# Chemically Induced Dynamic Nuclear Polarization*

## VII. Reaction Products of Independently Generated Alkyl Radicals

M. Lehnig and H. Fischer

Physikalisch-Chemisches Institut der Universität Zürich, Schweiz

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Alkyl radicals are generated by reactions of phenyl radicals in binary mixtures of substituted alkanes. CIDNP-NMR spectra of their reaction products are explained by $S - T_0$-transitions in radical pairs formed in free radical encounters. From comparisons of calculated and observed CIDNP spectra the $g$-factor and the proton hyperfine coupling constant of $\cdot CHCl_2$ are determined [$g = 2.0080 \pm 0.0003$, $a = (-17.0 \pm 1.0)$ G]. The inclusion of nuclear relaxation in free radicals in quantitative CIDNP treatments is discussed, and evidence for the radical pair mechanism causing CIDNP of phenyl derivatives during dibenzoylperoxide decompositions is presented.

## 1. Introduction

In a previous paper[1] a kinetic formulation of the radical pair mechanism explaining NMR-emission and/or enhanced absorption spectra during radical reactions (CIDNP) was given and equations for calculations of CIDNP patterns were derived. This theory is now applied in the interpretation of CIDNP of reaction products of independently generated radicals. CIDNP has been observed during such reactions previously by Closs[2], but has not yet found detailed investigation. We will show that there is fair agreement between experimental and theoretical results and will give an example for the application of CIDNP in determinations of free radical $g$-factors and hyperfine coupling constants.

Radical reactions were initiated by photolysis of dibenzoylperoxide (BPO) or, occasionally, other peroxides in binary solvents RX/R′X′. They are represented by

$$\mathrm{BPO} \rightarrow 2\,\Phi\mathrm{CO_2}\cdot \rightarrow 2\,\Phi\cdot + 2\,\mathrm{CO_2} \tag{1a}$$

$$\mathrm{BPO} \rightarrow \Phi\mathrm{CO_2}\Phi + \mathrm{CO_2} \tag{1b}$$

$$\Phi\cdot + \mathrm{RX} \xrightarrow{k_1} \Phi\mathrm{X} + \mathrm{R}\cdot \tag{1c}$$

$$\Phi\cdot + \mathrm{R'X'} \xrightarrow{k_2} \Phi\mathrm{X'} + \mathrm{R}\cdot' \tag{1d}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot' \rightarrow \mathrm{R} - \mathrm{R'} \tag{1e}$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{k_3} \mathrm{R} - \mathrm{R} \tag{1f}$$

$$\mathrm{R}\cdot' + \mathrm{R}\cdot' \rightarrow \mathrm{R'} - \mathrm{R'} \tag{1g}$$

$$\mathrm{R}\cdot + \mathrm{R'X'} \rightarrow \mathrm{RX'} + \mathrm{R}\cdot' \tag{1h}$$

$$\mathrm{R}\cdot' + \mathrm{RX} \rightarrow \mathrm{R'X} + \mathrm{R}\cdot \tag{1i}$$

CIDNP was observed for all the reaction products.

## 2. Experimental

The samples were solutions of peroxides (0.1 m) in binary mixtures of methyliodide, methylformiate, methylenchloride, carbon tetrachloride, mono-chloroacetic acid, and acetone. They were photolyzed within suitably modified[3] probes of VARIAN DP-60 or HA-100 spectrometers by the radiation of an AH-6 1 kW high pressure mercury lamp. During some experiments the flow technique and the method of irradiation in a separate magnet described previously[4] were also applied. For equal magnetic fields and irradiation conditions the structure of CIDNP effects did not depend on the experimental technique. Enhancement factors of individual NMR-transitions of the product protons were determined using Eq. (2)

$$V_{\mathrm{exp}} = \frac{A^*}{A_0} \cdot \frac{t}{T_1} \tag{2}$$

from the amplitudes of the transitions during ($A^*$) and after ($A_0$) irradiations with the in-situ-irradiation technique. $t$ is the total irradiation time, and $T_1$ is the longitudinal relaxation time for the transition. This quantity was measured from the decays of CIDNP effects after interruptions of the irradiation. (2) is applicable only if $|A_0| \ll |A^*|$. This condition was observed in all the examples given below.

Commercially available chemicals were used. Sample temperatures were $(26 \pm 4)$ °C.

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[1] Part VI: H. Fischer, Z. Naturforsch. **25 a**, 1957 [1970].

[2] G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc. **92**, 2186 [1970].

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## 3. Experimental Results and Calculated CIDNP Spectra

### 3.1. *Phenyl derivatives*

The CIDNP of the products of reactions (1b), (1c), (1d) is outlined briefly, because the main aspects of this paper refer to CIDNP of the other reaction products. In solutions not containing acetone, the benzene, chloro- or iodobenzene exhibit the emission patterns described previously [4]. The same result is obtained for solutions containing acetone when unfiltered radiation is applied. However, benzene, chloro- or iodobenzene show enhanced absorptions when light filtered by a WG-6 filter and of wavelengths $\lambda > 300$ nm (SCHOTT und Gen., Mainz) is used. Further, the minor product phenylbenzoate (1b) shows enhanced absorption for the ortho proton transitions of the phenoxy ring if benzene, chloro- or iodobenzene exhibit emission, and emission if these products show enhanced absorption. This agrees with observations of TROZZOLO [5] and KAPTEIN [6] and with the results of a recent study of the routes for CIDNP in thermal BPO decompositions [7]. The product polarizations and their phase relations support the previous suggestion [8] that CIDNP of phenyl derivatives during BPO decompositions are caused by $S$-$T_0$-transitions in the intermediate pair $\Phi CO_2 \cdots \Phi$. During thermal and direct photodecompositions this pair is formed from BPO decomposing from singlet states. During photodecompositions sensitized by acetone or other ketones [6] a BPO decomposition from triplet states seems likely.

This explanation of CIDNP during BPO decompositions will be treated in more detail in future publications. It has been offered by KAPTEIN [6], independently, and is certainly superior to the original interpretation [9].

### 3.2. *Products derived from solvent radicals*

Table 1 summarizes the CIDNP effects in the NMR spectra of products of reactions (1e) to (1i) for several binary solvent mixtures. Experimental CIDNP spectra are given in the upper parts of Figures 1 to 4. The assignments of the individual

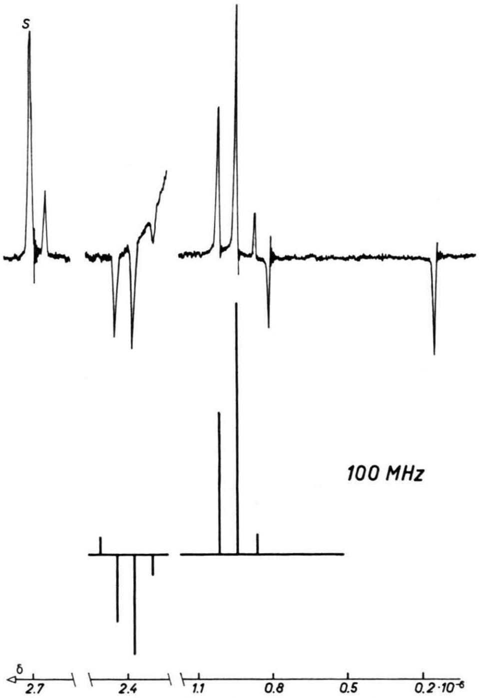

Fig. 1. CIDNP during photolysis of BPO in a 1 : 100 mixture of $CH_3I$ and $CH_3COCH_3$.

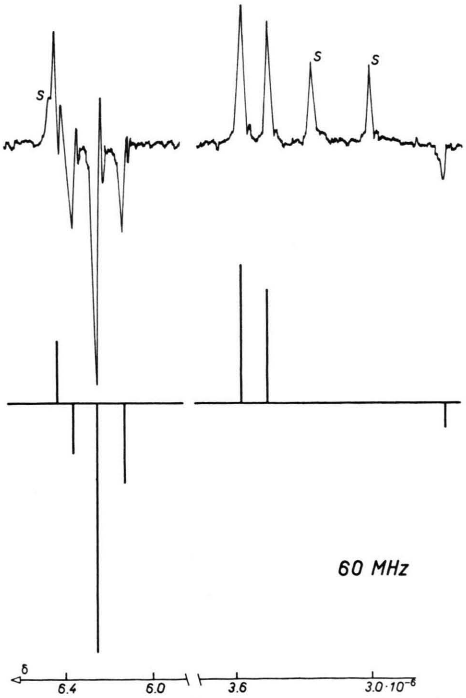

Fig. 2. CIDNP during photolysis of BPO in a 1 : 2 mixture of $CH_2Cl_2$ and $CH_3COCH_3$ (60 MHz).

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[5] A. TROZZOLO, Paper presented at the CIDNP-Symposium, Houston, USA, February, 1970.

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| R – R′ | | R – R, RX′, R′ – R′, R′X | |
|---|---|---|---|
| 1. $CH_3I/HCOOCH_3$ (1 : 20), 100 MHz<br>$R\cdot = \cdot CH_3$ ($g = 2.00252$, $a = -22.83$ G)[10–12]<br>$R\cdot' = \cdot COOCH_3$ ($g' = 2.0013$)[13] | | | |
| $\mathbf{CH_3}-COOCH_3$ | $\delta = 2.03\ E$ | $\mathbf{CH_3-CH_3}$ | $\delta = 0.82\ A$ |
| | | $\mathbf{CH_4}$ | $\delta = 0.16\ A$ |
| 2. $CH_3I/CH_3COCH_3$ (1 : 100), 100 MHz, Fig. 1<br>$R\cdot = \cdot CH_3$ ($g = 2.00252$, $a = -22.83$ G)[10–12]<br>$R\cdot' = \cdot CH_2COCH_3$ ($g' = 2.00441$, $\lvert a' \rvert = 19.75$ G)[10] | | | |
| $\mathbf{CH_3}-CH_2COCH_3$ | $\delta = 1.03\ A$ | $\mathbf{CH_3-CH_3}$ | $\delta = 0.82\ E$ |
| | $\delta = 0.95\ A$ | $\mathbf{CH_4}$ | $\delta = 0.16\ E$ |
| | $\delta = 0.88\ A$ | | |
| $CH_3-\mathbf{CH_2}COCH_3$ | $\delta = 2.51\ A$ | $\mathbf{CH_2}COCH_3)_2$ | $\delta = 2.63\ A$ |
| | $\delta = 2.44\ E$ | | |
| | $\delta = 2.37\ E$ | | |
| | $\delta = 2.29\ E$ | | |
| 3. $CH_3I/CCl_4$ (1 : 100), 100 MHz<br>$R\cdot = \cdot CH_3$ ($g = 2.00252$, $a = -22.83$ G)[10–12]<br>$R\cdot' = \cdot CCl_3$ ($g' = 2.0091$)[14] | | | |
| $\mathbf{CH_3}-CCl_3$ | $\delta = 2.72\ A$ | $\mathbf{CH_3-CH_3}$ | $\delta = 0.82\ E$ |
| | | $\mathbf{CH_3}Cl$ | $\delta = 2.94\ E$ |
| 4. $CH_2Cl_2/CH_3I$ (100 : 1), 56.4 MHz<br>$R\cdot = \cdot CHCl_2$ ($g = ?$, $a = ?$)<br>$R\cdot' = \cdot CH_3$ ($g' = 2.00252$, $a' = -22.83$ G)[10–12] | | | |
| $\mathbf{CHCl_2}-CH_3$ | $\delta = 6.02\ E$ (1) | $\mathbf{CHCl_2-CHCl_2}$ | $\delta = 5.96\ A$ |
| | $\delta = 5.90\ E$ (3.5) | | |
| | $\delta = 5.78\ E$ (3) | | |
| | $\delta = 5.67\ E$ (1) | | |
| $CHCl_2-\mathbf{CH_3}$ | $\delta = 2.09\ A$ (7.8) | $\mathbf{CH_3-CH_3}$ | $\delta = 0.82\ E$ |
| | $\delta = 1.98\ A$ (6.6) | $\mathbf{CH_4}$ | $\delta = 0.16\ E$ |
| 5. $CH_2Cl_2/CH_3COCH_3$ (1 : 2), 100 MHz, Fig. 3<br>$R\cdot = \cdot CHCl_2$<br>$R\cdot' = \cdot CH_2COCH_3$ ($g' = 2.00441$, $\lvert a' \rvert = 19.75$ G)[10] | | | |
| $\mathbf{CHCl_2}-CH_2COCH_3$ | $\delta = 6.32\ E$ | $\mathbf{CHCl_2-CHCl_2}$ | $\delta = 6.47\ A$ |
| | $\delta = 6.26\ E$ | | |
| | $\delta = 6.20\ E$ | | |
| $CHCl_2-\mathbf{CH_2}COCH_3$ | $\delta = 3.53\ A$ | $\mathbf{CH_2}COCH_3)_2$ | $\delta = 2.68\ E$ |
| | $\delta = 3.47\ A$ | | |
| 6. $CH_2Cl_2/CH_2ClCOOH$ (3 : 1), 100 MHz, Fig. 4<br>$R\cdot = \cdot CHCl_2$<br>$R\cdot' = \cdot CHClCOOH$ ($g' = 2.00677$, $\lvert a' \rvert = 20.2$)[15] | | | |
| $\mathbf{CHCl_2}-CHClCOOH$ | $\delta = 6.19\ E$ | $\mathbf{CHCl_2-CHCl_2}$ | $\delta = 6.06\ A$ |
| | $\delta = 6.13\ E$ | | |
| $CHCl_2-\mathbf{CHCl}COOH$ | $\delta = 5.11\ A$ | | |
| | $\delta = 5.04\ A$ | | |
| 7. $CH_2Cl_2/CCl_4$ (1 : 10), 100 MHz<br>$R\cdot = \cdot CHCl_2$<br>$R\cdot' = \cdot CCl_3$ ($g' = 2.0091$)[14] | | | |
| $\mathbf{CHCl_2}-CCl_3$ | $\delta = 6.14\ A$ | $\mathbf{CHCl_2-CHCl_2}$ | $\delta = 5.96\ E$ |

Table 1. CIDNP of reaction products during photolysis of BPO in mixed solvents (solvent compositions are given as volume ratios RX: R′X′).

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[10] H. ZELDES and R. LIVINGSTON, J. Chem. Phys. **45**, 1946 [1966].

[11] R. W. FESSENDEN and R. H. SCHULER, J. Chem. Phys. **39**, 2147 [1963].

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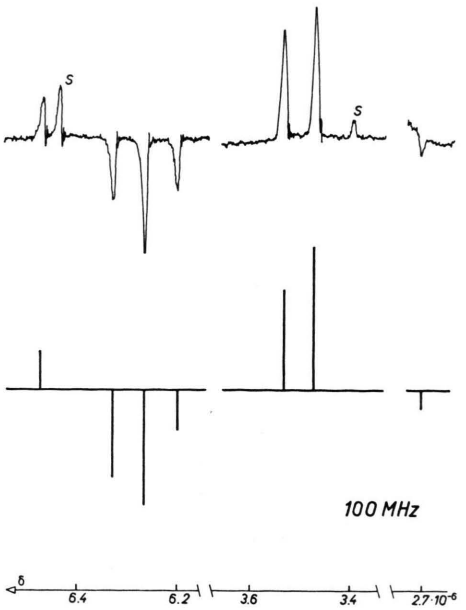

Fig. 3. CIDNP during photolysis of BPO in a 1 : 2 mixture of $CH_2Cl_2$ and $CH_3COCH_3$ (100 MHz).

Fig. 4. CIDNP during photolysis of BPO in a 3 : 1 mixture of $CH_2Cl_2$ and $CH_2ClCOOH$.

lines are found in Table 1 ($\delta$-units, standard TMS). Peaks denoted by $S$ are $C^{13}$ satellites of the solvents.

The products listed in Table 1 were the only derivatives of reactions (1e) to (1i). Therefore the radicals R· and R·′ given in the table are the only ones involved. To test whether the CIDNP of the products of R· and R·′ depended on the radical generation steps (1a), (1c), (1d), several experiments were performed. tert-butylperbenzoate, hydrogenperoxide and di-tert-butylperoxide were used as initiators instead of BPO, and filtered as well as unfiltered light was applied. The CIDNP patterns of the products were not found to change. Nuclear polarizations of R· or R·′ by reactions (1c), (1d) must therefore be of negligible importance, and product polarizations arise during reactions (1e) to (1i) only.

From the pair mechanism[1] the CIDNP effects may be attributed to $S$-$T_0$-transitions in pairs R· ·R′, R· ·R, and R′· ·R′ formed by diffusive encounters (1e), (1f), (1g). Now, transitions in the symmetric pairs R· ·R and R′· ·R′ can cause multiplet type polarizations only. In our examples (Table 1) the symmetric products have single line NMR spectra of the relevant protons, and multiplet type polarizations are thus not observable. Therefore the observed CIDNP effects are attributed entirely to transitions of the unsymmetric pair R· ·R′ and the following route for polarizations is proposed

$$\begin{array}{llll}
R\cdot + R\cdot' \rightarrow R\cdot & \cdot R' - & \begin{cases} \rightarrow \underline{R} - \underline{R}' \\ \rightarrow \underline{R}\cdot + \underline{R}\cdot' \end{cases} & \\
 & \underline{R}\cdot\ + \underline{R}\cdot & \rightarrow \underline{R} - \underline{R} & \\
 & \underline{R}\cdot' + \underline{R}\cdot' & \rightarrow \underline{R}' - \underline{R}' & \\
 & \underline{R}\cdot\ + R'X' & \rightarrow \underline{R}X' + R\cdot' & \\
 & \underline{R}'\cdot + RX & \rightarrow \underline{R}'X + R\cdot\,. &
\end{array} \tag{3}$$

Underlined symbols indicate polarized species. Rule A.1 of a previous paper[1] now immediately explains the observation (Table 1) that polarizations of symmetric coupling and transfer products have signs opposite to those of corresponding groups of the unsymmetric coupling products. Since the polarizations of R· and R·′ built up in R· ·R′ decay by nuclear relaxation in the free radicals, scheme (3) also explains why the amplitudes of the CIDNP effects are generally much lower for the symmetric coupling and transfer products than for the unsymmetric coupling products (Figs. 1 to 4). In particular, this relaxation will also be responsible for observed variations of CIDNP intensity ratios $|I_S/I_A|$ of corresponding transitions of symmetric and unsymmetric products with solvent compositions (see below). For the compositions noted in

Table 1 these ratios were $|I_S/I_A| < 10^{-1}$, meaning that polarizations of radicals entering $R\cdot\ \cdot R'$ must be much lower than the polarizations produced in these pairs.

Neglecting these small polarizations, the enhancement factors of the unsymmetric coupling products $R-R'$ should be given by Eqs. (5), (10), (14), and (19) of Ref. [1]. Immediate application of these formulas is rendered somewhat difficult, however, because the pertinent $g$-factors and proton hyperfine constants $a$ of some of our radicals are not known. So we are not aware of any literature value of $g$ and $a$ for $\cdot CHCl_2$ and of any experimental or theoretical determination of the signs of $a$ for $\cdot CH_2COCH_3$ and $\cdot CHClCOOH$. Therefore, we first deduce relations between the unknown parameters from our CIDNP results using a simple rule for the CIDNP of combination products of pairs formed by radical encounters which follows from approximations of Eqs. (5), (10), (14), and (19): If the $g$-factors of $R\cdot$ and $R\cdot'$ are different and if the coupling constants of $R\cdot$ and $R\cdot'$ are both negative (positive) the group of $R-R'$ corresponding to the radical with the larger $g$-factor shows net emission (enhanced absorption), the other group shows enhanced absorption (emission).

Inspection of Table 1 shows that the net polarizations of R and R' in $R-R'$ are of unlike signs for all cases with $|a|, |a'| \neq 0$. Thus the sign of the proton coupling constants is like for $\cdot CH_3$, $\cdot CH_2COCH_3$, $\cdot CHCl_2$, and $\cdot CHClCOOH$, i.e. negative. Further, the first three examples involving radicals with known $g$-factors are in perfect accord with the rule stated above. Applying this rule to the other examples, we then obtain that the $g$-factor of $\cdot CHCl_2$ must be larger than that of $\cdot CH_3$, $\cdot CH_2COCH_3$, and $\cdot CHClCOOH$ but lower than that of $\cdot CCl_3$. From the $g$-factors listed in Table 1 thus $2.00677 < g\,(\cdot CHCl_2) < 2.0091$.

With the knowledge of the signs of $a$ and the range for $g$ ($\cdot CHCl_2$) the final calculations of theoretical CIDNP patterns are readily carried out. Results are given in Table 2 ($V_{\text{calc}}$) and displayed as stick diagrams in Figs. 1 to 4

$$\left(A^*_{\text{calc}} = \frac{A_0 \cdot T_1}{t}\, V_{\text{calc}}\right)\,.$$

For $CH_3CH_2COCH_3$ the two parameters $k_d/k_d + k_c$ and

$$K = \frac{v^2 \cdot k_d}{(\Delta R)^2\,(k_d + k_c) \cdot 2\,n_c}$$

in formulas (10) and (14) of Ref. [1] were varied to obtain good fits of experimental and calculated results. For the other examples $a$ ($\cdot CHCl_2$) and $g$ ($\cdot CHCl_2$) were varied as well, and optimum agreement was found for $a\,(\cdot CHCl_2) = (-17.0 \pm 1.0)$ G, $g\,(\cdot CHCl_2) = 2.0080 \pm 0.0003$.

Considering the approximations made in developing the theory[1] we think the overall agreement of experimental and calculated CIDNP spectra most gratifying. In fact there are indications that the only major disagreement, the overestimation of the multiplet type polarization in the triplet of $CHCl_2-CH_2COCH_3$ (Fig. 2 and 3), may be caused by intramolecular Overhauser effects which tend to equalize the outer lines of the triplet and which have not been taken into account.

Our treatment does even reproduce the peculiar phase change of the multiplet type polarization of $CHCl_2-CH_2COCH_3$ from $A/E$ at 60 MHz to $E/A$ at 100 MHz (Fig. 2 and 3). As was noted previously[1], such or related[16,17] phase changes are explainable only with the aid of equations not linear in $|\Omega_{ji_\sigma}|^2$ as used in our treatment or the corresponding ones of Kaptein[18] or Closs[2,16,17].

By a simple extension of our formalism the enhancement factors of the symmetric coupling and transfer products can also been quantitatively discussed. The corresponding polarizations are produced in the unsymmetric pairs and decay by nuclear polarization in the free radicals. As an example we consider the ratio of the total intensities of the $CHCl_2$-transitions of $CHCl_2-CHCl_2$ ($I_S$) and of $CHCl_2-CH_2COCH_3$ ($I_A$) and its dependence on the solvent composition. Assuming that the nuclear relaxation in the radicals $\cdot CHCl_2$ may be described by one relaxation time $T_R$ and that cross-relaxation mechanisms are unimportant, simple calculations lead to

$$\frac{I_A}{I_S} = -\frac{T_{1A}}{T_{1S}}\left\{1 + \frac{1}{T_R}\sqrt{\frac{2}{k_3\,p}\,x}\right\} \qquad (4)$$

where

$$x = 1 + \frac{k_2}{k_1}\,\frac{[CH_3COCH_3]}{[CH_2Cl_2]}\,. \qquad (5)$$

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[16] G. L. Closs and A. D. Trifunac, J. Am. Chem. Soc. **92**, 2183 [1970].

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[18] R. Kaptein and L. J. Oosterhoff, Chem. Phys. Letters **4**, 195, 214 [1969].

| group | $T_1$ [sec] | $\delta$ | $V_{\mathrm{exp}}$ | $V_{\mathrm{calc}}$ | $\frac{k_d}{k_d + k_c}$ | $K$ [sec$^{-2}$] |
|---|---|---|---|---|---|---|
| 1. **$CH_3-CH_2COCH_3$**, 100 MHz, Fig. 1 | | | | | | |
| $CH_3$ | 13.4 | 1.03 | + 429 | + 416 | 0.95 | $2.0 \cdot 10^{17}$ |
| | | 0.95 | + 370 | + 393 | | |
| | | 0.88 | + 125 | + 63 | | |
| $CH_2$ | 14.1 | 2.51 | + 58 | + 308 | | |
| | | 2.44 | − 317 | − 287 | | |
| | | 2.37 | − 424 | − 450 | | |
| | | 2.29 | − 299 | − 250 | | |
| 2. **$CHCl_2-CH_2COCH_3$**, 56.4 MHz, Fig. 2 | | | | | | |
| $CHCl_2$ | 25.0 | 6.37 | − 765 | − 392 | 0.93 | $2.0 \cdot 10^{17}$ |
| | | 6.26 | −1180 | −1110 | | |
| | | 6.16 | − 803 | − 681 | | |
| $CH_2$ | 12.3 | 3.55 | +1108 | +1136 | | |
| | | 3.45 | + 965 | + 935 | | |
| 3. **$CHCl_2-CH_2COCH_3$**, 100 MHz, Fig. 3 | | | | | | |
| $CHCl_2$ | 25.0 | 6.32 | − 381 | − 645 | 0.93 | $2.0 \cdot 10^{17}$ |
| | | 6.26 | − 351 | − 354 | | |
| | | 6.20 | − 305 | − 236 | | |
| $CH_2$ | 12.3 | 3.53 | + 481 | + 425 | | |
| | | 3.47 | + 573 | + 633 | | |
| 4. **$CHCl_2-CHClCOOH$**, 100 MHz, Fig. 4 | | | | | | |
| $CHCl_2$ | 15.8 | 6.19 | − 320 | − 334 | 0.94 | $1.0 \cdot 10^{17}$ |
| | | 6.13 | − 630 | − 670 | | |
| CHClCOOH | 17.4 | 5.11 | + 816 | + 798 | | |
| | | 5.04 | + 522 | + 465 | | |

Table 2. Enhancement factors for products R — R′.

$k_1$, $k_2$, and $k_3$ are the rate constants of reactions (1 c), (1 d), and (1 f), and $p$ is the total rate of radical production. For two different values of $p$ the experimental ratios $|I_A/I_S|$ are given in Fig. 5 for various values of $x$ calculated from $k_2/k_1 = 0.36$[19] and the solvent composition. Since for $x \to 0$ $|I_A/I_S| \to 1$, $T_{1A} = T_{1S}$. The slopes of both straight lines give $1/T_{\mathrm{R}} = 3.1 \cdot 10^2 \sqrt{k_3}$. Taking $k_3 \approx 5 \cdot 10^9$ m$^{-1}$ sec$^{-1}$ $T_{\mathrm{R}}$ thus becomes $T_{\mathrm{R}} \approx 4.5 \cdot 10^{-4}$ sec. In an elegant trapping experiment Closs[20] has found $T_{\mathrm{R}} = 3.5 \cdot 10^{-4}$ sec for the α-protons of a benzyl type radical.

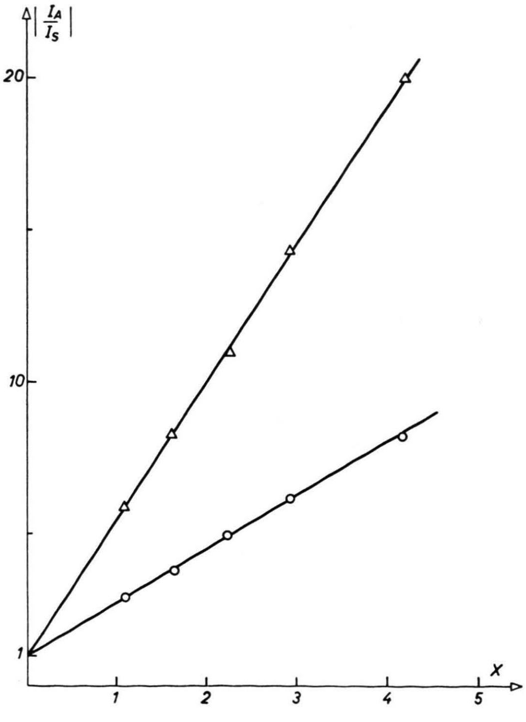

Fig. 5. Ratios of $CHCl_2$-transition intensities of $CHCl_2-CHCl_2$ and $CHCl_2-CH_2COCH_3$ in $CH_2Cl_2/CH_3COCH_3$ mixtures. (100 MHz, △: $p = 10^{-4}$ m · sec$^{-1}$, ○: $p = 6 \cdot 10^{-4}$ m · sec$^{-1}$).

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[20] G. L. Closs, private communication.

## 4. Discussion

The parameters used in fitting $V_{\text{exp}}$ and $V_{\text{calc}}$ (Table 2) deserve further comments.

$g$ (·$CHCl_2$) = 2.0080 is well within the range of $g$-factors of similar radicals[14, 15], and the negative sign of a ($CH_2COCH_3$) also agrees with expectation. Noteworthy, however, are the negative signs of a for ·CHClCOOH and, in particular, for ·$CHCl_2$, since a might be positive for ·$CHF_2$ [21]. We have tried to determine $g$ and $a$ of ·$CHCl_2$ by ESR, so far without success. An independent determination of these parameters would be very helpful indeed, since it would further support the validity of the radical pair explanations of CIDNP and the applicability of CIDNP experiments in determinations of radical $g$-factors and of absolute values *and* signs of hyperfine coupling constants.

In the systems studied $k_d/k_d + k_c$ was found to be 0.93, 0.94, and 0.95. These numbers indicate that only 5 to 7% of encounters of R· and R·′ lead to combination. Although somewhat high, they are compatible with values determined by SZWARC[22]. For the other parameter

$$K = \frac{v^2 \cdot k_d}{(\Delta R)^2 (k_d + k_c) \cdot 2\, n_c}$$

values $1.0 \cdot 10^{17}$ and $2.0 \cdot 10^{17}$ sec$^{-2}$ were used.

Assuming $n_c \approx 100$, $v \approx 10^{11}$ to $10^{12}$ Å/sec, and $\Delta R \approx 1$ Å a theoretical prediction would be $K \approx 10^{20}$ sec$^{-2}$. Obviously, the crude approximation of the rates of intersystem crossing[1] $k_{ij_\sigma} = k_d\,(|\Omega_{ij_\sigma}|^2/K)$ seriously underestimates this process. Since values $K \approx 10^{20}$ sec$^{-2}$ lead to CIDNP patterns disagreeing with the experimental results, the challenge for a better theoretical estimation of the dynamic factor $K$ remains.

The communications of results prior to publication by Drs. G. L. CLOSS and R. KAPTEIN are greatfully acknowledged.

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