

89. Chemically Induced Dynamic Nuclear Polarization VIII: Thermal Decomposition of Dibenzoyl peroxides in Solution [1]

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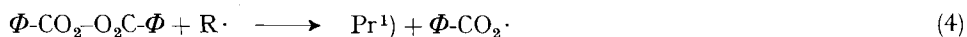
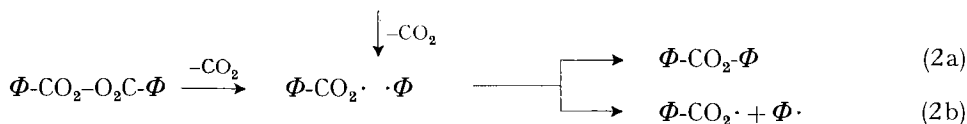
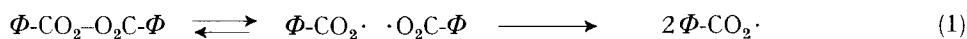
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Summary. - Thermolysis of di-(4-chlorobenzoyl)-peroxide was carried out in the probe of an NMR. spectrometer. The dependence of product distribution and chemically induced dynamic nuclear polarization (CIDNP.) patterns on the concentrations of radical trapping agents gives evidence that the CIDNP. effects are caused by singlet-triplet transitions, dependent on nuclear spin, in transient benzoyloxy/phenyl radical pairs and by the selective formation of radical-radical products from singlet state pairs.

1. Introduction. - One of the first examples of chemically induced dynamic nuclear polarization (CIDNP.), (*i.e.* NMR.-emission or enhanced absorption of radical reaction products) was the observation of an emission line of benzene in the course of thermolysis of dibenzoyl peroxide (BPO) in cyclohexanone [2]. This observation permitted an explanation of CIDNP. effects, in terms of electron-nuclear-cross-relaxations in intermediate free radicals [3], which became untenable as more evidence of CIDNP. phenomena, in this and other systems, was reported. The current, more important, CIDNP. theories [4] attribute the effects to singlet-triplet transitions, dependent on nuclear spin, in transient radical pairs and to the selective formation of radical-radical reaction products from singlet state pairs. As has already been pointed out [1] [5], the radical pair mechanism also explains the emission line of benzene during dibenzoyl peroxide thermolysis, if the polarization is caused by interactions within intermediate benzoyloxy/phenyl radical pairs.

Evidence for this explanation is here reported; it results from the observed dependence of CIDNP. effects on concentrations of radical trapping agents during dibenzoyl peroxide thermolysis in non-aromatic solvents. Our study has been guided by the relative amounts of products reported for the same reactions by authors [6]-[10].

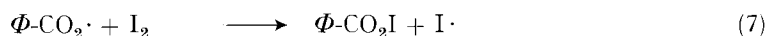
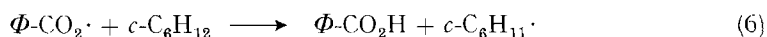
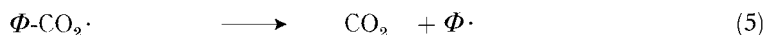
For dibenzoyl peroxide four initial decomposition modes are possible:



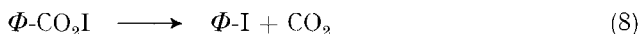
1) Pr denotes the product; in the specific case above it may be $\Phi\text{-CO}_2\cdot\text{R}$ but it cannot always be defined.

Three of them involve the formation of radical pairs ((1) benzoyloxy/benzoyloxy, (2) benzoyloxy/phenyl, (3) phenyl/phenyl) which may combine to give the corresponding pair (or cage) products ((1) dibenzoyl peroxide [6], (2) phenyl benzoate [7] [8], (3) biphenyl [8]) or may involve separation into free radicals ((1) benzoyloxy, (2) benzoyloxy and phenyl, (3) phenyl). From scavenging studies [7] [8] (1) is known to be the most important decomposition reaction, and for the reaction products, phenylbenzoate (2a) and biphenyl (3a) amount to only about 4% and 0.1%, respectively. The induced decomposition of dibenzoyl peroxide [9], is denoted by (4) the extent of which depends on the nature of the radicals $R\cdot$ derived from the solvent.

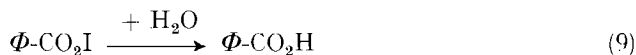
In general the benzoyloxy radicals formed in reactions (1), (2), and (4) may undergo decarboxylation (5). In cyclohexane ($c\text{-C}_6\text{H}_{12}$) [8] or in solutions containing iodine [7] they may also undergo the transfer reactions (6), (7).



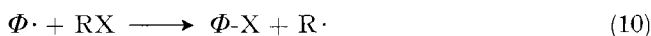
In fully chlorinated solvents reactions analogous to (6) have been excluded [10]. The hypoiodide (7) is unstable and is transformed (8) into CO_2 and phenyliodide. In the presence of water (9) it is quantitatively



hydrolyzed [7].



The phenyl radicals formed in (2), (3), and (5) react with non-aromatic solvents (RX ; $\text{X} = \text{H}$ or Cl) according to (10); in the presence of iodine phenyliodides are also observed (11).



(a) The emission line of benzene ((10), $\text{X} = \text{H}$) during dibenzoylperoxide thermolysis in cyclohexanone [2] and (b) the emission lines of the related compounds during dibenzoylperoxide photolysis in chlorinated solvents ($\text{X} = \text{Cl}$), and during di-(4-chlorobenzoyl)-peroxide (CBPO) thermolysis and photolysis [11], may be derived from phenyl radicals which themselves are intermediates in reactions (2), (3) and (5).

Three types of phenyl radicals can be distinguished, those arising from decomposition of benzoyloxy radicals (5), those formed directly from the radical pairs benzoyloxy/phenyl (2b), and those from phenyl/phenyl (3b). From the CIDNP. studies reported hitherto no safe deduction can be drawn concerning which type causes the nuclear polarization. Reactions (7) and (9) however, do provide means to establish the path of polarization. During thermolysis of the peroxide of dibenzoyl or that of di-(4-chlorobenzoyl), in fully chlorinated solvents, emission of products type (10) ($\text{X} = \text{Cl}$) is expected. If molecular iodine is added, in the absence of water, the products shown in (11) are formed. If overall polarization is not reduced drastically by

iodine addition the benzoyloxy radicals arising in (4) do not cause the polarizations since iodine prevents induced dibenzoyl peroxide decomposition [7] [9]. If iodine is added in the presence of water the benzoyloxy radicals are converted to benzoic acid (7), (9). In case the nuclear polarizations of the products of (10) and (11) are not grossly reduced by the addition of water and iodine, it is evident that the polarizations originate from the phenyl radicals escaping the radical pairs (2) or (3).

In the corresponding experiments di-(4-chlorobenzoyl) peroxide was used to simplify the NMR.-patterns of the reaction mixtures.

2. Experimental. – The thermolysis of di-(4-chlorobenzoyl)peroxide (*Elektrochemische Werke*, München) was carried out at 125°C in the probe of a *Varian* HA 100 D NMR. spectrometer. The solvent hexachloroacetone (*Fluka AG.*, Buchs) was purified by vacuum distillation and column chromatography (P_2O_5). Di-(4-chlorobenzoyl) peroxide was purified by reprecipitation and dried in vacuo; doubly sublimated iodine (*Merck AG.*, Darmstadt) was used; solvents and other chemicals were stored under nitrogen; samples not containing water were prepared under nitrogen; octamethylcyclotetrasiloxane was used as internal standard.

In all experiments the peroxide concentration was 0.1 M; concentrations of reaction products were determined by NMR.; the concentrations of the minor product 4-chlorophenyl 4-chlorobenzoate were obtained from samples after partial solvent evaporation. The first order decay constant of di-(4-chlorobenzoyl) peroxide was found to be $k_D = (6.0 \pm 1.5) \cdot 10^{-8} \text{ s}^{-1}$. Nuclear polarization intensities, proportional to the areas of the emission or enhanced absorption spectra, were determined for the individual products at maximum polarization. For 4-chlorophenyl 4-chlorobenzoate this was reached after $(120 \pm 10) \text{ s}$, for other products after $(160 \pm 20) \text{ s}$ following insertion of the samples tubes.

The spin-lattice relaxation times (T_1) of the products were measured by *W. Müller-Warmuhth* (*ISPRÄ*) and are given in the Table.

Relaxation times of products (125°C, in hexachloroacetone)

Product	$[I_2] = 0$	$[I_2] = 0.1 \text{ M}$
4-Cl-phenyl 4-Cl-benzoate	4.5 s	2.7 s
1,4-dichlorobenzene	26.4 s	4.4 s
1-iodo-4-chloro-benzene	31.0 s	17.6 s

3. Results. – In Fig. 1 the relation between product concentration and iodine concentration is given for samples containing small and large amounts of water. Biphenyl has not been detected, in agreement with the small yields reported by *Swain et al.* [8]. The yield of phenyl benzoate is 0.046 M per mole peroxide for $[I_2] = 0$, also in agreement with [7] [8]. It is noteworthy that the phenyl benzoate concentration decreases with increasing iodine concentration for $[H_2O] \approx 0.03 \text{ M}$ and $[H_2O] \approx 1.6 \text{ M}$. The relation between concentration of other products and iodine concentration is also as expected from (7) to (11). For $[I_2] = 0.1 \text{ M}$ 1,4-dichlorobenzene and 1-iodo-4-chlorobenzene are the main products when $[H_2O] \approx 0.03 \text{ M}$, on the other hand 4-chlorobenzoic acid is the main product when $[H_2O] \approx 1.6 \text{ M}$. For $[I_2] = 0$ no benzoic acid is formed, excluding reaction (6).

Fig. 2 shows NMR. spectra taken (a) during and (b) after decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone for $[I_2] = 0$ and $[H_2O] \approx 0.03 \text{ M}$. The spectrum observed for $[I_2] = 0$ and $[H_2O] \approx 1.6 \text{ M}$ is identical with that shown in the

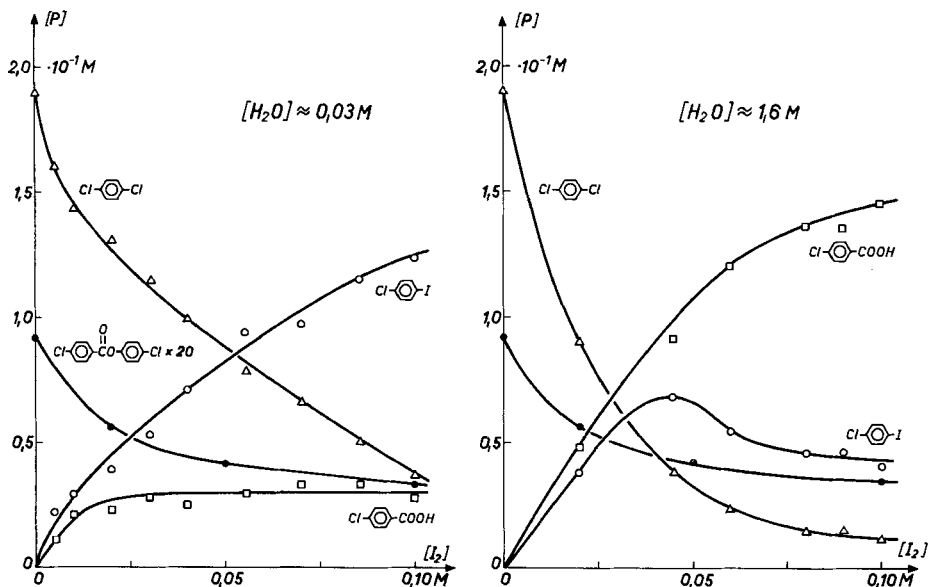


Fig. 1. Decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone at 125°C, for various concentrations of iodine and water; product yields (4-chlorophenyl 4-chlorobenzoate, enlarged scale)

figure. Apart from the A_2B_2 -spectrum of the peroxide we point out the strong emission of 1,4-dichlorobenzene at $\delta = 7.12$ ppm, the only product appearing in fig. 2b, and weaker enhanced absorption lines in the region $\delta = 7.00$ – 7.09 ppm, which belong to the *ortho*-proton transitions in the A_2B_2 -spectrum of the phenoxy ring of 4-chlorophenyl 4-chlorobenzoate. These weak enhanced absorptions have been reported before [1] [12]; they are expected for reasons of spin balancing if the pair occurring in reaction (2) causes the polarization (*vide infra*). Further, very weak emission and enhanced absorption lines are visible at $\delta \approx 7.30$ ppm, a region where transitions of the *meta*-protons of the phenylbenzoate and of biphenyl may occur. These lines are not assigned to specific products; their weakness excludes, however, that highly polarized 4,4'-dichlorobiphenyl (3a) is formed.

NMR. spectra taken (a) during and (b) after decompositions, for $[I_2] = 0.1$ M, $[H_2O] \approx 0.03$ M and ≈ 1.6 M, are given in fig. 3 and 4; the spectra shown in fig. 3b and 4b indicate the different yields at these $[H_2O]$ values. In fig. 3b 1-iodo-4-chlorobenzene (A_2B_2 -spectrum with prominent lines at $\delta = 6.90, 6.99, 7.39, 7.48$ ppm) is the main product, whereas in fig. 4b the main transitions are due to 4-chlorobenzoic acid (A_2B_2 -spectrum, $\delta = 7.26, 7.35, 7.91, 8.00$ ppm). During the reaction, the spectra (fig. 3a, 4a) are very similar showing emission lines of 1,4-dichlorobenzene ($\delta = 7.12$ ppm) and of 1-iodo-4-chlorobenzene (*ortho*-transitions at $\delta = 7.39, 7.48$ ppm) and the enhanced absorption lines of the 4-chlorophenyl 4-chlorobenzoate ($\delta = 7.00$ – 7.09 ppm). Normal absorption lines of the peroxide ($\delta = 7.29$ – 7.38 ppm) and of the *meta*-proton transitions of 1-iodo-4-chlorobenzene ($\delta = 6.90, 6.99$ ppm) are also to be seen; the 4-chlorobenzoic acid seems also to be not polarized (fig. 4a, $\delta = 7.26, 7.35$ ppm).

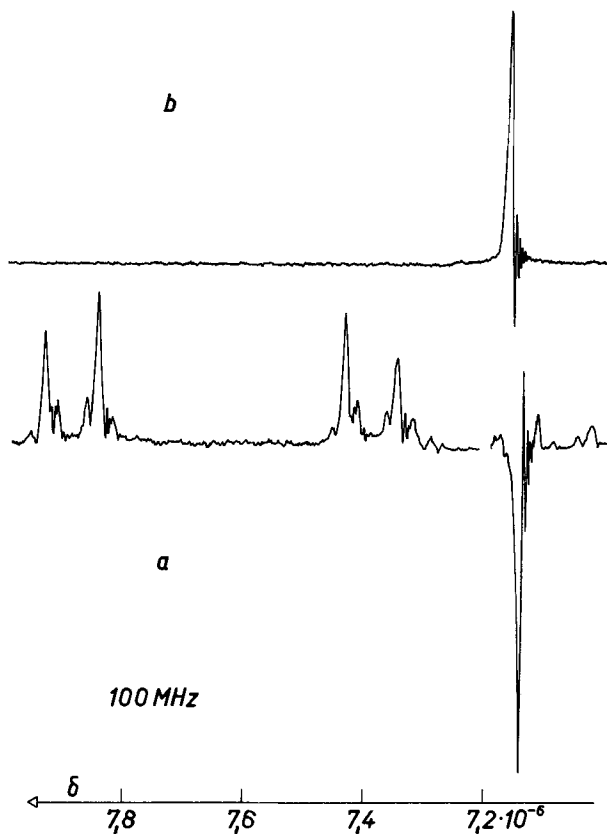


Fig. 2. CIDNP. for decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone at 125°C, $[I_2] = 0$

The close resemblance of the CIDNP. effects, during reaction for samples containing small and large amounts of water, holds also for other iodine concentrations; see fig. 5, where the relation between polarization intensities of the polarized products and iodine concentration is given.

As discussed in the introduction, the independence of the CIDNP. effects on water concentration gives evidence that the radical pairs appearing in (2) and (3) are the only possible sources of nuclear polarization. Of these we may outrule the phenyl/phenyl pair (3), since the polarization of 4,4'-dichlorobiphenyl is very weak, if present at all. This leaves benzoyloxy/phenyl radical pairs (2) as the polarizing system. Obviously all the polarization of the substituted benzenes is caused by the relatively few phenyl radicals escaping these pairs. It may be mentioned that this proof of the pair mechanism of CIDNP. is based entirely on chemical arguments and not on any consideration of the phases and amplitudes in the CIDNP. patterns.

4. Discussion. – The signs of the various nuclear polarizations are, of course, readily explained by interactions within benzoyloxy/phenyl radical pairs [1] [5]. Assuming the dibenzoyl peroxide decompositions to occur from singlet states, putting

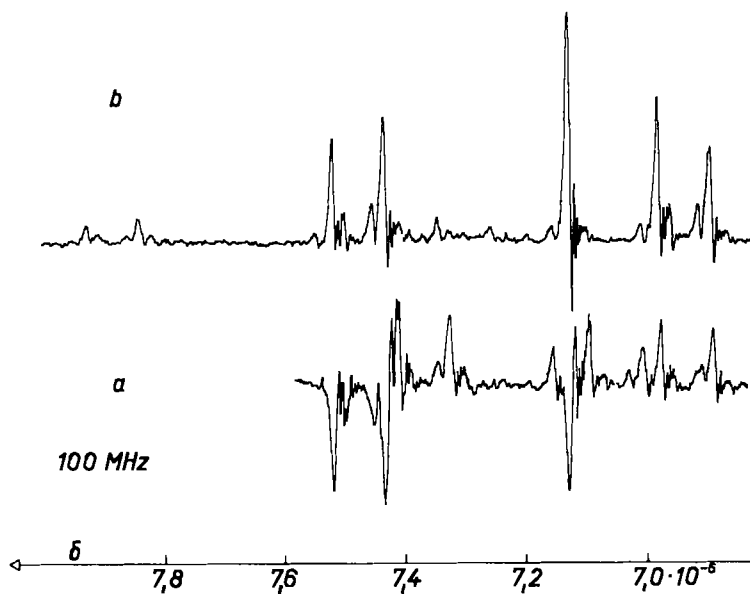


Fig. 3. CIDNP. for decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone at 125°C,
 $[I_2] = 0.1 \text{ M}$, $[H_2O] \approx 0.03 \text{ M}$

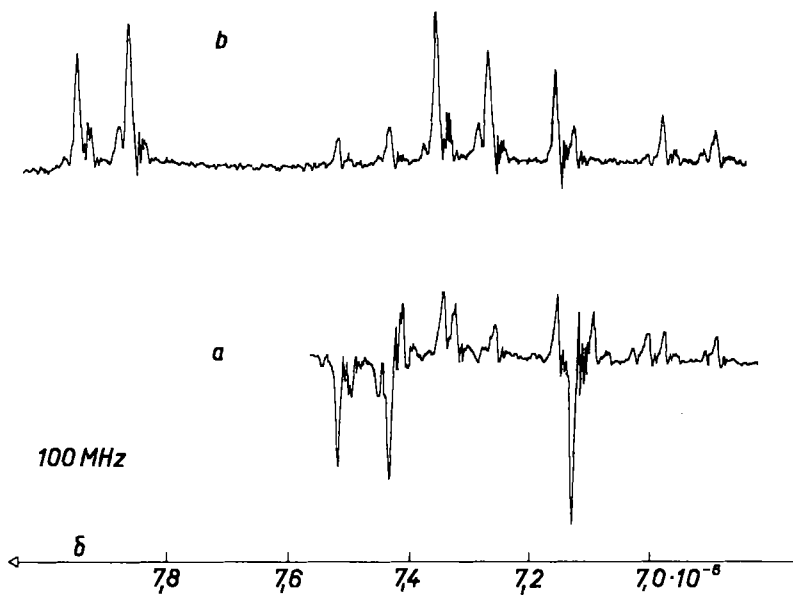


Fig. 4. CIDNP. for decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone at 125°C,
 $[I_2] = 0.1 \text{ M}$, $[H_2O] \approx 1.6 \text{ M}$

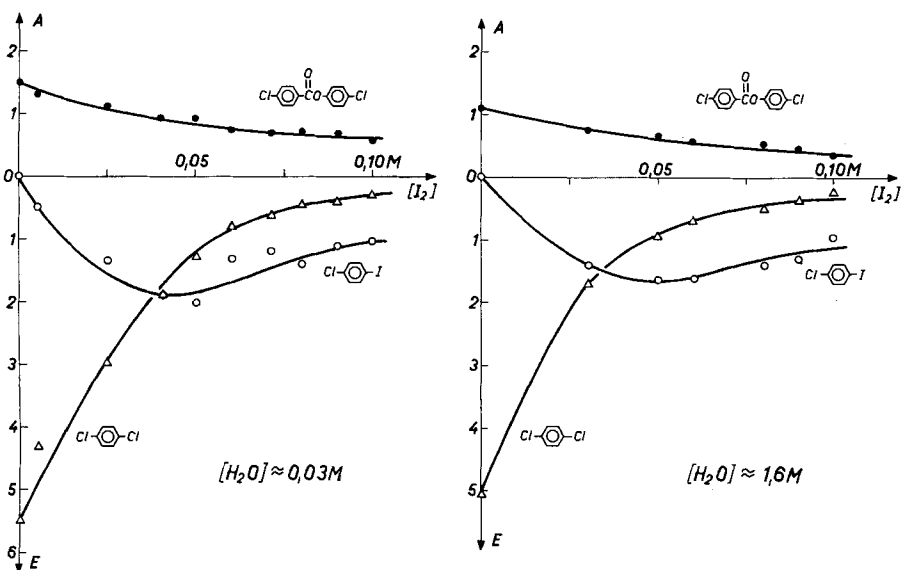


Fig. 5. CIDNP. intensities (arbitrary units) for decomposition of di-(4-chlorobenzoyl) peroxide in hexachloroacetone at 125°C, for various concentrations of iodine and water

the hyperfine coupling constants for the 4-chlorophenyl radicals a (*ortho*) > 0 and a (*meta*) $< a$ (*ortho*) [13], and setting g (4-chlorobenzoyloxy) $> g$ (4-chlorophenyl) = 2.0020 [13]), the theoretical equations [4] give enhanced absorption for the combination product 4-chlorophenyl 4-chlorobenzoate and emission for transfer products of the 4-chlorophenyl radicals, if only $S-T_0$ -transitions occur. With reasonable assumptions with regard to the ^{13}C -hyperfine coupling constants of the same radicals, the benzoyloxy/phenyl radical pair can also be responsible for the ^{13}C polarizations of phenylbenzoate, benzene and CO_2 observed during dibenzoyl peroxide thermolysis in cyclohexanone by *Lippmaa et al.* [14].

In fig. 2 to 5 we note that the observed intensities of the enhanced absorption are considerably smaller than those of the emission. This however, is not in disagreement with the theoretical prediction [4] that the differences in level population built up in the radical pairs should appear with equal magnitude in the coupling product and the radicals escaping the pairs. Expressing these as $|V \cdot R|$, where R is the rate of formation and V the enhancement factor of a special product observed, the polarization intensities I , measured under quasi-steady state conditions, may be approximated

$$I = V \cdot R \cdot T_1 \quad (12)$$

[1] by (12) where T_1 is the spin-lattice relaxation time of the product under consideration. Inserting the relaxation times given in the table, we obtain from the intensities (fig. 5) for the ratio $|V \cdot R|_A / |V \cdot R|_E$, the values 2.0 and 1.9 for $[\text{I}_2] = 0$ and $[\text{I}_2] = 0.1\text{M}$ respectively, so that, in contrast to the apparent behaviour (fig. 2 to 5), $|V \cdot R|$ is even higher for the phenylbenzoate than for the transfer products. The deviations

of $|V \cdot R|_A / |V \cdot R|_E$ from unity are very likely caused by the limited validity of (12) under our experimental conditions.

As seen from the table, the decrease of the polarizations with increasing iodine concentration is also mainly due to the decrease of the relaxation times.

Though (12) is not strictly valid, it may be used to obtain a rough estimate of the enhancement factor for phenylbenzoate. Putting $R = n \cdot k_D \cdot [\text{CBPO}]$, where n is the yield of phenylbenzoate (fig. 1), a calibration of the intensities gives $V = 690$ for $[\text{I}_2] = 0$ and $V = 1160$ for $[\text{I}_2] = 0.1 \text{ M}$, values which are within the limits of theoretical prediction.

Summarizing the results we may conclude that the CIDNP. effects observed during aroylperoxide decomposition can be explained exclusively by the $S-T_0$ -transitions in benzoyloxy/phenyl radical pairs. Cross-relaxation in free phenyl radicals [3] must contribute only to a minor extent, if at all. Further, there is no indication that polarizations may also occur during transfer reactions. Finally we consider our findings concerning the behaviour of CIDNP. effects during addition of radical trapping agents lend strong support to current CIDNP. theories [4].

We wish to express our gratitude to *Prof. Dr. Müller-Warmuth (ISPR)* for the determination of the relaxation times, and to the *Elektrochemische Werke München* for a gift of peroxides.

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