Sulphines. Part VIII.† Kinetics and Mechanism of the Reaction between Aryl Sulphines and Perbenzoic Acid

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Aryl sulphines are converted by perbenzoic acid into benzophenones. sulphur, and sulphur dioxide. The reaction shows kinetic features. namely the rate law as well as substituent and solvent effects, similar to those reported for the oxidation of thiones. sulphides. alkenes. acetylenes. and diazoalkanes with the same peroxyacid. The reaction is an example of oxidation of a cumulative. double-bond system and a multi-step reaction mechanism is advanced. The rate-limiting step is electrophilic attack of the peracid on the carbon–sulphur double bond of the CSO group to form a cyclic sulphinic ester: this intermediate. by rapid cleavage. gives the ketone and sulphur monoxide. the latter disproportionating into sulphur and sulphur dioxide. The reaction rates of the *E*- and *Z*-isomers of mesityl phenyl sulphine compared with that for diphenyl sulphine, give further evidence for the proposed mechanism.

Peroxyacid oxidation of thiones leads to the *S*-oxides (sulphines),[1] and subsequently to the ketones by reactions of considerably different rates, the first being much faster than the second.[2] A recent kinetic study [2]

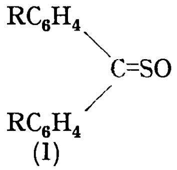
$$>C{=}S \xrightarrow{A} >C{=}SO \xrightarrow{B} >C{=}O \qquad (1)$$

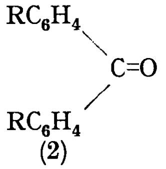
of stage A using perbenzoic acid (PBA) as oxidant gave results compatible with a one-step mechanism involving a nucleophilic displacement by sulphur on peroxidic oxygen, similar to that outlined for the oxidation of sulphides to sulphoxides and for the epoxidation of olefins.[3]

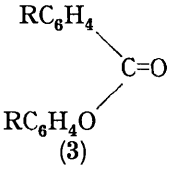
We now report results which elucidate the mechanism of stage B which, in addition to their significance to the chemistry of sulphines, also represent a novel oxidation of a cumulative, double-bond system by a peroxyacid.[4]

RESULTS AND DISCUSSION

The reactions of diaryl sulphines (1a—f) with PBA in carbon tetrachloride give primarily the corresponding benzophenones (2) in practically quantitative yields.[2] When a large excess of PBA is employed, the ketones partly undergo the Bayer–Villiger reaction [5] to form the aryl benzoates (3). This reaction, however, did not appreciably interfere with the kinetics of ketone formation.


(1)


(2)


(3)

a, R = H; b, R = *p*-OMe; c, R = *p*-Me; d, R = *m*-Me; e, R = *p*-Cl; f, R = *m*-Cl.

Analysis of the products for the case of di-*p*-tolyl sulphine (1c) showed the presence of di-*p*-tolyl ketone (2c), benzoic acid, sulphur, and sulphur dioxide conforming to the stoicheiometric equation (1). Analogous

$$(p\text{-}MeC_6H_4)_2CSO + PhCO_3H \longrightarrow (p\text{-}MeC_6H_4)_2CO + 1/2\ S + 1/2\ SO_2 + PhCO_2H \qquad (1)$$

products from the other sulphines gave confidence to the general validity of the stoicheiometry represented by equation (1).

The kinetics of the reactions of sulphines (1) with PBA have been studied in some detail. To obtain reproducible rates, the kinetic runs were carried out under nitrogen and the unchanged sulphine was monitored spectrophotometrically. In some cases, particularly for the less reactive sulphines (1e and f), the re-

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† Part VII, B. F. Bonini and G. Maccagnani, *Tetrahedron Letters*, 1973, 3585.

[1] B. Zwanenburg and J. Strating, *Quart. Reports Sulphur Chem.*, 1970, **5**, 79.

[2] A. Battaglia, A. Dondoni, P. Giorgianni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc.* (*B*), 1971, 1547.

[3] (*a*) R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740; (*b*) R. Curci and J. O. Edwards, 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970, vol. 1, ch. IV.

[4] (*a*) D. Swern, 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1971, vol. 2, ch. 5, pp. 479—482; (*b*) R. Curci, F. Di Furia, and F. Marcuzzi, *J. Org. Chem.*, 1971, **36**, 3774; (*c*) J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, 1968, **90**, 7292, 7347; J. K. Crandall, W. H. Machleder, and M. J. Thomas, *ibid.*, 1968, **90**, 7346.

[5] For a review see C. H. Hassall, 'Organic Reactions,' ed. R. Adams, Wiley, New York, 1957, vol. IX, p. 73. For mechanistic studies see: ref. 3*b*, p. 241; T. Mitsuhashi, M. Miyadera, and O. Simamura, *Chem. Comm.*, 1970, 1301; Y. Ogata and Y. Sawaki, *J. Amer. Chem. Soc.*, 1972, **94**, 4189.

actions were also carried out in the presence of small quantities of *p*-benzoquinone or allyl acetate in order to scavenge radicals derived from thermal or photochemical decomposition of the peroxyacid.[3]

Kinetic experiments at different initial concentrations of sulphine and PBA showed that the reaction is a second-order process, first order with respect to each reactant (Table 1). A log–log plot of k_1 *vs.* $[\mathrm{PBA}]_0$ for runs 1—5 (Table 1) gave a straight line of slope 0·97 and the k_1 value did not depend on the initial concentration of sulphine (runs 4 and 5); finally, k_2 values obtained as $k_1/[\mathrm{PBA}]_0$ were reproducible within experimental error (*ca.* ±3%) and agree with the value obtained in run 6 where comparable concentrations of the reactants were employed. For the reactions of sulphines (1e and f) in carbon tetrachloride and of (1b) in dioxan and isopropyl alcohol, the rate constants could not be obtained as described since concurrent decomposition of the sulphine occurred at a rate comparable to the peroxyacid oxidation. In fact the second-order rate constants k_2', calculated from the ratio $k_{\mathrm{obs}}/[\mathrm{PBA}]_0$, vary inversely with $[\mathrm{PBA}]_0$ (Table 2), thus indicating that the observed rate constants k_{obs} may be the sum of two terms, a first-order rate constant k_{D} for the decomposition of the sulphine and a pseudo-first-order term $k_1 = k_2[\mathrm{PBA}]_0$ for the peroxyacid oxidation. Plots of k_{obs} against $[\mathrm{PBA}]_0$ are linear and their slopes correspond to the second-order rate constant k_2.

TABLE 1

Rate constants for the reaction of di-*p*-tolyl sulphine (1c) (CSO) with perbenzoic acid in carbon tetrachloride at 25°

Run No.	1	2	3	4	5	6
$10^3[\mathrm{CSO}]_0/\mathrm{M}$	2·43	2·43	1·15	7·40	1·23	22·0
$10^2[\mathrm{PBA}]_0/\mathrm{M}$	4·89	4·87	8·05	13·1	14·5	14·25
$10^5k_1/\mathrm{s}^{-1}$ [a]	2·77	2·63	4·28	6·95	7·78	
$10^4k_2/\mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ [b]	5·66	5·40 [c]	5·32	5·30	5·37 [d]	5·08

[a] Values obtained from pseudo-first-order integrated plots. [b] Second-order rate constants were obtained as $k_2 = k_1/[\mathrm{PBA}]_0$ with the exception of run 6. [c] In the presence of 0·0024M-*p*-benzoquinone. [d] In the presence of 0·1M-benzoic acid.

TABLE 2

Rate constants for the reactions [a] between perbenzoic acid and sulphines (1e and f) (CSO) in carbon tetrachloride at 25°

Bis-*p*-chlorophenyl sulphine (1e)					
$10^3[\mathrm{CSO}]_0/\mathrm{M}$	3·01	2·40	2·86	2·40	2·47
$10^2[\mathrm{PBA}]_0/\mathrm{M}$	3·70	8·33	10·75	15·6	17·9
$10^5k_{\mathrm{obs}}/\mathrm{s}^{-1}$ [b]	0·950	1·80	1·78	2·86	2·95
$10^4k_2'/\mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ [c]	2·57	2·16	1·70	1·84	1·65
Bis-*m*-chlorophenyl sulphine (1f)					
$10^3[\mathrm{CSO}]_0/\mathrm{M}$	3·00	2·93	3·18		
$10^2[\mathrm{PBA}]_0/\mathrm{M}$	4·17	9·00	13·4		
$10^6k_{\mathrm{obs}}/\mathrm{s}^{-1}$ [b]	6·87	7·25	8·40		
$10^5k_2'/\mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$ [c]	16·2	8·07	6·27		

[a] Some of the reactions were carried out in the presence of *p*-benzoquinone (5—10% of $[\mathrm{PBA}]_0$). [b] Values obtained from pseudo-first-order integrated plots. [c] Second-order rate constants were obtained as $k_2' = k_{\mathrm{obs}}/[\mathrm{PBA}]_0$.

The rate constants and related data for the oxidation of sulphines (1) are collected in Table 3. A Hammett-type plot of the rate data gave the best linear correlation by using the sum $(\sigma^+ + \sigma)$[6] (ρ −1·16; r 0·982) or the sum $2\sigma^+$ (ρ −0·927; r 0·989) for each substituent; the correlation with 2σ values (ρ −1·45; r 0·924) is less satisfactory.* Nonetheless, the direction of the substituent effect is shown by the negative value of ρ, indicating that the sulphine acts as a nucleophile toward PBA. This result is common to the peroxyacid oxidation under neutral conditions of several substrates such as sulphoxides,[9] thiones,[2] pyridines,[10] dimethylanilines,[11] diazomethanes,[4b] stilbenes,[12] styrenes,[13] and phenylacetylenes;[14] in all these reactions the ρ values were negative, of modest size, and derived from correlation with σ^+ or σ-values.

TABLE 3

Rate constants [a] for the oxidation of sulphines (1) to ketones (2) with PBA in carbon tetrachloride at 25°

Sulphine	$10^4k_2/\mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$	Analytical λ/nm [b] (ε)
(1a)	1·28	330 (12,240)
(1b)	31·5	348 (15,900)
(1c)	5·32	335 (14,400)
(1d)	1·93	332 (12,530)
(1e)	1·20	335 (14,310)
(1f)	0·187	328 (13,070)

[a] Average values from four or more independent runs. [b] Analytical wavelength in carbon tetrachloride–cyclohexane (1 : 25 v/v).

Data chosen to elucidate the solvent effect on rates are given in Table 4. The reaction rates show little dependence on the solvent polarity as expressed by the dielectric constant, and they can be accounted for by specific solvent–solute interactions. The lower values of the rate constants are found in dioxan and isopropyl alcohol which are solvents capable of hydrogen bonding

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* The ρ value determined for systems having two identically substituted phenyl rings by assuming the additivity of σ values, may represent an upper or lower limit of the actual reaction constant.[7] This may be the case of the ρ values deduced from the correlations with $2\sigma^+$ or 2σ, whereas the value of −1·16 obtained from the correlation with $(\sigma^+ + \sigma)$ should be very close to the ‘ true ’ reaction constant. This also suggests that one substituent operates by a ‘ through resonance ’ effect and the other by a polar effect. In agreement with this suggestion, molecular models show that conjugation of the CSO group with both phenyl rings is prevented since the least crowded arrangement is that in which one phenyl ring is coplanar and the other is twisted out of planarity with the CSO group. Similar arguments have been advanced for the bromination of 1,1-diphenylethylenes[8] and the reaction of thiolate ions with 1,1-diphenyl-2-halogenoethylenes.[7a]

[6] L. P. Hammett, ‘ Physical Organic Chemistry,’ McGraw-Hill, New York, 1970, 2nd edn., p. 356.

[7] (*a*) P. Beltrame, D. Pitea, and M. Simonetta, *J. Chem. Soc.* (*B*), 1967, 1108; (*b*) D. F. Bender, T. Thippeswamy, and W. L. Rellahan, *J. Org. Chem.*, 1970, **35**, 939.

[8] J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, 1972, **37**, 2218; A. F. Hegarty, J. S. Lomas, W. V. Wright, E. D. Bergmann, and J. E. Dubois, *ibid.*, p. 2222.

[9] A. Cerniani and G. Modena, *Gazzetta*, 1959, **89**, 843.

[10] A. Dondoni, G. Modena, and P. E. Todesco, *Gazzetta*, 1961, **91**, 613.

[11] A. Dondoni and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1962, **20**, 79.

[12] D. R. Campbell, J. O. Edwards, J. Maclachlan, and K. Polgar, *J. Amer. Chem. Soc.*, 1958, **80**, 5308; B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1955, 1525.

[13] Y. Ishii and Y. Inamoto, *Kogyo Kagaku Zasshi*, 1960, **63**. 765.

[14] Y. Ogata, Y. Sawaki, and H. Inoue, *J. Org. Chem.*, 1973, **38**. 1044.

TABLE 4

Rate constants (k_2) for the oxidation of bis-*p*-methoxyphenyl sulphine (1b) (PMPS) to bis-*p*-methoxyphenyl ketone (2b) by perbenzoic acid and the ratios of the thiobenzophenone oxidation rate[a] k *vs.* PMPS oxidation rate in various solvents

Solvent[b]	Dielectric constant[c] (ε)	Temp. (°C)	10^3k_2/l mol^{-1} s^{-1}	k/k_2
CH_2Cl_2	9·08	25	6·28	7900
$CHCl_3$	4·81	25	5·07	15,700
CCl_4[d]	2·24	5	0·533	
		15	1·55	
		25	3·15	7300
		37	6·45	
Dioxan[e]	2·21	25	0·542	3500
Pr^{i}OH[e]	18·2	25	0·227	7600

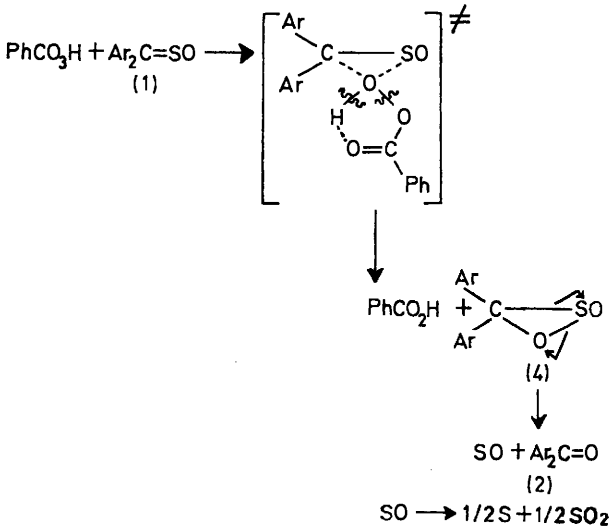
[a] k Values (at 20°) are from ref. 2 or calculated from linear trends cited therein. [b] The analytical wavelength after dilution with cyclohexane is that indicated in Table 3. [c] Data taken from ref. 3*a*. [d] Activation parameters were: $E_a = 13{\cdot}2$ kcal mol^{-1}, $\Delta S^{\ddagger}$ (25°) $= -28$ cal mol^{-1} K^{-1}. [e] The reactions were carried out in the presence of *p*-benzoquinone or allyl acetate (5—10% of $[PBA]_0$).

with PBA.[3,15] As discussed in detail,[3,15] this suggests for the reaction under study that PBA reacts through an internally stabilized five-membered ring; however, in alcoholic solvents this chelate form may not operate. Therefore, the observed trend of the rate constants mainly reflects the differences between ground-state and transition-state solvation of PBA. This is also supported by the log–log linear correlations[3] between the rate of oxidation by PBA of sulphine (1b) and those of other substrates for a given series of solvents. Actually, the rate data of Table 4 for methylene dichloride, carbon tetrachloride, and dioxan solutions correlate with those for oxidation of *p*-nitrophenyl phenyl sulphide,[3a] cyclohexene,[3a] and thiobenzophenone[2] in the same solvents. The values for chloroform and isopropyl alcohol do not give such a good correlation. This is probably due to solvation of the sulphine ground state which is no longer negligible in protic solvents.[16] Similar behaviour observed for the oxidation of sulphoxides to sulphones has been shown[17] to arise from specific interactions between the solvent and the sulphoxide group.

Final comment is reserved for the activation parameters evaluated in carbon tetrachloride (Table 4, footnote *d*). The activation entropy is almost the same as for related systems,[2,3a,4b] while the activation energy is higher and thus appears to be responsible for the lower rates of oxidation of sulphines than for sulphides, thiones, alkenes, and diazomethanes. Specifically, the possibility of obtaining sulphines by partial oxidation of thiones is due to the noticeable difference in activation energy between steps A and B.

Two reaction mechanisms fit the experimental data. In both the peroxyacid is considered to take part in the reaction through its chelate structure as deduced from the effect of solvent. Only for isopropyl alcohol it is likely[3a,15] that more complex mechanisms, involving solvent molecules in the transition state, are operating.

The first mechanism is a multi-step process (Scheme 1) involving the rate-determining primary formation of the cyclic sulphinic ester (4) from electrophilic attack of the peroxyacid on the carbon–sulphur double bond of CSO. Rapid cleavage of (4) gives the ketone (3) and sulphur monoxide, the latter disproportionating into sulphur and sulphur dioxide.



SCHEME 1

Transition states similar to that for the mechanism in Scheme 1 have been advanced for other reactions of peroxyacids with unsaturated centres, namely the epoxidation of olefins[12] and the primary formation of oxirens by oxidation of acetylenes.[14,*] Moreover, intermediate cyclic sulphinates of type (4) have been invoked[18] to account for the thermolytic conversion of thietan 1,1-dioxides into carbonyl compounds and sulphur monoxide. Finally, in the reaction of the cumulative, double-bond system of ketens with peroxyacids the transient formation of an α-lactone formally similar to (4) has been assumed.[19]

The mechanism in Scheme 2 resembles that outlined for the reaction of peroxyacids with diazoalkanes;[4b] this would require a one-step electrophilic attack of PBA on the carbon atom of the CSO group and the concerted extrusion of sulphur monoxide. This mechanism, however, even though in accord with the results of molecular orbital calculations[1,20] which indicate a small negative charge on carbon of the CSO group, does not find the support listed for the mechanism in Scheme 1. This,

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[*] Evidence for the transient formation of oxirens in the peroxyacid oxidation of acetylenes has been also reached through a study of solvent effects (J. O. Edwards, personal communication).

[15] R. Curci, R. A. Di Prete, J. O. Edwards, and G. Modena, 'Hydrogen-bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 301.

[16] B. F. Bonini, S. Ghersetti, G. Maccagnani, and G. Mazzanti, *Boll. sci. Fac. Chim. ind. Bologna*, 1969, **27**, 401.

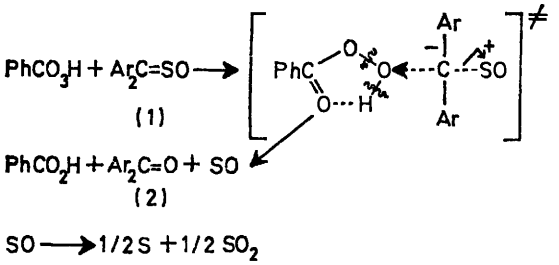
[17] G. Modena and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 31 (*cf.* ref. 3*a*, p. 237 and ref. 15, p. 316).

[18] C. L. McIntosh and P. De Mayo, *Chem. Comm.*, 1969, 32.

[19] J. K. Crandall and S. A. Sojka, *Tetrahedron Letters*, 1972, 1641.

[20] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 557.

especially in view of the similarity of our oxidation with those of olefins and acetylenes, seems more probable. It may also be observed that a modification of the mechanism in Scheme 2 into a multi-step process, in which the rate-determining step is formation of a dipolar intermediate,[1] is hardly acceptable on the basis of the insensitivity of the reaction rate to solvent polarity.

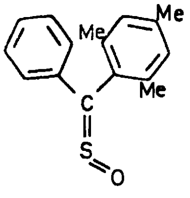
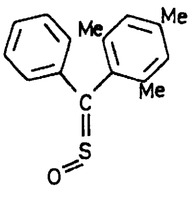
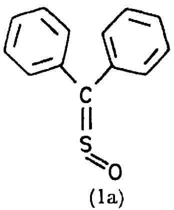


SCHEME 2

In order to find further evidence in favour of the mechanism in Scheme 1 the rates of oxidation of mesityl phenyl sulphine (5a) and its geometrical isomer (5b) have been measured and are reported in Table 5 along with those of diphenyl sulphine (1a) for comparison. These results show a small difference between the rate constants of the *E*- and *Z*-isomers of mesityl phenyl sulphine (5) and between these and the rate for (1a). This indicates that the configuration of the substrate and the presence of the *o*-methyl groups in one phenyl ring are not relevant in oxidation by PBA.

TABLE 5

Rate constants for the oxidation of sulphines (5) and (1a) with perbenzoic acid in carbon tetrachloride at 25°

Sulphine [a]			
	(5a) (*E*-isomer)	(5b) (*Z*-isomer)	(1a)
10^5k/l mol^{-1} s^{-1}	1·57	6·75	12·8

[a] The analytical wavelengths [λ/nm (ε)] in carbon tetrachloride–cyclohexane (1 : 25 v/v) were: 332 (11,500) for (5a) and 337 (13,420) for (5b); for (1a) see Table 3.

This suggests an attack by the peroxyacid on a reaction zone removed from the region of structural changes,[21] *i.e.* on the carbon–sulphur double bond rather than on the carbon atom. In the oxidation of thiones where attack on sulphur has been demonstrated,[2] the steric and conformational effects are even less important since mesityl phenyl thione reacts with PBA (k 35 l mol^{-1} s^{-1} in CCl_4 at 25°) almost at the same rate as thiobenzophenone.[2] Conversely, the reactivity ratio for thioanisole and mesityl methyl sulphide [22] to give the corresponding sulphoxides is *ca.* 13. These results thus give further support for the mechanism in Scheme 1.

Other mechanisms besides those examined here, for instance that involving rapid hydrogen exchange between PBA and the sulphine and subsequent rate-determining nucleophilic attack by the peroxide anion on the protonated sulphine, are hardly acceptable as discussed in detail for similar cases.[4b] Added benzoic acid (Table 1), which is a stronger acid than PBA, does not affect the rate and this is in accord with this conclusion.

Besides the elucidation of mechanism which was our primary aim, the present study and the previous one [2] on the oxidation of thiones to sulphines provide results of synthetic utility. In fact the ratio between the rate constants of steps A and B (Table 4) is sensitive to solvent and reaches a maximum value * in chloroform which thus appears to be the most suitable solvent for obtaining selective oxidation of thiones to sulphines.

EXPERIMENTAL

Materials.—Solvents were purified by standard procedures [23] and fractionally distilled. Commercial *p*-benzoquinone and allyl acetate were purified [24] before use. Perbenzoic acid of high purity (99%) was obtained as described.[2] The majority of thiobenzophenones, starting materials for the synthesis of sulphines, were prepared as reported [2] or as described.[25] The following new thione was prepared by a standard method: [26] *di*-m-*chlorothiobenzophenone*, m.p. 64—66° (from light petroleum) (Found: C, 58·4; H, 3·05; S, 12·6. $C_{13}H_8Cl_2S$ requires C, 58·4; H, 3·0; S, 12·0%).

Sulphines (1) and (5) were prepared by oxidation of the corresponding thiones with perbenzoic or monoperphthalic acid and gave physical data in agreement with those in the literature.[2,20,25,27] The new compound, *bis*-m-*chlorophenyl sulphine* (1f), was prepared, m.p. 62—64° (from benzene–light petroleum) (Found: C, 54·9; H, 2·75; S, 11·5. $C_{13}H_8Cl_2OS$ requires C, 55·1; H, 2·85; S, 11·3%).

Characterisation of Products.—Benzophenones (2) and mesityl phenyl ketone as well as phenyl benzoates (3) were obtained from small-scale preparations under conditions identical to the kinetic experiments. The products were isolated, together with elemental sulphur, by chromatography of the reaction mixture on silica plates using benzene–light petroleum (1 : 2) as eluant; in the case of (2b) and (3b) the eluant was diethyl ether–light petroleum–benzene (1 : 5 : 15). In all experiments the ketone was by far the major product and in some cases the ester was isolated only in traces. The total yields of products were 90—95% and the identities were checked by mixed m.p.s and/or comparison of the i.r. spectra with those of authentic specimens.[24]

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* The ratios of Table 4 have to be considered as merely indicative because of the different temperatures at which two reactions were carried out.

[21] M. S. Newman, 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 4; ref. 6, p. 369.

[22] G. M. Gasperini, G. Modena, and P. E. Todesco, *Gazzetta*, 1960, **9**, 12.

[23] A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, 1955, vol. VII.

[24] 'Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[25] A. Tangerman, L. Thijs, A. P. Anker, and B. Zwanenburg, *J.C.S. Perkin II*, 1973, 458.

[26] N. Lozac'h and G. Guillouzo, *Bull. Soc. chim. France*, 1957, 1221.

[27] J. Strating, L. Thijs, and B. Zwanenburg, *Tetrahedron Letters*, 1966, 65.

*Reaction Stoicheiometry.**—The reaction was shown to have the stoicheiometry of equation (1) by using di-*p*-tolyl sulphine (1c) as a typical example. Sulphur [28] and sulphur dioxide [29] were determined by standard methods. Similarly the organic products, benzoic acid [24] and di-*p*-tolyl ketone,[2] were estimated as before.

*Kinetics.**—The peroxyacid solution (40—50 ml) was placed in a thermostatted flask (±0·2°) and pure nitrogen [30] was bubbled through for 5 min. The reaction was initiated by the addition of a weighed amount of sulphine. At suitable intervals, aliquot portions (2·5 or 5 ml) were withdrawn and after rapid dilution to 50 or 100 ml in cyclohexane, the sulphine was monitored spectrophotometrically (Cary 14 spectrophotometer) by measuring the absorbance at the wavelengths indicated in Tables 3 and 5. Reactions were carried out under pseudo-first order conditions by using at least a ten-fold excess of PBA. The initial concentrations of the sulphines were in the range 0·002—0·02M.

The rate constants determined at different temperatures (Table 4) obeyed the Arrhenius equation and the activation parameters were evaluated by standard methods.[31]

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* Details of the apparatus and procedure are available from the authors on request.

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