Chemically Induced Dynamic Nuclear Polarization. Triplet and Singlet State Photosensitization of Peroxide Decompositions

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Summary Nuclear spin polarization in photolysis products of peroxides in the presence of ketones is opposite to the polarization in products both from direct photolysis and from thermal decomposition.

ONE prediction of the current theory of CIDNP[1–3] is that the nuclear polarization found in cage recombination products from radical pairs will depend upon the multiplicity of the electronic state, singlet (S) or triplet (T), of the precursor from which the pair is generated. Thus both net polarization [emission (E) or enhanced absorption (A)] and multiplet effects (E/A or A/E within a multiplet) will be reversed for products from T pairs as compared to products from S pairs. This opposite behaviour will hold also for the polarization of transfer products from radicals escaping from the cage of formation, provided that the free-radical lifetimes are not much longer than the nuclear spin-lattice relaxation times in the radical (*ca.* 10^{-5} s).[1b] This suggests[2b] that the observation of CIDNP during photochemical reactions could yield valuable information on the multiplicity of precursors of radical pairs or biradicals.† However, there is an ambiguity here because the theory also predicts[2d] that combination (or disproportionation) products of secondary radical encounters will be polarized like T-pair products, so that when T-pair polarization is observed one has *a priori* two alternative explanations for its origin: (i) primary cage recombination of a T pair or (ii) combination from secondary encounters of free radicals. In the second case the spin-state of the radical precursor could not be determined. Closs *et al.*[2] explain their results for the reactions of carbenes and benzophenones with alkylbenzenes as cage recombinations from T pairs [case (i)]. Although this interpretation may turn out to be correct (there can be little doubt about the spin-states of the precursors in these systems), the second possibility should be considered also, since the chemistry of the systems indicates that the radicals are mainly consumed by secondary encounters.

Here we show unambiguously the role of the precursor multiplicity. We studied ^{1}H n.m.r. spectra during photolysis of some peroxides in the presence of photosensitizers. Several authors have shown that the decomposition of peroxides can be photosensitized.[4] Two examples will be discussed here. The experiments were carried out on a Varian DA-60 spectrometer, modified in order to irradiate the sample in the probe with the light of an Osram HBO 1000 w high-pressure mercury arc, filtered with a $CuSO_4$ solution (transparent in the region 310—600 nm).

The spectra in Figure 1a—c were obtained from a solution of 0·26 M-benzoyl peroxide (BPO) (δ8·2—7·3 p.p.m.) in CCl_4 before, during, and after irradiation. The E lines in Figure 1b (δ7·25 p.p.m.) belong to chlorobenzene. Figure 1d—f shows a similar series for the same solution, to which 0·11M-acetophenone was added. Chlorobenzene clearly shows enhanced absorption in this case. In addition some emission lines (δ 7·0—7·2 p.p.m.) can be seen, that could be assigned to phenyl benzoate. The A effect is larger in Figure 1e than the E effect in Figure 1b due to a higher rate of decomposition of peroxide in the presence of acetophenone. In solutions containing 0·008 M-acetophenone, A can still be observed for chlorobenzene.

FIGURE 1. *60 MHz n.m.r. spectra of* 0·23 M-*benzoyl peroxide in* CCl_4 (a) *before,* (b) *during,* (c) *after irradiation and of the same solution with* 0·11 M-*acetophenone added* (d) *before,* (e) *during, and* (f) *after irradiation. The spectra* (c) *and* (f) *were run after a time long enough for thermal equilibrium to be established.*

This reversal can be observed also in the spectra of Figure 2a and b recorded during the photolysis of 0·13 M-propionyl peroxide [δ (CH_2) 2·37, δ (CH_3) 1·18 p.p.m.] in CCl_4 and the same solution containing 0·11 M-acetophenone [δ (CH_3) 2·53 p.p.m.]. The effect can be seen most clearly in the ethyl chloride lines [δ (CH_2) 3·52, δ (CH_3) 1·42 p.p.m., A/E multiplets in Figure 2a, E/A multiplets in Figure 2b],‡ but also in the butane CH_3 lines (δ 0·90 p.p.m.). The spectra of Figures 1b and 2a are similar to spectra that we obtained during thermal decomposition of the peroxides in CCl_4 at 85° (*cf.* refs. 5 and 6).

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† The observation of CIDNP in biradical products has been mentioned in ref. 1b and will be published shortly in more detail.

‡ The high-field line of the ethyl chloride CH_3 triplet overlaps with the low-field line of the peroxide CH_3 triplet.

The similarity to the thermal decomposition indicates that the direct photolysis proceeds *via* an excited singlet state and the reversal of the polarization in the presence of acetophenone is direct evidence for photosensitization of the decomposition by triplet acetophenone.[4d] With benzophenone we observed the same effects, but weaker, which is probably due to a lower triplet energy[7] of benzophenone (E_T 69 kcal/mole) compared with acetophenone (E_T 74 kcal/mole). With fluorenone (E_T 53 kcal/mole) we did not observe the reversal of polarization.§

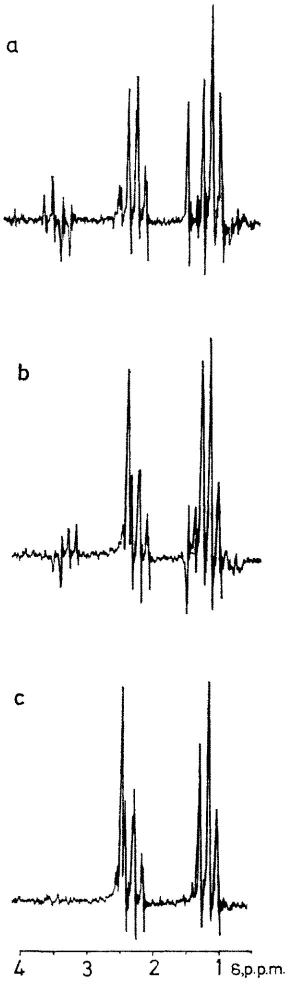
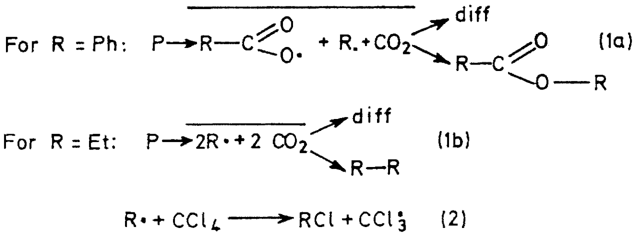


FIGURE 2. *60 MHz n.m.r. spectra of* 0·13 M*-propionyl peroxide in* CCl_4 (a) *during irradiation and of the same solution with* 0·11 M*-acetophenone added* (b) *during and* (c) *after irradiation.*

Surprisingly, addition of 0·07 anthracene resulted in an increase of the *emission* signal for chlorobenzene by a factor of 5 and of *A*/*E* for ethyl chloride and *E*/*A* for butane by a factor of 9, indicating sensitization by excited *singlet* anthracene¶ (E_S 76, E_T 42 kcal/mole), contrary to the assumption by Walling and Gibian[4d] of sensitization by triplet anthracene. This result is in accord with suggestions of sensitization of peroxide decompositions by excited *S*-states of benzene,[4] toluene,[4b] and naphthalene.[4c]

The spectra can be understood in terms of the Scheme.



SCHEME

P represents peroxide (S_0) in the thermal decomposition, peroxide (S_1) in the direct photolysis, a triplet precursor, *e.g.* peroxide (T_1) or some peroxide-sensitizer (T_1) complex, in the photosensitized decomposition in the presence of ketones and similarly a singlet precursor in the presence of anthracene. Diffusion from the cage (indicated by a bar) is denoted by "diff." For BPO a second and probably major reaction path[9] yielding two benzoyloxy-radicals escaping from the cage will not give the reversal of nuclear polarization. As the benzoyloxy-radical is expected to have a larger *g* value than the phenyl radical and the hyperfine coupling constants are positive in the phenyl radical, theory[2c] predicts *A* in phenyl benzoate for cage recombination from an *S* pair (equation 1a) and *E* in the transfer reaction product chlorobenzene (equation 2) from phenyl radicals that escaped from the primary cage by diffusion.[1b] For *T* pairs: phenyl benzoate *E*, chlorobenzene *A*.

The formation of propionyloxy-radicals followed by rapid decarboxylation before appreciable diffusion from the cage has occurred is also possible. The hyperfine coupling constants in the ethyl radical have opposite signs [$A(CH_3)$ = 27G, $A(CH_2)$ = − 22G].[10] The observed phases for the multiplet effects in Figure 2a are in accordance with the theory for recombination from an *S* pair of ethyl radicals (butane, *E*/*A*) and diffusion followed by rapid transfer reaction (ethyl chloride, *A*/*E*). For *T* pairs: butane *A*/*E*, ethyl chloride *E*/*A*. Other interpretations such as combination and diffusion from secondary encounter pairs are very unlikely in these cases. We note that the diffusive process and also the hyperfine-coupling-induced intersystem-crossing rate, yielding polarization *via* selection in the second part of (equation 1), will be very similar for *S* and *T* pairs so that n.m.r. intensities are expected to be opposite but similar in magnitude for equal rates of decomposition, although chemically the amount of cage effect may differ.

The observations described here firmly support the recent theory of CIDNP[1-3] and suggest that the early experiments by Bargon and Fischer[5] (thermal decomposition of BPO in cyclohexanone) should be explained in a similar way and that cross-relaxation in free radicals does

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§ Trozzolo[8] has recently observed *A* for the benzene line during photolysis of BPO in cyclohexanone. We have verified this and we observed *A* for benzene also in cyclopentanone and acetone using a $NiSO_4$ filter solution (transparent below 310 nm). With a $CuSO_4$ filter, however, benzene shows *E* in these solvents. Apparently there is competition of direct photolysis with triplet-sensitized decomposition in these systems.

¶ In accordance with this conclusion we observed the quenching of anthracene fluorescence by benzoyl peroxide.

not play a significant role in this case. It may be noted that a suggested[11] mechanism of polarization by transfer reaction (equation 2) cannot be reconciled with the observed reversal of polarization.

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