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CHEMICALLY INDUCED DYNAMIC NUCLEAR POLARIZATION. DECARBOXYLATION OF PHOTOCHEMICALLY GENERATED BENZOYLOXY RADICALS

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Abstract—CIDNP has been studied during thermal decomposition, photolysis, and sensitized photolysis of benzoyl chloroacetyl peroxide. The ratio of the CIDNP intensities for the recombination products benzyl chloride and chloromethyl benzoate is dependent on the mode of decomposition, reflecting the extent of rapid decarboxylation of the primary formed benzoyloxy radicals.

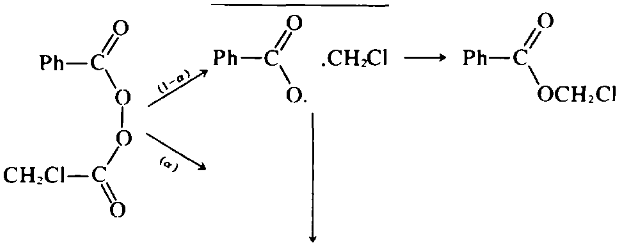
The primary photochemical process of the photodecomposition of aroyl and acyl peroxides[1,2] is the rupture of the peroxide bond, in the case of aroyl peroxides leading to aroyloxy radicals. Initially these radicals carry a large excess energy, resulting in decarboxylation before thermal equilibrium is reached. CIDNP[3] offers an opportunity to study the fraction (α) of the radicals which decarboxylate in an early vibration after the rupture of the peroxide bond. Unlike the radicals which decarboxylate very rapidly on the CIDNP timescale ($\ll 10^{-9}$ sec) and do not affect the CIDNP patterns of the recombination products, the radicals decarboxylating in about 10^{-9} s have a profound influence.[4] This effect has been used to determine the rate of decarboxylation of thermally generated benzoyloxy radicals.[5] Since these effects on CIDNP are presently well understood they can be used conveniently for the study of multi-bond rupture in photochemical reactions.

CIDNP during thermal and photochemical decomposition of benzoyl peroxides has been studied extensively.[6] Poranski *et al.* studied ^{13}C CIDNP during the photolysis of benzoyl peroxide. Their experimental results did not allow of an unambiguous decision in favour of the multi-bond cleavage. We found that benzoyl chloroacetyl peroxide (BCAP) rather than benzoyl peroxide is suitable for a CIDNP study of the decarboxylation of benzoyloxy radicals. Both intermediate radical pairs (viz the benzoyloxy/chloromethyl and the phenyl/chloromethyl) have appreciable g-factor differences, which moreover are of opposite sign. CIDNP seems to have the advantage over product analysis methods for the study of radical reactions in that no CIDNP effects appear in products formed by ionic pathways[7] and that also the interference of induced decomposition[8] can be considered.

RESULTS

Thermal Decomposition of BCAP in CCl_4

Figure 1 shows the CIDNP spectrum obtained during thermal decomposition of BCAP in CCl_4, the observed CIDNP signals are summarized in Table 1. The polarizations can be readily interpreted by the reaction sequence of Scheme 1, in which for the thermal decomposition $\alpha = 0$. The possible intermediate chloroacetoxy radical is too short-lived to affect the CIDNP of the products. The g-factor is 2.0117 for benzoyloxy,[9] 2.00234 for phenyl,[10] and 2.0065 for chloromethyl radicals;[11] the hyperfine interactions for the phenyl radical are +17.4 (H_0), +5.9 (H_m) and +1.9 (H_p) and for the chloromethyl radical −20.7 gauss. From Kaptein's rules[12] it follows that we expect emission for the methylene protons of chloromethyl benzoate ($\Gamma_{ne} = -.+.-.-$) and enhanced absorption for the escape product methylene chloride, explaining the most striking features of the CIDNP spectrum. The emission for the product benzylchloride is an extreme



$$\overline{Ph.\qquad .CH_2Cl} \longrightarrow Ph{-}CH_2Cl$$

$$Ph. + CCl_4 \longrightarrow PhCl + .CCl_3$$

$$.CH_2Cl + CCl_4 \longrightarrow CH_2Cl_2 + .CCl_3$$

$$2\quad .CH_2Cl \longrightarrow \overline{2\qquad .CH_2Cl}^{F} \longrightarrow CH_2ClCH_2Cl$$

$$.CCl_3 + .CH_2Cl \longrightarrow \overline{.CCl_3\qquad .CH_2Cl}^{F} \longrightarrow CCl_3CH_2Cl$$

Scheme 1.

Table 1. Decomposition of benzoyl chloroacetyl peroxide

Product	Chemical shift (δ, ppm)	Signal	T	P	A	B
$PhCOOC\underline{H}_2Cl$	5.97	(c)	E	E	E	A
$PhCH_2Cl$	7.34	(a)	—	A	A	E
$PhC\underline{H}_2Cl$	4.56	(a)	E	A	A	E
PhCl	7.28	(b)	—	E	E	A
CH_2Cl_2	5.30	(d)	A	E	A	E
CCl_3CH_2Cl	4.30	(e)	A	A	A	A
CH_2ClCH_2Cl	3.72	(f)	A	E	A	E
CH_3Cl	3.01	(g)	A	—	A	E
CH_2(peroxide)	4.26		N	N	N	N

T: Thermal decomposition (Fig. 1).
P: Photolysis (Fig. 2).
A: Anthracene sensitized photolysis (Fig. 3).
B: Benzophenone sensitized photolysis (Fig. 4).

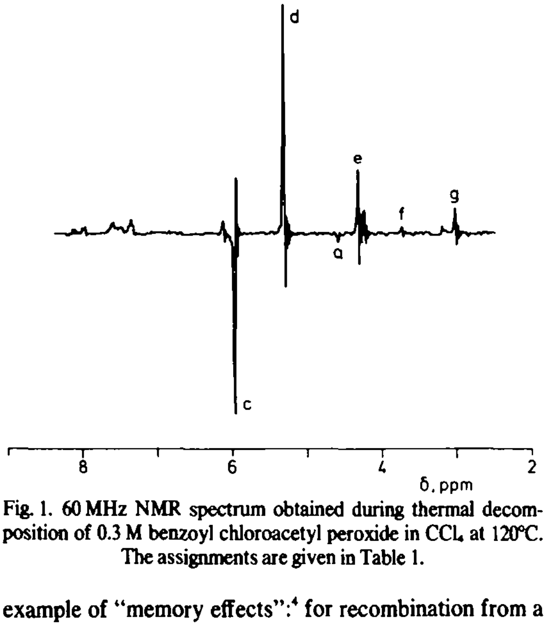


Fig. 1. 60 MHz NMR spectrum obtained during thermal decomposition of 0.3 M benzoyl chloroacetyl peroxide in CCl_4 at 120°C. The assignments are given in Table 1.

example of "memory effects":[4] for recombination from a singlet phenyl/chloromethyl pair we would expect enhanced *absorption* for the methylene protons of benzylchloride. However, the g-factor difference of the parent benzoyloxy/chloromethyl pair is much larger than that of the phenyl/chloromethyl pair and has the opposite sign, resulting in an emission for benzylchloride. Thus the observation of a small emission for benzylchloride demonstrates the occurrence of the benzoyloxy radical as an intermediate.

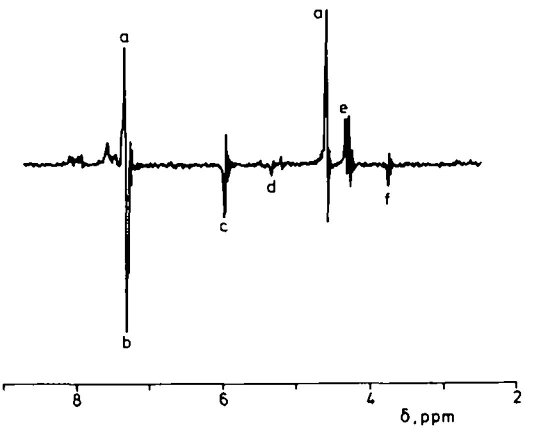


Fig. 2. 60 MHz NMR spectrum obtained during photolysis of 0.3 M benzoyl chloroacetyl peroxide in CCl_4.

Photolysis and Sensitized Photolysis of BCAP

The CIDNP spectrum obtained during photolysis of BCAP in CCl_4 (Fig. 2) shows a striking difference with that obtained during thermal decomposition. Again an emission is observed for the chloromethyl benzoate which can be explained by a reaction sequence analogous to Scheme 1, showing that the photodecomposition occurs predominantly from the singlet state. However, a difference is observed for benzyl chloride and chlorobenzene. The large absorption of the methylene and phenyl protons of benzyl chloride and the emission of the phenyl protons of chlorobenzene can only be accounted for by assuming that for an important fraction the phenyl/chloromethyl radical pair is formed directly, viz without the benzoyloxy radical as intermediate. The CIDNP ratio of the benzylchloride and the chloromethyl benzoate reflects the extent of rapid decarboxylation of the benzoyloxy radical. We found that this ratio is sensitive to the wavelength of the irradiating light. Filtering the light by a Corning CS 7-54 glass filter (transparent for $\lambda > \sim 240$ nm) the ratio measured is about 5.0; using a Corning CS 0-53 ($\lambda > \sim 290$ nm) we found about 3.5.

Using the Corning CS 4-97 ($\lambda > \sim 340$ nm) no CIDNP during irradiation of a sample BCAP without sensitizer could be detected. Using this filter we studied CIDNP during the photolysis of BCAP in the presence of anthracene (Fig. 3). In this way direct photolysis is excluded and the signals observed in the presence of anthracene are solely due to the sensitized decomposition. This compound acts as a singlet sensitizer, and accordingly the CIDNP spectrum is analogous to that obtained during photolysis.[12] Compared with the photolysis the signal of chloromethyl benzoate has become larger relative to benzyl chloride, indicating a lower value of the fraction α.

In the CIDNP spectrum obtained during benzophenone sensitized photolysis (Fig. 4), again using the CS 4-97 glass filter, the signals are reversed compared with direct photolysis due to triplet sensitization.[12] Furthermore the ratio of the CIDNP intensities for benzylchloride and chloromethyl benzoate is smaller, from which it follows that α has further diminished.

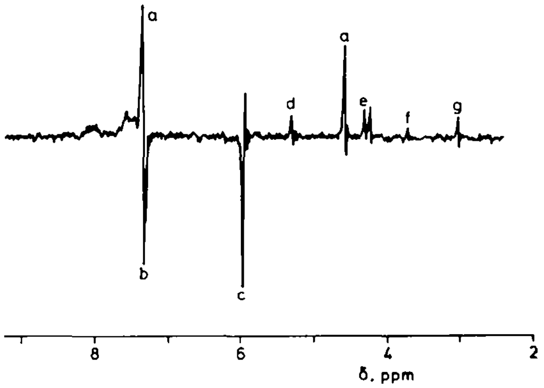


Fig. 3. 60 MHz NMR spectrum obtained during photolysis of 0.3 M benzoyl chloroacetyl peroxide in CCl_4 in the presence of anthracene.

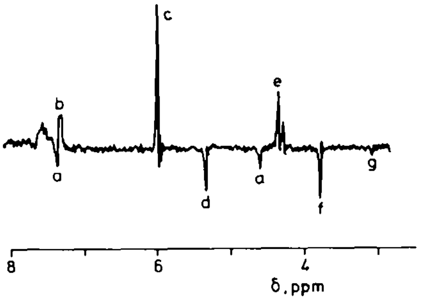


Fig. 4. 60 MHz NMR spectrum obtained during photolysis of 0.3 M benzoyl chloroacetyl peroxide in CCl_4 in the presence of benzophenone.

We measured the nuclear relaxation times (T_1) for the products from the appearance of the CIDNP signals after turning on the light. The relaxation time found for the methylene protons of chloromethyl benzoate is 5.5 (±0.4) sec, for the corresponding protons of benzyl chloride 8.7 (±0.4) sec.

DISCUSSION

From the ratio of the CIDNP signals for chloromethyl benzoate and benzyl chloride the ratio for the two pairs benzoyloxy/chloromethyl and phenyl/chloromethyl can be estimated and hence the fraction α of the benzoyloxy radicals which decarboxylate in an early vibration after the primary rupture of the peroxide bond. Since the CIDNP intensities are proportional to the relaxation time T_1 for the product we have to divide these intensities by T_1. Assuming a similar diffusive behaviour of the two pairs a computer simulation showed that the predicted enhancement factors[13] for the methylene protons of the recombination products of a benzoyloxy/chloromethyl and of a phenyl/chloromethyl radical pair are virtually equal. The fractions α are now estimated for the photolysis and for the sensitized photolysis experiments, an uncertainty remains the probability of recombination during a singlet collision which may be different for the two pairs (Table 2).

Because of the reactive solvent the induced decomposition cannot be an important source of formation of chloromethyl benzoate. This is evidenced by product analysis for the recombination products (chloromethyl benzoate and benzyl chloride) and the escape products (CH_2Cl_2, CH_2ClCCl_3, CH_2ClCH_2Cl and CH_3Cl). For the photolysis (a singlet reaction) the ratio recombination/escape was found to be 0.95; for the benzophenone-sensitized decomposition 0.05. This clearly shows that the amount of recombination products is very small as expected for a triplet precursor and that other pathways leading to ester formation are unimportant under our conditions. Moreover we found that for a much lower peroxide concentration the ratios of both the CIDNP signals and of the product yields did not change much.

Table 2. Ratio benzylchloride/chloromethyl benzoate and the estimated fraction α of fast decarboxylation

	CIDNP ratio	Estimated fraction α	Product ratio
Direct photolysis	4.0	0.75	1.0
Anthracene sensitization†	0.5	0.25	—
Benzophenone sensitization	0.11	0.07	—

†First stage of the reaction.

The product yields can also be used for an estimate of the relative importancy of the two pairs. This was only possible for the direct photolysis because in the case of anthracene-sensitization this compound is consumed by reaction with the radicals. In the case of benzophenone-sensitization the ratio of the product yields is probably not representative because of the low yield of the recombination products. For the direct photolysis it is found that considerably more ester is formed than expected from the analysis of the CIDNP results. This discrepancy could be caused by a difference in size of the two pairs. According to the treatment given by Kaptein[13] the product yields are proportional to (λp), in which λ is the probability of recombination during a singlet collision of the radical pair, and p is the total probability of at least one re-encounter for a pair separating from a collision. The CIDNP intensities on the other hand are proportional to (λ m),

$$p \sim 1 - \left(\frac{1}{2} + \frac{3\rho}{2\sigma}\right)^{-1}$$

$$m = 1.036(1-p)^2\left(\frac{\rho}{\sigma}\right)^2 \Big/ \nu^{1/2}$$

ρ is the encounter diameter of the radical pair, σ the root mean square displacement for diffusion and ν the frequency of the diffusive displacements. From this it follows that if the benzoyloxy/chloromethyl radical pair has a larger encounter diameter ρ than the phenyl/chloromethyl pair, rather the product *yields* than the CIDNP intensities are affected. Another possible explanation of the discrepancy is primary recombination of benzoyloxy and chloromethyl radicals, yielding additional ester formation which does not contribute to CIDNP.

The estimated fractions α for rapid decarboxylation are very sensitive to the way in which the peroxide is decomposed: much larger for direct photolysis than for sensitized decompositions. In our view this reflects the influence of the excess energy available to the benzoyloxy radical after the primary rupture of the peroxide bond. This was demonstrated by the sensitivity of the chloromethyl benzoate/benzyl chloride CIDNP ratio to the wavelength of the irradiating light: at shorter wavelength relatively more benzyl chloride is formed. The observed difference for anthracene- and for benzophenone-sensitization can also be explained in this way since excited singlet anthracene (E_S = 76 kcal/mole) has a higher energy than triplet benzophenone (E_T = 69 kcal/mole).

Our study demonstrates that it is essential for a CIDNP study of mechanistic and kinetic aspects of radical reactions to design a system that is bound to give distinct CIDNP effects.

EXPERIMENTAL

BCAP was prepared by autoxidation of benzaldehyde with chloroacetic anhydride.[14] The peroxide was purified carefully from residual benzaldehyde by recrystallization from a mixture of ether and 1,1,2-trichloro-1,2,2-trifluoro-ethane (1:1). An A-60 NMR spectrometer was applied for the study of CIDNP during thermal decomposition, and the DA-60 IL (modified to allow irradiation of the sample) during the photolysis, both operating at

60 MHz. The light source was an HBO 1000 W high pressure mercury lamp, the light was filtered by a $NiSO_4$ solution.

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