonium compounds. For \(E_{\text{Pr}}\) eq. (5) is valid:

\[
E_{\text{Pr}} = E_{\text{Pr}}^{\text{donor}} - E_{\text{Pr}}^{\text{acceptor}} \text{(eV)}
\]

The radical pairs \((\text{Ar}^-\text{N}=\text{N}, \text{pyrene}^+)\) formed during the electron transfer have generally high energies. Therefore, it is to be expected that the electron back transfer \(k_{e^-}\) requires only a very low activation energy, and \(E_{\text{Pr}} = -\Delta G\) determines the rate \(k_{e^-}\) of the electron back transfer within the geminate

* Value for \(a_{^{14}\text{N}(a)} = 2.25\text{ mT}\) [6], multiplied with \(-1.46275\) to get \(a_{^{15}\text{N}(a)}\), cf. [3].
Fig. 2. Time-dependent evolution of the singlet character within the radical pair (Ph–N=N, pyrene*) according to equation (4);
a) under the influence of nuclear spins $\alpha$ and $\beta$ of $^1\text{H}(3)$;
b) under the influence of nuclear spins $\alpha$ and $\beta$ of $^{15}\text{N}(\alpha)$. 
radical pair. The energies of the radical pairs with differently substituted aryldiazonium radicals as calculated from the half-wave oxidation potential of pyrene ($E_{ox}^{\alpha} = 1.20$ V, see, in acetonitrile) and the half-wave reduction potentials $E_{red}^{\alpha}$ of the diazonium salts [7] are included in Table I. It can be seen that the maximum CIDNP effect arises with 4-chlorobenzene diazonium salt. In this case not only enhanced absorption of $^{13}$C(1) was observed but furthermore a weaker enhanced absorption of $^{13}$C(3).

Generally it is to be expected that the rates of the reverse electron transfer $k_{e}$ increase with increasing $E_{rp}$ values, that is, from 4-nitrobenzene diazonium salt to 4,N,N-dimethylaminobenzene diazonium salt. But the most intensive CIDNP signals of the series studied arise if $E_{rp} \approx 0.85-1$ eV. Hence $k_{e}$ and $k_{p}$ must be of the same order of magnitude. This is confirmed by the quantum yields of diazotation under the same conditions: $\psi_{Me} = 0.35$, $\psi_{Cl} = 0.47$, $\psi_{NO_{2}} = 0.79$. Using the expression $\Phi = k_{p}/(k_{p} + k_{e})$ one obtains the ratios $k_{p}/k_{e}$ ($\psi_{Me}$) = 0.5, $k_{p}/k_{e}$ ($\psi_{Cl}$) = 0.9, $k_{p}/k_{e}$ ($\psi_{NO_{2}}$) = 3.7. With 4,N,N-dimethylaminobenzene diazonium salt on the other hand the driving force for the reverse electron transfer amounting to 1.30 eV is so high that $k_{e} \gg k_{p}$. Thus the appropriate balance between $k_{e}$ and $k_{p}$ no longer exists and only a very weak $^{13}$N-CIDNP effect was observed, cf. Table I.

To prove this assumption rubrene ($E_{ox}^{\alpha} = 0.90$ V, see, in acetonitrile) was used as the electron donor instead of pyrene**. $E_{rp}$ is now 1.0 eV, and the driving force for the reverse electron transfer comes into the favorable region of strong CIDNP effects. In fact, an intensive $^{13}$C-CIDNP signal (enhanced absorption for $^{13}$C(1)) was observed for the 4,N,N-dimethylaminobenzene diazonium salt/rubrene system. However, no emission signal of the escape product, N,N-dimethylaniline, was found. This is not surprising, because the life time of 4-dimethylaminophenyl diazo radical (3.5 $\mu$s) exceeds the time domain boundary of the electron spin-lattice relaxation. This result verifies condition (2). Vice versa it proved possible to estimate rates of the reverse electron transfer and correlate these with the energies of the respective radical pairs. This will be published separately.

It should be emphasized that in the $^1$H-CIDNP experiments only polarization of the protons in 3-position of the arene diazonium salt and for the corresponding protons in the escape products, respectively, was observed. In connection with this, the CIDNP effects of the $^{15}$N($\alpha$) atoms were invariably of higher intensity than those of $^{15}$N($\beta$) atoms, cf. Fig. 1. According to quantum-mechanical calculations [8] and the results of ESR spectroscopy [6] this result is only compatible with a bent planar structure of the aryldiazonium radicals. The spin density in these $\alpha$-radicals is delocalized over both N-atoms of the diazonium group, but is somewhat higher in the $\alpha$-position. The quotient of the respective hyperfine coupling constants which are proportional to the spin densities amounts to $\alpha_{N(\alpha)}/\alpha_{N(\beta)} = 2.50$. The same value can be calculated from the CIDNP intensities of $p$-chlor- and $p$-cyanobenzene diazonium salt/pyrene systems (2.57 and 2.67, respectively) which were measured most accurately. The aryldiazonium radicals are therefore close analogues of the benzoyl radical [9, 10].

It should be noted that 4-chlorobenzene diazonium salt in the presence of the crown ether benzo-18-crown-6 in acetonitrile showed a weak $^{15}$N-CIDNP effect (enhanced absorption for Ar$^{15}$N$_{2}^{+}$, emission for $^{15}$N$_{2}$). Dibenzo-18-crown-6 gave a strong $^{15}$N-CIDNP effect of the same sign, but the saturated analogue, 18-crown-6, produced no CIDNP signal. From the oxidation potentials of these crown ethers and using equation (5) the electron transfer to diazonium salts should be possible. It can be concluded that for an effective electron transfer to arene diazonium salts a $\pi,\pi$-interaction is far better, if not a precondition, than is a $n,\pi$-interaction. Thus, the relatively high stability of arene diazonium salts in dioxane can be explained.

Experimental

Arene diazonium tetrafluoroborates

The arene diazonium tetrafluoroborates were synthesized by diazotation of the respective anilines with NaNO$_{2}$ or Na$^{12}$NO$_{2}$ respectively, in HBF$_{4}$ [11].

Aniline-$^{15}$N and p-methoxyaniline-$^{15}$N were available commercially (ISOCOMM ERZ, Leipzig).

Anilines-$^{15}$N with 4-X = Me, F, Cl, Br, NO$_{2}$, respectively, were synthesized by HOFMANN degradation of the respective benzamides-$^{15}$N.

4-Iodoaniline-$^{15}$N was synthesized by iodination of aniline-$^{15}$N [12].

** As shown by laser impulse fluorometry singlet-excited rubrene transfers an electron to arene diazonium salts with a diffusion-controlled rate, $k_{e} = 2 \times 10^{10}$ M$^{-1}$s$^{-1}$. 
4-Trimethylammoniumbenzene diazonium tetrafluoroborate chloride, $4\cdot\text{NMe}_3\cdot\text{C}_6\text{H}_4\cdot\text{N}_2^+\cdot\text{BF}_4\cdot\text{Cl}^-$, was synthesized by reaction of 4-chlorobenzene diazonium tetrafluoroborate,$\text{N}_2^+$ with trimethylamine [13].

4-Cyanobenzene diazonium tetrafluoroborate-$\text{N}_2^+$, $4\cdot\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2^+\cdot\text{BF}_4^-$, was prepared via the following steps:

a) SANDMEYER reaction [14] of 4-cyanobenzene diazonium tetrafluoroborate,$\text{N}_2^+$ with $\text{Na}^{15}\text{NO}_2$ to form 4-cyano-nitrobenzene-$\text{N}$. 

b) Reduction of the former product (purified by column chromatography on Al$_2$O$_3$ using benzene as eluent) with SnCl$_2$ in concentrated hydrochloric acid, cf. [15].

c) Diazotization of 4-cyanoaniline-$\text{N}$, $4\cdot\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{H}_2\text{N}^+$ with $\text{Na}^{15}\text{NO}_2$ in HB$iF_4$ [11].

The diazonium salts were recrystallized twice from acetonitrile/ether and acetonitrile/methylene chloride, dried in vacuo over KOH and concentrated H$_2$SO$_4$ and used immediately.

**Photo-CIDNP experiments**

The photo-CIDNP experiments were performed on a BRUKER NMR spectrometer HX-90-R equipped with an irradiation device, similar as described in [10], using a 500 W high pressure Hg lamp which was run with a.c. and overvoltage to produce a light output as high as possible. By means of a chopper, which was started by the trigger impulse for the gated decoupler of the NMR spectrometer, alternating irradiation and FID periods of the PFT mode were possible.

The following conditions were usually used:

<table>
<thead>
<tr>
<th>$t_{\text{rep}}$</th>
<th>$t_{\text{comp}}$</th>
<th>$t_{\text{irr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{15}$C-photo-CIDNP:</td>
<td>1.3–5.0 s</td>
<td>1.0–3.0 s</td>
</tr>
<tr>
<td>$^{15}$N-photo-CIDNP:</td>
<td>20.0 s</td>
<td>3.6 s</td>
</tr>
</tbody>
</table>

$t_{\text{rep}}$ pulse repetition time of the PFT mode,
$t_{\text{comp}}$ time for triggering the computer,
$t_{\text{irr}}$ duration of irradiation.

Saturated solutions of arene diazonium salts and 0.1 M of pyrene in acetonitrile without exclusion of air were used.

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