Table IV. Second-Order Rate Constants for the Oxidation of Alkyl Phenyl Sulfides with PIA at 40 $^{\circ}$ C and Relative Rates of Oxidation^{*a*}

		rel rates of oxidation		
sulfide	$10^{3}k_{2}, \mathrm{M}^{-1} \mathrm{s}^{-1}$	PIA	P2084-b	$S_{2}O_{8}^{2-c}$
PhSMe	9.44 ± 1.09	100	100	100
PhSEt	8.28 ± 0.54	88	66	41
PhS-n-Pr	7.55 ± 0.52	80	56	31
PhS- <i>i</i> -Pr	6.76 ± 0.31	72	32	15
PhS-t-Bu	4.01 ± 0.41	42	6.0	1.8

^a General reaction conditions: solvent 95% CH₃CN-5% H₂O (v/v); [PIA] = 7.5×10^{-4} M. ^b Values from ref 8. ^c Values from ref 7.

The linear relationship between ΔH^* and ΔS^* suggests that the oxidation occurs by a similar mechanism for all aryl methyl sulfides.

Steric Effects in the Oxidation of Alkyl Phenyl Sulfides. The observed second-order rate constants (Table IV) for the oxidation of alkyl phenyl sulfides, C_6H_5SR (R = Me, Et, *n*-Pr, *i*-Pr, *t*-Bu) by PIA reveal that the rate decreases in the order PhSMe > PhSEt > PhS*n*-Pr > PhS-*i*-Pr > PhS-*t*-Bu. The same order has also been observed in the oxidation of these sulfides by peroxoanions.^{7,8} If the contribution of the +I effect of the alkyl groups predominates over the steric effect exerted by the increasing bulkiness of the alkyl groups, one would expect a reverse order in the rate. Further, there is a good correlation between log $(k_2/k_2(Me))$ values with Taft's steric substituent constant,²⁰ E_s (slope = 0.229 ± 0.05, r= 0.993, s = 0.02). All these facts are enough indications to show that the reaction is sensitive to steric congestion at the reaction center.

Experimental Section

Materials. PIA was prepared by the method of Böeseken and Schneider;²¹ mp 158 °C. All the sulfides were prepared by known

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(21) J. Böeseken and G. C. C. C. Schneider, J. Prakt. Chem., 131, 285 (1931).

methods.⁷ The sulfides were purified by vacuum distillation/ recrystallization from suitable solvents. The boiling point, melting point, n^{30}_{D} and d^{30}_{4} of these sulfides were found to be identical with the literature values.¹³ Further, the sulfides showed no impurity peaks in the ¹H NMR spectra, and the TLC analyses proved the presence of a single entity in each sulfide. Acetonitrile was purified by the standard method. All the other chemicals used were of AR/GR grade.

Kinetic Measurements. The kinetic studies were carried out in a 95% acetonitrile-5% water (v/v) mixture under pseudofirst-order conditions in vessels coated on the outside with black paint. The reaction was followed by estimating the unchanged PIA by the iodometric procedure.¹¹ Reproducible results, giving good first-order plots (r > 0.995), were obtained for reactions run in duplicate in each substrate and at all the temperatures studied. Since k_1 decreases with an increase in [PIA]₀, the runs were carried out at constant [PIA]₀ with all the aryl alkyl sulfides. The pseudo-first-order rate constants (k_1) were calculated by the least-squares method by using a Micro 2200 computer (Hindustan Computers). The second-order rate constants (k_2) were obtained from $k_2 = k_1/[sulfide]$. The precision of the k value is given in terms of 95% confidence limit.⁸

Product Analysis. The reaction mixture from an actual kinetic run with MPS was analyzed by TLC (silica gel), and the product was found to be methyl phenyl sulfoxide. This is also confirmed by the fact that the oxidation of sulfoxide to sulfone is slow in comparison with the oxidation of sulfide (pseudo-first-order rate constants for the oxidation of MPS and methyl phenyl sulfoxide are $5.74 \pm 0.32 \times 10^{-5}$ and $5.72 \pm 0.78 \times 10^{-6}$ s⁻¹, respectively, under identical experimental conditions).

The stoichiometry of the reaction has been taken to be 1:1 and the reaction is represented by eq 10.

PhSCH₃ + PhI (OCOCH₃)₂ + H₂O \rightarrow PhSOCH₃ + PhI + 2CH₃COOH (10)

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Effect of Pressure on Chemically Induced Dynamic Nuclear Polarization

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Chemically induced dynamic nuclear polarization (CIDNP) has been observed in the thermolysis of acetyl benzoyl peroxide over a pressure range of 0–200 MPa. Analysis of the CIDNP spectra shows that the application of pressure retards the rate of peroxide cleavage and increases the ratio of cage product to escape product but has no effect on the enhancement factors. The spin-lattice relaxation times of the methyl protons in methyl benzoate and chloromethane have been determined over the same pressure range; both decrease as pressure is applied. The activation volumes for these processes are -13 and -6.4 cm³/mol, respectively. The principal advance gained by means of this study is that the observation of CIDNP under pressure allows a rapid and reasonably accurate evaluation of the activation volume of the initiator decomposition (4 cm³/mol) and of the difference in activation volume for the formation of escape and cage products (8 cm³/mol).

Enhanced absorption and emission in nuclear magnetic resonance spectra obtained during radical decomposition of acyl peroxides are well-established phenomena.² The "chemically induced dynamic nuclear polarization" (CID-

431



NP) spectra have been successfully explained with the radical-pair mechanism by Closs and by Kaptein and Oosterhof.³ This mechanism is shown in Scheme I for the thermolysis of acetyl benzoyl peroxide (P) in chlorobenzene containing carbon tetrachloride as a radical scavenger. The asterisks indicate polarization; in their absence, the species have thermalized spin populations. This system is particularly amenable to study because both emission (by the methyl protons of the *cage* product C, methyl benzoate) and enhanced absorption (by those of the *escape* product E, chloromethane) occur, and both are singlets. The kinetics of the decomposition can be followed simply by means of acquisition of single 90° pulses, repeated at equal intervals over the course of the reaction.

The reaction kinetics can be adequately modeled by two sequential first order reactions (eq 1 and 2). The rate

$$P \xrightarrow{k'_c} C^* \xrightarrow{k_{rc}} C \tag{1}$$

$$\mathbf{P} \xrightarrow{k'_{\bullet}} \mathbf{E}^{*} \xrightarrow{k_{re}} \mathbf{E}$$
(2)

constants $k_{\rm rc}$ and $k_{\rm re}$ are the spin-lattice relaxation rate constants $(1/T_1)$. Application of the steady-state approximation to the radical pairs in Scheme I then gives eq 3 and 4. Acyl peroxides are believed not to be subject to

$$k'_{\rm c} = \left(\frac{k_2}{k_{-1} + k_2}\right) \left(\frac{k_{\rm c}}{k_{\rm c} + k_{\rm e}}\right) k_1 \tag{3}$$

$$k'_{e} = \left(\frac{k_2}{k_{-1} + k_2}\right) \left(\frac{k_{e}}{k_{c} + k_{e}}\right) k_1 \tag{4}$$

return in the first step (see further below); hence, the leading parenthetic factors in eq 3 and 4 reduce to unity. The second factors in these equations are, in fact, the fractions of peroxide going on to form the products C and E, respectively; i.e., they are the yields. Hence, one obtains eq 5 and 6. Recognition⁴ that the signal intensity at any

$$fk_1 = k'_c \tag{5}$$

$$(1 - f)k_1 = k'_e (6)$$

time is given by eq 7, where α and β are proportionality

$$I_{\rm c} = \alpha_{\rm c}[{\rm C}^*] + \beta_{\rm c}[{\rm C}] \tag{7}$$

constants related to spin population, and that these con-

stants are pressure independent allows application of the steady-state approximation to the concentration of polarized species. The argument is developed for C^* , but that for E^* is, of course, completely analogous.

According to this approximation

$$d[C^*]/dt = fk_1[P] - k_{rc}[C^*] = 0$$
(8)

so that

$$[C^*] = fk_1[P] / k_{rc}$$
(9)

If we apply

$$d[C]/dt = k_{\rm rc}[C^*] \tag{10}$$

to eq 9, we obtain

$$\mathbf{d}[\mathbf{C}] = fk_1[\mathbf{P}]\mathbf{d}t \tag{11}$$

We also have

$$[\mathbf{P}] = [\mathbf{P}]_0 \exp(-k_1 t) \tag{12}$$

Combining eq 9 and 12 gives

$$[C^*] = fk_1[P]_0 \exp(-k_1 t) / k_{rc}$$
(13)

From eq 11 and 12

$$[C] = {}_{0} \int {}^{[C]} d[C]$$

= ${}_{0} \int {}^{t} f k_{1}[P]_{0} \exp(-k_{1}t) dt$
= $f[P]_{0} - f[P]_{0} \exp(-k_{1}t)$ (14)

Hence

and

$$[C]_{\infty} = fP_0 \tag{15}$$

=

$$I_{\rm c}^{\ \infty} = \beta_{\rm c} f P_0 \tag{16}$$

By substitution of eq 13 and 14 into

$$\frac{I_{\rm c} - I_{\rm c}^{\infty}}{I_{\rm c}^{\infty}} = \frac{\alpha_{\rm c}[{\rm C}^*] + \beta_{\rm c}[{\rm C}] - \beta_{\rm d}f[{\rm P}]_{\rm 0}}{\beta_{\rm d}f[{\rm P}]_{\rm 0}}$$
$$\frac{\frac{\alpha_{\rm d}fk_1[{\rm P}]_{\rm 0}\exp(-k_1t)}{k_{\rm rc}} - \beta_{\rm d}f[{\rm P}]_{\rm 0}\exp(-k_1t)}{\beta_{\rm d}f[{\rm P}]_{\rm 0}}$$
(17)

$$= \frac{\alpha_{\rm c}k_1}{\beta_{\rm c}k_{\rm rc}} \exp(-k_1 t) - \exp(-k_1 t)$$
(18)

The enhancement factor v is defined as the ratio of the polarized to the unpolarized population, e.g.,

$$\nu_{\rm c} = \alpha_{\rm c} / \beta_{\rm c} \tag{19}$$

This gives

$$\frac{I_{\rm c} - I_{\rm c}^{\infty}}{I_{\rm c}^{\infty}} = \frac{v_{\rm c} k_{\rm 1} - k_{\rm rc}}{k_{\rm rc}} \exp(-k_{\rm 1} t)$$
(20)

or

$$\ln \frac{I_c - I_c^{\infty}}{I_c^{\infty}} = \ln \frac{v_c k_1 - k_{rc}}{k_{rc}} - k_1 t$$
(21)

Eq 21 allows linear regression analysis of a plot of the logarithmic term vs. time to yield the rate constant for peroxide bond cleavage, k_1 , as the negative of the slope. The *f* factor (composite of rate constants) does not appear in the final form. If we follow I_e , the factor (1 - f) will similarly cancel out, and the result is eq 22.

$$\ln \frac{I_{\rm e} - I_{\rm e}^{\infty}}{I_{\rm e}^{\infty}} = \ln \frac{v_{\rm e} k_{\rm 1} - k_{\rm re}}{k_{\rm re}} - k_{\rm 1} t$$
(22)

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Figure 1. CIDNP spectrum obtained from thermolysis of acetyl benzoyl peroxide in chlorobenzene containing carbon tetrachloride at 96.4 °C (190 MPa) 22 min after insertion of capillary NMR cell into the preheated pressure-transmitting fluid (tetrachloro-ethylene). The scale is in δ units. The principal emission and enhanced absorption are due to methyl benzoate and chloromethane, cage and escape products, respectively.

Table I. Effect of Pressure on the Product Distribution

P, MPa	<i>I</i> c [∞]	<i>I</i> e [∞]	
2.5	3.7	8.0	
60	4.2	8.8	
120	4.3	7.2	
190	4.7	6.3	

If k_r is obtained from separate experiments (e.g., by means of inversion-recovery),⁵ the intercept of the plot allows calculation of the enhancement factor.

Since the CIDNP phenomenon depends on differential combination vs. escape from the initial solvent cage, it would be expected that a change in cage lifetimes would be reflected in the observed CIDNP effects. Our recently developed method for observing NMR spectra under high pressure⁶ allows us to investigate the effect of pressure on CIDNP, the hope being that this might furnish a novel glimpse at the detailed behavior of radical pairs under conditions of changing solvent interaction.

Results and Discussion

Figure 1, the first example of a CIDNP spectrum obtained under high pressure, shows the emission by methyl benzoate and enhanced absorption by chloromethane. CIDNP kinetics were obtained over the pressure range of 0-190 MPa (~ 1900 atm).

Table I shows the effect of pressure on the I^{∞} values observed. These values show a not unexpected variation as pressure is increased; I^{∞} for methyl benzoate increases while I^{∞} for chloromethane decreases.

A plot of $\ln I_c {}^{\circ}I_e {}^{\circ}$ vs. pressure (see Figure 2) allows calculation of the difference of the activation volumes for formation of cage and escape products by simply multiplying the slope by RT (see below); $\Delta\Delta V^* = V_e^* - V_c^*$ is



Figure 2. Effect of pressure on the ratio of signal intensities of cage and escape products.

Table II.	Effect of Pressure ^{<i>a</i>} on the Slope a	and
	Intercept of Eq 4	

		inte	ercept	
P, MPa	$10^{6}k_{1}, s^{-1}b$	cage ^c	escape ^d	
2.5	512	2.84	1.95	
60	514	2.37	1.66	
120	456	2.04	1.72	
190	408	1.58	1.60	

^{*a*} Acetyl benzoyl peroxide (0.140 M) and CCl₄ (3.11 M) in chlorobenzene at 96 °C. ^{*b*} Average of slopes obtained from both methyl benzoate and chloromethane lines. ^{*c*} Methyl benzoate data. ^{*d*} Chloromethane data.

found to be ca. 8 cm³ mol⁻¹. This effect is most simply explained by invoking an increase in solvent viscosity, hence increased cage life, leading to an increase in the relative yield of cage as compared to escape product. Similar observations based on more conventional product analyses have been reported by Neuman.⁷

The slope and intercept resulting from linear regression analysis of eq 21 are shown in Table II. These CIDNP data at once confirm one result expected from the application of pressure to decomposing acyl aroyl peroxide: the decrease of k_1 . This decrease in k_1 as a function of pressure can be analyzed⁶ by application of eq 23. When this is

$$\partial \ln k / \partial P = -\Delta V^* / RT \tag{23}$$

done, one finds that the retardation of peroxide decomposition (i.e., the homolysis of one single bond) by pressure has an activation volume of about 4 cm³/mol. A positive ΔV^* of approximately this magnitude is predicted for the bond-stretched transition state leading to homolysis of such compounds in which return is not significant.^{8,9}

Interpretation of the effect of pressure on the intercept is a more complicated problem. First of all, this intercept is a composite value depending heavily on the determination of I^{∞} which is the smallest and hence the most

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Table III. Effect of Pressure on Spin-Lattice Relaxation Times

P, MPa	T_1 , s ^a	$10^2 k_{\rm rc},{\rm s}^{-1}$	T ₁ , s ^b	$10^2 k_{\rm re}, {\rm s}^{-1}$
4	10.10	9.9	12.70	7.8
10	8.67	11.5	9.55	10.5
50	6.65	15.0	7.88	12.7
100	6.56	15.2	8.11	12.3
143	5.07	19.7	7.22	13.9
190	4.08	24.5	7.90	13.5

^a Methyl benzoate. ^b Chloromethane.

Table IV. Effect of Pressure on the Enhancement Factors

P, MPa	ν _c	ν _e	
2.5	3800	1500	
60	3100	1300	
120	3500	1800	
190	3500	2100	

difficult intensity to obtain accurately; second, it contains the enhancement factor, k_1 , and T1; all three can vary as a function of pressure (vide supra). In order to determine if the observed decreases in intercept for both cage and escape products (corrected for changes in I^{∞}) are due to a decrease in the enhancement factor, because of longer cage lifetimes, or to an increase in k_r (shortening of T_1), it was necessary to determine T_1 for both methyl benzoate and chloromethane under the same experimental conditions as a function of pressure. This was done by inversion-recovery experiments⁵ with solutions of methyl benzoate and chloromethane in chlorobenzene, each about 0.1 M, at 96° C. Table III shows the pressure dependence of T_1 over a 200-MPa range. Application of eq 23 to these data allows the volumes of activation for these relaxation rate processes to be determined experimentally. It can be seen that the spin-lattice relaxation of methyl benzoate $(\Delta V^* = -13 \text{ cm}^3/\text{mol})$ is more pressure sensitive than that of chloromethane ($\Delta V^* = -6.4 \text{ cm}^3/\text{mol}$). The decreases in T_1 may be attributable to an increased dipole-dipole interaction at high pressure, although our present limited data do not allow us to verify this speculation.¹⁰ Nevertheless, these experimental results now permit us to calculate the enhancement factors for both cage and escape products, and this enables us to look for the effect of pressure on nuclear spin populations, and hence on cage lifetime.

The enhancement factors for both cage and escape products are presented in Table IV. These data show no

systematic variation in enhancement factor as a function of applied hydrostatic pressure.

Summary and Conclusion

The effect of high pressure on CIDNP has been investigated for the first time by means of the thermolysis of acetyl benzoyl peroxide. Increased pressure increases the yield of cage over escape products, slows the rate of peroxide decomposition, and increases the rate of nuclear spin-lattice relaxation of products but has no significant effect on the nuclear population of polarized products. All of these effects can be evaluated quantitatively in terms of volume changes or volume differences. The relative constancy in the ratio of cage product to escape product enhancement factors may probably be explained in terms of the rapid relaxation (ca. 10^{-5} s)¹¹ of the intermediate radicals. This rate is evidently too fast to be significantly affected by applied pressure, and thus, it alone controls the overall polarization and enhancement factors.

Experimental Section

Acetyl benzoyl peroxide was prepared by AIBN-initiated photooxygenation of benzaldehyde in glacial acetic acid in a modification of Walling's procedure.¹² Concentrations were determined by iodometric titration.

CIDNP Spectra. Solutions were placed in the capillary cell, and spectra were obtained by means of a Bruker WP-60 as previously described.⁵ The pressure-transmitting fluid used was tetrachloroethylene, selected for its boiling point and dielectric constant. Initial measurements could be made 8–10 min after pressurization; they were recorded as free induction decays every 2 min.

 T_1 Determinations. A solution ca. 0.1 M in both methyl benzoate and chloromethane in chlorobenzene was prepared on a high-vacuum line and placed in the capillary cell. The standard Bruker inversion-recovery sequence was used to obtain T_1 values.

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Registry No. Acetyl benzoyl peroxide, 644-31-5.

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