Carbon-13 and Proton Chemically Induced Dynamic Nuclear Polarization from the Thermal Decomposition of Benzoyl Peroxide in Tetrachloroethylene[1]

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Abstract: Polarized ^{13}C and ^1H nmr spectra have been observed during the decomposition of benzoyl peroxide in tetrachloroethylene at 90–125°. Peaks have been identified by comparison with reaction products and signs of polarization (enhanced absorption or emission) shown to be consistent with generally accepted steps in the decomposition mechanism. Most polarizations observed apparently arise from initial sorting encounters between phenyl and benzoyloxy radicals within an initial solvent cage, the strongest being enhanced absorption at α and 1′ carbons of phenyl benzoate. Emission from C-1 of trichlorostyrene, the major product, is an interesting case of memory effect in which polarized phenyl adds to C_2Cl_4, followed by fast chlorine loss to yield the polarized product. The utility of ^{13}C nmr in identifying otherwise undetectable polarization is pointed out.

In spite of the current interest in chemically induced dynamic nuclear polarization (CIDNP), almost all the data available are from proton spectra.[2] In this work we wish to discuss the nature and utility of CIDNP techniques in naturally occurring ^{13}C spectra. Only two other enriched[3] and natural abundance[4] CIDNP studies in ^{13}C have been reported, and this work along with these previously published accounts stress the very significant importance of the ^{13}C magnetic isotope in providing otherwise unavailable information on the details of free-radical interactions in solution. Benzoyl peroxide in tetrachloroethylene has been selected for investigation as this is a system for which little information may be obtained using ^1H CIDNP results. Furthermore, details of the benzoyl peroxide chemistry are relatively well known[5] and proton CIDNP results from several other reactions of this peroxide[6] are available for comparison purposes.

Results

A. Polarized Spectrum of Reacting Mixture. The polarized spectrum from the thermal reaction of a 15% solution of benzoyl peroxide in tetrachloroethylene exhibits several intense enhanced absorption and emission bands detectable in single-scan ^{13}C measurements (obtained with proton decoupling at natural isotopic abundance). A number of lesser CIDNP peaks for which chemically induced enhancements are quite evident are also observed in time accumulated spectra (see Figure 1). The ^{13}C peaks given in Table I for the polarized spectra are assigned to products on the basis of ^{13}C spectra obtained on known compounds listed in Table II. These results on the enhanced absorptions in phenyl benzoate and biphenyl confirm the results of Lippmaa, *et al.*,[4] for benzoyl peroxide in cyclohexanone. New peaks resulting from reaction with tetrachloroethylene are encountered in the emission bands of α,β,β-trichlorostyrene and chlorobenzene. No attempt has been made to assign unequivocally the several weakly enhanced ^{13}C peaks in the aromatic region because of the large number of possible products (*cf.* Table II) which could contribute to the polarized spectra in this region. In addition, bands from the 10–15% unidentified products originating from the aromatic peroxide could also contribute in this region. The distinctive CO_2 emission is significantly weaker than that reported[4] in the cyclohexanone solvent system. The decrease in intensity is presumably due to de-

Table I. ^{13}C Observations during the Reaction of Benzoyl Peroxide in Tetrachloroethylene

Assignment	Chemical shift $\delta_{C_6H_6}$	Obsd rel intensities[a]	"Polarization"[b]
Phenyl benzoate, α	-35.42 ± 0.2	180	1700
1′	-23.4 ± 0.1	540	5200
Biphenyl, 1	-13.2	50	180
p-Biphenylcarboxylic acid, 1′	-11.9	−25	
Trichlorostyrene, 1	-7.9 ± 0.2	−410	−130
Chlorobenzene, 1	-6.7 ± 0.1	−82	−160
Aromatics	-2.5 ± 0.1	21	
	-1.55	31	
	-1.06	26	
	-0.83	67	
	-0.36 ± 0.1	48	
CO_2	3.17 ± 0.05	−35	
C_2Cl_4	7.67	100	1
$CHCl_2CCl_3$, 2	29.6 ± 0.4	17	170

[a] Average values normalized to a solvent intensity of 100. [b] Ratio of signal intensity to that calculated for the same amount of material assuming 85% conversion of peroxide to products during 15 accumulated scans with distribution as measured by gc for reactions at reflux, *e.g.*, phenyl benzoate 10^{-3} *M*. This is not the true enhancement factor which would also involve the relative rates of product formation and nuclear relaxation.[14]

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(1) Support of this work by grants from the National Science Foundation (GP 24300) and the National Institutes of Health (GM-08521) is gratefully acknowledged.

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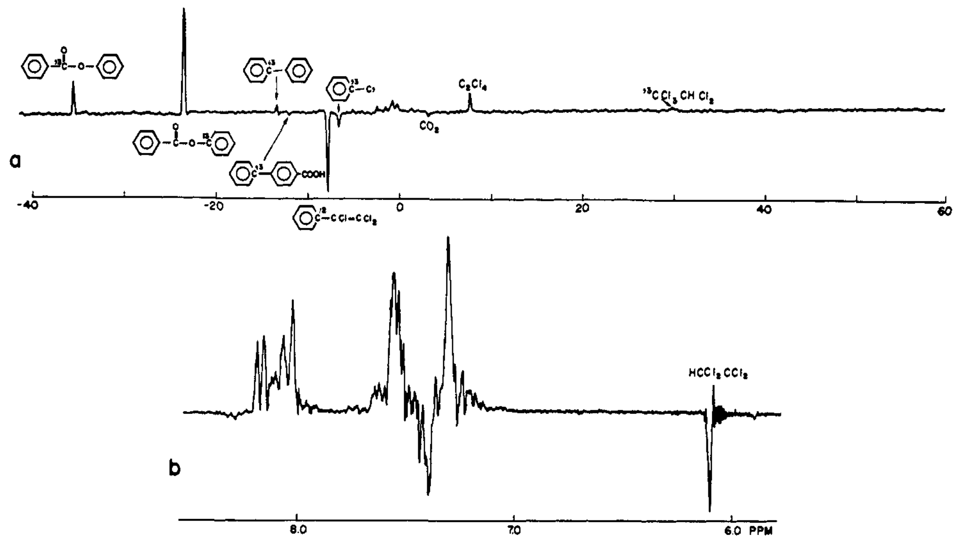

Figure 1. Emission and enhanced absorption peak assignments for the reaction of 15% benzoyl peroxide in tetrachloroethylene: (a) 25.2-MHz ^{13}C spectrum at 118°, 15 accumulated scans; (b) single-scan 60-MHz ^{1}H spectrum after 2 min at 120°.

Table II. Chemical-Shift Data for Reaction Products and Other Compounds Related to the Benzoyl Peroxide Decomposition in Tetrachloroethylene

Compd	Position	^{1}H δ_{TMS}[a]		^{13}C $\delta_{C_6H_6}$[b]
		Ambient	115°	
Benzoic acid	α	13.23 s	11.45 s	−44.06
	1			−2.01
	2	9.15 m	8.25 m	−1.52
	3	7.54 m	7.48 m	+0.12
	4			−4.96
Benzoyl peroxide[c]	α			−34.04
	1			−5.52
	2	7.45 m		−1.69
	3	7.38 m		−0.50
	4			+1.54
Biphenyl	1			−13.18
	2, 3	7.38 m	7.34 m	−0.43
	4			+1.09
p-Biphenylcarboxylic acid[d,e]	1			−1.9
	1′			−11.3
	4			−16.4
	4′			+0.1
Chlorobenzene	1			−6.42
	2	7.38 m	7.34 m	−0.44
	3			−1.30
	4			+2.00
Hexachloroethane				+22.77
Pentachloroethane	1	6.10 s	6.10 s	+48.23
	2			+28.33
Phenyl acetate	α			−39.97
	1			−22.99
	2			+6.47
	3			−0.98
	4			+2.74
	CH_3			+107.40
Phenyl benzoate	α			−35.61
	1,1′			−1.99, −23.12
	2,2′	8.33 m	8.31 m	−0.99, +6.46
	3,3′	7.45 m	7.41 m	−0.20, −1.97
	4,4′			−4.84, +2.85
Tetrachloroethylene				+7.67
α,β,β-Trichlorostyrene	α			−1.92
	β			+8.75
	1			−7.47
	2	7.50 m 8.33 m	7.50 m 8.25 m	−0.07
	3			−0.84
	4			−1.18

[a] Measured relative to $HCClCCl_2$ and converted to the TMS scale using δ 6.45 ppm for the olefinic proton. [b] Measured relative to C_2Cl_4 and converted to the benzene scale using δ 7.67 for the olefinic carbon. [c] ^{13}C spectrum run on saturated solution at 60°. [d] Run as 20% solution in DMF, relative to internal benzene. [e] Other peaks measured at −1.96, −0.73, +1.14, and +1.40, assignments in limbo. Further studies of chemical shifts in biphenyl compounds are under way. Our thanks to Dr. K. A. Christensen for ^{13}C measurements in this series.

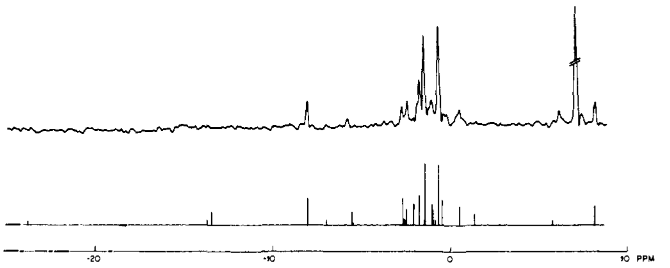

Figure 2. ^{13}C nmr spectrum from 244 scans after completion of thermal reaction (Figure 1a) and the calculated simulation from relative peak intensities of pure compounds and gc product distributions.

Table III. Product Distribution from the Thermal Decomposition of Benzoyl Peroxide in Tetrachloroethylene

Product	Reijnhart[a] 110° 2.5 *M*	CWS[b] 120° ~0.3 *M*[c]	This work 115° 0.7 *M*
	% yield		
C_6H_6			1.6
C_6H_5Cl	36	0	17.7
HC_2Cl_5			1.7
C_2Cl_6	0.64	11	14.6
$C_6H_5CCl{=}CCl_2$	19	28	52.3
$(C_6H_5)_2$			4.4
$C_6H_5CO_2C_6H_5$			3.6
$C_6H_5CO_2H$		19	14[d,e]
$C_6H_5C_6H_4CO_2H$			*f*

[a] Reference 9. [b] Reference 10. [c] Slow addition of 109 g of benzoyl peroxide in 500 cc of tetrachloroethylene to 100 cc of solvent maintained at 120° under an N_2 atmosphere. [d] Gc identification as methyl ester. [e] Yield calculated from neutralization equivalent assuming all acid product was benzoic acid. [f] Ortho and para isomers identified by ambient temperature phosphorescence spectrum of salt when irradiated at 290 nm; ref 11.

creased solubility of CO_2 in the tetrachloroethylene system. This assignment of the CO_2 peak depends upon the resonance position and is confirmed by off-resonance proton-decoupling techniques.[7,8]

B. Spectrum of Products. Spent samples show the normal ^{13}C peaks from products after completion of reaction predominantly centered in the aromatic absorption region as may be observed in Figure 2, and after the peaks which were enhanced in the polarized spectrum no longer dominate the spectral features. In the absence of CIDNP enhancements, accumulation of 200–600 scans is essential to the development of detailed spectra even though chemical equivalence and nuclear Overhauser enhancements of two–threefold[8] contribute to the intensities from most CH-decoupled aromatic carbon atoms. The relatively large concentration of resonance peaks for the spent sample in the narrow region of the spectrum from -2.5 to 0 ppm precludes specific peak assignments except perhaps for the major product trichlorostyrene. Many of the ^{13}C peaks detected are within experimental error of those measured for several of the pure compounds expected as reaction products and listed in Table II. Indeed, the large number of decoupled peaks even for a single compound, such as phenyl benzoate, required the assignments in the related but simpler phenyl acetate before the assignment of both phenyl rings could be completed. Overhauser enhancement data and off-resonance experiments were also utilized in making the assignments for compounds contained in Table II.

C. Gas Chromatographic Results. Gas chromatography (gc) confirmation of the characterized compounds in the spent sample and their relative quantities are given in Table III. Peak coincidence in the gc substantiated all of the volatile products previously reported for this system[9,10] plus those new substances found by ^{13}C CIDNP (*vide supra*). Yields of chlorobenzene roughly agree with earlier quantitative distributions, see Table III, for the intermediate benzoyl peroxide concentrations used. However, considerably larger quantities of trichlorostyrene and hexachloroethane are now detected. Weight factors were measured and applied to our gc analysis, and the low values in earlier efforts are probably due to mechanical separation problems. We also encountered these problems during distillation as a result of the crystalline solid, hexachloroethane, having a slightly higher vapor pressure than the more prevalent liquid, trichlorostyrene. The gc data, which refer to decompositions carried out at reflux, are quite applicable to actual product distributions encountered in the CIDNP experiments. The gc data provide a mass balance of volatiles of 80% based on peroxide phenyl groups and are in reasonable agreement with the titratable acid residue. The 65% chlorine balance obtained compares the chlorine lost by solvent in forming trichlorostyrene with that found in the chlorobenzene, pentachloroethane, and hexachloroethane. The acidic residues, although predominantly benzoic acid as seen from gc on the methyl ester, gave a room temperature phosphorescence spectrum for a dried basic solution on paper which had the excitation and emission characteristics of the two distinguishable anion components, *o*- and *p*-biphenylcarboxylate.[11]

D. Simulated ^{13}C Spectrum of Products. Simulation of the spent sample ^{13}C spectrum was based on the gc data (Table III), the chemical shift (Table II), and relative intensity results for known compounds. Intensities between compounds were weighted properly by using one of the spectral peaks which did not exhibit Overhauser enhancement to calibrate those peaks manifesting a nuclear Overhauser enhancement. The weighting factor used to combine these normalized spectral intensities was taken as the percentage of product in the spent sample determined by gc. Accumulation of these peaks for all identified compounds is also shown in Figure 2 and gives a good approximation of the observed spectral features. This agreement is quite reasonable considering the limitations imposed by an incomplete mass balance and the lack of identification for a number of minor gc peaks.

E. Proton CIDNP Data. The proton CIDNP results appearing in the aromatic region as shown in Figure 1b were only observed during the first few (<5) minutes of reaction and were not particularly informative because of the overlap in starting material and product

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spectra. However, the sharp singlet emission at δ 6.10 ppm characteristic of pentachloroethane is of long duration (>15 min). The unusual persistence of this emission suggested the measurement of the proton and attached ^{13}C relaxation times to account for the unique time features encountered in these results. The adiabatic rapid passage method[8,12] was used to obtain these T_1 values at the temperature of CIDNP reactions, and the results are given in Table IV along with values on chloroform for comparison purposes.

Table IV. Relaxation Times, T_1, for Pentachloroethane and Chloroform

Atom	Temp, °C	HC_2Cl_5 T_1, sec	$CHCl_3$ T_1, sec
^1H	37	56 ± 10	84[a]
	110	74 ± 7	
^{13}C	118	17 ± 3	24 ± 2[b]

[a] T. L. Pendred, A. M. Pritchard, and R. E. Richards, *J. Chem. Soc. A*, 1009 (1966). [b] At 38°; J. R. Lyerla, private communication.

Discussion

A. Reaction Mechanisms. A plausible mechanism of product formation for the thermal benzoyl peroxide reaction in tetrachloroethylene is outlined in eq 1–14. These reactions, which offer multiple pathways to the observed products, however, will exhibit different CIDNP results depending upon the reaction route taken. Although the quantitative determination of the magnitude of each reaction rate cannot adequately be determined from accumulated or individual instantaneous intensities of enhanced peaks as both physical and chemical processes affect the enhancement factors,[13,14] the principle results found in this study may be rationalized solely in terms of the predominant reaction pathways expected for this system. Thus, there is no need to invoke any of the less favorable reaction steps to account for any major CIDNP peak. Therefore, as a working hypothesis, the major polarized signals are attributed to nuclear spin sorting in the high flux intermediates associated with the principle reaction steps.

Radical Initiation

$$(C_6H_5CO_2)_2 \longrightarrow \overset{\text{caged}}{\overline{2C_6H_5CO_2\cdot}} \longrightarrow \overset{\text{free}}{2C_6H_5CO_2\cdot} \tag{1}$$

Radical Conversion

$$C_6H_5CO_2\cdot \longrightarrow C_6H_5\cdot + CO_2 \tag{2}$$

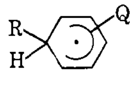
$$C_6H_5\cdot + CCl_2{=}CCl_2 \longrightarrow C_6H_5CCl_2CCl_2\cdot \tag{3}$$

$$C_6H_5CCl_2CCl_2\cdot + CCl_2{=}CCl_2 \longrightarrow C_6H_5CCl{=}CCl_2 + CCl_3CCl_2\cdot \tag{4}$$

$$CCl_3CCl_2\cdot + RH \longrightarrow CCl_3CCl_2H + R\cdot \tag{5}$$

$$C_6H_5\cdot + RH \longrightarrow C_6H_6 + R\cdot \tag{6}$$

$$R\cdot + C_6H_5Q \longrightarrow \tag{7}$$



Termination

$$C_6H_5CO_2\cdot + \cdot C_6H_5 \longrightarrow C_6H_5CO_2C_6H_5 \tag{8}$$

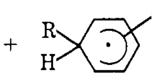
$$2C_6H_5\cdot \longrightarrow (C_6H_5)_2 \tag{9}$$

$$C_6H_5CCl_2CCl_2\cdot + \cdot C_6H_5 \longrightarrow C_6H_5CCl{=}CCl_2 + ClC_6H_5 \tag{10}$$

$$C_6H_5CCl_2CCl_2\cdot + CCl_3CCl_2\cdot \longrightarrow C_6H_5CCl{=}CCl_2 + C_2Cl_6 \tag{11}$$

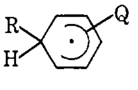
$$CCl_3CCl_2\cdot + C_6H_5\cdot \longrightarrow CCl_2{=}CCl_2 + C_6H_5Cl \tag{12}$$

$$CCl_3CCl_2\cdot +$$



$$\longrightarrow CCl_3CCl_2H + RC_6H_4Q \tag{13}$$

$$C_6H_5\cdot +$$



$$\longrightarrow C_6H_6 + RC_6H_4Q \tag{14}$$

Equations 1, 2, 6–9, and 14 in the reaction mechanism are solvent independent and derive from other studies[5,6] on benzoyl peroxide in general and those with CIDNP effects[3,4] in particular. Initiation *via* peroxy bond cleavage in eq 1 provides benzoyloxy radicals which undergo subsequent CO_2 loss to form phenyl radicals in eq 2. Termination by coupling of the two radicals from eq 1 and 2 or conversion to acid accounts for benzoyloxy components in products. Phenyl radical is more reactive and addition to solvent (eq 3) is the essential step in chlorine-containing product formation, although some dimerization (eq 9), hydrogen abstraction (eq 6), and addition to form cyclohexadienyl species (eq 14) occur.

Solvent-derived radicals participate in radical transfer (eq 4 and 5) and disproportionation (eq 10–13) reactions providing routes to trichlorostyrene, penta- and hexachloroethane, and chlorobenzene.

B. Mechanism Discrimination with CKO Theory. The work of Closs,[15] Kaptein, and Oosterhoff[16] (CKO) on chemical and physical effects on polarization in proton systems may be used to rationalize the ^{13}C results as both proton and carbon-13 are spin $^1/_2$ nuclei. Since heteronuclear decoupling was used in our ^{13}C experiments, only the net polarization effects are observable.[17] Hence, Kaptein's[18] simple equation given in eq 15 may be used for determining the sign in net polarization, Γ_{ne}. The Γ term in eq 15 is used to compare the sign of the polarized peaks based on the above mechanism and the observed results in Figure 1 and Table I.

$$\Gamma_{ne} = \mu\epsilon\Delta g a \tag{15}$$

Net polarization in CKO theory occurs only when a dissimilar pair of radicals interacts and, through partial reaction, undergoes preferential sorting leaving a predominance of singlet or triplet electronic configurations. The sense of the resulting nuclear polarization in the products then depends on the product of signs from the four terms given in eq 15. These terms and their qualitative chemical origin may be summarized as follows.

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(16) R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

(17) A balance of CIDNP absorption and emission in a multiplet collapses on decoupling to eliminate all resonance lines as has been confirmed in other experiments by one of us (A. R. L).

(18) R. Kaptein, *Chem. Commun.*, 732 (1971).

Table V. Comparison of Nuclear Polarizations Predicted by Various Reaction Routes and Observed in Spectra[a]

		Sorting		Product forming		Δg	a[b]	Polarization	
Product	Position	Eq	Sign	Eq	Sign	sign	sign	Calcd	Obsd
$C_6H_5CO_2C_6H_5$	α-C	8	−	8	+	+	−	A	A
	C-1	8	−	8	+	+	(−)	A	(A)
	C-1′	8	−	8	+	−	+	A	A
	C-2′	8	−	8	+	−	(+)	A	(A)
$(C_6H_5)_2$	C-1	8	−	9	+	−	+	A	A
	C-1	8	−	9	−	−	+	E	
C_6H_6	C-1	8	−	6	−	−	+	E	
	C-1	14	+	14	+	~0	+	n	n
C_6H_5Cl	C-1	8	−	12 (10)	−	−	+	E	E
	C-1	12 (10)	+	12 (10)	+	−	+	E	
$C_6H_5CCl{=}CCl_2$	C-1	8	−	3, 4 (10, 11)	−	−	+	E	E
	α-C	10	+	10	+	+	−	E	
	α-C	11	+	11	+	~0	−	n	n
	β-C	10	+	10	+	+	+	A	
	β-C	11	+	11	+	~0	+	n	n
$CCl_2{=}CCl_2$	C-1	12	+	12	+	+	+	A	(n)
	C-2	12	+	12	+	+	−	E	
$CHCl_2CCl_3$	C-1	13	+	13	+	−	+	E	
	C-2	13	+	13	+	−	−	A	(A)
	H-1	13	+	13	+	−	+	E	E
p-$C_6H_5C_6H_4COOH$	C-1′	8	−	15	−	−	+	E	E

[a] Parentheses indicate uncertainty; A, enhanced absorption; E, emission; n, negligible. [b] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(1) **Radical Pair Formation** (μ). In bond scission, thermal dissociation gives a singlet pair with a minus sign, while phototriplet production yields a triplet pair with a positive sign for the μ term. In free-radical encounters triplet spin pairs also predominate in the sorting process because of their longer lives.

(2) **The Product-Forming Step** (ϵ). A positive sign is obtained for ϵ if the product is formed in a spin sorting step (*e.g.*, a radical pair combination or disproportionation); otherwise, a negative ϵ obtains if the radical escapes without reaction from the radical pair cage where the sorting collision takes place and then participates in any reaction which is not a sorted reaction (*e.g.*, addition, radical transfer, coupling, etc.).

(3) **Inequality of Electronic g Factors** (Δg). The sign of the net polarization is affected by the sign of $\Delta g = g_1 - g_2$ as shown in eq 15. Here g_1 designates the radical bearing the atom showing net polarization. Thus, if $g_1 = g_2$ (either fortuitously or because of symmetry), $\Delta g = 0$ and no net polarization can occur during the reaction. If $g_1 > g_2$ the sign is positive; for $g_2 > g_1$ a negative sign is realized.

(4) **The Sign of the Hyperfine Coupling Constant** (a). The sign of the electron-nucleus interaction as determined by the sign of the hyperfine coupling constant, a, in eq 15 affects the sign of the net polarization directly.

The application of these qualitative rules for predicting the expected polarization (enhanced absorption is positive; emission is negative) of the products from the thermal benzoyl peroxide decomposition in tetrachloroethylene is summarized in Table V for the various proposed reaction mechanisms. In several cases the alternatives generated by more than one route may be compared, and the dominant polarization pathway determined from the sign of the enhanced peak.

C. **Anticipated Mechanism Results.** The polarized peaks for α-C and C-1′ of phenyl benzoate are the most intense enhanced absorptions observed in the CIDNP ^{13}C spectrum. This result is consistent with a mechanism in which singlet radical pairs are predominant in the sorting step, which would be eq 8 in this instance. The singlet pair obtains when eq 2 occurs prior to separation of the caged benzoyloxy pair. Sequential extrusion of a second CO_2 and collapse within the cage are also necessary to account for enhanced absorption in biphenyl since emission is predicted for coupling of presorted phenyl pairs in random collisions. The low intensity is explained on the basis of the depleted concentration due to competition of diffusion and other reactions with the multistage process, eq 1, 2, 2, 9, required for biphenyl production.

Any retained phenyl radical polarization after escaping the initial caged sorting step would also appear in any benzene produced, as was found in the strong emissions for benzene reported at both C-1[4] and H-1[6a] when phenyl radical reacts with cyclohexanone, an excellent hydrogen source for reaction 6. In this study the low probability of reactive hydrogen source encounter in eq 6 ensures relaxation before or during abstraction, and thus the absence of such a benzene peak. The radical–radical process in eq 14 would not be expected to give polarized benzene for the same reason and, furthermore, the small Δg would discriminate against net polarization. Thus, the minor amount of benzene produced is not polarized.

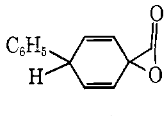
Production of chlorobenzene C-1 polarization in eq 10 or 12 as well as from the initial sorting encounter, eq 8, presents a case where unequivocal assignment of the principle polarizing step is not possible as each radical pair interaction would give the same net polarization. In this case any one of the reactions (8, 10, or 12) could account solely for the result obtained. Conversely, this may be an example where the polarization could come from more than one reaction and reenforcement from successive steps may be important in the polarized chlorobenzene. Nevertheless, the long-lived pentachloroethyl radical process 12 is favored over that of eq 10 due to the greater radical concentrations. The lower probability of biradical processes encourages nuclear spin relaxation from previous sorting steps. Thus, polarization *via* sorting in eq 12 probably offers a better opportunity for polarization. Solvent polarization in eq 12 is self-cancelling since the hyperfine coupling constants at C-1 and -2 of the pentachloroethyl radical are of opposite sign but similar magnitude.[19] However, detailed kinetics[14] would be essential to distinguish relative polarization contributions by the several routes.

D. New Features in the Mechanism. The most significant new effect noted in this study is a manifestation of a "memory effect," occurring in addition reactions. We report here for the first time CIDNP arising from products in which polarization of the initial radical is followed by a chain of addition and elimination steps in which memory of the original polarization is maintained in the product. The only CIDNP previously noted in addition reactions (in the thermolysis of AIBN with nitrosobenzene,[20] nitrones,[21] and 9-bromoanthracene,[22] and the reversible addition of pentafluorobenzoyloxy to benzene[23]) was the result of sorting steps following addition. The C-1 of trichlorostyrene must have been polarized during the initial cage sorting process, eq 8. This fact has profound implications on the rate processes involved. First, the rates of addition of phenyl to solvent, eq 3, and subsequent loss of chlorine (*via* eq 4, 10, and 11) must be much faster than the relaxation rates for both the phenyl and the phenyltetrachloroethyl radicals. The lack of polarization in the α and β positions of trichlorostyrene is indicative of the fact that no polarization occurs during addition, eq 3, or subsequent radical encounter leading to disproportionation, eq 10 and 11. None would be expected in eq 3 or 4, since only one radical is involved. Although two radicals do interact in eq 11, the difference in g values between the two polychlorinated radicals would be negligible and lead to no net polarization. Since the α-C is not polarized, one may assume that reaction 10 is not in fact acting as a sorting step. This enables us to clear up part of the uncertainty as to the origin of chlorobenzene polarization (*vide supra*) since removal of eq 10 as a sorting step implies polarization in chlorobenzene also arises in eq 8 and is yet another memory effect, although eq 12 is still a possible sorting step.

The main mechanistic route to trichlorostyrene would have to be addition, eq 3, followed by loss of chlorine to solvent, eq 4, rather than by disproportionation, eq 10 and 11. The relative importance of the dechlorination routes can be found by comparing the concentrations of the acceptors and the rates of transfer reactions. The solvent is at least 10^7 times more concentrated than pentachloroethyl radical (maximum radical concentrations possible are limited by the fact that no paramagnetic broadening is found in the nmr). The rate of disproportionation of the two radicals involved in eq 11 would be near diffusion control, *i.e.*, about 10^9 mol^{-1} sec^{-1}, while the rate of loss to solvent, eq 4, would be much greater than 10^3 mol^{-1} sec^{-1}, and might be up near diffusion control also. Thus, the relative contributions of eq 4/eq 11 $\geq 10^7 \times 10^3/1 \times 10^9 \geq 10$. Thus, once again, the polarization route to the product—trichlorostyrene—is coincident with the predominant production route and no minor reactions must be invoked to explain CIDNP.

The emission detected at -11.9 ppm can be assigned to the C-1′ of *p*-biphenylcarboxylic acid (which was detected in very low yield by room temperature phosphorescence[11]). The most likely route to this CIDNP would also involve presorting in eq 8 and be yet another manifestation of the memory effect. The production of polarized biphenylcarboxylic acid is most interesting in that it involves the phenyl radical induced decomposition of benzoyl peroxide for which the following sequence has been proposed (eq 16).[24] It is quite apparent here that the combined rates of addition and subsequent rearrangement of the intermediate α-lactone must be much greater than the relaxation rates in both the phenyl radical and α-lactone. This is an analogous rate requirement to the trichlorostyrene case discussed above. Rate requirements for observation of polarization have been quantitatively studied by Walling and Lepley[14] who calculate a T_1 for benzyl radical of 10^{-4} sec. The fact that we see such a respectable intensity (Table I) for the C-1′ of *p*-biphenylcarboxylic acid despite its extremely low yield indicates that the steps in eq 16 are exceedingly fast and that the pertinent T_1 values are relatively long.

$C_6H_5\cdot + (C_6H_5CO_2)_2 \longrightarrow$



$+ C_6H_5CO_2\cdot \longrightarrow C_6H_5C_6H_5COOH$ (16)

One apparent anomaly in the CIDNP phenomena associated with the thermolysis of benzoyl peroxide in tetrachloroethylene is that the most prominent ^{1}H emitter, pentachloroethane, is practically inactive in the ^{13}C spectrum. No signal at all was detected for the proton-bearing carbon either with or without noise decoupling; that is to say, we observed neither net nor multiplet effect polarization during the reaction. A very weak signal was obtained from the C-2 during reaction which would indicate at least some enhanced absorption. Hydrogen abstraction by pentachloroethyl from an aromatic substrate as indicated in eq 5 could not lead to ^{1}H polarization as it involves only a single radical. The source of the polarization in pentachloroethane is best explained by invoking a sequence related to, but not directly involving, the induced decomposition path, eq 16, discussed above. We assume that a radical, undefined, adds to an aromatic substrate, again undefined, to produce a cyclohexadienyl radical intermediate, eq 7. The driving force of rearomatization makes this intermediate an extremely good hydrogen atom source. However, the collision of pentachloroethyl with the intermediate, eq 13, involving encounter of two radicals, is a potential sorting step.[25] This interaction does in fact account for the observed

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[19] A more important feature influencing solvent intensity (and the related apparent enhancements) is the long ^{13}C relaxation time which may cause partial saturation during accumulated CIDNP scans.

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polarization (*cf.* Table V). Parallel production of polarized benzene, as might be expected from reactions 7 and 14, is obviated by the nearly identical g values expected for phenyl and cyclohexadienyl radicals. The lack of CIDNP at the C-1 of pentachloroethane is best explained by comparison of relaxation times (Table IV). The T_1 for the C-2 would be about the same as that for the proton, and thus about a factor of 4 greater than that for the C-1. Thus, the relative intensity of the C-1 to the C-2 would be 0.25 (assuming approximately equal polarization) and would be hopelessly lost in the noise as can be seen in Figure 1a. In this case, the longer relaxation time of the proton compared with the C-1 combined with the ~400-fold greater sensitivity of the A-60 for ^{1}H detection compared with the XL-100-15 for ^{13}C detection (combination of natural abundance, machine signal-to-noise specifications, and gyromagnetic ratios) makes the detection of ^{1}H CIDNP in this product 10^3 times as facile as ^{13}C CIDNP. Thus, as is discussed below, ^{13}C CIDNP has its greatest advantage in sensitivity when it is most valuable (*i.e.*, carbons with no protons attached).

The value of the ^{13}C technique combined with CIDNP is strikingly exemplified in our study. The definitive assignments for the large number of aromatic products were made possible only through ^{13}C spectroscopy. Conversely, the proton emission is much simpler in character and therefore does not contain comparable information. For example, the mechanistic scheme leading to pentachloroethane would be but poorly implied from ^{1}H CIDNP even when supported by gc data since the sequence of reaction steps, eq 2–4 and 7, is essential in addition to initiation, eq 1, and termination, eq 13. The proton polarization data for pentachloroethane are interpretable only upon a correct understanding of the relationship between the ^{1}H and ^{13}C results. This required relaxation data and an estimate of relative instrument sensitivities. Very large relative enhancement factors for carbon offer one of the primary potentials of carbon CIDNP as signals on very dilute species can be detected after only a single scan at natural abundance. It has also been shown that qualitative features of the kinetics are discernible from relative enhancements when radicals sorted in one step participate in a sequence of subsequent steps without additional sorting.

The extremely large "polarizations" estimated for phenyl benzoate (Table I) probably result because the unpaired electron in the radical precursor resides directly on the ^{13}C atom detected. The $1/r^3$ field dependence of an electron dipole upon the carbon nucleus is thus maximized when the unpaired electron resides in the atom containing the magnetic nucleus. Furthermore, in the absence of directly attached protons, the resulting ^{13}C CIDNP signals offer the only probe for biradical reactions. Thus, in addition to primary aliphatic ^{13}C CIDNP which has been reported in enriched compounds,[3,4] quaternary aliphatic and tertiary aromatic natural abundance carbon atoms at reactive radical sites may be studied conveniently with these techniques. With the advent of Fourier transform carbon-13 spectroscopy, there is little doubt that routine ^{13}C CIDNP spectra can easily be obtained with all the benefits that carbon-13 spectroscopy enjoys over proton techniques.

Experimental Section

Chemicals. Benzoyl peroxide from the Lucidol Division of Wallace and Tiernan, Inc., was titrated iodimetrically and found to be >98% pure. Tetrachloroethylene from Matheson Coleman and Bell (MCB) was found to be >99% pure by gc (see conditions below) with the principal impurity being trichloroethylene. Trichlorostyrene was separated from the reaction mixture by reduced pressure distillation. *p*-Biphenylcarboxylic acid (Aldrich) was sublimed under reduced pressure. Trichloroethylene (MCB), biphenyl (Eastman), benzoic acid (Baker Analyzed), hexachloroethane (MCB), chlorobenzene (MCB), and phenyl benzoate (Eastman) were all used as received.

Gas Chromatography. A Hewlett-Packard Model 700-12 chromatograph equipped with a Model 5771A electrometer and 7127A recorder with disc integrator was used for analysis of reaction product mixtures. Separation was on a 6 ft × $^1/_8$ in. column of 10% UCW 98 (methyl vinyl silicone) on silanized 80–100 mesh Chromosorb W with 40 ml/min of He or N_2 flow and a temperature program of 5 min at 88° followed by an increase at 10°/min to a maintained maximum of 250°. Qualitative product identifications are based on superposition of gc peak on adding knowns to reaction mixtures and are supported by nmr analysis. Quantitative analysis was made by adding a weighed amount of *o*-dichlorobenzene to the reaction mixture and determining relative integral areas. Weight factors with respect to this standard were determined by analyzing known mixtures and were used in calculation of the mole per cent yields in Table III.

Nuclear Magnetic Resonance Measurements. ^{1}H spectra were obtained using a Varian A60 spectrometer with Model V-6040 temperature controller and Model V6058A decoupler. Ambient (37°) and elevated (90–125°) temperatures were carefully determined by using a 4-mm thermometer in place of sample tube at fixed controller settings. Equilibration of the thermometer (and presumably nmr samples) was within 0.5° of the final temperature within 2 min. Spectra of all identified materials were run as 5–20% solutions in tetrachloroethylene at ambient temperature and 115° (see Table II) to confirm gc assignments. The T_1 for pentachloroethane was measured *via* adiabatic rapid passage procedures at a high-field H_1 of 2.5 mG using a 20 Hz/sec sweep rate and 7-min delay for relaxation.

^{13}C spectra were measured at 25.2 MHz with a Varian XL-100-15 spectrometer equipped with a Gyrocode decoupler, variable temperature controller, and C-1024 time averaging computer. Samples were contained in open 10 mm o.d. thin-walled tubes which were placed inside 12 mm o.d., 11 mm i.d. tubes containing 0.5 ml of DMSO-d_6 which served to activate the ^{2}H internal field frequency locking circuits. Temperatures were measured by placing the thermometer in a spent reaction sample. Temperature equilibration at a fixed controller setting in the 90–125° range required at least 5 min for samples which were at 55–60° before insertion in the preheated probe. Spectra of all identified materials were run as 25% solutions in tetrachloroethylene at ambient temperature with a D_2O lock and these spectra were used in simulating those of reaction mixtures (see below). Heteronuclear proton decoupling was used except when assigning structure by employing off-resonance proton decoupling. The relaxation time, T_1, of the α carbon in neat, outgassed pentachloroethane was determined at 118° using the adiabatic rapid passage method. Single scan spectra at 20 Hz/sec with the concentric DMSO-d_6 lock gave adiabatic condition at 110 db. Calculations were based on 14 measurements taken over the first 2 half-lives.

Benzoyl Peroxide Reactions in Tetrachloroethylene. Benzoyl peroxide, 1.25 g (5.16 mmol), was added with stirring to 7 ml of tetrachloroethylene at 60°. Solutions (0.7 *M*) were held at 50–60° to prevent crystallization of peroxide and aliquots were removed for CIDNP experiments or determination of safety factors in such experiments by carrying out peroxide decompositions in an oil bath at 10–20° higher than maximum temperatures used for CIDNP. Spinning sample tubes comparable to those employed in the actual nmr experiments were used in the safety tests. Reactions were allowed to proceed for 45 min at 135° (115° reflux) and then cooled prior to gc analysis for product identification and yield determinations (see above). Distillation of accumulated reaction mixtures provided pure α,β,β-trichlorostyrene, while basic extraction of the residue gave organic acids (comparable to benzoic acid by ir on acidification). These were separated into two components by the use of *i*-PrOH–NH_3 (aqueous) on silica gel. Treatment of the mixed acids with diazomethane in ether and gc analysis indicated one component was benzoic acid by the presence of methyl benzoate.

Total acids were determined by adding an aliquot to sodium hydroxide and back-titrating with hydrochloric acid to a phenolphthalein end point.

CIDNP Reactions. Spectrometers were tuned on previously reacted samples (after equilibrating for 20–30 min at elevated temperatures from 90 to 120° to determine qualitative effects of peroxide decomposition rate on spectroscopic abnormalities). ^1H external lock spectra were run on 0.5-ml aliquots of the above peroxide solution in 5-mm thin-walled nmr tubes. Sample tubes were inserted in the preheated probe and repeatedly scanned over selected ranges (generally 350–600 or 200–700 Hz) at 2.5–5 Hz/sec. Initial scans were in progress within 15 sec after inserting the sample in the probe and repeated scans were continued until emission ceased (2 hr at 90°). ^{13}C spectra using a DMSO-d_6 ^2H concentric tube internal lock (see above) were run on 2.5-ml aliquots of the peroxide solution. Normally 15–30 sec was required to establish lock and fine tune so that at best one scan was initiated in the first minute. Strong emission or enhanced absorption peaks were easily detected in single scans at 25 Hz/sec, but other reported signals were observed using the CAT with 25–35 scans at 40 Hz/sec. The distribution of peaks in a spent sample was determined by time averaging (244 scans at 10 Hz/sec) and gave a good correlation with a simulated spectrum based on spectra of the gc identified components and their relative concentrations.

An INDO Theoretical Study of the Geometry of Fluorinated Methyl and Allylic Cations and Radicals[1]

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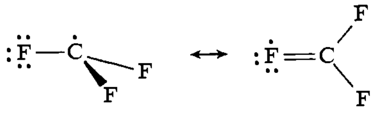
Abstract: LCAMO-SCF calculations in the INDO approximation have been performed on CH_3^+ (**2**), CH_2F^+ (**3**), CHF_2^+ (**4**), and CF_3^+ (**5**), a series of four fluorinated allylic radicals including $CH_2{=}CH{-}CF_2\cdot$ (**6**), $CH_2{=}CF{-}CF_2\cdot$ (**7**), *trans*-$CFH{=}CF{-}CF_2\cdot$ (**8**), and *cis*- $CFH{=}CF{-}CF_2\cdot$ (**9**), and a series of five fluorinated allylic cations including $CH_2{=}CH{-}CF_2^+$ (**10**), $CH_2{=}CF{-}CF_2^+$ (**11**), *trans*-$CHF{=}CF{-}CF_2^+$ (**12**), *cis*-$CHF{=}CF{-}CF_2^+$ (**13**), and $CF_2{=}CF{-}CF_2^+$ (**14**). Fluorinated methyl cations (**3**–**5**), unlike their radical analogs, were planar as was CH_3^+. The barrier to out-of-plane deformation is shallow at small angles but increases rapidly at large angles. The preference for the planar geometry is due in part to substantial F → C back π donation which increases per F–C bond in the series **5** < **4** < **3**. Accompanying F → C π donation is a strong C → F σ polarization. The two nearly balance so that the net charge density on fluorine does not change appreciably. By attaching a strongly conjugating vinyl group to the $-CF_2\cdot$ function in place of H or F, the preferred geometry at that carbon becomes planar (sp^2) in **6**–**9**. In addition, the $CF_2\cdot$ plane is also that of the vinyl group. This all planar geometry is rather strongly favored as a result of substantial C–C π-bond character as well as a moderate π contribution in the $\cdot$C–F bonds where F → C back π bonding occurs. The unpaired spin density is found mostly on C_1 (and C_3) with a significant portion at C_2 but very little on the terminal fluorines. The magnitude of F → C π donation increases markedly going from fluoroallylic radicals **6**–**9** to fluoroallylic cations **10**–**14**. In addition, rather large (0.35–0.28) C_1–C_3 π-bond orders were found in the cations. As the number of terminal fluorines was increased, the 1–3 π-bond order decreased. The C_1–C_2 rotation barriers in radicals **6**–**9** and cations **10**–**14** were obtained and compared. Although complete structure optimization (and symmetrization) was not carried out, moderate changes in the bond lengths and angles do not markedly change the magnitude of the calculated quantities and do not affect the conclusions.

Experimental studies (*i.e.*, infrared, electronic, and esr spectroscopy) have demonstrated that the methyl radical is planar, or almost planar, and that $CF_3\cdot$, $CF_2H\cdot$, and $CFH_2\cdot$ are pyramidal.[2–6] Theoretical studies by Morokuma, Pedersen, and Karplus,[7] using the LCAO–MO–SCF method with Gaussian AO-basis sets, and by Beveridge, Dobosh, and Pople,[8] using the LCAO–SCF method in the INDO approximation, were in agreement with experiment for these radicals. Pauling[9] argued that the electronegativity difference between carbon and fluorine atoms is the major factor which determines the nonplanar configuration of these radicals. Furthermore, Pauling stated that the structure of $CF_3\cdot$ would have FCF angles significantly smaller than the observed value of 112° if there was no double bond contribution to the normal state of the radical (see below) and if nonbonded fluorine repulsions were not operating. Thus, the observed value of 112° for FCF angles is expected. Detailed theoretical calculations comparing the analogous cation series CH_3^+, CFH_2^+, CF_2H^+, and CF_3^+ have not appeared although



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