Mechanistic Implications of the Chemically Induced Dynamic Nuclear Polarization Spectra Derived from Radical-Pair Interactions in Aliphatic Diacyl Peroxide Decompositions[1]

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Abstract: CIDNP spectra taken during the thermal decomposition of aliphatic diacyl peroxides $(RCO_2)_2$ in solutions containing alkyl iodides, R′I, show multiplet effect polarization for R′I, for RI, and for the coupling and disproportionation products of R· and R·′. Except for acetoxy, there is no evidence that an acyloxy radical survives for a time sufficient to lead to net nuclear polarization, and no enhancements are observed in the alkoxy protons of esters (excepting methyl acetate). The carbonic anhydride produced in isobutyryl peroxide decomposition also shows no polarization, suggesting that, if radical pairs with ionic character are valid intermediates in the carboxy inversion process, these pairs must be intimate. Characteristic nuclear polarization results from spin selection in diffusive encounters of two R·′ and is easily distinguished from polarization in geminate pairs.

Aliphatic diacyl peroxides thermally decompose at 50–100° at rates which are suitable for kinetic study and also have proven to be useful initiators for radical-chain reactions. The combination of experimental accessibility and practical importance has led to a substantial number of investigations of the mechanism of thermolysis and many of the details of this reaction seem to be established beyond reasonable doubt.[2] It is clear, for example, from the insensitivity of decomposition rate to structure for the straight-chain diacyl peroxides that the initiative step is cleavage of the oxygen–oxygen bond to form a pair of acyloxy radicals. Whether these radicals recombine to form peroxide, separate by diffusion, or react by decarboxylation depends on radical structure, reaction temperature, and solvent interactions, and the effects of these interrelated parameters are by no means exactly understood. A common feature to many of the uncertainties in decomposition mechanism is that the reactions and interactions of interest occur in radical pairs. These details have remained obscure, since, because of the high rate of reaction between paired radicals, it is difficult to exert any outside influence on reactivity, and, therefore, to gain information on the pair interactions. In fact, the addition of scavenging agents has been used to isolate pair reactions by intercepting all free radicals, on the very assumption that paired radicals remain inviolate.

The realization that the enhanced nmr signals that result from chemically induced dynamic nuclear polarization (CIDNP)[3] arise from radical pair interactions[4,5] suggests simultaneously that CIDNP may be used to study the aspects of peroxide decompositions which are poorly understood, and that, conversely, results from mechanistically well-established peroxide reactions may be useful in the evaluation of CIDNP theory. Indeed, one of the earliest examples of a CIDNP spectrum was taken by Fischer[6] during the thermal decomposition of benzoyl peroxide, and preliminary reports of polarizations during other peroxide decompositions have appeared.[1,7] The purpose of this paper is to describe the character of the CIDNP spectra observed in such peroxide reactions, to relate the spectral types to reaction mechanisms, and to present the unique features that are revealed when alkyl iodides are present as scavenging agents.

Experimental Section

General Procedure for Recording CIDNP Spectra. An nmr tube containing a solution which was 0.5 *M* in peroxide and 1.0 *M* in alkyl iodide was placed in the preheated probe of a Varian A-60-A spectrometer and the spectral region of interest was scanned repeatedly. After an initial period of time for the sample to warm (about 15 sec), polarization could be observed for periods of several minutes. Spectra were taken until an unchanging, unenhanced absorption pattern was obtained for the product mixture.

Product Analysis. Product yields were measured in selected reactions by comparison of integrated nmr peak areas with areas from added internal standards (Table I). For a few reactions, product mixtures were analyzed by gas chromatography. For products of the decomposition of lauroyl peroxide in *o*-dichlorobenzene (ODCB) and octane solvents a 5-ft, 5% SE-30 on 60–80 Chromosorb W column with programmed column temperatures (60–200°) proved suitable (Table II). For the decomposition of isobutyryl peroxide in the presence of 1-iodooctane, a 15-ft, 15% TCEP 80–100 Chromosorb P column (45°) and the SE-30 column (145°) gave the following product composition (corrected for detector sensitivity): 2-iodopropane, 11%; 2,3-dimethylbutane, 8%; isopropyl butyrate, 67%; and 2-methyldecane, 2%.

Table I. Yields and Enhancements for $C_{11}H_{23}X$ in the Decomposition of Lauroyl Peroxide in the Presence of Alkyl Halides

RX	Yield of $C_{11}H_{23}X$, %	$(I - I^0)/I^0$
3-Iodopentane	53	73
2-Iodopentane	50	85.5
2-Iodopropane	49	80
3-Bromopropene	32	68
Iodomethane	23	81

Reagents. Commercial alkyl iodides were purified by washing with sodium bisulfite solution and distillation at reduced pressure,

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[1] A portion of this work has appeared in preliminary form: H. R. Ward, R. G. Lawler, and R. A. Cooper, *Tetrahedron Lett.*, 527 (1969).

[2] For a recent comprehensive review, see: R. C. P. Cubbon, *Progr. React. Kinet.*, **5**, 29 (1970).

[3] (a) H. R. Ward, *Accounts Chem. Res.*, **5**, 24 (1972); (b) R. G. Lawler, *ibid.*, **5**, 32 (1972).

[4] G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

[5] R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 214 (1969).

[6] J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch. A*, **22**, 1551 (1967).

[7] R. Kaptein, *Chem. Phys. Lett.*, **2**, 261 (1968).

Table II. Product Distributions in the Decomposition of Lauroyl Peroxide in Octane and ODCB

	1-Undecene, %	Undecane, %	Docosane, %
Octane	9	36	56
ODCB	4	16	58

and were stored at 0° over copper wire. Propionyl and isobutyryl peroxides were prepared by standard methods.[8] Commercial lauroyl peroxide was used as received.

Calculation of Relative Intensities. The method used to calculate the relative polarized intensities canceled out differences in degeneracy ($D^i/2^n$ where n is the total number of protons), in the hyperfine fields [$\delta_p^2 - \delta_q^2$ where p and q denote the two nuclear levels involved in the transition and $\delta^2 = (g - g')\Sigma am + (\Sigma am)^2$] and in the spin lattice relaxation times (T_1) of the products in question. The polarized intensity, I, and the contribution due to unpolarized material, I_t^0, were both taken at time t (69 sec), the latter measured after quenching the reaction by immersion in liquid nitrogen. The relative polarized intensity for 1-iodoundecane compared to 2-iodopropane (formed in the decomposition of lauroyl peroxide in the presence of 2-iodopropane) was 1.3, as calculated by eq 1 and 2. (The intensities were measured from the $m = +{}^1/_2$

$$I - I_t^0 = \kappa \sum (\delta_p^2 - \delta_q^2) D^i/2^n \tag{1}$$

$$\text{relative intensities} = \frac{\kappa_{\text{C}_{11}\text{I}}}{\kappa_{i\text{-PrI}}} \frac{T_{1(i\text{-PrI})}}{T_{1(\text{C}_{11}\text{I})}} \tag{2}$$

and $-{}^1/_2$ lines for 1-iodoundecane and 2-iodopropane, respectively.) The progressive saturation technique was used to measure the relative T_1 values ($T_1(i\text{-PrI})/T_1(\text{C}_{11}\text{I}) = 1.5$).

In the calculation of the enhancements reported in Table I for undecyl halides, I was the maximum observed intensity and I_∞^0 was the absorption intensity at the end of the reaction. Since no correction was applied for T_1 and since I_∞^0 was used instead of I_t^0, these numbers are useful only for comparative purposes, and do not reflect absolute maximum enhancements.

Results and Discussion

Phases of CIDNP Spectra. The decomposition of an aliphatic diacyl peroxide in a solution containing an alkyl iodide generally allowed observation of the polarization of protons contained in the olefins derived from both peroxide and iodide, the iodide derived from the alkyl portion of the peroxide, and the reagent alkyl iodide itself. Line positions of the coupling products of alkyl radicals were usually coincident with reagent absorptions, and polarization from these products could not be observed clearly. This overlap presents little mechanistic difficulty because the same information is conveyed by olefin polarization (except for reactions of methyl and ethyl radicals). Observed polarizations are reported in Table III for the protons on the α carbon in the iodides and for the vinyl protons in the olefins.

CIDNP spectra can be qualitatively described by combinations of the features of the two "pure" types of polarization (*vide infra*). *Net polarization*, which arises only in radical pairs where the partners differ in g factors, was not observed in any of the aliphatic diacyl peroxide decompositions (save for acetyl peroxide), and the spectra reported here are all examples of pure *multiplet effects*. Multiplet effect polarization arises from spin selection in radical pairs where the g factors of the partners differ little (the case for all hydrocarbon radicals), and, for first-order spectra, show both enhanced absorption (A) and emission (E) of equal magnitude in the same multiplet. The phase, that is the order with which E and A appear with increasing field, is a most useful description, and in Table III is listed as EA for emission appearing downfield of enhanced absorption and AE for enhanced absorption downfield of emission.

Table III. Summary of CIDNP Spectra Taken during Reaction

$(\text{RCO}_2)_2 + \text{R}'\text{X or X}_2 \longrightarrow \text{RX} + \text{R}_{-\text{H}} + \text{R}'_{-\text{H}}$

R	R′X or X_2	RX	R′X	R_{-H}	R'_{-H}
Ethyl	Iodobenzene	AE[e]	*d*	*a*	*c*
	Iodomethane	AE	*a*	*a*	*c*
	3-Bromopropene	AE	*d*	*a*	*c*
	1-Iodobutane	AE	EA	*a*	AE
	2-Iodopropane	AE	EA	*a*	AE
	2-Iodobutane	AE	EA	*a*	AE
	3-Iodopentane	AE	EA	*a*	*d*
	I_2	AE	*c*	*a*	*c*
Isopropyl	Iodobenzene	AE	*d*	EA	*c*
	Iodomethane	AE[e]	*a*	EA	*a*
	3-Bromopropene	AE	*d*	*b*	*c*
	Iodoethane	AE	EA	EA	*a*
	1-Iodobutane	AE	EA	EA	*b*
	1-Iodooctane	AE	EA	EA	*b*
	2-Iodobutane	AE	EA	EA	*b*
	3-Iodopentane	AE	EA	EA	*b*
	I_2	AE	*c*	EA	*c*
Undecyl	Iodobenzene	AE[e]	*d*	EA	*c*
	Iodomethane	AE	*a*	EA	*c*
	3-Bromopropene	AE	*d*	EA	*c*
	Iodoethane	AE	EA	EA	*a*
	2,2,2-Trifluoro-iodoethane	AE	EA	EA	*c*
	2-Iodopropane	AE	EA	EA	*b*
	2-Iodobutane	AE	EA	EA	*b*
	3-Iodopentane	AE	EA	EA	*b*
	I_2	AE	*c*	EA	*c*

[a] Multiplet effect polarization cannot be observed. [b] Spectrum obscured by other signals. [c] Product is not formed. [d] Polarization is not observed. [e] RCl showed AE polarization.

Spectral Expectations. The radical pair model has had almost total success in the qualitative explanation and prediction of CIDNP spectra. Its occasional failure at quantitative simulation need not be of concern here, since, because of the complexity of the chemical systems and the inavailability of sufficiently advanced instrumentation, accurate experimental spectral enhancements have not yet been measured for these reactions. Thus, no choice is required between the various mutants of the pair model[4,9–11] for, while they differ in quantitative predictions, they agree totally in their expectation of spectral phase. The details of the derivation of the pair model and its application to spectral prediction are available in the original reports[4,5,9–11] and in summary[3b] and need not be reiterated. However, for convenience, the relation between CIDNP spectra and pair interactions which are directly relevant to peroxide decompositions will be reviewed.

According to the pair model, the nuclear hyperfine field experienced by the unpaired electrons in a radical pair may induce mixing of nearly degenerate singlet and triplet electronic states and thereby affect the spin multiplicity of the pair. The probability of radical–radical reaction is assumed to be high only for singlet

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(8) M. S. Kharasch, J. Kuderna, and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1954).

(9) H. Fischer, *Chem. Phys. Lett.*, 4, 611 (1970).

(10) S. H. Glarum, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, No. ORGN-40.

(11) F. J. Adrian, *J. Chem. Phys.*, **53**, 3374 (1970).

pairs, and so a mechanism for nuclear spin selection is created through which nuclei which provide certain hyperfine fields are more likely than others to change the spin multiplicity (and hence the reactivity) of the radical pair. In the specific case of the thermal decomposition of diacyl peroxides, pairs will be formed in the singlet state, since the peroxide is certainly in a singlet (ground) electronic state and, in the time required for bond homolysis, no mechanism is available to change the spin multiplicity. If the peroxide decomposition leads to pairs in which the unpaired electrons in the partners have different Zeeman interactions with the magnetic field of the spectrometer (*i.e.*, $\Delta g \neq 0$, as for an acyloxy–alkyl pair), this difference in g will itself induce singlet–triplet mixing at a rate which can be reduced or increased by the nuclear hyperfine field. This effect will lead to the appearance of net polarization, A or E, of lines arising from a single kind of proton. Conversely, the absence of net polarization (other parameters being suitable) can be taken to suggest that pairs in which Δg would be expected to be substantial do not exist for times sufficient to induce singlet–triplet mixing (10^{-10}–10^{-9} sec). Pairs of alkyl radicals ($\Delta g = 0$) formed in the singlet state will lead to multiplet effects in the geminate combination[12] products which, for the substitution patterns and signs of the nuclear spin–spin coupling constants in the products discussed herein, will always be of EA phase.[13] It is an important corollary that radicals which do not react with their partner and are scavenged (in these reactions by iodine abstractions) must show the complementary AE phase. Restated, the nuclei which exert the greatest absolute hyperfine field on the electron spin (those nuclear levels with the largest values of $(am)^2$, where a is the value of the hyperfine field constant and m is the nuclear spin quantum number) will be "drained" to the triplet radical pair causing an AE-like[14] population in the free radical with a corresponding EA-like population resulting in the singlet radical pair, which will be reflected in the cage products.[15]

If pairs are formed by the diffusive encounter of free radicals, the singlet (S) and the one triplet state (T_0) which are mixed by the hyperfine fields will be equally populated.[16] It might seem, *a priori*, that mixing could have no effect in such a situation, but a consideration of the macroscopic spin multiplicity of a number of diffusive pairs, formed simultaneously, reveals that the equal populations of S and T_0 are not maintained.[17] Since radicals certainly do react on diffusive singlet encounters, but not in triplet encounters, after some time ($<10^{-9}$ sec) the remaining pairs will have a net triplet character. These triplet pairs can react only if they undergo intersystem crossing to the singlet. Intersystem crossing can, in turn, be induced by the hyperfine field and will result in spin selection. Just as before, AE-like spin populations will induce mixing, but in this case will dominate in *products* of coupling and disproportionation, while EA-like radicals are more likely to separate without reaction and, perhaps, be scavenged. Thus, the phase of the multiplet effect can differentiate between products which form from geminate and diffusive pairs and between the products of radicals scavenged upon escape from these pairs.

If the same product results from both geminate and diffusive pairs, an opposing polarization will develop. It is not yet possible to say at which point cancellation is exact since the relative efficiencies of geminate and diffusive spin selection are not known precisely. For these reasons, and in view of the additional comments made earlier about the quantitative aspects of CIDNP, the observation of, say, EA for an olefin does not mean necessarily that *more* olefin forms in a geminate encounter, but rather that more spin selection occurred in geminate pairs leading to olefins.

Decomposition Mechanisms

It has been conclusively and repeatedly demonstrated that the only important initial step in the thermal decomposition of *n*-alkyl diacyl peroxides is the homolysis of the oxygen–oxygen bond (eq 3), and the evidence

$$(RCO_2)_2 \longrightarrow \overline{2RCO_2\cdot} \qquad (3)$$

supporting this conclusion[2] will not be reproduced here. The subsequent reactions of the geminate acyloxy pair so formed are heavily dependent upon the structure of the alkyl group.

Acetyl Peroxide. The acetoxy pairs formed from acetyl peroxide dissipate in three possible ways: by recombination to the peroxide, by decarboxylation, and by diffusive separation.[18] The methyl protons are probably only weakly coupled to the unpaired electron in the acetoxy radicals, and so the nuclear hyperfine field from these protons should have a negligible effect on the relative importance of the three routes, eq 4. The return to form peroxide is an important process, for, at 93°, 34% of geminate acetoxy pairs recombine and about 50% separate by diffusion.[19] The remaining 16% proceed, probably *via* stepwise

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[12] (a) Following the nomenclature of Noyes,[12b] the term geminate pair will be used to describe radicals which are formed simultaneously and in close proximity, in this case by oxygen–oxygen bond homolysis. Geminate products include both primary combination products of radicals confined by a solvent cage, and secondary combination products, formed from radical pairs which may become separated by one or more solvent molecules, but are, by diffusion, reunited. Because of the time scale required for nuclear spin selection, it appears that most polarization must result from radicals which do not undergo primary recombination. (b) R. M. Noyes, *J. Amer. Chem. Soc.*, **72**, 2042 (1955).

[13] The sign and magnitude of the hyperfine coupling constant (a) in the radical, and of the nuclear spin–spin coupling constant (J) in the product, in addition to pair multiplicity and g factors, affect the spectral predictions.[3a] Generalization is allowed in this case because, in each product, J is positive, and each radical contains both α and β protons (where a is $-$ and $+$, respectively). All of the predictions of enhanced spectra presented here are valid only for reactions run at high fields (*e.g.*, in the spectrometer field). Substantially different polarization might be expected for reactions run at zero fields or at low fields: see H. R. Ward, R. G. Lawler, H. Y. Loken, and R. A. Cooper, *ibid.*, **91**, 4928 (1969).

[14] The nmr spectrum of these radicals is, of course, never measured directly. For simplicity in discussion the operational designation of AE-like or EA-like is given to a radical based on the phase of polarization which would be observed if the radical were trapped by, say, an iodine donation.

[15] Assuming the signs of the hyperfine fields of protons α and β to electron spin are opposite, the inner nuclear levels will have the largest $(am)^2$. Thus, the triplet radical pair will have the inner nuclear levels overpopulated (AE-like population, assuming $J > 0$), while the singlet radical pair will have the outer levels overpopulated (EA-like population).

[16] The other triplet states, T_{-1} and T_{+1}, also receive equal population but, at high field, do not mix with the S_0 state.[3b]

[17] (a) F. Gerhart and G. Osterman, *Tetrahedron Lett.*, 4705 (1969); (b) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2186 (1970).

[18] J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967).

[19] S. A. Dombchik, Ph.D. Dissertation, University of Illinois, 1969.

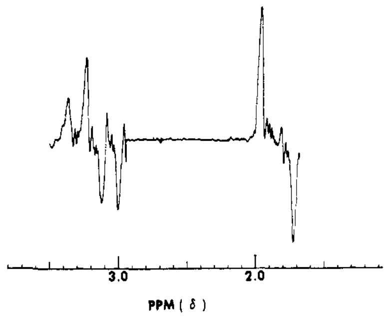
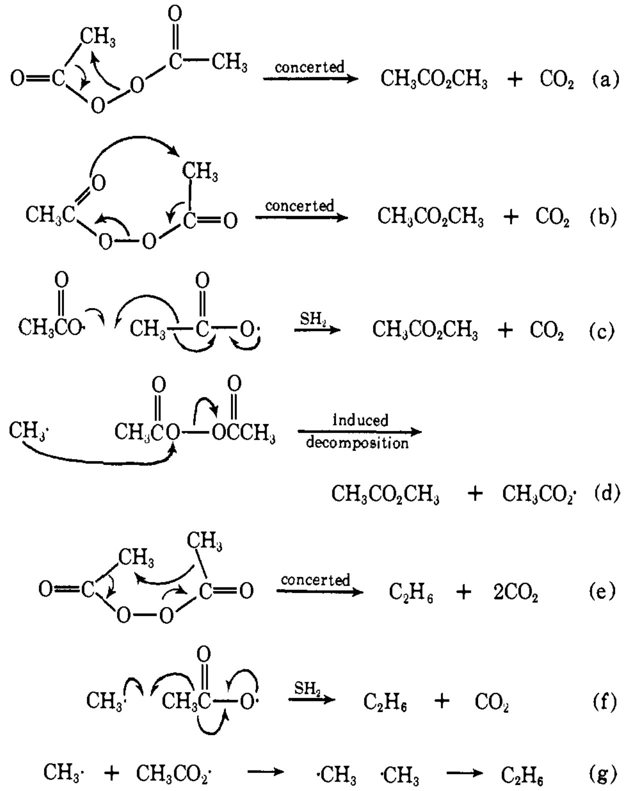


Figure 1. Spectrum recorded during the thermolysis of propionyl peroxide in ODCB saturated with iodine at 120°.

decarboxylations, to form 10% methyl acetate and 6% ethane. Spin selection is expected to occur in the methyl–acetoxy pairs and, because of a substantial difference in the two g factors, should be demonstrated by net polarization in the products. Kaptein,[7] in the first report of CIDNP in alkyl diacyl peroxide decompositions, found emission for the methoxy protons of methyl acetate, and enhanced absorption for methyl chloride (formed by abstraction of chlorine from the hexachloroacetone solvent by methyl radicals escaping the geminate encounter). This is the polarization pattern expected for a geminate pair reaction, with a high g factor assigned to acetoxy. No enhancement is observed for the acetyl methyl protons of the ester, confirming the expectation of weak coupling of the methyl protons to the electron in acetoxy. The emission that Kaptein reports for ethane confirms the formation of geminate pairs of two methyl radicals,[18] *via* decarboxylation in methyl–acetoxy pairs. Spin selection in pairs of methyl radicals cannot give net polarization ($\Delta g = 0$) and, because of degeneracies, multiplet effects are unobservable. The emission from ethane must result from the same spin selection process that led to emission for the methoxy protons of methyl acetate. Thus the entire CIDNP spectrum is quite consistent with the decomposition pattern as proposed by Martin and Taylor,[18] featuring a competition between decarboxylation and diffusion for destruction of acetoxy pairs. None of the other suggested[18, 19] modes of formation of methyl acetate (Scheme I, a–d) would have led to the observed polarization. The concerted decomposition to ethane and carbon dioxide (Ie) also is inconsistent with the CIDNP spectra. The bimolecular homolytic displacement of carbon dioxide in a geminate methyl–acetoxy pair (If) is not excluded and remains as an alternative to Ig.

$$\begin{tikzcd}
(CH_3CO_2)_2 \arrow[r, phantom, "\rightleftharpoons"] & \overline{2CH_3CO_2\cdot} \arrow[r] \arrow[d] & 2CH_3CO_2\cdot \\
\underset{\mathrm{E}}{CH_3CO_2CH_3} & \overline{CH_3\cdot CH_3CO_2\cdot} \arrow[l] \arrow[r] \arrow[d] & \underset{\mathrm{A}}{CH_3\cdot} + CH_3CO_2\cdot \quad (4) \\
\underset{\mathrm{E}}{C_2H_6} & \overline{2CH_3\cdot} \arrow[l] \arrow[r] & 2CH_3\cdot
\end{tikzcd}$$

Scheme I



Propionyl Peroxide. The CIDNP spectra obtained during the decompositions of propionyl and all of the higher n-alkyl peroxides which have been investigated differ markedly from that observed during the acetyl peroxide thermolysis, in that they exhibit only multiplet polarization.[1,7] Further, no polarization of any type is observed in the ethoxy protons of ethyl propionate during propionyl peroxide decomposition (in the presence of iodine) (CH_2, δ 4.12, CH_3, δ 1.25, Figure 1) even though it is known to form.[19] This absence of polarization may mean either that the ester forms by a nonradical route, through carboxy inversion or a concerted rearrangement, or that the radical pair leading to the ester does not lead to polarization. There is little reason to accept the former possibilities,[20] but the latter is quite reasonable. The time required for noticeable mixing of singlet and triplet pairs of alkyl radicals is set in the range of 10^{-9}–10^{-10} sec by hyperfine frequencies of the order of 4×10^8 radians/sec. This is about the time that geminate pairs are expected to exist at "usual" viscosities.[21] Since acetoxy decarboxylation obviously proceeds at a rate comparable to diffusion, its lifetime (under CIDNP conditions) must be in this same range. Propionoxy radicals, however, decompose 15–20 times as rapidly as does acetoxy,[19] presumably because ethyl is of greater stability than methyl. It is therefore not unreasonable to suggest that the decarboxylation of a propionyl pair to an ethyl–propionyl pair and on to geminate pairs of ethyl radicals simply occurs too rapidly to allow spin selection. Those pairs which form ethyl propionate are both short lived and intimate, while, conversely, polarization increases both with the lifetime of the pair and the distance of temporary partner separation.[22]

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(20) The carboxy inversion product, $C_2H_5OCO_2COC_2H_5$, although it should give ester under forcing conditions, would not lead to ^{18}O scrambling, and should display a higher sensitivity in ester yield to changes in solvent polarity than is observed. A concerted reaction also is virtually eliminated by the oxygen-labeling studies of Martin.[18]

(21) R. M. Noyes, *J. Chem. Phys.*, **22**, 1349 (1954).

(22) Dombchik[19] found that (a) more ethyl acetate formed in the thermolysis of acetyl propionyl peroxide than did (b) methyl acetate in acetyl peroxide decomposition or (c) ethyl propionate in propinyl peroxide decomposition. His rationalization for this variation is that, while decarboxylation in b is slow, so that few methyl–acetoxy pairs

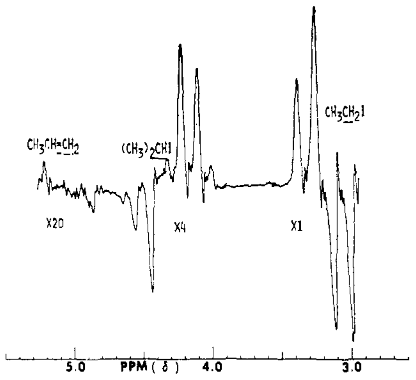
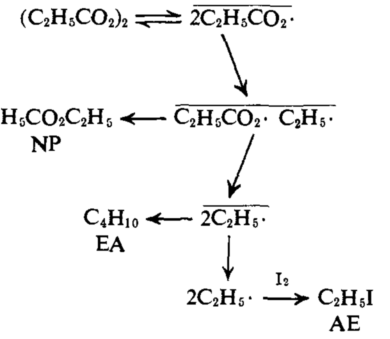


Figure 2. Spectrum recorded during the thermolysis of propionyl peroxide in ODCB and 2-iodopropane. Amplification factors are given beneath each absorption.

The geminate pairs of ethyl radicals which form by such a dual decarboxylation spin select to show a pure AE multiplet effect in the 1-iodoethane (CH_2, δ 3.2; CH_3, δ 1.83) formed when ethyl radicals escaping the pair react with molecular iodine (Figure 1) or abstract iodine from an alkyl iodide (Figure 2). The multiplet effect, again because of magnetic equivalence, cannot be observed in ethylene and ethane, but is present, EA, in butane.



Lauroyl Peroxide. The decomposition of lauroyl peroxide in the presence of an alkyl iodide generates CIDNP spectra entirely analogous to that of propionyl peroxide excepting only that, because of spin-spin splitting, the 1-undecene formed by disproportionation reveals an EA phase (Figure 3). Again no polarization is observed from the α-alkoxy protons of undecyl lauroate, although these protons could be observed (at high-spectrum amplitude) at the completion of the reaction. If this decomposition is done in a medium which is immune to radical attack (Kel-F, 120°), the 1-undecene forms not only in geminate but also in diffusive encounters. The opposing spin selections nearly cancel, but the geminate polarization prevails (possibly because of scavenging of undecyl radicals by peroxide molecules) and a weak EA spectrum is seen for the vinyl protons. The effect of addition of 3-iodopentane on the EA intensity of 1-undecene in Kel-F and octane solvents is shown in Figure 4. The increase of the EA intensity with increasing amounts of 3-iodopentane indicates interception of the undecyl radicals by the reactive radical scavenger. The rate of decomposition is unaffected by the change in solvent.

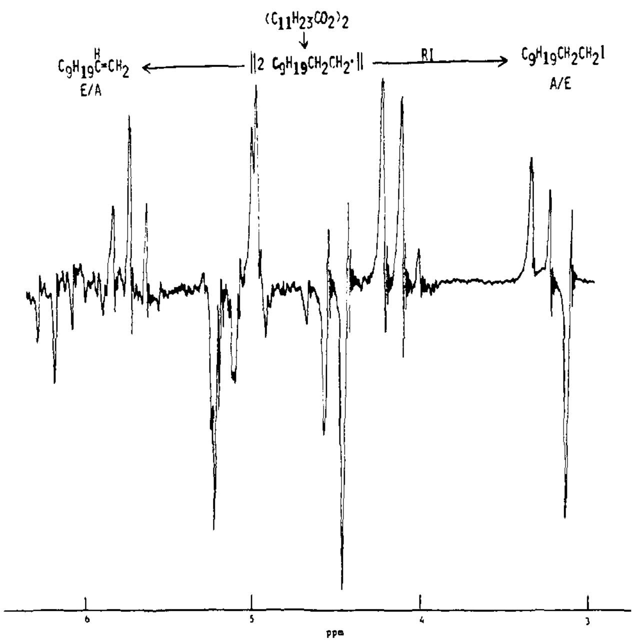


Figure 3. Spectrum recorded during the thermolysis of lauroyl peroxide in ODCB and 2-iodopropane.

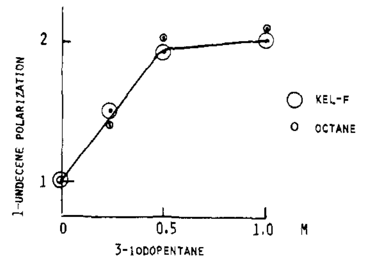


Figure 4. Plot of the intensity of the vinylmethylene polarization for 1-undecene formed during the decomposition of lauroyl peroxide as a function of the concentration of 3-iodopentane.

The AE intensity of the α-CH_2 in 1-iodoundecane correspondingly increases with RI concentration and levels off at concentrations above 1.5 *M*. An accurate measurement of the yields of the disproportionation and coupling products of the undecyl radicals was not possible for reactions run in Kel-F because of solvent interference with the gas-chromatographic separations. Analyses for these products were possible, however, for thermolyses in octane and ODCB (solvents which have nearly the same viscosities at 97.5°) and are reported in Table II. Even though twice as much 1-undecene is formed in the octane solvent, the enhancements of the vinyl protons of this compound are eight times greater in ODCB, most probably because reactions with solvent prevent undecene formation in diffusive encounters. Weak AE polarization is in fact observed from both 1-chloroundecane and a ring-alkylated ODCB,[23] and is eliminated by the addition of 3-iodopentane, a superior radical trap. The close agreement of the docosane yield in both solvents suggests that it is principally a geminate combination product. The larger amounts of undecane and 1-undecene in octane solvents must result mainly from reaction

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form, and in c is rapid, decreasing ethyl-propionyl pair concentration, the rapid decarboxylation of propionoxy and the slow decarboxylation of acetoxy provide a substantial number of acetoxy-ethyl pairs.

(23) It is interesting to note that 1-chloroundecane is still observed when iodobenzene is added (Table III) which is consistent with the high endothermicity of the iodine transfer. In fact, 1-iodoundecane may be formed by a mechanism similar to that of chloride formation.

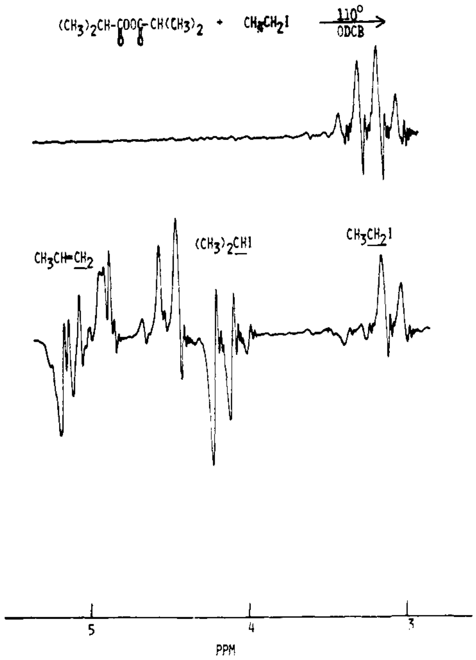
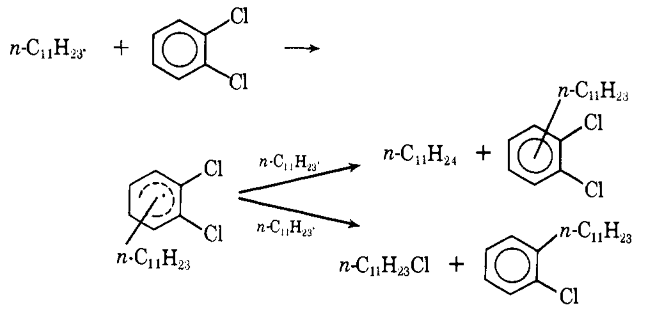


Figure 5. Spectra recorded during (lower) and after (upper) the thermolysis of isobutyryl peroxide in ODCB and iodoethane at 110°.

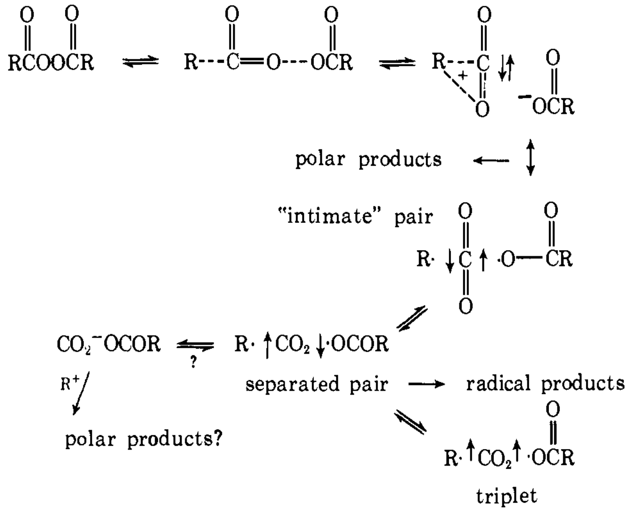
of 1-undecyl radicals with solvent and solvent-derived radicals forming 1-undecene in the diffusive encounter.



Dependence of Enhancement on Reactivity of Scavenger. The enhancement observed in the product of a scavenged radical (*e.g.*, 1-iodoundecane) depends not only on the initial geminate polarization and the number of undecyl radicals scavenged but also on the rapidity with which the scavenging occurs. Proton relaxation times in the radicals, because of dipolar coupling with the unpaired electron, are *ca.* 10^{-4} sec, and the polarization, created in a pair interaction, will be lost in the free radical unless it can be scavenged within this time limit. The invariance (Table I) in the enhancement of 1-haloundecane when the structure of the scavenging agent was changed from 2-iodopropane to 2-iodobutane to 3-iodopentane means that abstraction occurs from each in a time $\ll 10^{-4}$, although not necessarily at the same rate for each scavenger.[24] The decrease in the amount of haloundecane formed in the presence of 3-bromopropene and iodomethane is consistent with the variance in bond strengths of the alkyl halides, but the enhancement factors reflect no change in efficiency of transfer on the time scale of nuclear spin relaxation in the radical. This apparent incongruity probably results from the more successful competition of solvent for undecyl radicals in the case of these less reactive alkyl halide scavengers.

Isobutyryl Peroxide. A number of reports[2] have made it very clear that the decomposition of secondary alkyl diacyl peroxides is mechanistically rather more complicated than the decomposition of the *n*-alkyl homologs.[25] The rates of decomposition are greater and are sensitive to the structure of the alkyl group. The formation of ester with alkoxy stereochemistry retained (from optically active peroxides), and the isolation of the carbonic anhydrides which precede ester formation suggest an additional reaction path. The moderate sensitivity of rate to solvent polarity further indicates a slight polar character in this rearrangement. The radical and the polar characteristics of this decomposition have been merged by Walling[26] and are reproduced in Scheme II.

Scheme II



This decomposition, carried out in the presence of 1-iodoethane under conditions suitable for CIDNP purposes (Table III), gives a product composition quite consistent with those reported by Walling, and a spectrum shown in Figure 5. Multiplet polarization is clearly evident for the vinyl protons in propene (CH_2, δ 4.9–5.2; CH, δ 5.6–6.2; EA) and the methyne proton of 2-iodopropane (δ 4.34, AE). Isopropyl isobutyrate (OCH, δ 4.98) and the carboxy inversion product $(CH_3)_2CHOC(=O)OC(=O)CH(CH_3)_2$ (OCH–, δ 4.83) on the other hand do not show polarization of any sort. If Scheme II is to be retained it must be modified (Scheme III, where $k_{-CO_2} \gg W_{SS}$) to achieve consistency with these observations. (Of course, isopropyl–isobutyroxy pairs probably do form but would be expected to exist so transiently that spin selection would not occur.) Most significantly, the existence of a singlet solvent-separated pair composed of an isopropyl and an iso-

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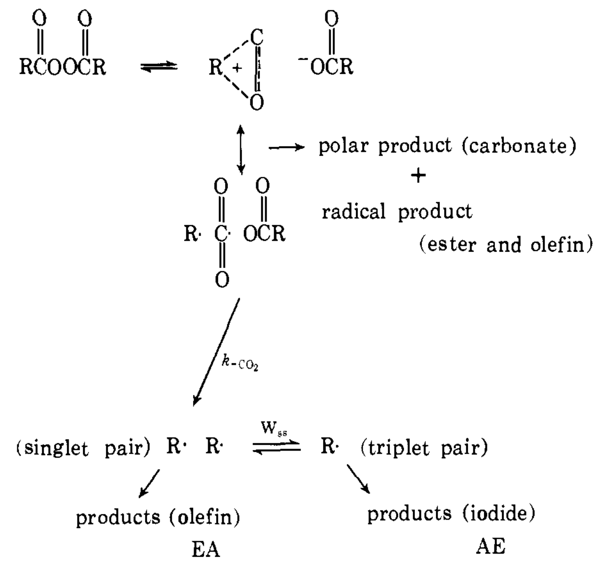
(24) (a) The enhancements are insensitive to small changes in alkyl iodide concentrations, which suggests that all radicals escaping a geminate encounter are trapped in a time less than T_1. (b) The haloundecane, once formed, probably will not serve as a halogen donor because it is always in lower concentration than the reagent halide, and is usually of lower reactivity.

(25) Benzoyl peroxide is a special case because of the unusual stability of the benzoyloxy radical. A CIDNP study of its decomposition in alkyl iodide solutions is described in the following paper: R. A. Cooper, R. G. Lawler, and H. R. Ward, *J. Amer. Chem. Soc.*, **94**, 552 (1972).

(26) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, **93**, 4927 (1970).

Scheme III



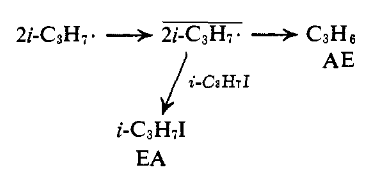
butyroxy radical is contraindicated, for it should have led, *via* mixing with the triplet pair, to net polarization in isopropyl isobutyrate, propene, and 2-iodopropane. It is unlikely that singlet–triplet mixing would occur without spin selection in such a pair. If reversion to the initial pair occurred, polarization should also have appeared in the alkyl–acyl carbonate. The CIDNP spectra, instead, are most consistent with geminate pairs of isopropyl radicals as the sole source of spin selection, and thus the only pairs which exist for a time sufficient for separation and recombination. The fact that the CIDNP spectra are entirely analogous for the primary and the secondary peroxide decompositions, while the chemistry is quite different, should serve as a useful reminder of the inherent limitations of CIDNP.

Polarization in Diffusive Encounters. The use of alkyl iodides as scavenging agents for free radicals provides not only a rapid sequestering of radicals escaping a geminate encounter, but also a method by which radicals can be formed free of any previous pair involvement. For iodine transfers which are exothermic or even mildly endothermic, at the alkyl iodide concentrations used in this study, nearly all escaping radicals are captured in a time short compared to that required for diffusive encounters,[24] and so the number of free radicals resulting from the iodide can be derived directly from the "cage effect," *ca.* 40–60%. There is no evidence to support the idea[17a] that the act of iodine transfer in itself provides a route for spin selection, and the nuclear spin state population of the alkyl iodide should be accurately reflected in the free radical which derives from it. (Certainly, no polarizing mechanism has been suggested which can act within the 10^{-13} sec required for an atom transfer.)

It is instructive to follow the path of one such radical, after it is formed by iodine donation. Since iodine transfer is rapid for transfers which are slightly endothermic,[27] thermoneutral transfers should also be swift,[28] and many regenerate iodine transfers (*ca.* 100) between like alkyl moieties may occur before any other reaction is probable. Reactions other than iodine transfers are apparently not able to compete, at these radical concentrations, with radical–radical reactions. Since each transfer takes place in a time short compared to nuclear relaxation in the radical, the nuclear spin state populations in the alkyl iodide should remain virtually unchanged by the sequence of atom transfers. After about 10^{-3}–10^{-4} sec, two of these radicals will encounter each other, and will form product with the characteristic AE phase. A proper example is the propene formed in the decomposition of propionyl peroxide in 2-iodopropane (Figure 2).

$$(C_2H_5CO_2)_2 \longrightarrow \longrightarrow C_2H_5\cdot$$

$$C_2H_5\cdot + i\text{-}C_3H_3I \longrightarrow C_2H_5I + i\text{-}C_3H_7\cdot$$



$$2i\text{-}C_3H_7\cdot \longrightarrow \overline{2i\text{-}C_3H_7\cdot} \longrightarrow \underset{\text{AE}}{C_3H_6}$$
$$\overline{2i\text{-}C_3H_7\cdot} \xrightarrow{i\text{-}C_3H_7I} \underset{\text{EA}}{i\text{-}C_3H_7I}$$

Those isopropyl radicals which do not react must carry the complementary spin information, and will be trapped by yet another iodine transfer from 2-iodopropane. Chemically this transfer results in no change but the nuclear spin state population of the product 2-iodopropane will be different from that of the reagent. (It is useful to note in passing that CIDNP offers an additional approach to the study of this degenerate type of exchange, beyond the established techniques of double labeling and loss of optical activity.) In this way an EA phase is imposed in the reagent iodide (see the methyne proton of 2-iodopropane, δ 4.34, Figure 2), which will decay with the characteristic T_1 for the iodide.

The efficacy of spin selection in the diffusive encounter compared to a geminate encounter has not been predicted theoretically or tested experimentally. The proper experimental test is difficult because of an inherent complication. The efficiencies to be compared for the two types of encounters must be from pairs which are in every other way identical, even including the cage effect, which figures prominently in the calculation of enhancement factors. Unfortunately, cage effects for diffusive encounters cannot be straightforwardly measured, since the available measuring techniques interfere with the very formation of diffusive encounter pairs. A very approximate measure of the relative efficiencies in two different pairs, measured in the same reaction, is available from the decomposition of lauroyl peroxide in 2-iodopropane–*o*-dichlorobenzene. The ratio of enhancements, corrected for T_1 in the products and degeneracies in the peaks used for measurement, was 1.3, for enhancement of 1-iodoundecane–2-iodopropane. Of course, the encounters leading to these enhancements are different in many ways, in structure of partners, distance of initial separation, and probably in cage effect, but the message is clear that diffusive encounters cannot be drastically less efficient in spin selection than geminate encounters.

It is expected that peroxide systems will continue to provide convenient systems for the study of CIDNP, and in a symbiotic relation will supply experiments to test the theory while deriving profit in mechanistic clarification.

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(27) Isopropyl radicals are able to abstract iodine from 1-iodoethane in a time short compared to T_1 in the radical.

(28) R. G. Lawler, H. R. Ward, R. B. Allen, and P. E. Ellenbogen, *J. Amer. Chem. Soc.*, **93**, 789 (1971).

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Radical Pair Substitution in Benzoyl Peroxide Thermolyses Observed by Chemically Induced Dynamic Nuclear Polarization

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Abstract: During the thermolysis of benzoyl peroxide in solutions containing alkyl iodides, CIDNP spectra of alkyl benzoates have been observed which must result from interactions in benzoyloxy–alkyl geminate radical pairs. Such pairs may arise *via* a rapid iodide abstraction leading to a "pair substitution" of an alkyl radical for a phenyl radical. The same benzoyloxy–alkyl pair, generated independently by the thermolysis of the appropriate benzoyl alkyl acyl peroxide, gave rise to CIDNP spectra entirely analogous to those resulting from pair substitution. The type of polarization which is observed from the alkylbenzene which forms in both reactions must result from spin selection in a phenyl–alkyl geminate pair which is a direct descendant of a benzoyloxy–alkyl pair. From the known rate of decarboxylation of the benzoyloxy radical, it can be shown that the geminate pair must exist for times of 10^{-6}–10^{-7} sec.

Benzoyl is favored among diacyl peroxides, carrying the same high status among free-radical sources that benzophenone has as a photosensitizer. Since it is the peroxide used by more chemists than any other, it is no surprise that one of the first reported examples of chemically induced dynamic nuclear polarization (CIDNP) was the benzene nmr emission signal recorded by Fischer[3] during the thermolysis of benzoyl peroxide in cyclohexanone. Characteristically, the decomposition of benzoyl peroxide has been the most popular CIDNP subject, figuring in more of these studies[4–12] than any other compound. We continue in the tradition by reporting that benzoyl peroxide decompositions in solutions containing alkyl iodides can lead to substitution in the geminate radical pair to form a benzoyloxy–alkyl radical pair.

Mechanism of the Decomposition. Most of the useful information on benzoyl peroxide decomposition (and subsequent reactions) was brought together in a paper by DeTar,[13] which has required only minimal updating. The initial step is unquestionably an oxygen–oxygen bond cleavage to form a geminate pair of benzoyloxy radicals, which have been shown by ^{18}O labeling to revert only slightly (~5%) to the peroxide.[14] Benzoyloxy is, for an acyloxy radical, quite stable, and its rate of decarboxylation at the conventional decomposition temperature of *ca.* 90° has been taken to be slower than diffusive separation.[13] As a consequence, those benzoyloxy geminate pairs which do not recombine (the majority) diffuse apart and may be trapped by addition to carbon–carbon unsaturation or by hydrogen abstraction. The modest amounts of phenyl benzoate and biphenyl which persist even at high concentrations of trapping agents are ascribed[13] to a minor amount (<5%) of multiple bond cleavage, generating phenyl–benzoyloxy and phenyl geminate pairs (a point to which we shall return).

$$\begin{tikzcd}
(\mathrm{PhCO_2})_2 \arrow[r, shift left, "\Delta"] & \overline{2\mathrm{PhCO_2}\cdot} \arrow[l, shift left] \arrow[r, "\text{major}"] \arrow[d, "\text{minor}"] & 2\mathrm{PhCO_2}\cdot \arrow[r, "\mathrm{SH}"] & \mathrm{PhCO_2H} \\
& \overline{\mathrm{PhCO_2}\cdot,\mathrm{Ph}\cdot} \arrow[r] \arrow[d] & \mathrm{PhCO_2Ph} & \\
& \mathrm{PhCO_2}\cdot + \mathrm{Ph}\cdot & &
\end{tikzcd}$$

Annals of Benzoyl Peroxide CIDNP Studies. In the first disclosure of nmr enhancements observed in benzoyl peroxide thermolyses in cyclohexanone, Fischer[3] focused on a strong benzene emission line, which he explained by a chemical Overhauser effect.[15] As CIDNP theory has developed, and the radical pair model has gained the ascendency,[16–21] the significance

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