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

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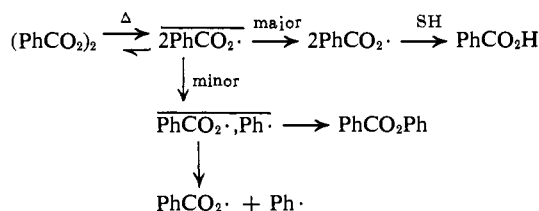
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Abstract: During the thermolysis of benzoyl peroxide in solutions containing alkyl iodides, CIDNP spectra of alkyl benzoates have been observed which must result from interactions in benzyloxy-alkyl geminate radical pairs. Such pairs may arise *via* a rapid iodide abstraction leading to a "pair substitution" of an alkyl radical for a phenyl radical. The same benzyloxy-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 benzyloxy-alkyl pair. From the known rate of decarboxylation of the benzyloxy 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 Fischer³ 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 benzyloxy-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 benzyloxy radicals, which have been shown by ¹⁸O labeling to revert only slightly (~5%) to the peroxide.¹⁴ Ben-



zyloxy 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 benzyloxy 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 ascribed¹³ to a minor amount (<5%) of multiple bond cleavage, generating phenyl-benzyloxy and phenyl geminate pairs (a point to which we shall return).

Annals of Benzoyl Peroxide CIDNP Studies. In the first disclosure of nmr enhancements observed in benzoyl peroxide thermolyses in cyclohexanone, Fischer³ 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 ascendancy,^{16–21} the significance

(1) National Defense Education Act Trainee, 1967; National Science Foundation Predoctoral Fellow, 1970.

(2) Alfred P. Sloan Foundation Research Fellow, 1969–1971.

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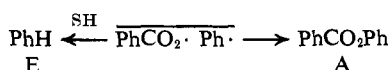
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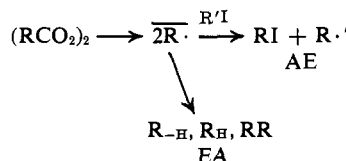
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of the benzene emission line has been reinterpreted²² (along with the enhanced absorption which subsequently has been discovered for phenyl benzoate) to be a result of spin selection in a geminate benzoyloxy-phenyl pair. The manner²¹ in which the hyperfine field of the phenyl protons, in concert with the difference in *g* factors between phenyl and benzoyloxy, conspires to induce singlet-triplet mixing in the pair need not be repeated here. It is sufficient to say that the dependency of this mixing on the nuclear magnetic quantum number of the phenyl protons provides a mechanism for nuclear spin selection, in which the ortho protons with spin $-1/2$ predominate in phenyl radicals escaping the geminate encounter, and phenyl radicals with ortho proton spins of $+1/2$ remain to dominate the *o*-phenoxy protons of phenyl benzoate. This is a specific instance of the generalization that protons with positive hyperfine splitting on the radical with the lower *g* factor of a pair formed initially in the singlet state, as in this example, give enhanced absorption in combination products and emission in products arising from radicals which have escaped the geminate pair.



When correction is made for the longer T_1 which prolongs the emission in benzene, the enhancements for both products are the same.²² Trozzolo has shown,²³ through the use of perdeuteriobenzoyl peroxide, that the polarization is in the benzene protons which reside on the phenyl radical and that the proton transferred from solvent shows no enhancement. Enhancements in ^{13}C spectra⁹ taken during benzoyl peroxide thermolyses are consistent with this model, as are triplet-photosensitized decompositions^{12, 24, 25} which lead to reversal of the sign of enhancement by virtue of the initial triplet multiplicity of the radical pairs.

Decomposition in Solutions Containing Alkyl Iodides. In the previous paper,²⁶ we have reported that the decomposition of aliphatic diacyl peroxides in solvents containing alkyl iodides ($\text{R}'\text{I}$) is a convenient method for the generation of alkyl radicals with no past record of partnership in a radical pair. The products, R_-H and $\text{R}'\text{I}$, show a multiplet effect polarization, of phase EA and AE, respectively, a result of geminate pair spin selection. The disproportionation product, $\text{R}'_-\text{H}$ (AE),



and the reagent alkyl iodide, $\text{R}'\text{I}$ (EA), itself show multiplet effects which arise from spin selection in diffusive encounters. The decomposition of propionyl peroxide²⁶ in an *o*-dichlorobenzene (ODCB) solution

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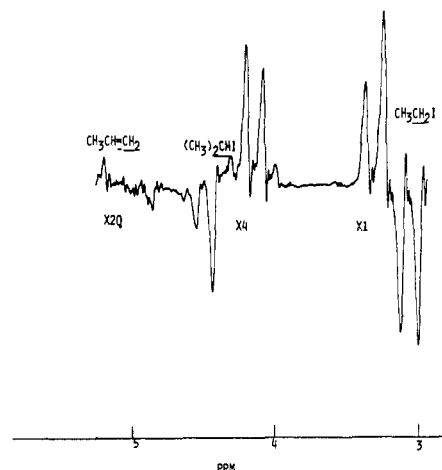
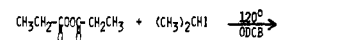
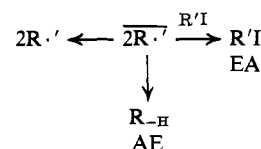


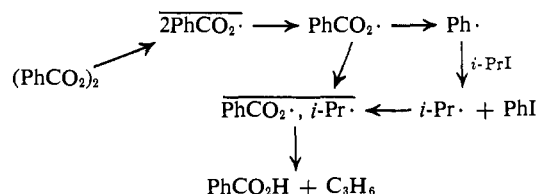
Figure 1. Polarization observed during the thermolysis of propionyl peroxide in the presence of 2-iodopropane in ODCB solvent at 120°C.

containing 2-iodopropane (Figure 1) shows many of these features, with an AE phase for propene (CH_2 , δ 4.9–5.35) and 1-iodoethane (CH_2I , δ 3.2), and an EA phase for 2-iodopropane (CH , δ 4.3).



Benzoyl Peroxide-2-Iodopropane. We were somewhat perplexed when the decomposition of benzoyl peroxide in solutions containing alkyl iodides afforded polarizations for which the study of the aliphatic peroxides had not prepared us. Some aspects of these spectra were comfortably familiar; for example, 2-iodopropane showed EA during benzoyl peroxide decomposition (Figure 2) and the emission from the ortho protons of iodobenzene was to be expected from Fischer's work.³ The net emission from the vinyl methylene (δ 5.7–6.2) and the net enhanced absorption from the vinylmethylene of propene were not expected, however, and demanded a polarizing interaction of an isopropyl radical with a radical with a different *g* factor (*i.e.*, not a hydrocarbon radical). Virtually the only such radical in this system is benzoyloxy, and one might imagine its diffusive encounter with an isopropyl radical in the manner of Scheme I.

Scheme I



There are two difficulties with this scheme. First, the rate of benzoyloxy decarboxylation is certain to be greater than that of diffusive encounter so that for a benzoyloxy radical to survive to form such a pair

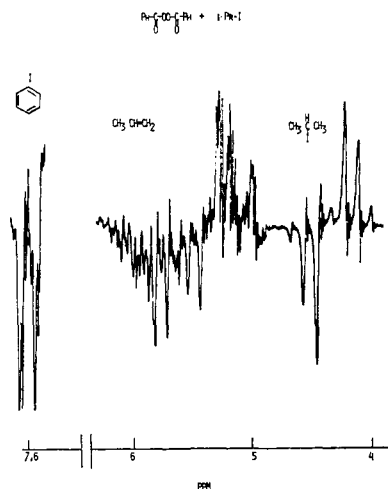


Figure 2. Polarization observed during the thermolysis of benzoyl peroxide in the presence of 2-iodopropane in ODCB solvent at 130°.

would at best be unlikely. Second, the phase of polarization is incorrect, for a diffusive encounter would have given emission for the 1-protons and enhanced absorption for the 2-proton of propene.

Benzoyl Peroxide—Iodoethane. The thermolysis of benzoyl peroxide in iodoethane-*o*-dichlorobenzene (Figure 3) also gives rise to net polarization and, in this case, a product, ethyl benzoate (2.2% yield), which demands an ancestral benzoyloxy-ethyl pair. Further, the phase of the polarization (emission for the methylene (δ 4.3) and enhanced absorption for methyl (δ 1.3)) requires that the pair be *geminate*, not diffusive. The most rational way in which such a pair might be formed is the abstraction of iodine from iodoethane by a geminate partner of benzoyloxy, thereby replacing itself with an ethyl radical. Since the abstraction act is rapid, it should proceed with spin conservation, and the spin multiplicity of the new radical pair should be the same as its predecessor pair. This type of radical trapping has been called the "cage-wall effect," but since we wish to focus on the further reactions of the pair so formed, we prefer the term "pair substitution."²⁷

Another possible route for ethyl benzoate formation is the SH₂-like induced decomposition of benzoyl peroxide by ethyl radicals. However, the predicted polarization for α and β protons of the ethyl moiety for this mechanism is EA, since this is the dominant phase of free ethyl radicals. Further, Trozzolo and Fahrenholtz¹² have shown that induced decomposition of benzoyl peroxide of itself does not give rise to CIDNP.

We may now examine the spectral implications of a pair substitution for the iodoethane system (Scheme II).

In addition to the ethyl benzoate, this second generation geminate pair of benzoyloxy and ethyl radicals can lead, by disproportionation, to benzoic acid and ethylene. The carboxylic proton derives from the β position of the ethyl radical and properly displays enhanced absorption. The forecast of the ethylene polarization is more complex. Two protons on the α position, polarized E, and two on the β position, polarized A, contribute to the ethylene singlet and if the two polarizations were equal, this singlet would be expected to grow in as a normal absorption signal

(27) As far as we are aware, the application of pair substitution to the explanation of CIDNP spectra was first suggested by Robert Kaptein.

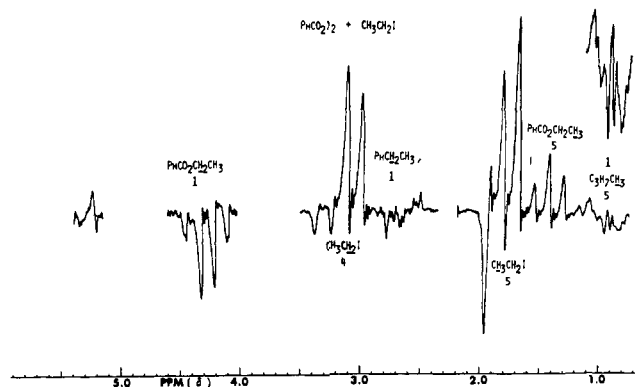
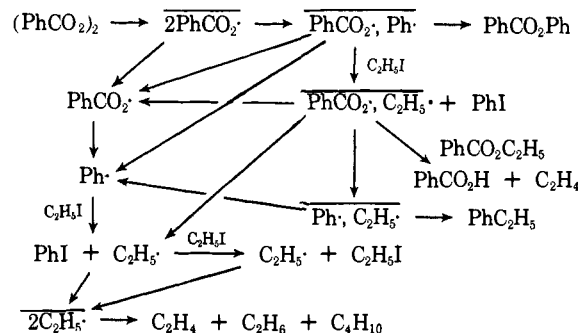


Figure 3. Polarized spectrum taken during the thermolysis of benzoyl peroxide in the presence of iodoethane in ODCB solvent at 130°.

during the reaction. The polarizations are not equal, however, because of an inequality in the absolute magnitudes of the hyperfine coupling constants²⁸ for

Scheme II



the α (22.5 G) and the β positions (27.1 G). The larger hyperfine field from the β position leads to the weak enhanced absorption which is observed for ethylene. The decomposition of benzoyl peroxide in 2,2,2-trideuterioiodoethane-*o*-dichlorobenzene solutions forms ethylene (presumably *d*₂) which shows *emission* (from the protons which were α in the ethyl radicals), thus certifying this explanation.²⁹

The enhancements for ethylbenzene also are small, but, for the methylene protons (δ 2.7), are unmistakably a combination of E and EA. This is consistent only with a composite of E from the geminate benzoyloxy-ethyl pair and EA from a phenyl-ethyl geminate pair derived by decarboxylation. Other modes of formation (polarization), by diffusive encounter of phenyl and ethyl radicals (AE, perhaps with attendant A) or direct, multiple bond cleavage in the peroxide followed by pair substitution (EA only), are both inconsistent with the observed polarization and mechanistically improbable. We believe that this CIDNP spectrum alone establishes benzoyloxy decarboxylation in a geminate pair (although it certainly does not describe its degree).

Ethyl radicals are participants in two distinct polarizing actions; geminate encounters with benzoyloxy radicals and diffusive encounters with other ethyl radicals. Iodoethane is formed by iodine abstraction by ethyl radicals on escape from both encounters, and from the former should show net polarization

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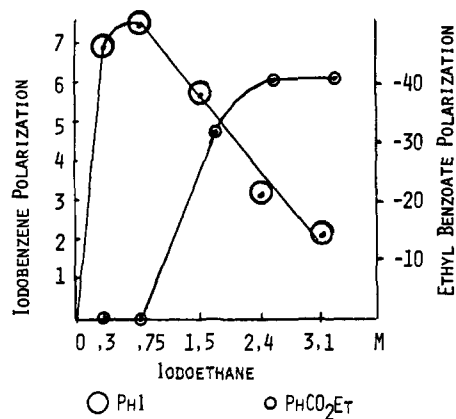


Figure 4. Plot of enhancements for iodobenzene and intensities for ethyl benzoate *vs.* iodoethane concentration.

(CH₂ A, CH₃ E) and from the latter a pure EA multiplet effect. The net polarization is partially masked by the much larger multiplet effect (many more diffusive encounters occur).

The pattern of polarization on changing iodoethane concentration is consonant with the idea of pair substitution. Scheme II suggests that as iodoethane concentration increases, the polarization of products from the "original" geminate pair should decline and polarization from the derivative geminate pair should increase. We have monitored the signals from iodobenzene, from phenyl radicals polarized in the original pair, and from the methylene protons of ethyl benzoate, which forms in the substitution pair. (Unfortunately ODCB absorption prevented direct monitoring of phenyl benzoate, the corresponding product of the original geminate pair.) The formation of both products depends on reaction with iodoethane, but on a substantially differing time scale. Iodobenzene, if it is to display maximum polarization, must be formed before proton relaxation occurs in the antecedent phenyl radical ($<10^{-4}$ sec). The plot of iodobenzene polarization as a function of iodoethane concentration (Figure 4) shows that at 0.4 M the polarization reaches a maximum. Pair substitution is more demanding, since reactions must occur during a pair lifetime, and at 0.4 M iodoethane very little polarization can be seen for ethyl benzoate. As the iodoethane concentration increases, however, iodobenzene polarization drops and ethyl benzoate polarization rises. As expected, the more efficient the pair substitution process, the weaker should be the iodobenzene polarization, since by definition (retention of spin multiplicity in the derivative pair) pair substitution must diminish the degree of spin selection, by cutting short the lifetime of the original pair. The leveling of ethyl benzoate polarization at 2.5 M iodoethane concentration suggests that nearly all phenyl-benzoyloxy pairs are being intercepted, and also that the benzoyloxy radical itself does not abstract iodine from iodoethane, at least within a pair lifetime. Product analysis (Table I) confirms that at high iodoethane concentration (>2.5 M) all phenyl benzoate formation is prevented. Even though iodobenzene polarization is nearly extinguished by iodoethane concentrations >2.5 M, the amount which forms in the 0.5–3.1 M range decreases only slightly, presumably because most of the iodobenzene is formed by an extra-

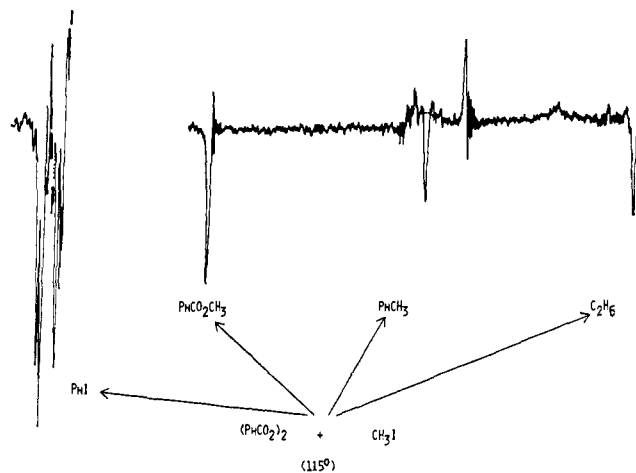


Figure 5. Thermal decomposition of benzoyl peroxide in ODCB with added iodomethane at 130°.

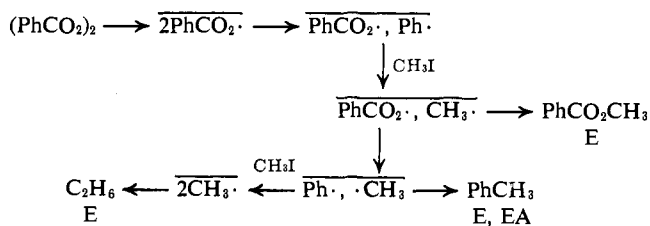
cage decarboxylation of benzoyloxy (to give unpolarized phenyl radicals), followed by iodine abstraction.

Table I. Effect of Iodoethane Concentration on Product Composition

[EtI], M	PhCO ₂ Ph, %	PhCO ₂ Et, %	PhI, %
	3.5		
1.4 M	1.3	0.5	57
2.5 M	<0.1	2.2	50

The polarization observed¹¹ during the decomposition of benzoyl peroxide in solutions containing iodomethane (Figure 5) is largely explicable by pair substitution (Scheme III) to form both benzoyloxy-methyl and

Scheme III



phenyl-methyl geminate pairs. Again, the emission³⁰ of the methyl protons of toluene most strongly indicates toluene formation from a third-generation pair, in which the polarization developed in the second-generation benzoyloxy-methyl pair is maintained. Indeed, the weak emission from ethane may result from a *second* pair substitution, of methyl for phenyl, the polarization having survived from the benzoyloxy-methyl pair. If this lengthy chain of events strains the credulity, we can offer in mild defense that there is independent evidence (emission for methyl benzoate and toluene) for each geminate pair along the way, and, more to the point, no reasonable alternative route to emission in ethane suggests itself. This process of double pair substitution may well have occurred with iodoethane and 2-iodopropane, but in the coupling products has

(30) In certain scans, under particularly high resolution, an EA, arising from splitting by the ortho protons, can be seen superimposed on the net methyl emission, confirming a geminate encounter origin for toluene.

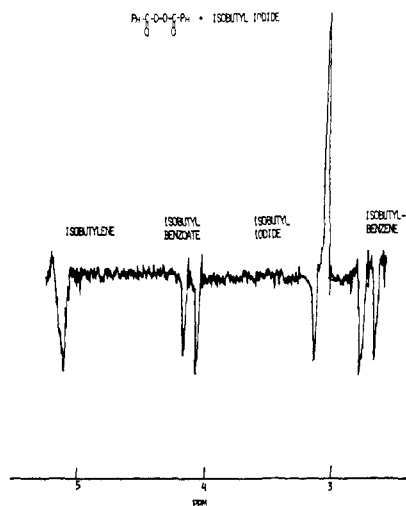
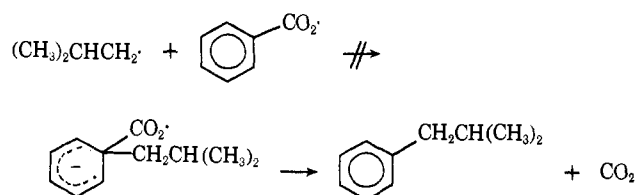


Figure 6. Thermal decomposition of benzoyl peroxide in ODCB with added 1-iodo-2-methylpropane at 130°.

been obscured by multiplet effect polarization from diffusive encounters.

Benzoyl Peroxide-1-Iodo-2-methylpropane. The polarization observed during this thermolysis (Figure 6) is in every way analogous to the CIDNP spectra taken during the benzoyl peroxide decomposition in iodoethane (Figure 3). However, the relative intensities observed from the protons of the benzoate ester and the alkylbenzene are quite different in the two cases, ethyl benzoate showing a much stronger signal than ethylbenzene, while signals from the methylene protons of isobutyl benzoate (δ 4.1) and isobutylbenzene (δ 2.7) are of nearly equal intensity. This may result from a decrease in reaction rate of the benzoyloxy-isobutyl geminate pair (relative to a benzoyloxy-ethyl pair) because of increased steric resistance to both coupling and disproportionation. Again, the emission in isobutylbenzene is clear evidence that its formation proceeded by route of a benzoyloxy-isobutyl pair. The EA multiplet effect which accompanies this emission is most clearly seen by comparison of the intensities of the doublet lines for the ester (high-field line more intense than the low-field line as in the normal absorption spectrum) and the isobutylbenzene (low-field line more intense than the high-field line, the opposite of the normal absorption spectrum). Clearly the isobutylbenzene must have resulted from a pair in which additional multiplet effect polarization was added to the polarization from the benzoyloxy-isobutyl pair. The most reasonable suggestion, again, is a benzoyloxy decarboxylation during the geminate pair lifetime, to form a phenyl-isobutyl geminate pair. The fact that both alkylbenzene and ester do not form from the same pair eliminates the possibility of isobutylbenzene formation by a displacement of carbon dioxide by the isobutyl radical or by any other *direct* reaction of isobutyl and benzoyloxy radicals. The slight AE phase



which is detectable along with the net emission of the methylene protons in isobutylene (δ 5.1) probably also has its source in the disproportionation of the phenyl-isobutyl pair.

Geminate Pair Lifetime. The extent of pair substitution will increase both with increasing geminate pair lifetime and with an increase in the rate of reaction leading to substitution (e.g., the rate of iodine abstraction by phenyl radical from an alkyl iodide). Unfortunately, the rate of iodine abstraction is not known for this case, and the only comparisons (methyl radical and 1-iodopropane,³¹ $4 \times 10^5 M^{-1} \text{sec}^{-1}$ at 100°, gas phase; allyl radical and 3-iodopropene,³² $3 \times 10^7 M^{-1} \text{sec}^{-1}$ at 100°) do not provide adequate models. Certainly, because of the exothermicity of the iodine transfer from an alkyl iodide to a phenyl radical, the rate would be expected to exceed that of a transfer between alkyl moieties. The necessity of a benzoyloxy decarboxylation during the lifetime of a geminate pair, in order to explain the alkylbenzene polarization, does provide a lower limit for this lifetime. This decarboxylation rate is calculated³³ to be $2.5 \times 10^5 \text{sec}^{-1}$ at 130°, which leads to an estimated minimum half-life of the pair of $4 \times 10^{-6} \text{sec}$. This value is certainly compatible with the probable rate of iodine transfer, and with the rate of pair substitution reported by Kaptein.³⁴ It is, of course, far longer than the lifetime of 10^{-10} – 10^{-9}sec which is usually taken for geminate pairs. This discrepancy is not as severe as it may initially appear since the two lifetimes are intended to describe different events. The usual reference is to the probability of product formation by combination in geminate pairs, which will decrease as some function of time (the exact function depends on the solution model which is chosen). The observed intensity of the CIDNP spectra, however, depends not only on the combination probability, but also on the spin selection process, which is of *increasing* efficacy as time increases. Thus, although the amount of geminate combination decreases with time, the observed polarization may remain relatively high (at least up to 10^{-8} – 10^{-7}sec , when singlet-triplet mixing should be complete). Because the polarization in some of the alkylbenzenes is quite comparable with that observed for other reaction products we must conclude that in this and other CIDNP spectra, the polarization may result principally from those few radical pairs which exist for relatively long times (up to 10^{-6}sec).

Mixed Alkyl Aryl Diacyl Peroxides. If the idea of a pair substitution process giving rise to geminate polarization has any validity, it should be possible to duplicate the CIDNP spectrum by independently generating the same geminate pair. Fortunately, for benzoyloxy-alkyl pairs, this is a simple exercise since the appropriately constituted mixed diacyl peroxides are easily prepared. The initial acyloxy pair certainly degrades with alacrity to the desired pair, because the decarboxylation of the alkyl acyloxy radical far outstrips both benzoyloxy decarboxylation and diffusive separation.

(31) Estimated from data reported by D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, **70**, 1579 (1966).

(32) R. G. Lawler, H. R. Ward, R. B. Allen, and P. E. Ellenbogen, *J. Amer. Chem. Soc.*, **93**, 791 (1971).

(33) Extrapolated from rate measurements at 60 and 80°: J. U. Bevington and J. Toole, *J. Poly. Sci.*, **28**, 413 (1959).

(34) R. Kaptein, F. W. Verhens, and L. J. Oosterhoff, personal communication.

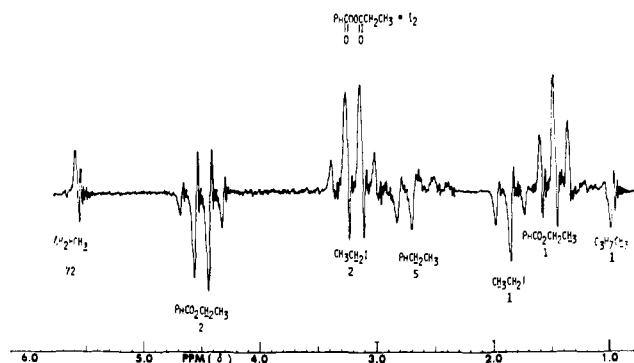


Figure 7. Thermal decomposition of benzoyl propionyl peroxide in ODCB solvent with added iodine at 120°.

Benzoyl Propionyl Peroxide. The polarization phases in the spectrum taken during the decomposition of benzoyl propionyl peroxide in a solution of ODCB containing iodine (Figure 7) proved to be identical with those in Figure 3, for all of the relevant products. Of course, since many more benzyloxy-ethyl pairs are produced in the direct formation than by pair substitution, the enhancements in Figure 7 are rather larger. Polarizations of ethylene, ethyl benzoate, and ethylbenzene are all explicable by the portions of Scheme II which follow benzyloxy-ethyl pair formation. Iodoethane polarization is expectedly different, since now, with no diffusive encounter of ethyl radicals, a clear A for the methylene and E for the methyls can be seen. Iodobenzene appears to show a relatively weak enhanced absorption for which we can offer no reasonable explanation at this time.

The decomposition of benzoyl propionyl peroxide in the presence of 2-iodopropane gives no hint of substitution of isopropyl for ethyl in the geminate pair. We conclude that the transfer of iodine from 2-iodopropane to ethyl must be much less facile than the transfer to phenyl from iodoethane or 2-iodopropane in line with the thermodynamics of the process. Any iodine abstraction by benzyloxy would lead to an ethyl-isopropyl pair, but if any such pairs are formed the resultant polarization is totally obscured by other polarization processes.

Benzoyl Isobutyryl Peroxides. Benzoyl isobutyryl peroxide was prepared and decomposed in iodine-*o*-dichlorobenzene solutions to provide spectra (Figure 8) for comparison with the pair substitution process in benzoyl peroxide decomposition in 2-iodopropane-*o*-dichlorobenzene solutions (Figure 2). The agreement is satisfactory, and in most respects is analogous to the benzoyl propionyl peroxide thermolysis. It differs in the polarization intensity observed for the ester, isopropyl benzoate, which is so weak as to be scarcely observed (CHO, δ 5.4, E). The propene protons and the carboxylic proton of benzoic acid are strongly polarized, however, which may mean simply that benzyloxy-isopropyl pairs prefer disproportionation to combination. A substantial amount of carboxy inversion product should be formed in this thermolysis,³⁵ but appears to form by a path which does not involve spin selection.²⁶

(35) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *J. Amer. Chem. Soc.*, **92**, 4927 (1970).

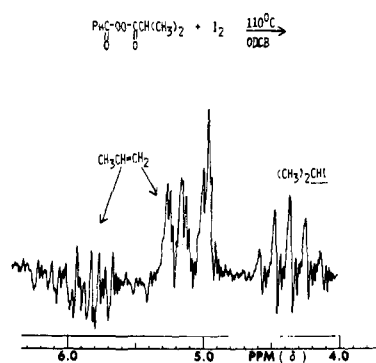


Figure 8. Polarization observed during the thermolysis of benzoyl isobutyryl peroxide in the presence of iodine in ODCB at 120°.

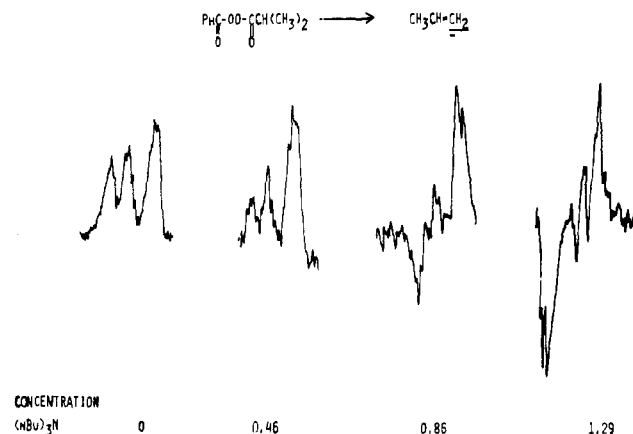
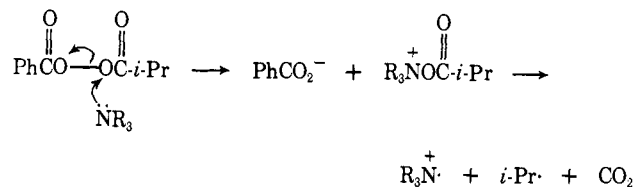


Figure 9. Polarization observed from the vinylmethylene protons of propene during the decomposition of benzoyl isobutyryl peroxide, displayed as a function of the concentration of added tri-*n*-butylamine.

The thermolysis of acetyl benzoyl peroxide reported by Buchachenko and Rykov³⁶ gives CIDNP spectra which are entirely interpretable by radical pair models, and are consistent with the polarization reported here for the higher homologs.

Amine-Induced Decompositions. The rate of decomposition of benzoyl isobutyryl peroxide is increased by the addition of tertiary amines and Walling³⁵ reports high yields of the products of the isopropyl radical and the nearly quantitative formation of benzoic acid. The reaction is believed to proceed by a nucleophilic attack of the amine on a peroxidic oxygen, in this case to produce the benzoate ion and an acyl ammonium ion which fragments to the amine radical cation, an isopropyl radical, and carbon dioxide. The polarization ob-



served from the methylene protons of propene formed during this decomposition is displayed in Figure 9, as a function of the concentration of tri-*n*-butylamine. As the amine concentration increases this polarization

(36) A. L. Buchachenko, S. V. Rykov, A. V. Kessenikh, and G. S. Bylina, *Dokl. Akad. Nauk, SSSR*, **190**, 839 (1970).

changes from enhanced absorption to a pure EA multiplet effect. In the presence of iodine, 2-iodopropane is formed, and, for the methyne proton, proceeds (with increasing amine concentration) from enhanced absorption to an AE multiplet. It appears that the amine-induced decomposition totally overcomes the normal decomposition at $\sim 0.8 M$ amine concentration. The observed polarization apparently derives from a geminate pair, containing the isopropyl and some other radical of similar g factor.

The amine-induced decomposition of benzoyl propionyl peroxide does not produce ethyl benzoate (although it does form, and show strong polarization (Figure 7) in the normal decomposition). In the presence of an iodine source (2-iodopropane) iodoethane displays an AE phase, as it should for formation by iodine abstraction on escape from a geminate encounter.

At the present time, we are unable to assign the identity of the partner of the alkyl radical in the geminate pair. The most chemically reasonable partner, the amine radical cation, should have a substantially higher g factor than ethyl or isopropyl (the g factor for $(\text{CH}_3)_2\text{N}\cdot^+$ is 2.0044),³⁷ and the resulting Δg effect would produce net polarization. Further, no polarization is observed in any amine-derived product. The absence of ethylbenzene polarization in the induced decomposition of benzoyl propionyl peroxide eliminates the possibility of a phenyl-ethyl geminate pair. A geminate pair of alkyl radicals would satisfy the requirements for polarization, but a rational way by which such a pair might be formed is not apparent.³⁸

(37) A. J. Tench, *J. Chem. Phys.*, **38**, 593 (1963).

(38) Professor John Garst has suggested that a geminate pair of alkyl radicals might be formed from the alkyl diacyl peroxide (a possible impurity in the benzoyl alkyl acyl peroxide or, alternatively, the product of an unspecified reaction of the benzoyl alkyl acyl peroxide with the tertiary amine). Such an impurity is difficult to exclude, especially if it is formed during the induced decomposition. However, the amine-catalyzed decomposition of lauroyl peroxide (which should serve as a reasonable model for propionyl peroxide) in solutions containing isopropyl iodide does *not* show geminate polarization for 1-undecene.

Experimental Section

CIDNP Spectra. All reactions were run by placing a 0.5 M solution of the peroxide in *o*-dichlorobenzene (ODCB) (usually containing a twofold excess of an alkyl iodide) in the preheated probe of a Varian A60A spectrometer.

Reagents. The alkyl iodides were distilled under vacuum and stored over copper wire at 0°. Benzoyl peroxide was obtained commercially and not purified further. The mixed benzoyl-alkyl acyl peroxides were prepared in the usual way.

Analysis. Product analyses for benzoyl peroxide-iodoethane decompositions were obtained by glc using a 9-ft silicone 710 on 90-100 Chromosorb (100°) and a 5-ft silicone SE-30, 60-80 Chromosorb (60-120°) column. The results of a decomposition of 0.5 M benzoyl peroxide in a 2 M solution of iodoethane in ODCB at 130° were: ethyl benzoate = 2.2%, iodobenzene = 57.0%, benzene = 4.8%, ethylbenzene = 3.2%, biphenyl = 1.0%, phenyl benzoate = <0.1%.

Enhancement Factors for Iodobenzene. The intensities of polarization (I) were measured by taking the area of the iodobenzene emission at 160 sec after placement of the solution in the preheated probe (130°), and the unpolarized intensity (I_0) was measured at room temperature after the above reaction was quenched, immediately after I was measured, by immersion in liquid N_2 . Normal absorption intensities were corrected by comparing the solvent peak areas at the elevated and at room temperatures. The enhancement factors, P , were calculated from the ratio $(I - I_0)/I_0$.

Intensities for Ethyl Benzoate. The benzoyl peroxide-iodoethane solutions were placed in a preheated probe at 130° and the methylene quartet of the ethyl benzoate was repeatedly scanned. The intensities were measured by taking the area of the $m = 1/2$ line at 160 sec after placement in the probe. Enhancements could not be measured because the small amount of ethyl benzoate which is formed leads to an inaccurate value for I_0 .

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(The isopropyl iodide does exhibit diffusive polarization, which establishes that free radicals certainly do result from the induced decomposition.) We regard the mode of formation of the radical pairs in these reactions as an open question.