For **30a**: ^{1}H NMR ($CDCl_3$) δ 7.65–7.0 (m, 3 H), 3.4–3.0 (m, 2 H), 1.93–1.77 (m, 1 H), 1.50 (s, 3 H), 0.77 (dd, J = 9.3, 2.1 Hz, 1 H); mass spectrum, calcd m/e 181.0891, found 181.0896.

3-Methyl-9-methoxy- and 2-Methyl-10-methoxytetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene (29b and 30b). Due to severely limited quantities of **15b**, its irradiation was conducted only on a single 30-mg scale. The resultant colorless oil was quantitatively analyzed by ^{1}H NMR spectroscopy through appropriate integration of the methoxyl and methyl peaks of the two isomers: δ 3.83 and 1.47 for **29b**; δ 3.87 and 1.53 for **30b**. The ratio of the products was 60:40.

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Registry No. 7a, 71925-34-3; **7b**, 71925-42-3; **7c**, 71906-49-5; **8a**, 31893-13-7; **8b**, 80160-36-7; **8c**, 80160-37-8; **9a**, 71925-43-4; **9b**, 71906-45-1; **10a**, 80160-38-9; **10b**, 80160-39-0; **13a**, 71906-41-7; **13b**, 80160-40-3; **14**, 21806-67-7; **15a**, 71906-43-9; **15b**, 80160-41-4; **18a**, 71925-36-5; **18b**, 80160-42-5; **20a**, 71925-37-6; **20b**, 80160-43-6; **21**, 80160-44-7; **22**, 80160-45-8; **23**, 80160-46-9; **24**, 80160-47-0; **25a**, 80160-48-1; **25b**, 80160-49-2; **26a**, 80160-50-5; **26b**, 80160-51-6; **27a**, 80160-52-7; **27b**, 80160-53-8; **28a**, 80160-54-9; **28b**, 80160-55-0; **29a**, 80160-56-1; **29b**, 80160-57-2; **30a**, 80160-58-3; **30b**, 80160-59-4; *exo*-2-hydroxy-7-iodobenzonorbornene, 80160-60-7; *exo*-7-methoxy-2-benzonorborneol, 21845-86-3.

Mechanism of the Oxidation of Alkyl Aryl Sulfides by Phenyliodoso Diacetate

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The rates of oxidation of 16 alkyl aryl sulfides by phenyliodoso diacetate have been studied in acetonitrile–water mixtures. Those sulfides containing electron-donating groups in the benzene ring accelerate the rate while those with electron-withdrawing groups retard the rate. A plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for the aryl methyl sulfides is linear and suggests that the oxidation processes for all the sulfides are the same. A Hammett ρ value of -0.796 ± 0.13 obtained at 35 °C indicates an electron-deficient transition state. The kinetic results have been analyzed by the Yukawa–Tsuno equation. The separation of inductive and resonance effects shows that the reaction is controlled more by the delocalized factor (62.5%) rather than by the localized factor (37.5%). Rate studies with different alkyl phenyl sulfides C_6H_5SR (R = Me, Et, n-Pr, i-Pr, t-Bu) results in a good correlation with Taft's steric substituent constant, E_s. A mechanism involving the rate-limiting step of formation of an iodine(III)–sulfonium ion intermediate complex decomposing by the attack of water in a fast step has been proposed.

Several studies have been reported on the kinetics of oxidation of organic sulfur compounds.[1-9] Both the mechanism and rate of oxidation of these compounds are largely affected by the nature of the oxidant. For example, the oxidation of alkyl aryl sulfides to sulfoxides by halogen[2] is generally assumed to proceed via the halogenosulfonium cation as in eq 1. However, our recent studies[7] have

$$R_2S + X_2 \rightleftharpoons R_2{}^+SX + X^- \xrightarrow{H_2O} R_2SO + 2H^+ + 2X^- \qquad (1)$$

revealed that such a preequilibrium is not present in the oxidation of alkyl aryl sulfides by peroxodisulfate ion, a fact which has been confirmed by the fact that the addition of sulfate ions does not influence the rate, and the mechanism suggested is represented by Scheme I.

Scheme I

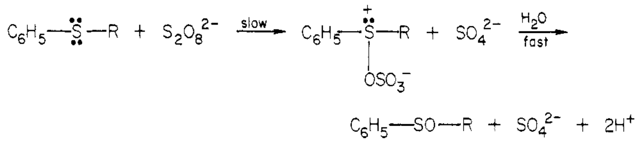

Table I. Pseudo-First-Order and Second-Order Rate Constants for the Reaction of MPS with PIA in 95% CH_3CN-5% H_2O (v/v) at 35 °C

$10^2 \times$ $[MPS]_0$, M	$10^3 \times$ $[PIA]_0$, M	10^5k_1,[a] s^{-1}	10^3k_2,[a] M^{-1} s^{-1}
0.75	0.75	5.74 ± 0.32	7.65 ± 0.43
1.00	0.75	8.32 ± 0.46	8.32 ± 0.46
1.25	0.75	10.0 ± 0.20	8.00 ± 0.16
1.50	0.75	12.1 ± 0.83	8.08 ± 0.55
2.00	0.75	15.5 ± 1.66	7.73 ± 0.83
1.50	0.52	24.1 ± 1.53	16.1 ± 1.02
1.50	1.00	10.7 ± 0.51	7.15 ± 0.34
1.50	1.26	6.39 ± 0.20	4.26 ± 0.14
1.50	1.50	4.96 ± 0.21	3.31 ± 0.14

[a] The error quoted in k is the 95% confidence limit of the Student's t test.[8]

Though Szmant and Lapinski[10] prepared diphenyl sulfoxide by the oxidation of diphenyl sulfide by employing phenyliodoso diacetate (PIA), the kinetics of the oxidation of organic sulfur compounds by PIA have not been carried out so far. The mechanism of the oxidation of several

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Table II. Effect of Added $HClO_4$ and NaOAc and Variation of the Percentage of Solvent Composition on the Rate of Oxidation[a]

$10^5[HClO_4]$, M	10^5k_1,[b] s^{-1}	10^6[NaOAc], M	10^5k_1,[b] s^{-1}	% CH_3CN-H_2O (v/v)	10^5k_1, s^{-1}
0.00	5.74 ± 0.32	0.00	5.74 ± 0.32	95	5.74 ± 0.32
1.12	10.9 ± 0.20	8.00	1.15 ± 0.07	90	13.6 ± 0.85
1.60	12.5 ± 0.47	12.0	0.87 ± 0.03	80	20.1 ± 1.02
2.40	15.8 ± 1.30	16.0	0.58 ± 0.11	75	24.0 ± 0.87
4.00	26.2 ± 1.71	24.0	0.42 ± 0.05	70	30.6 ± 1.59
		40.0	0.31 ± 0.04		

[a] At 35 °C; [MPS] = 7.5×10^{-3} M; [PIA] = 7.5×10^{-4} M. [b] Solvent 95% CH_3CN - 5% H_2O (v/v).

Table III. Second-Order Rate Constants and Enthalpies and Entropies of Activation for the Oxidation of XC_6H_4SMe by PIA[a]

		10^3k_2, M^{-1} s^{-1}						
no.	X	25 °C	35 °C	40 °C	45 °C	55 °C	$\Delta H^\ddagger$,[b] kJ mol^{-1}	$-\Delta S^\ddagger$,[b] JK^{-1} mol^{-1}
1	H	1.91 ± 0.17	7.96 ± 0.49	9.44 ± 1.09	16.1 ± 1.29		79.8 ± 6.8	28.3 ± 24
2	*p*-MeO	12.3 ± 0.60	26.2 ± 2.26		65.0 ± 8.60		63.0 ± 7.0	70.5 ± 24
3	*p*-Me	4.02 ± 0.19	10.1 ± 0.34	15.1 ± 1.02	25.3 ± 2.01		69.0 ± 4.5	59.6 ± 16
4	*p*-*i*-Pr	4.14 ± 0.22	8.95 ± 0.81		22.5 ± 1.75		64.1 ± 5.8	75.9 ± 20
5	*m*-Me		6.05 ± 0.14		14.3 ± 0.64	31.2 ± 1.60	66.3 ± 3.3	72.5 ± 11
6	*p*-Br	2.79 ± 0.16	5.58 ± 0.25		17.4 ± 1.59		69.4 ± 5.1	61.8 ± 18
7	*p*-F		4.86 ± 0.56		11.9 ± 1.48	30.1 ± 3.82	73.9 ± 10	49.7 ± 34
8	*m*-MeO		4.14 ± 0.19		11.1 ± 0.72	21.3 ± 1.48	66.3 ± 5.1	75.3 ± 17
9	*p*-Cl		3.93 ± 0.30	5.94 ± 0.24	10.3 ± 0.93	27.7 ± 4.79	80.6 ± 8.0	30.2 ± 27
10	*m*-Cl		2.01 ± 0.04		4.26 ± 0.22	7.98 ± 0.50	55.3 ± 3.8	117 ± 13
11	*p*-$COCH_3$		1.22 ± 0.07		2.99 ± 0.16	5.42 ± 0.13	60.1 ± 3.8	106 ± 13
12	*p*-NO_2		1.03 ± 0.19	1.66 ± 0.18	2.05 ± 0.36	4.11 ± 0.47	53.8 ± 12	128 ± 41

[a] General conditions: solvent 95% CH_3CN-5% H_2O (v/v); [PIA] = 7.5×10^{-4} M. [b] The precision of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values were calculated by using the method of Petersen et al.[19]

organic substrates by PIA has been studied by various workers.[11] It is generally assumed that the decomposition of the intermediate complex formed from the reactants is the rate-controlling step, as in eq 2. We are interested

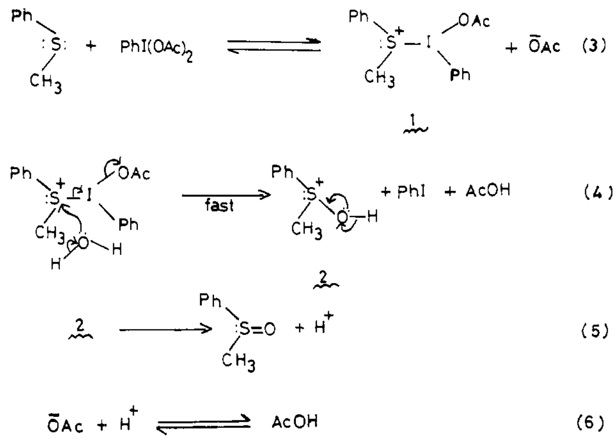
$$\text{substrate} + \text{PIA} \rightleftharpoons \text{intermediate complex} \xrightarrow{\text{slow}} \text{products} \quad (2)$$

in the oxidation of organic sulfur compounds by various oxidants like peroxo anions, chloramine T, Cr(VI), and *N*-bromosuccinimide, and hence we have decided to use PIA as the oxidant for organic sulfur compounds. We present here an account of the kinetics of oxidation of a number of aryl methyl sulfides and a few alkyl phenyl sulfides by PIA and the mechanism of the oxidation in a 95% acetonitrile–5% water (v/v) mixture.

Results and Discussion

The kinetic studies were carried out under pseudo-first-order conditions with the [sulfide] ≫ [PIA]. The oxidation of methyl phenyl sulfide (MPS) by PIA is of total second-order, first-order with respect to each reactant. The pseudo-first-order rate constants (k_1) and second-order rate constants (k_2) at different $[MPS]_0$ and $[PIA]_0$ are presented in Table I. A plot of log k_1 vs. log $[MPS]_0$ is linear with a slope of 1.00 ± 0.16 (r = 0.996, s = 0.02), and the plot of k_1 vs. $[MPS]_0$ also gives a good straight line (r = 0.997) passing through the origin. These observations lead to the conclusion that the order in [MPS] is unity. The rate of disappearance of PIA follows first-order rate law in each kinetic run.

Scheme II



The rate of the oxidation of MPS is accelerated by the added $HClO_4$ and retarded by NaOAc. The rate of the reaction increases as the percentage of water increases in the reaction medium. The kinetic data at different $[HClO_4]$, [NaOAc], and percentage composition of solvent mixture are recorded in Table II. It has also been observed that k_1 decreases with an increase in $[PIA]_0$ (Table I). Since the rate is markedly affected by the introduction of small amount of NaOAc (Table II), we attribute the decrease in k_1 to traces of alkaline impurity in PIA. When the reaction was conducted in the presence of a vinyl monomer, acrylamide in a nitrogen atmosphere, no polymerization product was obtained. This clearly established the absence of free-radical formation during PIA oxidation of MPS. The product was found to be methyl phenyl sulfoxide. MPS and a number of substituted phenyl methyl sulfides were subjected to reaction with PIA (at constant [PIA]), and the rates have been followed in a binary mixture of acetonitrile–water over the temperature range of 20 °C. Table III gives the temperature dependence of the reaction rate in 95% acetonitrile–5% water The experimental data fit the Arrhenius equation, and the activation parameters are collected in Table III. The negative value of the entropies of activation suggests

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[11] K. Swaminathan and N. Venkatasubramanian, *J. Chem. Soc., Perkin Trans. 2*, 1161 (1975), and references cited therein.

that the activated complex formed from aryl methyl sulfide and PIA should have an exacting specificity of orientation.

Mechanism and Rate Law. On the basis of the foregoing kinetic picture, a polar mechanism (Scheme II) may be proposed for the oxidation of MPS by PIA. The mechanism envisages the attack of PIA on the nucleophilic sulfide sulfur to form iodine(III)–sulfonium ion intermediate complex 1 which is decomposed to sulfoxide by the attack of water. The acceleration of the rate by $HClO_4$ and retardation of the rate by NaOAc substantiate the presence of preequilibrium (eq 3) and the formation of the intermediate complex 1. Similar intermediate complexes have been postulated in the reaction of PIA with other organic substrates.[11] The linear increase in the rate of the reaction with an increase in the percentage of water may tempt one to postulate that eq 4 is the slow and rate-determining step. But a study of the substituent effects reveal that electron-donating groups in the phenyl ring of $ArSCH_3$ accelerate the rate of the reaction (Table III). The dominant delocalized effect especially with electron-donating substituents would certainly diminish the electrophilicity of $>S^{+}-$ in the complex 1 and hence retard the water attack. But the same delocalized effect will stabilize and hence increase the PIA–MPS complex formation and hence the rate. All these indicate that the forward reaction in eq 3 is likely to be the rate-determining step. An explanation may also be given for the increase in rate with water content in the medium. The formation of the complex 1 in the rate-determining step involves charge separation which would naturally be stabilized by an increase in the dielectric constant as well as the nucleophilicity (water content) of the medium.[12] It is pertinent to mention here that almost similar types of mechanisms have been suggested for the oxidation of alkylaryl sulfides[7] and phenylthioacetic acids[9] by potassium peroxodisulfate (Scheme I). We have also observed in these reactions an acceleration of rate with an increase in the water content of the medium, and this has been taken as evidence for the formation of a charge-separated complex in the rate-determining step. On the basis of Scheme II the rate law for the oxidation of MPS by PIA can be written as eq 7.

$$-\mathrm{d}[\mathrm{PIA}]/\mathrm{d}t = k_2[\mathrm{MPS}][\mathrm{PIA}] \qquad (7)$$

Substituent Effects. To gain more information about the nature of the transition state and the mechanism, we studied the rates of oxidation with several meta- and para-substituted phenyl methyl sulfides. The data in Table III indicate that electron-releasing substituents in the benzene ring accelerate the rate while the electron-withdrawing substituent produce the opposite effect. It is of interest to find out if any Hammett-type correlation exists for the oxidation of aryl methyl sulfides by PIA. The reactivity pattern is brought out by two different correlations at 35 and 45 °C, one a log k_2 with σ plot and the other with log k_2 and σ^{+}/σ^{-} (Figure 1). Since sulfur can act as an electron donor or acceptor depending upon the substituent para to the methylthio group,[13] we have used both σ^{+} and σ^{-} simultaneously in the second correlation. There are several reactions involving a sulfur center where both σ^{+} and σ^{-} were simultaneously employed.[7-9,14] Though a fair correlation is observed with σ values[7] ($\rho = -1.23 \pm 0.30$, $r = 0.945$, $s = 0.14$ at 35 °C; $\rho = -1.28 \pm 0.34$, $r = 0.938$, $s = 0.15$ at 45 °C), a satisfactory correlation exists between log k_2 with σ^{+}/σ^{-} values[7] ($\rho = -0.796 \pm 0.13$, $r = 0.975$, $s = 0.09$ at 35 °C; $\rho = -0.834 \pm 0.15$, $r = 0.971$, $s = 0.10$ at 45 °C). The negative ρ value indicates that the nucleophilic sulfur atom of the sulfide is more positively charged in the transition state than it is in the reactant.

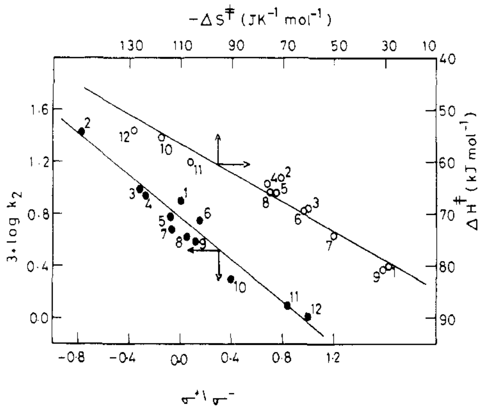

Figure 1. Hammett plot for substituted phenyl methyl sulfides at 35 °C (●); plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ for substituted phenyl methyl sulfides (○). The points in the figure are referred to by the same numbers as the substituents in Table III.

Since a better correlation exists with σ^{+}/σ^{-} values, the kinetic data have been analyzed by the Yukawa–Tsuno equation,[15] eq 8, with σ^{n} constants. This treatment can

$$\log k = \rho[\sigma^{n} + r(\sigma^{+}/\sigma^{-} - \sigma^{n})] + \log k_0 \qquad (8)$$

give an idea regarding the extent of involvement of cross conjugation of the substituent in the transition state. Multiple regression yields correlation ($R = 0.975$ and 0.971 at 35 and 45 °C, respectively) with eq 8 and is justified by F- and t-test significance at better than the 99.9% level. The resonance parameter r is found to be 0.977 and 0.981 at 35 and 45 °C, respectively. The positive r value[16] shows that the transition state is stabilized by an additional resonance between a positively charged reaction center and electron-releasing substituents.

A quantitative picture regarding the operation of polar effects in the reaction can be gained by using eq 9 proposed

$$\log k = L\sigma_{\mathrm{I}} + D\sigma_{\mathrm{R}}^{0} + h \qquad (9)$$

by Taft and Lewis.[17] In eq 9 L and D are the susceptibility constants of the localized and delocalized effects, respectively, and h is the intercept term. Correlations with the rate data ($R = 0.957$ and 0.964 at 35 and 45 °C, respectively) are justified by F- and t-test significance (>99.9%). The results point out that the reaction is controlled more by the delocalized factor (62.5%).

Figure 1 shows that there is a regular linear variation in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (isokinetic temperature, β, slope = 264 ± 43 K, $r = 0.974$). Since the observed range of experimental $\Delta H^{\ddagger}$ value is $>2\delta$, the relation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be assumed to be valid[18,19] in the present study.

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[12] K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York 1964, p 381.

[13] V. Baliah and M. Uma, *Tetrahedron*, **19**, 455 (1963).

[14] O. Exner in "Advances in Linear Free-Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, p 34.

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[16] Y. Yukawa, Y. Tsuno, and Y. Ibata, *Bull. Chem. Soc. Jpn.*, **40**, 2622 (1967).

[17] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958); 81, 5343 (1959).

[18] We have applied the method of error analysis by Petersen et al. and Wiberg to our $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ data. According to this analysis, in order for an isokinetic plot as shown in Figure 1 to be significant, the range of observed $\Delta H^{\ddagger}$ ($\Delta\Delta H^{\ddagger}$) must exceed twice the maximum possible error (δ) in $\Delta H^{\ddagger}$, i.e., $\Delta\Delta H^{\ddagger} > 2\delta$. The calculated maximum possible error (δ) for our data is 12 kJ/mol. For our system the range of observed $\Delta H^{\ddagger}$ values ($\Delta\Delta H^{\ddagger} = 26.8$ kJ/mol) is sufficiently large that the above condition is satisfied. Therefore, the error analysis is additional evidence that the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ correlation shown in Figure 1 is significant.

[19] R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961); K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, 1964, p 376–379.

Table IV. Second-Order Rate Constants for the Oxidation of Alkyl Phenyl Sulfides with PIA at 40 °C and Relative Rates of Oxidation[a]

sulfide	10^3k_2, $M^{-1}\ s^{-1}$	rel rates of oxidation		
		PIA	$P_2O_8^{4-}$ [b]	$S_2O_8^{2-}$ [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*-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% CH_3CN–5% H_2O (v/v); [PIA] = 7.5×10^{-4} M. [b] Values from ref 8. [c] Values from ref 7.

The linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ 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 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 pseudo-first-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 $k_2 = k_1/[\text{sulfide}]$. 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.

$$PhSCH_3 + PhI\ (OCOCH_3)_2 + H_2O \rightarrow PhSOCH_3 + PhI + 2CH_3COOH \qquad (10)$$

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Registry No. **1**, 100-68-5; **2**, 1879-16-9; **3**, 623-13-2; **4**, 70026-35-6; **5**, 4886-77-5; **6**, 104-95-0; **7**, 371-15-3; **8**, 2388-74-1; **9**, 123-09-1; **10**, 4867-37-2; **11**, 1778-09-2; **12**, 701-57-5; PhSEt, 622-38-8; PhSPr, 874-79-3; PhSPr-*i*, 3019-20-3; PhSBu-*t*, 3019-19-0; phenyliodoso diacetate, 3240-34-4.

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[20] R. W. Taft, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., J. Wiley New York, 1956, Chapter 13.

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

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 cm^3/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 cm^3/mol) and of the difference in activation volume for the formation of escape and cage products (8 cm^3/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-

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