Chemically Induced Dynamic Nuclear Polarization in the Products of Reaction of Phenylacetyl Peroxide with Bromotrichloromethane and Trichloromethanesulfonyl Chloride[1]

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Abstract: Decomposition of phenylacetyl peroxide at 40° in the presence of CCl_3Br and CCl_3SO_2Cl yields, respectively, nmr spectra showing strong polarization of benzylic protons of benzyl bromide and chloride (emission) and also in both cases of $C_6H_5CH_2CCl_3$ (enhanced absorption). No polarization of other products is detected. Benzyl halide polarization varies in intensity with substrate concentration with a maximum at 0.4 *M* CCl_3Br. It is proposed that benzyl radical polarization occurs *via* sorting accompanying diffusive encounters of benzyl and CCl_3 radicals. This model accounts for the maximum observed and yields values for the rate constants for benzyl radical substrate reactions, the relaxation of polarized benzyl radicals, and the polarization produced per encounter. The model predicts the proper sign and the observed greater magnitude for the polarization of the coupling product $C_6H_5CH_2CCl_3$, but not its variation with substrate concentration which indicates an intensity proportional to the average number of sorting encounters of benzyl radicals.

Although it is generally accepted that chemically induced dynamic nuclear polarization (CIDNP) is only observed in the nmr spectra of molecules recently formed from free-radical precursors, the details of the polarization process are still being elaborated. The most convincing treatments have been those of Kaptein and Oosterhoff[2] and Closs,[3] who assume that nuclear polarization is a consequence of singlet–triplet crossovers in radical pairs held near each other in a solvent cage. Although total spin distributions are unchanged, different polarizations and different reaction probabilities are associated with singlet and triplet states of the radical pairs so that a sorting process occurs, and those which couple (or disproportionate) and those which separate have polarization of opposite sign.

Although this model has been very successful in predicting signs of polarization of radical products produced in various ways, it was applied originally only to coupling or disproportionation products. A number of cases of polarized spectra for radical displacement products have also been reported.[4] Although at the time we began our investigation no real interpretation of the polarization mechanism in displacement products existed, some have subsequently appeared.[5] As we shall see, the point at which polarization occurs can be quite different in different systems. Our approach has been to choose a reaction for which the chemistry is relatively well understood, to examine the effect of reaction conditions on the polarizations observed, and then to construct a model consistent with the results.

The Decomposition of Phenylacetyl Peroxide. Phenylacetyl peroxide decomposes rapidly by concerted multibond scission[6] to yield a mixture of "polar" and "radical" cage products, plus reaction products of free benzyl radicals. The decomposition rate increases with solvent polarity[6,7] and it has been proposed[7] that the decomposition occurs *via* a single rate-determining transition state to yield a very short-lived radical pair–ion pair intermediate which partitions to the products observed. At 40° in CCl_4 containing varying amounts of CCl_3Br the half-life for decomposition is 3–4 min, and product distribution is readily determined by nmr analysis utilizing signals from the various benzylic protons present.

The effect of CCl_3Br addition on product distribution is shown in Figure 1. Major products yield a material balance of 93–94%. In addition to those products shown, decomposition in CCl_4 alone yielded a trace (<1%) of benzyl chloride, and C_2Cl_6 was detected by gc in the presence of CCl_3Br. From Figure 1 we see that phenylacetyl benzyl carbonate and benzyl phenylacetate yields are independent of CCl_3Br as would be expected for cage products. On the other hand, bibenzyl is evidently both a cage and noncage product in CCl_4, but in the presence of CCl_3Br its yield drops and levels out, while benzyl bromide and phenyltrichloroethane appear *via* the efficient scavenging of

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[1] Support of this work by grants from the Petroleum Research Fund of the American Chemical Society and the National Science Foundation is gratefully acknowledged. For preliminary reports, *cf.* A. R. Lepley and C. Walling, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, No. PHYS 7; C. Walling and A. R. Lepley, *J. Amer. Chem. Soc.*, **93**, 546 (1971).

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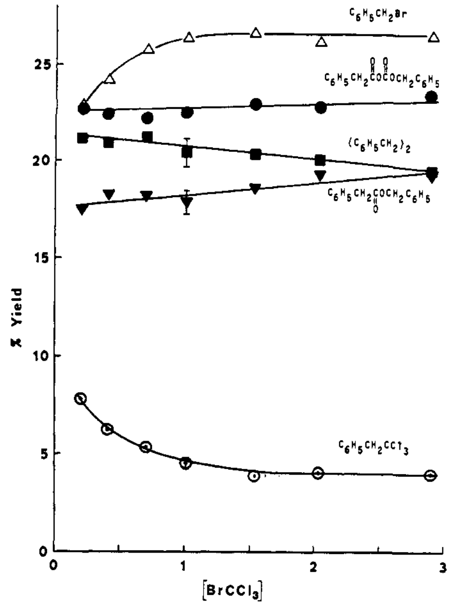

Figure 1. Yield variation for major products with initial concentration of $BrCCl_3$ after 40° decomposition of 0.18 *M* phenylacetyl peroxide in CCl_4.

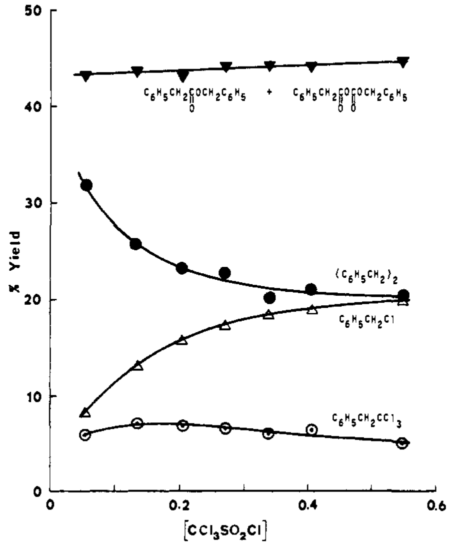

Figure 2. Trapped and cage product yield dependence on initial concentration of CCl_3SO_2Cl after decompositions of 0.16 *M* phenylacetyl peroxide in CCl_4 at 40°.

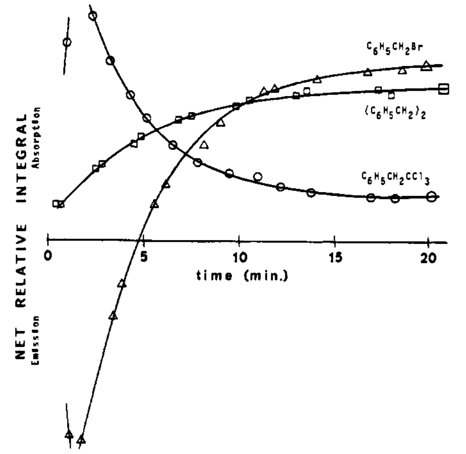

Figure 3. Integral sign and magnitude dependence on time for three products during the reaction of 0.18 *M* phenylacetyl peroxide and 0.41 *M* $BrCCl_3$ in CCl_4 at 40°.

benzyl radicals (eq 1 and 2). Reactions 1 and 2 thus

$$PhCH_2\cdot + CCl_3Br \longrightarrow PhCH_2Br + \cdot CCl_3 \qquad (1)$$

$$\cdot CCl_3 + PhCH_2\cdot \longrightarrow PhCH_2CCl_3 \qquad (2)$$

yield the only significant noncage products containing benzylic protons, and approximately 35% of peroxide fragments escape the initial solvent cage.

If trichloromethanesulfonyl chloride is substituted for CCl_3Br, eq 1 is replaced by eq 3. Product distribu-

$$PhCH_2\cdot + ClSO_2CCl_3 \longrightarrow PhCH_2Cl + SO_2 + CCl_3 \qquad (3)$$

tions for this system appear in Figure 2. Benzyl bromide is replaced by benzyl chloride, and, since the reactivity of the sulfonyl chloride is lower than CCl_3Br (direct competitive measurements indicate relative reactivities of $CCl_3Br/CCl_3SO_2Cl = 3.6$), the bibenzyl yield declines more slowly with increasing substrate concentration. Further, since the conversion of carbonate ester to ester is catalyzed by SO_2, relative yields of these two cage products are time dependent, although their sum is essentially constant.

Nmr Spectra during Reaction. When decomposition of phenylacetyl peroxide is carried out in CCl_4 in the probe of a 60-MHz nmr spectrometer at 40° no polarized spectra are observed for any major products. However, in the presence of CCl_3Br (or CCl_3SO_2Cl) we find strong emission and enhanced absorption, respectively, from the benzylic protons of benzyl bromide (or chloride) and phenyltrichloroethane. Signals from benzyl protons of other species grow normally with no indication of polarization, and that from bibenzyl, in particular, provides a convenient monitor of reaction rate. Typical results appear in Figure 3. For quantitative discussion, however, we must distinguish between the polarization of molecules at the moment of formation and the observed polarization which is the sum of contributions from new polarized molecules and older ones which have undergone relaxation. In general we are dealing with a process

$$A \longrightarrow B^* \xrightarrow{k_r} B \qquad (4)$$

where B* are the polarized molecules (produced from starting material A) and k_r is their rate constant for relaxation. The observed signal intensity *I* is given by

$$I = \alpha B^* + \beta B \qquad (5)$$

where α and β are parameters proportional to extinction coefficients. In the case of benzyl bromide, B* is produced *via* eq 4 at a rate $2k_df[P]$ where k_d is the rate constant for decomposition of the peroxide P, and *f* is the approximately constant fraction of peroxide fragments undergoing eq 4. Since B* is a low concentration transient intermediate we may use a steady-state approximation for its concentration

$$B^* = 2k_df[P]/k_r \qquad (6)$$

and set

$$B = 2f([P]_0 - [P]) \qquad (7)$$

Table I. Rate Constants (k_d) for 0.18 *M* Phenylacetyl Peroxide Decomposition and Enhancement Factors (p) for Polarized Products in $BrCCl_3$-CCl_4 at 40°

	$10^3 \times k_d{}^a$			p^b	
$[BrCCl_3]$, *M*	$(PhCH_2)_2$	$PhCH_2Br$	$PhCH_2CCl_3$	$PhCH_2Br$	$PhCH_2CCl_3$
0.203	3.06	3.81	4.45	−40.3 (−39.6)	350 (345)
0.406	3.24	4.35	5.38	−45.7 (−47.4)	256 (254)
0.71	3.49	4.27	5.75	−42.9 (−43.5)	182 (175)
1.01	3.65	4.57	4.77	−39.3 (−42.6)	161 (157)
1.52	3.02	4.10		−35.7 (−36.0)	74.0
2.03	4.05	4.35		−29.4 (−32.0)	50.4
2.89	4.48	4.40		−21.1 (−23.3)	31.8
Av	3.6 ± 0.4	4.3 ± 0.2			

[a] Calculated *via* least-squares fits using eq 11. [b] Calculated at a fixed time of 240 sec and an average k_d of 4.0×10^{-3} sec^{-1} or for values in parentheses by using individual k_d and the intercept of least-squares plot of eq 11 using the following T_1 values: $PhCH_2Br$, 11.7 sec; $PhCH_2CCl_3$, 6.15 sec.

Table II. Rate Constants (k_d) for 0.163 *M* Phenylacetyl Peroxide Decomposition and Enhancement Factors (p) for Polarized Products in CCl_3SO_2Cl-CCl_4 at 40°

	$10^3 \times k_d{}^a$			p^b	
$[CCl_3SO_2Cl]$, *M*	$(PhCH_2)_2$	$PhCH_2Cl$	$PhCH_2CCl_3$	$PhCH_2Cl$	$PhCH_2CCl_3$
0.136	4.77	3.33	3.46	−18.0 (−16.5)	418 (435)
0.204		3.41	3.91	−25.3 (−23.5)	516 (562)
0.271	4.06	3.92	3.68	−28.0 (−26.7)	574 (587)
0.339		3.90	4.14	−30.6 (−29.0)	605 (594)
0.407	3.93	3.61	4.62	−31.8 (−30.1)	458 (439)
0.544		3.82	6.17	−34.9 (−34.1)	428 (420)
0.544	3.21	4.20	5.11	−36.2 (−36.3)	501 (478)
Av		3.7 ± 0.3	4.4 ± 0.7		

[a] As in Table I. [b] As in Table I except that the fixed time was 215 sec so that the instantaneous peroxide concentration at this point was equivalent to that used for enhancement factor calculations in Table I; using T_1 (for $PhCH_2Cl$) of 14.4 sec.

At long times when all peroxide is decomposed and all B* relaxed

$$I_\infty = \beta B_\infty = 2f\beta[P]_0 \tag{8}$$

Combining eq 6–8 with eq 5 gives

$$(I_\infty - I)/I_\infty = (1 - \alpha k_d/\beta k_r)[P]/[P]_0 \tag{9}$$

which, since

$$[P]/[P]_0 = e^{-k_d t} \tag{10}$$

can be rewritten as

$$\ln (I_\infty - I)/I_\infty = \ln (1 - \alpha k_d/\beta k_r) - k_d t \tag{11}$$

The quantity α/β may be calculated from eq 9 for any particular value of I, using the rate of appearance of bibenzyl to calculate k_d and $[P]/[P]_0$ and knowing k_r, the rate constant for relaxation of the benzylic protons of benzyl bromide (we obtain $k_r = 0.086$ sec^{-1} by adiabatic fast passage measurements in CCl_4-CCl_3Br solvent). Alternatively, from eq 11 a semilog plot of $(I_\infty - I)/I_\infty$ *vs.* t yields both k_d and $\alpha k_d/\beta k_r$ and hence α/β. This treatment uses more data, but ignores the fact that (as follows from our analysis given below) α/β may vary somewhat with [P].

In eq 5 α and β contain instrument parameters, but these cancel in the ratio, so that $\alpha/\beta = p$, the desired enhancement factor or difference in population of the two possible proton spin states relative to the usual thermal difference. In the case of emission spectra, p is a negative quantity. Values of p for benzyl bromide and phenyltrichloroethane, calculated by both methods, are listed in Table I for a range of concentrations of CCl_3Br and peroxide. Values for benzyl chloride and phenyltrichloroethane for the CCl_3SO_2Cl system (to which the same treatment applies) appear in Table II, and the data in these two tables provide the basis for our subsequent analysis.

Some characteristics of eq 11 are worth pointing out before continuing to the analysis. First, it is essentially a first-order rate expression, but with a variable intercept, and may actually be applied to any two consecutive first-order reactions followed by a physical measurement in which the intermediate is present in only low concentration, but still makes an appreciable contribution to the measurement. It is also valid only after B* achieves its maximum value, and the steady-state treatment applies. Second (and this needs to be kept in mind by anyone investigating CIDNP phenomena), the *observed* intensity of polarization depends, not only on p, but also on k_d/k_r, and is greatest for fast reactions and products showing slow relaxation. Further, products with different values of k_r may show maximum observed polarizations at quite different times, even though formed in the same process. Finally, eq 10 may be put in the much more general form

$$I/I_\infty = [pB^* + B]/B_\infty \tag{12}$$

and p determined for any system in which B, B*, and B_∞ can be expressed as functions of time and initial concentrations of reagents.

The Radical Flux Model. Inspection of Table I shows that p for benzyl bromide varies considerably with CCl_3Br concentration, with a maximum at $[CCl_3Br] \cong 0.4$ *M*. Further, p for $PhCH_2CCl_3$ behaves quite differently, decreasing with increasing CCl_3Br concentration. We propose that both effects are the consequence of benzyl radical polarization by close approach to $\cdot CCl_3$ radicals (consistent with the Kaptein-Closs model for the polarization process)[2,3] and that benzyl bromide polarization then depends upon the $CCl_3\cdot$

concentration and the subsequent competition between relaxation of polarized *radicals* and their reactions to yield products. The reactions on which we base our analysis are the following where R· = PhCH$_2$·.

$$\mathrm{R\cdot + CCl_3Br \xrightarrow{k_1} RBr + CCl_3\cdot} \tag{13}$$

$$\mathrm{R\cdot + CCl_3\cdot \xrightarrow{k_2} R\cdot^{*} + CCl_3\cdot} \tag{14}$$

$$\mathrm{R\cdot^{*} \xrightarrow{k_3} R\cdot} \tag{15}$$

$$\mathrm{2R\cdot \xrightarrow{k_4} R\text{-}R} \tag{16}$$

$$\mathrm{2CCl_3\cdot \xrightarrow{k_5} C_2Cl_6} \tag{17}$$

$$\mathrm{R\cdot + CCl_3\cdot \xrightarrow{k_6} RCCl_3} \tag{18}$$

In our formulation k_2 is the rate constant for the process in which R· and CCl$_3$· undergo a polarizing encounter and then separate without reaction. We assume that each such encounter contributes an increment of polarization n to the pool of R· radicals, so that R· polarization is introduced at a rate nk_2·[R·][CCl$_3$·]. The quantity k_3 is the rate constant for nuclear spin relaxation of benzyl radicals. As we will see $k_3 \gg k_r$, the rate constant for relaxation of product *molecules*. The quantities k_4, k_5, and k_6 are rate constants for radical coupling processes. A value of $k_4 = 4 \times 10^9$ has been reported by Burkhardt.[8] Several values of k_5 ranging from 0.3 to 1 × 10^8 are available for the reaction in solution[9] and we have chosen to use $k_5 = 1 \times 10^8$. The cross coupling constant k_6 has not been measured, so we employ the old dodge of setting $k_6 = 2(k_4k_5)^{1/2}$ which drastically simplifies the analysis.[10] We may note that eq 14 and 18 between them are the "sorting processes" leading to polarization and this will be considered again when we discuss the polarization of RCCl$_3$.

Before working out the consequences of our model we may note that two polarization paths can immediately be eliminated for our particular system on the basis of the data of Table I. The first is one in which benzyl radicals are polarized during their initial formation, since here p would simply be proportional to k_1[CCl$_3$Br]/k_3, and not pass through a maximum as observed.[5a] The second is a polarization accompanying reaction 13 as has been suggested by Gerhard and Osterman,[11] since here p should be constant under all conditions.

Taking the total rate of polarization of benzyl radicals as nk_2[R·][·CCl$_3$], assuming the validity of the steady-state assumption for all transient intermediates and using eq 13–18 to eliminate radical concentrations (see Appendix), we obtain an expression for the predicted enhancement factor p for benzyl bromide

$$\frac{1}{p} = r + s[\mathrm{CCl_3Br}] + t[\mathrm{CCl_3Br}] \tag{19}$$

where

$$r = \{4(k_4k_5)^{1/2} + k_3(k_5/fk_\mathrm{d}[\mathrm{P}])^{1/2}\}/nk_2$$

$$s = k_1(k_5/fk_\mathrm{d}[\mathrm{P}])^{1/2}/nk_2$$

$$t = \{2k_3(k_4k_5)^{1/2} + 4k_4(k_5fk_\mathrm{d}[\mathrm{P}])^{1/2}\}/nk_1k_2$$

Least-squares fitting to the appropriate data from Table I gives $r = 1.35 \times 10^{-2}$, $s = -9.84 \times 10^{-3}$, and $t = -1.78 \times 10^{-3}$. The numerical values of r, s, and t provide three equations which may next be solved for k_1, nk_2, and k_3 and we obtain $k_1 = 8.52 \times 10^3$, $nk_2 = -8.64 \times 10^{11}$, and $k_3 = 9.13 \times 10^3$.

These values will be considered in the next section, but first we note that there are two checks on our treatment.

First, we have an independent check for our value of k_1. Relative yields of RBr and RCCl$_3$ are available from our analyses and are predicted from eq 13 and 18 as

$$\frac{[\mathrm{RBr}]}{[\mathrm{RCCl_3}]} = \frac{\int k_1[\mathrm{R}\cdot][\mathrm{CCl_3Br}]\mathrm{d}t}{\int 2(k_4k_5)^{1/2}[\mathrm{R}\cdot][\cdot\mathrm{CCl_3}]\mathrm{d}t} \tag{20}$$

Reexpressing the quantities to be integrated in terms of initial concentration and carrying out the integration (see Appendix for details) gives

$$\frac{[\mathrm{RBr}]}{[\mathrm{RCCl_3}]} = \frac{Q_0 + a \ln a/(a + Q_0)}{a + Q_0 + 2a \ln a/(a + Q_0) - a^2/(a + Q_0)} \tag{21}$$

where $Q_0{}^2 = 2k_4R_\mathrm{i}$ and $a = k_1$[CCl$_3$Br].

Solving eq 21 for k_1 for a series of experiments gives values ranging from 2 × 10^3 to 1.4 × 10^4 in complete agreement with our previous value.

Second, since [CCl$_3$Br] always appears in eq 19 in the form k_1[CCl$_3$Br], we can combine our CCl$_3$Br and CCl$_3$SO$_2$Cl data in using eq 19 by dividing [CCl$_3$SO$_2$Cl] by k_1/k_1' as normalized for trapping efficiency, where k_1' is the rate constant for reaction 3, and using this corrected concentration in place of [CCl$_3$Br]. As noted earlier, $k_1/k_1' = 3.6$. Combining both sets of data gives only slightly different values of r, s, and t, and $k_1 = 1.07 \times 10^4$; $nk_2 = -1.12 \times 10^{12}$; $k_3 = 1.32 \times 10^4$. The fit of both sets of data to the calculated curve for the variation of p with [CCl$_3$Br] (or [CCl$_3$SO$_2$Cl]) is shown in Figure 4.

Discussion

As we have seen, our results on the polarization of both benzyl bromide and benzyl chloride are consistent with a "radical flux" model in which benzyl radicals are polarized *via* "sorting encounters" with CCl$_3$· radicals. Qualitatively, the model predicts the observed maximum in polarization with varying CCl$_3$Br or CCl$_3$SO$_2$Cl concentration because, at higher concentrations, benzyl radicals are trapped *via* reactions 1 and 3 before polarization while, at lower concentrations, their polarization relaxes *via* eq 15 before eq 1 or 3 occurs.

Considering next the magnitude of the parameters required to fit our data to eq 19, our value for the rate constant for the benzyl radical–CCl$_3$Br reaction, $k_1 = 1.07 \times 10^4$, appears consistent with other properties of this process, *e.g.*, the yield of phenyltrichloroethane discussed above, and also the high transfer constant for CCl$_3$Br observed in styrene polymerization[12] and

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[8] R. D. Burkhardt, *J. Amer. Chem. Soc.*, 90, 273 (1968).

[9] H. W. Melville, J. C. Robb, and R. C. Tutton, *Discuss. Faraday Soc.*, 14, 150 (1953); W. I. Bengough and R. A. M. Thomson, *Trans. Faraday Soc.*, 57, 1928 (1961); D. J. Carlson and K. U. Ingold, *J. Amer. Chem. Soc.*, 89, 4891 (1967).

[10] Although this simplification has frequently been questioned, it must be approximately correct for reactions of simple radicals all of which have rates close to those of diffusion-controlled processes.

[11] F. Gerhart and G. Ostermann, *Tetrahedron Lett.*, 4705 (1969).

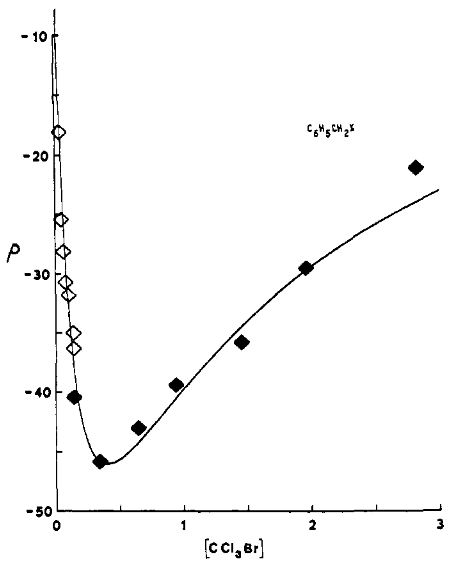

Figure 4. Nuclear polarization, p, at 0.069 M phenylacetyl peroxide for benzyl bromide or chloride, respectively: ◆, *vs.* CCl_3Br concentration; ◇, *vs.* CCl_3SO_2Cl equivalent. Calculated curve uses rate constants as described in text.

the radical chain nature of toluene bromination by CCl_3Br.[13] Indeed, we observe a weak polarized emission of benzyl bromide in this last reaction, when initiated by *tert*-butyl hyponitrite, but have not attempted to analyze it in detail. In contrast, the *tert*-butyl hypochlorite chlorination of toluene, involving much lower concentrations of possible polarizing radicals, shows no CIDNP phenomena whatsoever, although the decomposition of phenylacetyl peroxide in the presence of *tert*-butyl hypochlorite yields polarized benzyl chloride by a nonchain process.

Our value for relaxation of polarized benzyl radicals, $k_3 = 1.32 \times 10^4$, also seems consistent with other estimates and measurements of such processes.[2,14] The remaining parameter, $nk_2 = -1.12 \times 10^{12}$, requires more discussion. It is the product of two quantities inseparable in our analysis: k_2, the rate constant for the polarizing process, and n, the average amount of polarization produced in each encounter. A maximum value of k_2 may be estimated roughly from classical diffusion theory for spheres in a homogeneous media of viscosity η.[15] If the encounter involves actual contact between radicals

$$k_2 = \frac{RT}{1500\eta} \qquad (22)$$

If polarization actually occurs at an average separation of x molecular diameters, k_2, as calculated by eq 22, should be multiplied by x. The present state of CIDNP theory does not predict x, but, assuming a maximum value of 5[16] and taking $\eta = 0.9$ cP (the measured value in our reaction systems) we obtain $k_2 < 10^{10}$; accordingly $n > -10^2$. Since at thermal equilibrium at 40° in a field of 14 kG (the conditions in our experiments) the difference in population of benzylic protons in their two possible spin states is one part in 10^{-5}, we conclude that, among benzyl radicals separating from polarizing encounters, this population difference is inverted and amounts to at least one part in 10^3.

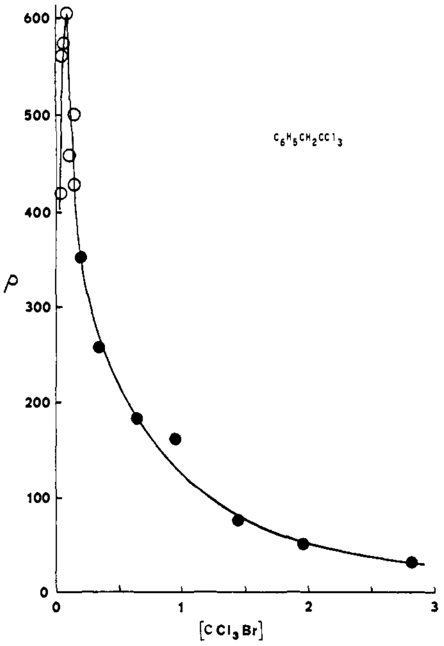

Figure 5. Variation of nuclear polarization for benzylic protons of 1-phenyl-2,2,2-trichloroethane with concentration of CCl_3Br (●) or a CCl_3SO_2Cl equivalent (○) as in Figure 4 but without the calculated curve.

If our treatment is correct, we would hope that our model would also predict the polarization observed in the coupling product, phenyltrichloroethane. Qualitatively, this is the case. Its sign is opposite to that for benzyl bromide (or chloride) as would be expected if both are the consequence of the same sorting process, and it is positive (enhanced absorption) as is predicted by Kaptein's analysis[5b] since polarization occurs as the consequence of a diffusive pair encounter, predominantly triplet in character, in which the benzylic protons have a negative proton hyperfine coupling constant (benzylic $a_H = -16$ G[17]) and a negative $\Delta g > -6 \times 10^{-3}$ ($(R\cdot)g \leq 2.003$;[18] $(\cdot CCl_3)g = 2.0091$[19]). Quantitatively, however, a simple model encounters difficulties. If the polarization process is truly an adiabatic sorting one, each encounter of benzyl and $CCl_3\cdot$ leads either to coupling or separation, and the polarization m produced in the coupling product should be given by

$$m = -k_2/2(k_4k_5)^{1/2} \qquad (23)$$

However, since the benzyl radicals already possess a polarization p_{RBr} the experimentally measured polarization p_{RCCl_3} (as given in Tables I and II) should be

$$p_{RCCl_3} = p_{RBr} - nk_2/2(k_4k_5)^{1/2} \qquad (24)$$

From eq 24, since nk_2 is negative, there should be a simple, inverse relation between the absolute magnitudes

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[12] M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Amer. Chem. Soc.*, **69**, 1105 (1947).

[13] E. S. Huyser, *ibid.*, **82**, 391 (1960).

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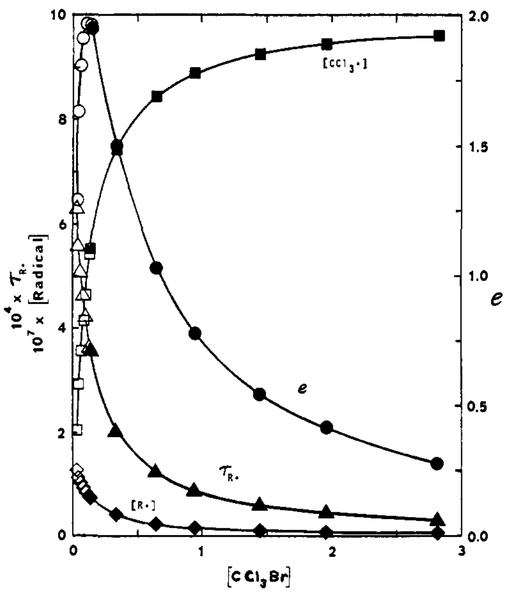

Figure 6. Dependence on CCl_3Br (solid) or equivalent CCl_3SO_2Cl (open) concentrations of the radical concentrations for R· (◆, ◇) and CCl_3· (■, □), the lifetime τ_{R}· (▲, △), and the average number of R· polarizing encounters e (●, ○).

of the two polarizations which, from inspection of Tables I and II, is plainly not the case. Rather, if $[CCl_3SO_2Cl]$ is corrected for its reactivity relative to $[CCl_3Br]$ as in Figure 4 all the data lie on a smooth curve with a maximum in polarization similar to that for p_{RBr} but occurring at lower substrate concentration (Figure 5). What the data appear to indicate is that polarization of the coupling product is closely proportional to the average number of polarizing encounters e which a benzyl radical R· undergoes during its lifetime. This in turn is determined by radical concentrations (*cf.* Appendix), $[R\cdot] = R_i/(a + Q)$ and $[CCl_3\cdot] = a\sqrt{R_i}/2\sqrt{k_5}(a + Q)$, and their lifetimes, $\tau_{R\cdot} = [R\cdot]/R_i$ and $\tau_{CCl_3\cdot} = [CCl_3\cdot]/k_1[R\cdot][CCl_3Br] = (2k_5R_i)^{-1/2}$, since

$$e = k_2[CCl_3\cdot]\tau_{R\cdot} \qquad (25)$$

The dependence of each of these terms is shown in Figure 6 except for $\tau_{CCl_3\cdot}$ which is constant, 5×10^{-3} sec, at the constant R_i used in our measurements. Comparison of Figures 5 and 6 shows that e and p_{RCCl_3} indeed have very similar concentration dependence and maxima at the same point.

This result is as though, for those benzyl radicals which eventually couple, positive polarization is being accumulated by successive encounters during their entire lives (0.3–7×10^{-4} sec) but without relaxation, k_3. Since the polarization introduced into those which go on to benzyl radicals is also proportional to e (although the maximum in polarization observed is shifted to higher CCl_3Br concentration due to relaxation) this result might be considered consistent with adiabatic sorting. Similarly, the greater enhancement factor observed in the coupling product is also plausible since most encounters lead to separation rather than coupling. Nevertheless, the details of the process are very difficult to picture in terms of any plausible model and we can only conclude that there are many aspects of CIDNP phenomena which are poorly understood and that the field is badly in need of much more quantitative data of the sort which we have attempted to gather here.

Finally, we may comment on the bearing of our results on the details of the mechanism of decomposition of phenylacetyl peroxide. In contrast to results reported for benzoyl[20] and acetyl[5b] peroxides, none of our cage products exhibit polarization. We conclude that both carboxyl inversion and ester products arise from extremely tight and short-lived radical–ion pairs which do not live long enough or separate sufficiently (or both) for polarization to occur, or, stated another way, CO_2 loss from phenylacetoxy radicals in the solvent cage must be extremely fast indeed, a conclusion which is certainly consistent with the products observed.

Experimental Section

Chemicals. Phenylacetyl chloride was prepared in 56% yield by the reaction of phenylacetic acid and thionyl chloride.[21] The acidic esterification[22] of phenylacetic acid with benzyl alcohol in CH_2Cl_2 gave a 67% yield of benzyl phenylacetate. All other compounds used, except those described below in detail, were commercially available.

1-Phenyl-2,2,2-trichloroethane. Aniline (10 ml, 0.11 mol) was dissolved in 24 ml of concentrated HCl, diluted with 10 ml of water, cooled to 0°, and kept below 4° during dropwise addition of a $NaNO_2$ solution (7.5 g in 20 ml of H_2O). The solution was kept cold while it was slowly added to an ice-cold rapidly stirred mixture of 16 ml (0.2 mol) of vinylidene chloride, 100 ml of acetone, 3 g of cupric chloride, 8 g of sodium acetate trihydrate, and 10 ml of water. After addition was complete, the solution was stirred at room temperature overnight, and then extracted with ether. The organic layer was washed with water, dried over anhydrous Na_2SO_4, decanted, and vacuum distilled to give 2.2 ml of phenyltrichloroethane, bp 121–123° (20 mm) [lit. 112° (15 mm),[23] 109° (7 mm)[24}].

Phenylacetyl Peroxide. Phenylacetyl chloride (4 ml, 30 mmol) in 10 ml of CCl_4 was cooled to −4° and kept below −2° while rapidly adding 3.5 ml (30 mmol) of cold 30% H_2O_2 and then very slowly (45–75 min), particularly initially, adding a cold solution of 6.4 g (160 mmol) of NaOH in 30 ml of water. The basic aqueous layer was separated and washed twice with 15-ml portions of cold CCl_4. The CCl_4 layers were combined, washed twice with ice water, dried over anhydrous Na_2SO_4 while cooling, and sampled for titration and reactions before freezing on Dry Ice. All samples were kept at Dry Ice temperatures until use. Iodometric determinations of peroxide were carried out on 3-ml samples of CCl_4 stock solution which were placed in chilled, CO_2 outgassed, glacial acetic acid (15 ml) containing 1 g of sodium iodide for 10–15 min before titration. Yields based on peroxide titer of the 0.20–0.25 *M* solution were 50–70%. The pmr spectra of CCl_4 solutions recovered after titration showed weak but characteristic benzylic singlets for bibenzyl, benzyl phenylacetate, and benzyl iodide. The use of less soluble potassium iodide in the titration procedure gave low and erratic peroxide concentrations.

Proton Magnetic Resonance Measurements. A. General. Although the qualitative characteristics of the bromotrichloromethane-phenylacetyl peroxide CIDNP reactions and quantitative benzylic product distributions from these reactions were confirmed using a Varian XL-100-15 with internal TMS lock, all of the data reported were obtained using a Varian A-60 equipped with temperature controller and decoupler. All samples were prepared and run in 5-mm thin-walled nmr tubes. Spectra for chemical-shift assignments (Table III) were measured on 5% solutions of pure compounds in CCl_4 with an internal (~1%) TMS standard. Chemical shifts are reported on the δ scale in parts per million relative to TMS.

B. Product Distributions. The sum of five or more integrals over the benzylic region (250 cycle sweep width, 150 cycle offset)

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Table III. Proton Magnetic Resonance Spectra of Reaction Products and Other Compounds Related to the Thermal Decomposition of Phenylacetyl Peroxide in CCl_4 with $BrCCl_3$ or CCl_3SO_2Cl[a]

	Chemical shifts (δ_{TMS}, ppm)		
Compound	OH	Alkyl	Aryl
$(PhCH_2)_2$		2.87 (s, 4)	7.27 (s, 10)
$PhCH_2CO_2CH_2Ph$		3.54 (s, 2), 5.03 (s, 2)	7.21 (m, 10)
$PhCH_2CO_2H$	12.17 (s, 1)	3.55 (s, 2)	7.21 (s, 5)
$(PhCH_2CO_2)_2$		3.63 (s, 4)	7.20 (s, 10)
$PhCH_2CO_2COCH_2Ph$[b]		3.64 (s, 2), 5.15 (s, 2)	*c*
$PhCH_2CCl_3$		3.88 (s, 2)	7.31 (m, 5)
$PhCH_2Br$		4.42 (s, 2)	7.29 (m, 5)
$PhCH_2OH$	3.42 (t, 5.3, 1)	4.44 (d, 5.3, 2)	7.21 (s, 5)
$PhCH_2Cl$		4.50 (s, 2)	7.29 (s, 5)
$(PhCH_2)_2O$		4.48 (s, 4)	7.25 (s, 10)

[a] Measured as 5% solutions of the pure compound in CCl_4 with 1% TMS. [b] Data based on peaks from reaction product which is thermally converted to ester. [c] Aromatic protons from this product are not distinct from other product peaks.

was used for quantitative determination of relative product distributions in phenylacetyl peroxide reactions. These measurements were made immediately after kinetic runs but generally instrument parameters were optimized for resolution before recording product integrals. At least six times the known benzyl halide relaxation time was allowed to elapse between retrace and recording of successive integrals. The accumulated amount of bibenzyl, ester, and carboxy inversion products in samples of known peroxide titer was determined relative to peroxide by benzyl integral measurements on stock solutions at −5 to −8°. Correction factors derived from stock solution evaluation were used in determining relative yields of trapping products and total noncage products.

C. Reaction Kinetics. The instrument probe was brought to approximately the correct temperature using the temperature controller calibration and then fine adjustments of the controller were made after 30-min equilibration with the aid of a thermometer in place of the sample. Temperature variation was not detectable (±0.1°) over an 8-hr period by repeated thermometer checks. The instrument parameters were optimized on a previously reacted sample in one of a set of precision nmr tubes. The scale expansion (100 cycles for $BrCCl_3$ and 250 cycles for CCl_3SO_2Cl) and offset (>150 cycles) were set so that bibenzyl and benzyl halide were both on scale and fine curvature adjustments were made so that integrals could be run during either up- or downfield sweeps. A previously prepared frozen sample containing all reaction components was rapidly armpit warmed. A timer was started when shaking completed melting and ensured improved sample homogeneity. The sample was immediately placed in the probe and integral scans were initiated. Times were recorded at the point of maximum integral rise. A maximum number of data points for the compounds of interest were obtained by integrating only the appropriate peaks. Smoothed curves through integral *vs.* time plots (*e.g.*, Figure 3) were used for rate constant and enhancement factor evaluation. The use of integrals rather than peak heights during CIDNP experiments is essential due to band narrowing and display of both absorption and emission components for a singlet in single scans during intermediate reaction periods.

D. Relaxation Times (T_1). Adiabatic rapid passage (ARP) conditions were used to determine relaxation times. Measurements were made on solutions of single compounds in CCl_4 with concentrations which bracketed (a) the particular compound concentration as generated by reaction and (b) the total proton density in phenylacetyl peroxide solutions. Solutions were placed in serum-capped nmr tubes and outgassed through a needle connected to a vacuum line by repeated freeze-pump-thaw cycles. Further simulation of reaction conditions was provided by flushing the sample tube twice with CO_2 during the outgassing cycles and final filling of the tube to a slight positive pressure of CO_2. ARP conditions were met by using the decoupler to generate high-field H_1 values of 1.7–3.0 mG and by using sweep rates of 25 sec over 500 cycles so that dH_0/dt was 20 cycles/sec. Least-squares fits of the first-order processes were made on 10–20 measurements ranging from 2 to 20 sec for each sample. The values of T_1 determined for methylene protons were: benzyl chloride, 14.4 ± 0.7 sec, benzyl bromide, 11.7 ± 0.7 sec, and phenyltrichloroethane, 6.15 ± 0.2 sec.

CIDNP Studies. Phenylacetyl Peroxide. Reactions were carried out in pressure-capped, 5-mm, thin-wall nmr tubes on 0.50 ml of 0.20–0.25 *M* stock solutions of phenylacetyl peroxide in CCl_4.

A. *tert*-Butyl Hypochlorite. The hypochlorite (25 μl) was added to the frozen peroxide solution. Rapidly, armpit warming to near probe ambient preceded placement in the instrument. Repeated scans of the δ 1.0–5.5-ppm region were initiated within 12 sec after melting the sample. A benzyl chloride emission singlet quickly appeared at 4.5 ppm (*cf.* Table III) but had undergone inversion to a normal absorption band within 1.5 min. No other spectral abnormalities were observed under these conditions which may be compared with those of high $BrCCl_3$ concentrations (*cf.* Table I) because of the high reactivity of the hypochlorite. Qualitative reactivity confirmation was the greatly increased benzyl chloride emission when trap concentration was reduced.

B. Bromotrichloromethane. Purified CCl_3Br (12–200 μl) and enough CCl_4 to make the total sample volume 700 μl were added to the 500 μl of frozen stock peroxide solution. Sets of five–nine samples prepared at one time were consecutively followed by pmr for qualitative or kinetic evaluation (Table I). The correspondence of chemical-shift locations to the data in Table III was good. The assignment for benzyl phenylacetyl carbonate was obtained by noting the pmr bands which disappeared and were quantitatively converted to benzyl phenylacetate after heating overnight at reflux. Other peaks all increased appropriately on addition of the assigned compounds. The gas chromatographs of a sample also gave peak enhancements on individual addition of bibenzyl, benzyl bromide, phenyltrichloroethane, and C_2Cl_6. Gc measurements were made on a HP 700 thermal conductivity chromatograph using a 10 ft × 0.25 in. column of 10% FFAP on 40–60 mesh Chromosorb W, ballistically programmed from 125 to 200° and with a He flow of 38 ml/min. Viscosities measured in nmr tubes by the falling ball method gave η at 40°, relative to a CCl_4 value of 0.74 cP, of 1.3 cP for pure CCl_3Br, and an average of 0.9 cP for solutions after reaction. The maximum trapping efficiency of CCl_3Br was 33–37% of peroxide.

C. Trichloromethanesulfonyl Chloride. Recrystallized CCl_3SO_2Cl (2.0 g) was dissolved in CCl_4 in a 5-ml volumetric flask. Titration of 200-μl samples iodometrically (*cf.* phenylacetyl peroxide preparation) indicated a concentration of 1.90 ± 0.01 *M*. This stock solution (14–200 μl) was used in place of CCl_3Br in preparing samples for pmr kinetic analysis (Table II) as above. The maximum trapping efficiency of total peroxide was 25%. Comparative reactivities were determined on solutions 0.16 *M* in phenylacetyl peroxide, 0.46 *M* in CCl_3Br, and 0.40–0.43 *M* in CCl_3SO_2Cl. Both benzyl halides gave pmr emission bands during reaction. The final ratio of benzyl bromide to chloride integrals as normalized for equivalent concentrations was 5.3 ± 0.4 which when adjusted for trapping efficiencies gave a CCl_3Br–CCl_3SO_2Cl reactivity of 3.6.

Toluene Reactions. A. *tert*-Butyl Hypochlorite and AIBN. A stock solution of 5 ml (47 mmol) of toluene, 1 ml (8.4 mmol) of *tert*-butyl hypochlorite, and 33 mg (0.2 mmol) of azobisisobutyronitrile was sampled in 0.5-ml aliquots. Spectra were run by placing an nmr tube in a hot water bath until color loss and vigorous reaction occurred and then quickly transferring the tube to the ambient temperature nmr probe for rapid scanning or placing the sample tube directly in a hot nmr probe of comparable (84°) temperature. The typical final methylene of benzyl chloride to methyl of *tert*-butyl alcohol integral ratio was 2:10 and while 1–4 min was necessary for reaction initiation under these conditions, the benzylic peak growth was not perturbed by CIDNP effects. Comparable results were obtained when four-fifths of the toluene was replaced with CCl_4.

B. CCl_3Br and *tert*-Butyl Hyponitrite. Samples were prepared using 0.25 ml of toluene, 231 μl of CCl_3Br, and 23–25 mg of hyponitrite. Reactions were run in the nmr probe which was preheated to 80°. During reaction a very weak emission for benzyl bromide inverted in 2 min, while the intense emission peak for chloroform prevailed for 8 min but no other CIDNP effects were evident. The final mole ratios relative to *tert*-butyl alcohol as calculated from integrals were: benzyl bromide, 1.1; $CHCl_3$, 0.9; acetone, 0.3; and bibenzyl, <0.03.

Appendix

Derivation of the Polarization Eq 19. In our scheme, reactions 13–18, polarization p is introduced into the pool of benzyl radicals *via* eq 14 and lost *via* eq 13, 15–16, and 18 at a rate proportional to the amount of p present in the pool, *i.e.*

$$nk_2[R\cdot][CCl_3\cdot] = (k_1[CCl_3Br][R\cdot] + k_3[R\cdot] + 2k_4[R\cdot]^2 + 2k_4[R\cdot]^2 + 2(k_4k_5)^{1/2}[R\cdot][CCl_3\cdot])p \quad (26)$$

whence

$$\frac{1}{p} = \frac{k_1[CCl_3Br] + k_3}{nk_2[CCl_3\cdot]} + \frac{2k_4[R\cdot]}{nk_2[CCl_3\cdot]} + \frac{2(k_4k_5)^{1/2}}{nk_2} \quad (27)$$

Radical concentrations may be eliminated *via* the steady-state expression for total radicals

$$2fk_d[P] = R_i = 2k_4[R\cdot]^2 + 4(k_4k_5)^{1/2}[R\cdot][CCl_3\cdot] + 2k_5[CCl_3\cdot]^2 \quad (28)$$

and for $CCl_3\cdot$

$$k_1[CCl_3Br][R\cdot] = 2(k_4k_5)^{1/2}[R\cdot][CCl_3\cdot] + 2k_5[CCl_3\cdot]^2 \quad (29)$$

Factoring eq 28 and 29 yields

$$R_i/2 = (\sqrt{k_4}[R\cdot] + \sqrt{k_5}[CCl_3\cdot])^2 \quad (30)$$

$$k_1[CCl_3Br][R\cdot] = 2\sqrt{k_5}[CCl_3\cdot] \times (\sqrt{k_4}[R\cdot] + \sqrt{k_5}[CCl_3\cdot]) \quad (31)$$

Equations 30 and 31 are easily solved for $[R\cdot]$ and $[CCl_3\cdot]$

$$[R\cdot] = R_i/(\sqrt{2k_4R_i} + k_1[CCl_3Br]) \quad (32)$$

$$[CCl_3\cdot] = k_1\sqrt{2R_i}[CCl_3Br]/(2\sqrt{2k_4k_5R_i} + 2k_1\sqrt{k_5}[CCl_3Br]) \quad (33)$$

Substituting eq 32 and 33 into 27 yields

$$\frac{1}{p} = \frac{4\sqrt{k_4k_5}}{nk_2} + \frac{2k_3\sqrt{k_5}}{nk_2\sqrt{2R_i}} + \frac{2k_1\sqrt{k_5}[CCl_3Br]}{nk_2\sqrt{2R_i}} + \frac{2k_3\sqrt{k_4k_5}}{nk_2k_1[CCl_3Br]} + \frac{2k_4\sqrt{2k_5R_i}}{nk_2k_1[CCl_3Br]} \quad (34)$$

which may be rearranged to eq 19 by consolidating terms in each power of $[CCl_3Br]$, or into an equivalent expression for use with varying peroxide concentration by consolidating terms in R_i.

Since, from eq 34, p is a function of R_i, and, hence, of [P], eq 11 used to determine experimental values of the polarization or enhancement factor p is not strictly accurate since p varies during reaction. As a consequence, both k_d's and p's are slightly larger than those calculated from bibenzyl appearance (Table I). For our subsequent fitting of our model, Figure 4, we have used an average $k_d = 4 \times 10^{-3}$ and the values of p calculated *via* eq 9.

Determination of k_1 from RBr–$RCCl_3$ Ratios. Equation 21 was obtained by first eliminating radical concentrations from eq 20 *via* eq 32 and 33, making the substitutions $Q^2 = 2k_4R_i$ and $a = k_1[CCl_3Br]$, and changing variables from dt to dQ *via* the relation $-d[P]/dt = k_d[P]$ and $Q^2 = 4fk_4k_d[P]$ to get

$$\frac{[RBr]}{[RCCl_3]} = \frac{\int Q\,dQ/(a + Q)}{\int Q^2\,dQ/(a + Q)^2} \quad (35)$$

Equation 35 is readily integrated between Q_0 and 0 to yield eq 21. Computer solutions of eq 21 by successive approximation yielded the values of k_1 cited.