Chemically Induced Dynamic Nuclear Polarization

X. On Effects of Nuclear Relaxation and the Magnetic Field Dependence

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The magnetic field dependence of CIDNP is presented for two reaction products of independently generated alkyl radicals. It is shown that nuclear spin relaxation of the products influences the intensity distributions within multiplets, and how this relaxation can be included in the calculation of CIDNP effects from the radical pair theory. Analysis of the experimental results supports the recent view that CIDNP is created in pairs of radicals which undergo many diffusive displacements before reencounter.

1. Introduction

Chemically induced dynamic nuclear polarization (CIDNP) is currently attributed to nuclear spin dependent singlet triplet intersystem crossing in correlated radical pairs and the exclusive formation of pair products from the singlet manifold. The correlated pairs are produced by either simultaneous formation of two radicals or non-reactive radical-radical collisions. Models for calculations of the rates of product formation in the different nuclear spin states have been developed. They have been shown to yield fair agreement between observed and predicted structures of CIDNP-patterns.

It has long been realized that absolute CIDNP-enhancements are strongly influenced by the nuclear relaxation of the products. Moreover, recently, evidence for relaxation effects changing relative multiplet line intensities has been presented. Therefore, any quantitative calculation requires the inclusion of nuclear relaxation and this aspect has so far found little attention. Further, it is known that CIDNP effects depend on the magnetic field strength during the reaction. The few examples have been discussed mainly qualitatively and with neglect of relaxation effects.

This paper extends our previous analysis of CIDNP effects during reactions of independently produced ·CHCl₂, ·CHClOOH and ·CH₂COCHO radicals in solution. The product relaxation rates are determined and included in calculations of absolute enhancements during steady state conditions and of the magnetic field dependencies of the CIDNP effects.

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where $T_1 = (2 W_{12})^{-1}$. Integration leads to

$$V = \frac{p_1 - p_2}{p_1 + p_2} \cdot 2 k T, \quad V_1 \left(1 - e^{-t/T_1}\right).$$

(5)

For $t < T_1$ the initial enhancement becomes

$$V_1 = \frac{p_1 - p_2}{p_1 + p_2} \cdot 2 k T$$

(6)

and for $t > T_1$ a steady state NMR signal corresponding to

$$V_S = V_1; T_1/t$$

(7)

is obtained.

For a multilevel system (2) leads to

$$\frac{d(n_K - n_L)}{dt} = r(p_K - p_L) - 2 W_{KL}(n_K - n_L)$$

$$\sum_{M=+K} W_{MK}(n_M - n_K) - \sum_{M=-K} W_{ML}(n_M - n_L)$$

(8)

and a closed expression for $V$ can not be obtained. However, for the initial period $t \ll (W_{KL})^{-1}$

$$V_1 = \sum \frac{\Delta E}{\sum D_{KL}(p_K - p_L)} \cdot Z_k T \cdot \frac{d(n_K - n_L)}{dt},$$

(9)

The steady state enhancement factor $V_S$ follows from a solution of (8) for $d(n_K - n_L)/dt = 0$. Would the last two terms of (8) reduce to a form $-\bar{w}(n_K - n_L)$ we would have again the proportionality between $V_S$ and $V_1$ as expressed by (7), now with $T_1 = (2 W_{KL} + \bar{w})^{-1}$. Since this is not generally the case $V_S$ is not simply proportional to $V_1$. This means, that except for the initial period, CIDNP patterns are influenced not only by the rates of product formation ($p_K$) but also by the relaxation rates $W_{KL}$. The latter may cause deviations from the patterns predicted from (9), i.e. under neglect of relaxation.

In the following sections we give steady state enhancement factors for $t \gg T_1$ const in terms of the quantities $\bar{V}_S, \frac{d}{dt}$

$$\bar{V}_{S, \exp} = V_{\exp} \cdot t/T_1$$

(10)

where $T_1$ is an appropriate time constant. $V_1$ is calculated from (9) and $V_S$ from (1), (3) and (8). If relaxation effects are negligible, $\bar{V}_S = V_1$, therefore the differences between $V_1$ and $\bar{V}_S$, and $V_1$ and $\bar{V}_{S, \exp}$ reflect the relaxation effects.

The $W_{KL}$ and $T_1$ are determined from the time dependencies of CIDNP signals after interrupt of the reaction ($r = 0$). For the calculations of the $p_K$ we use, preferentially, Adrian’s high field formula $^6$ for products of pairs formed by radical-radical collisions:

$$p_K = 0.31 k_R \left(\frac{1}{3} \cdot \frac{37}{37}\right) + 0.105 k_R \Omega_K^{1/2} \cdot t^h$$

(11)

where $k_R$ is the probability for reaction on a singlet encounter and $t$ is the time between diffusive pair displacements. The matrix element $\Omega_K$ for $S=T_0$ intersystem crossing

$$\Omega_K = \frac{1}{2} \left\{ (g_1 - g_2) \cdot H + \sum a_{ii} m_{11} - \sum a_{ii} m_{112} \right\}$$

(12)

is determined from the field strength during reaction $H_r$ and the $g$-factors and hyperfine coupling constants of the two radicals of the pairs. Hyperfine interactions of nuclei which do not lead to splittings in the product NMR spectra are taken into account by individual calculation of $p_K$ for each spin state of these nuclei and summation $^6$.

3. Experimental

The steady-state CIDNP proton NMR-spectra of 1,1,2-trichloropropionic acid ($\text{CHCl}_2 - \text{CHClCOOH}$) and 1,1-dichloro-2-acyethylene ($\text{CHCl}_2 - \text{CH}_{2}\text{COCH}_3$) were obtained during reactions of $\cdot\text{CHCl}_2$, $\cdot\text{CHClCOOH}$ and $\cdot\text{CH}_{2}\text{COCH}_3$ radicals initiated by photolysis of dibenzyloperoxide in $\text{CH}_2\text{Cl}_2 | \text{CH}_2\text{COOCl},$ and $\text{CH}_2\text{Cl}_2 | \text{CH}_2\text{COCH}_3$-mixtures. They have been described in Ref. $^5a$ together with the experimental details.

For the determination of the magnetic field dependences of CIDNP the chemical systems were irradiated for $t_r = (5 \pm 0.2)$ sec in the variable field $H_r$ of a separate magnet $^4b$. Within a few tenths of a second they were then transferred into the field $H_0 = 23.5$ Gauss of a 100 MHz-NMR-spectrometer. The transitions of the product were recorded $\tau_t = (7 \pm 1)$ sec after the end of irradiation. The relaxation of the polarizations at $H_0 = 23.5$ Gauss was studied by varying $\tau_t$, relaxation in the low field $H_L < 2$ Gauss of the laboratory was investigated by interrupting the transfer process for $t_1$ seconds.

$g$-factors and hyperfine coupling constants of the radicals were measured by ESR. The signs of $a_{ii}$ in Table 1 were chosen to accommodate the phases of the

<table>
<thead>
<tr>
<th>Radical</th>
<th>$g$</th>
<th>$a$ [Gauss]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\cdot\text{CHCl}_2$</td>
<td>2.00829</td>
<td>$H_0$: $-16.79 \pm 0.05$</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.00010$</td>
<td>$^{35}\text{Cl}$: $+3.4 \pm 0.3$</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0001$</td>
<td>$^{37}\text{Cl}$: $+2.9 \pm 0.3$</td>
</tr>
<tr>
<td>$\cdot\text{CHClCOOH}$</td>
<td>2.0070</td>
<td>$H_0$: $-19.96 \pm 0.05$</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.00010$</td>
<td>$^{35}\text{Cl}$: $+3.9 \pm 0.3$</td>
</tr>
<tr>
<td>$\cdot\text{CH}_2\text{COCH}_3$</td>
<td>2.0046</td>
<td>$H(\text{COO})$: $&lt;0.5$</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0001$</td>
<td>$H(\text{CH}_3)$: $&lt;0.5$</td>
</tr>
</tbody>
</table>
CIDNP-patterns. The parameters of CHCICOOH and CH$_2$COCH$_3$ agree with previous results of other authors. A previous CIDNP-estimate for CHCl$_2$ lead to $a_H = -17.0$ Gauss and $g = 2.0080$, i.e. to values nearly identical to those now obtained. We note that the parameter $|a_H| = 20.5$ Gauss reported by HUDSON for CHCl$_2$ is too high.

Total decomposition of dibenzoyl peroxide was lower than 5% in all experiments, thus $r = \text{const}$ holds to a very good approximation.

4. Results and Analysis

4.1. 1,1,2-Trichloropropionic Acid

The AB-system formed by the CHCl$_2$ and CHCICOH protons of CHCl$_2$ - CHCICOH is characterized by the coupling constant $J = 6$ Hz and the difference of chemical shifts $\Delta_{AB} = 1.39 \cdot 10^{-6} \nu_0$, where $\nu_0$ is the proton resonance frequency. The four transitions between the spin states $|K\rangle = \sum C_K \sigma^K_\alpha \sigma^K_\beta$

\[
\begin{align*}
|1\rangle &= \beta \beta \\
|2\rangle &= \sin \theta \cdot \alpha \beta + \cos \theta \cdot \beta \alpha \\
|3\rangle &= \cos \theta \cdot \alpha \beta - \sin \theta \cdot \beta \alpha \\
|4\rangle &= \alpha \alpha
\end{align*}
\]

with $\sin 2 \Theta = J \cdot (\Delta^2 \nu_0^2 + J^2)^{-1/2}$ form a characteristic AX-pattern at the observation frequency ($\nu_0 = 100$ MHz, $H_0 = 23.5$ kGauss) and are observed at the positions

\[
\begin{align*}
(1) & \quad \delta = 6.19 \cdot 10^{-6} & |1\rangle & \rightarrow |3\rangle, \\
(2) & \quad \delta = 6.13 \cdot 10^{-6} & |2\rangle & \rightarrow |4\rangle, \\
(3) & \quad \delta = 4.81 \cdot 10^{-6} & |1\rangle & \rightarrow |2\rangle, \\
(4) & \quad \delta = 4.74 \cdot 10^{-6} & |3\rangle & \rightarrow |4\rangle
\end{align*}
\]

(13)

Figures 1 and 2 show the magnetic field dependence of the CIDNP-intensities. A pattern observed

![Fig. 1](image1)

Fig. 1. Magnetic field dependence of the CHCl$_2$-CIDNP-intensities of 1,1,2-trichloropropionic acid. Solid and broken lines calculated, see text; (1) in the text is identical with 1 in a circle in the figure.

![Fig. 2](image2)

Fig. 2. Magnetic field dependence of the CHCICOOH-CIDNP-intensities of 1,1,2-trichloropropionic acid. Solid and broken lines calculated, see text.

![Fig. 3](image3)

Fig. 3. Effects of relaxation in $H_0$, transitions (3) and (4) of 1,1,2-trichloropropionic acid.

![Fig. 4](image4)

Fig. 4. Effects of relaxation in $H_1$, transitions (3) and (4) of 1,1,2-trichloropropionic acid.

after reaction at $H_r = 20$ Gauss is given in Fig. 3, and the steady state pattern for $H_r = H_0$ is shown in Figure 4.
Figure 3 also demonstrates effects of relaxation in \( H_0 \) for lines (3) and (4). Lines (1) and (2) behave similarly, as is seen in Fig. 5 where the absolute intensities of all lines [(1) and (2) in enhanced absorption, (3) and (4) in emission] are plotted versus time \( t_0 \).

Effects of relaxation in the low laboratory field are shown in Figures 4 and 6.

For the analysis of the results we consider relaxation processes caused by randomly fluctuating external magnetic fields \( H_{A,B} \) at the nuclei [intermolecular, \( \langle W_{KM} \rangle_1 \) and by the fluctuating intramolecular dipol-dipol-coupling between A and B [\( \langle W_{KM} \rangle_d \)]. For the intermolecular process \(^{10}\)

\[
(W_{12})_1 = (W_{21})_1 = \frac{1}{2} \left( \frac{\sin^2 \Theta}{TA} + \frac{\cos^2 \Theta}{TB} \right) + C \frac{\sin^2 \Theta}{\sqrt{TA \cdot TB}},
\]

\[
(W_{13})_1 = (W_{31})_1 = \frac{1}{2} \left( \frac{\cos^2 \Theta + \sin^2 \Theta}{TB} \right) - C \frac{\sin^2 \Theta}{\sqrt{TA \cdot TB}},
\]

\[
(W_{14})_1 = (W_{41})_1 = 0,
\]

\[
(W_{23})_1 = (W_{32})_1 = \frac{1}{2} \left( \frac{\sin^2 \Theta}{TA} + \frac{\sin^2 \Theta}{TB} \right), \quad (14)
\]

\[
(W_{24})_1 = (W_{42})_1 = \frac{1}{2} \left( \frac{\cos^2 \Theta + \sin^2 \Theta}{TA} \right) - C \frac{\sin^2 \Theta}{\sqrt{TA \cdot TB}},
\]

\[
(W_{34})_1 = (W_{43})_1 = \frac{1}{2} \left( \frac{\sin^2 \Theta}{TA} + \frac{\cos^2 \Theta}{TB} \right) - C \frac{\sin^2 \Theta}{\sqrt{TA \cdot TB}}.
\]

where for normal viscosities

\[
(T_{A,B})^{-1} = \frac{\gamma^2}{3} \left| H_{A,B} \right|^2 \gamma \cdot \tau_D
\]

are the relaxation times and \( \tau_D \) is the diffusional correlation time. For the intramolecular process \(^{10,11}\)

\[
(W_{12})_d = (W_{21})_d = (W_{24})_d = (W_{42})_d = \frac{1}{TD} 0.1 (1 + \sin 2 \Theta),
\]

\[
(W_{13})_d = (W_{31})_d = (W_{24})_d = (W_{43})_d = \frac{1}{TD} 0.1 (1 - \sin 2 \Theta),
\]

\[
(W_{14})_d = (W_{41})_d = 0.4 \frac{1}{TD},
\]

\[
(W_{23})_d = (W_{32})_d = \frac{1}{TD} 0.0667 \cos^2 2 \Theta. \quad (15)
\]

The dipolar relaxation time \( T_D^{-1} = \frac{3}{2} \frac{\gamma^4 h^2}{\tau_a^4} \tau_R \) depends on the rotational correlation time \( \tau_R \) and the internuclear distance.

In a relaxation study \(^{10}\) of a similar AB-system (2,3-dibromothiophene, 10% in CS\(_2\)) the parameters \( T_A = 92.2 \) sec, \( T_B = 100.2 \) sec, \( T_D = 87.3 \) sec and \( C = 0.67 \) were obtained. These values allow a pre-estimate of the relative importance of inter- and intramolecular processes for our case. For the pro-
pionic acid \( r_{AB} \) is larger than for the thiophene. The viscosity of our solution (0.5 cp) is comparable to that of CS\(_2\). Therefore we expect \( T_B \approx 87.8 \) sec. On the other hand the proton density of our CH\(_2\)Cl\(_2\) \( \mid \) CH\(_2\)ClCOOH mixture is about 10-fold larger than that of the thiophene solution. Since \( |H_{A,B}|_{AV} \) is proportional to the proton density\(^{12}\) \( T_{A,B} \ll 90 \) sec is anticipated. This means that \( T_{A,B} \ll T_D \), so that the intramolecular process can be neglected. C seems to depend only little on \( r_{AB} \)^{10}, and is thus preestimated to be \( C \approx 0.67 \). With neglect of the dipolar process analysis of the time dependence of Fig. 5 by Eq. (2) with \( r = 0 \) is straightforward. The symmetry immediately gives \( T_A = T_B \) and \( n_1 = n_4 \), and the parameters of Eq. (2) reduce to \( T_A \) and the ratio \( (n_2 - n_1)/(n_3 - n_1) \) at \( t_{1f} = 0 \). A good fit represented by the calculated solid lines of Fig. 5 was obtained for \( T_A = T_B = 19.2 \) sec and \( (n_2 - n_1)/(n_3 - n_1) = 0.16 \) for \( t_{1f} = 0 \). It will be noted that the parameter \( C \) does not enter these calculations since for the high field \( H_0 \) \( \sin 2 \Theta \approx 0 \).

The thus determined value of \( T_{A,B} \) is used as time constant \( T_1 \) in Eq. (10) to obtain the experimental steady state enhancement factors of Table 2. They differ slightly from the previously reported values\(^{5a} \) since slightly different but less defined parameters were used in the earlier study.

**Table 2. Enhancement factors of 1,1,2-trichloropropionic acid.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>( \bar{V}_{S, exp} )</th>
<th>( \bar{V}_{S, calc} )</th>
<th>( \bar{V}_{L, calc} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>-260</td>
<td>-410</td>
<td>-375</td>
</tr>
<tr>
<td>(2)</td>
<td>-520</td>
<td>-487</td>
<td>-524</td>
</tr>
<tr>
<td>(3)</td>
<td>+740</td>
<td>+613</td>
<td>+643</td>
</tr>
<tr>
<td>(4)</td>
<td>+470</td>
<td>+535</td>
<td>+504</td>
</tr>
</tbody>
</table>

\( T_A = T_B = 19.2 \) sec now also enables us to calculate enhancement factors from the formulae of Section 2, (13), (14) and the radical parameters of Table 1. In these calculations the chlorine atoms of \( \cdot \)CHCl\(_2\) and \( \cdot \)CHCICOOH were considered to be all of mass number 35.

\[ x = 0.31 \frac{1}{0.105} \frac{k_R}{k_R \cdot r^{1/2}} \]  

(16)

of Eq. (11) enters approximately as a linear scaling parameter into \( \bar{V}_{S, calc} \) and \( \bar{V}_{L, calc} \). It was determined to \( x \approx 0.615 \times 10^6 \) rad\(^{1/2}\) sec\(^{-1/2}\) by a least square fit of \( \bar{V}_{S, calc} \) to \( \bar{V}_{S, exp} \). The results of the calculation are given in columns 3 and 4 of Table 2.

Obviously, for this example, steady state conditions and \( H_0 = 23.5 \) kGauss, inclusion of relaxation does not improve the fit between experimental and calculated enhancements. The following analysis of the magnetic field dependence shows its importance more clearly.

The corresponding experiments (Figs. 1, 2, 4 and 6) involve the transfer of samples from \( H_L \) to \( H_0 \) and on to \( H_H \), and the analysis has to start from the behaviour of the spin state populations created in \( H_L \) during the periods of transfer. There are the two limiting cases of adiabatic and non-adiabatic behaviour. For the first, the population of an eigenstate \( |K\rangle \) of the product does not change with the magnetic field and follows the energy-versus-field correlation diagram. For the second, the population changes according to the projection of low field to high field eigenstates. In accord with others\(^{46,13} \) we believe that the adiabatic case holds for our systems, since we have compared CIDNP patterns obtained \( t_{1f} \) seconds after reaction for \( t_r \) seconds in \( H_0 \) and no transfer with those found \( t_{1f} \) seconds after reaction in the separate magnet for \( t_r \) seconds at \( H_L \approx H_0 \) and transfer and found identical spectra. For non-adiabatic transfer of populations drastic differences are expected. The finding also shows, that relaxation during transfer is negligible.

The final calculations were then performed for the conditions of adiabatic transfer, neglect of relaxation during transfer, relaxation with \( T_{A,B} = 19.2 \) sec in \( H_L \) and \( H_0 \), \( C = 0.67 \) and the previously given parameters. The results are represented by the solid lines of Figures 1, 2 and 6. One free adjustable scaling parameter which affects the absolute intensities only was fitted to the experimental data for transitions (2) and (3). The agreement between experimental and calculated data is very satisfactory. In particular, the agreement for transitions (1) and (4) of Fig. 6 supports \( C = 0.67 \) since this parameter strongly influences the relaxation of these lines at \( H_L \approx 0 \).

The importance of full inclusion of the relaxation behaviour is demonstrated by the much poorer fit given by the broken lines of Figures 1 and 2. For the corresponding calculations relaxation was taken into account by the assumption that (8) can be approximately represented by

\[ d(n_K - n_L)/dt = r(p_K - p_L) - (n_K - n_L)/T_A. \]  

(17)

Otherwise the same parameters and scaling factor as used for the solid lines was applied. It is note-
worthy that this treatment does not yield the correct values of $H_r$ for which the CIDNP intensities of (1) and (4) are zero.

4.2. 1,1-Dichloro-2-acetylethane

At 100 MHz the CHCl$_2$-CH$_2$C-group exhibits a typical AX$_2$-spectrum ($J_{AX} = 5$ Hz, $A_{AX} \nu_0 = 2.76 \cdot 10^{-6} \nu_0$) with transitions at (1) $\delta = 6.32 \cdot 10^{-6}$, (2) $\delta = 6.26 \cdot 10^{-6}$, (3) $\delta = 6.20 \cdot 10^{-6}$ (CHCl$_2$-group), (4) $\delta = 3.53 \cdot 10^{-6}$, (5) $\delta = 3.47 \cdot 10^{-6}$ (CH$_2$-group). Steady state CIDNP-spectra for $\nu_0 = 56.4$ MHz and for $\nu_0 = 100$ MHz have been reported previously $^5$.

The magnetic field dependence of the CIDNP-intensities are given in Figures 7 and 8. Because of experimental difficulties we were unable to measure the dependencies on $\delta$ and $\tau$.

For the analysis we adopt the following relaxation model:

The CH-proton shall relax via intermolecular processes ($T_A$), whereas the CH$_2$-protons shall relax by inter-molecular and intramolecular processes ($T_{A1}$, $T_{1B}$, and $T_D$). The inclusion of intramolecular dipolar relaxation for the CH$_2$-group is appropriate because the internuclear distance between the nuclei $B_1$ and $B_2$ is rather small. The same reasoning supports the further assumption that for the CH$_2$-group the correlation factor $C = 1$. Calculation of the elements of the relaxation matrix for high fields (AX$_2$) is straightforward and will not be reproduced here $^{14}$. One results of the model is the prediction that the sum of the intensities of the line group A [(1), (2), (3)] decays exponentially with the time constant $T_A = T_{1A}$, and that the sum of the intensities of group B [(4), (5)] decays with $T_{1B}^{-1} = T_{1B}^{-1} + T_D^{-1}$ for high fields.

To determine the relaxation parameters these time constants were measured from the decay of the CIDNP-signals after reaction in $H_2$. The values $T_A = 25.0$ sec and $T_{1B} = 12.3$ sec were found for 56.4 and 100 MHz. With the further assumption $T_B = T_A$, supported by the findings of Section 4.1, $T_B = 25.0$ sec and $T_D = 24.2$ sec are obtained.

These values and Eq. (10) lead to the steady state enhancement factors of column 2 in Table 3.

Table 3. Enhancement factors of 1,1-Dichloro-2-acetylethane.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\nu_0$</th>
<th>$V_s$ exp</th>
<th>$V_s$, calc</th>
<th>$V_1$, calc</th>
</tr>
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<td>380</td>
<td>-473</td>
<td>-563</td>
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</tr>
<tr>
<td>(2)</td>
<td>330</td>
<td>-413</td>
<td>-401</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>230</td>
<td>-398</td>
<td>-334</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>+480</td>
<td>+456</td>
<td>+438</td>
<td></td>
</tr>
<tr>
<td>(5) (100 MHz)</td>
<td>+570</td>
<td>+532</td>
<td>+552</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>-760</td>
<td>-800</td>
<td>-746</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>-1180</td>
<td>-920</td>
<td>-988</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>-800</td>
<td>-796</td>
<td>-713</td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>+1110</td>
<td>+1035</td>
<td>+1033</td>
<td></td>
</tr>
<tr>
<td>(5) (56.4 MHz)</td>
<td>+965</td>
<td>+1049</td>
<td>+1052</td>
<td></td>
</tr>
</tbody>
</table>

Columns 3 and 4 of this Table show enhancement factors calculated from the formulae of Section 2 and the radical parameters of Table 1. A chlorine coupling constant of 3.9 gauss was used, the small couplings with the COOH- and COCH$_3$-protons were neglected. The free scaling parameter $\kappa$ (16) was obtained as $\kappa = 0.575 \cdot 10^6$ rad$^{1/2}$ sec$^{-1/2}$ by fitting $V_s$, calc to $V_s$, exp. Inspection of the enhancement factors indicates that for this example relaxation diminishes the multiplet effect type contribution$^2$ to CIDNP.

The procedure described in Section 4.1 was used in the calculation of the magnetic field dependence (Figures 7, 8). The product was treated as AB$_2$-
system in the determinations of the probabilities $p_K$ and the transition probabilities $D_{KL}$, whereas the relaxation matrix for an $AX_2$-system was used for all fields. The latter approximation may be responsible for some deviations of calculated lines from experimental data for $H_r \leq 3$ kgauss. The scaling parameter was adjusted to the crossing point of transitions (4) and (5) (Figure 8). Again, proper treatment of relaxation (solid lines) gives better agreement than neglect of these processes (broken lines). However, for this example, there are significant differences between predicted and observed CIDNP effects of transitions (2) and (3) (Fig. 7) which remain to be explained.

5. Discussion

It is evident from the figures that in general relaxational effects do not grossly change the characteristics of CIDNP patterns, i.e. the net and multiplet type effects. They influence the intensity distribution within multiplets, however, and specifically tend to equalize the intensities of outer lines of the multiplets by intensity stealing processes. Lines predicted in emission from the $p_K$ alone may even appear in enhanced absorption if the multiplet to which they belong has net enhanced absorption, and vice versa.

If relaxation is taken into account Adrian's high field CIDNP treatment of the probabilities $p_K$ leads to fair qualitative and quantitative agreements of predicted and observed effects. We have not analyzed our low field data ($H_r \leq 1$ kgauss). Recently, Garst et al. have treated our data of Figs. 1 and 2 in terms of a generalized Closs-Kaptein-Oosterhoff approach. With a free parameter $\tau$ set to $5 \cdot 10^{-10}$ sec, they have found a good fit for low fields but a rather poor fit for high fields. Relaxation was not included.

For obtaining good fits from Adrian's theory the inclusion of small hyperfine coupling constants of the radical nuclei is essential even if these nuclei do not contribute to the observed NMR patterns of the products. We have previously published a magnetic field dependence of lines (3) and (4) of 1,1,2-trichloropropionic acid calculated with neglect of the chlorine couplings which gave only a very poor description of the experimental data. This reference also shows that under neglect of the chlorine couplings a good fit is obtained from Kaptein's diffusional treatment which in contrast to Adrian's includes a non-zero exchange interaction $J$ between the two radicals of the pair. For the specific example $J = 2 \cdot 10^8$ rad$^{-1}$sec$^{-1}$ was used. Our present results show that a non-zero $J$ hat not to be assumed and that this parameter simulates the effects of small nuclear coupling constants. Further, $J = 0$ supports the opinion that nuclear polarization is created in pairs which undergo many diffusive displacements before they reencounter.

The values $\kappa = 0.615 \cdot 10^6$ and $0.575 \cdot 10^6$ rad$^{-1/2}$sec$^{-1/2}$ allow estimates for the probabilities $k_R$ of reaction during pure singlet encounters. Inserting times $\tau$ between two successive diffusive encounters of $10^{-12} \leq \tau \leq 10^{-11}$ sec into Eq. (16) we obtain $0.43 \leq k_R \leq 0.86$. These values are in accord with the definition $k_R \leq 1$ and compatible with the results of Zwarc et al. who obtained for the probability $\alpha$ of reaction during an encounter of methyl radicals $0.09 \leq \alpha \leq 0.5$.

Finally, we wish to comment on calculations of magnetic field dependencies and enhancement factors of the CIDNP effects given in Section 4 which we have performed using other formulations of the radical pair theory, thus as the original Closs-Kaptein-Oosterhoff and our kinetic approach. These theories contain free selectable parameters $(J, \tau, K)$ the choices of which effect the qualitative appearances of CIDNP patterns. It was possible to find parameter sets for which good fits of the experimental data are obtained even if the small coupling constants or relaxation effects were neglected and our previous work contains some examples. Adrian's formulation does not contain such a parameter. Therefore, we believe that these parameters simply simulate effects of relaxation and small couplings which have hitherto not found attention, though the older treatments may still have their use in allowing good and quick preestimates of CIDNP spectra.

The ESR-data of Table 1 were kindly supplied by Dipl.-Phys. H. Paul of this laboratory.

I. Introduction

Since the classical work of Maxwell, it is known that velocity or temperature gradients near walls lead to the familiar surface effects of viscous and temperature slip in the range of sufficiently low pressures. These phenomena have been studied quite well both experimentally and theoretically. In the flow of gas mixtures, diffusive slip occurs due to the concentration gradient tangential to the wall. In contrast to the phenomena mentioned earlier, little was known about this almost unstudied effect. The diffusive slip was first discussed by Kramers and Kistemaker. These authors obtained an expression for the diffusive slip by using Maxwell's momentum balance at the wall and established the existence of diffusive slip by measuring the pressure difference that results in a closed system. Since that time, this effect has been studied, both experimentally and theoretically by several authors. The earlier theoretical treatments, however, included only the effects of the masses and the accommodation coefficients.

A theoretical relation for the diffusion slip coefficient $\sigma_{12}$ including the effects of intermolecular...