Kinetics of the Base-catalysed Oxidation of Sulphoxides with 1-Methyl-1-phenylethyl Hydroperoxide

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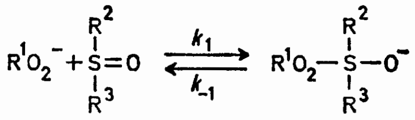
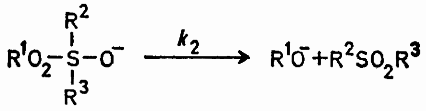
The kinetics of the base-catalysed oxidation of dialkyl sulphoxides with 1-methyl-1-phenylethyl hydroperoxide have been studied in mixtures of benzene and protic solvents. The reaction rate is expressed as $v = k[\mathrm{RSOR}][\mathrm{PhCMe_2O{\cdot}ONa}][\text{protic solvent}]^{-n}$, where n increases with increasing acidity of solvent. The rate of oxidation changes with solvent in the order n-butyl alcohol > isopropyl alcohol > 1-methyl-1-phenylethyl hydroperoxide > t-butyl alcohol. A positive ρ^* value of $+2{\cdot}8$ has been obtained. A probable mechanism which explains these results is discussed.

THE peroxyacid oxidation of dialkyl, diaralkyl, and diaryl sulphoxides to the corresponding sulphones has been studied extensively.[1] The SO group can be oxidized in basic media by nucleophilic attack of the peroxyacid anion (R = acyl). The addition stage (1) is



$$R^1O_2^- + \overset{R^2}{\underset{R^3}{S}}{=}O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^1O_2{-}\overset{R^2}{\underset{R^3}{S}}{-}O^- \quad (1)$$



$$R^1O_2{-}\overset{R^2}{\underset{R^3}{S}}{-}O^- \xrightarrow{k_2} R^1O^- + R^2SO_2R^3 \quad (2)$$

often much slower than the subsequent step (2) since the O–O bond energy is fairly small, resulting in an easy fission of the bond.[2]

Curci and Modena[3] reported that the oxidation of sulphoxide to sulphone with organic hydroperoxides (R = alkyl or aralkyl) did not occur in spite of the high nucleophilicity of peroxide, since the alkoxide ions formed are poor leaving groups. However, their reactions were conducted in aqueous alkaline media which can readily associate with the anion and the solvation may reduce the activity of the peroxide anion in the addition step (1). The reactivity of peroxide anion can be increased by carrying out the reaction in non-aqueous media.

During our study on organic hydroperoxides, it was found that oxidation of sulphoxide by hydroperoxide occurred quantitatively in non-aqueous alkaline media but not in aqueous ones.[4] Also the addition of protic components such as alcohols as well as water to the reaction solvent retarded the oxidation.

Our purpose is to elucidate the mechanism and the effect of solvent on the oxidation of sulphoxides with the sodium salt of 1-methyl-1-phenylethyl hydroperoxide.

RESULTS

Stoicheiometry.—Dimethyl sulphone and αα-dimethylbenzyl alcohol were obtained on oxidation of dimethyl sulphoxide with the sodium salt of 1-methyl-1-phenylethyl hydroperoxide (RO·ONa). The stoicheiometry shows that 1 equiv. of sulphoxide reacts with 1 equiv. of RO·ONa to give a mixture of 1 equiv. of sulphone and αα-dimethylbenzyl alcohol.

Kinetics.—The kinetics of oxidation of dimethyl sulphoxide with RO·ONa were studied in benzene–isopropyl alcohol (9 : 1, v/v) at 25 °C. The rates were followed by analysing the peroxide in aliquot portions by iodometry.

The rate of base-catalysed decomposition of peroxide was negligible, since the solution of sodium salt of 1-methyl-1-phenylethyl hydroperoxide in benzene–isopropyl alcohol (9 : 1) in the absence of dimethyl sulphoxide was stable for 1—2 h at 25 °C.

Pseudo-first-order rate constants for the disappearance of RO·ONa were measured in benzene–isopropyl alcohol at 25 °C. Table 1 shows that the reaction rate is expressed by equation (3).

$$v = k_{2.\mathrm{obs}}[\mathrm{Me_2SO}][\mathrm{RO{\cdot}ONa}] \qquad (3)$$

Substituent Effect.—The effect of substituents in the sulphoxide on the pseudo-first-order rate constants with peroxide, $k_{1,\mathrm{obs}}$, was studied. Table 2 shows that the Taft equation $\log(k/k_0) = \rho^*\sigma^*$ is satisfied. The Taft ρ^* value, which was calculated from dimethyl, diethyl, and di-n-propyl sulphoxides, was $+2{\cdot}8$.

TABLE 1

Effect of initial concentration of reactants in benzene–isopropyl alcohol (91 : 9) at 25 °C

[Reactant]/M		
RO·ONa	$\mathrm{Me_2SO}$	$10^4k_{1,\mathrm{obs}}/\mathrm{s}^{-1}$
Effect of initial concn. of RO·ONa		
0·014	0·20	1·50 [a]
0·027	0·20	2·80 [a]
0·054	0·20	5·40 [a]
Effect of initial concn. of $\mathrm{Me_2SO}$		
0·29	0·040	3·50 [b]
0·29	0·060	5·50 [b]
0·29	0·082	6·85 [b]
0·29	0·092	8·05 [b]

[a] In benzene–isopropyl alcohol (4 : 1). $v = k_{1.\mathrm{obs}}[\mathrm{RO{\cdot}ONa}]$.
[b] $v = k_{1,\mathrm{obs}}[\mathrm{Me_2SO}]$.

Solvent Effect.—The effect of protic compounds on the oxidation of dimethyl sulphoxide was examined in mixtures of benzene and a number of alcohols at 25 °C. In all experiments, the sodium salt of the hydroperoxide (0·08 mol) was added to excess of sulphoxide (0·8 mol) at various concentrations of alcohol in benzene–alcohol as solvent. Pseudo-second-order rate constants for the disappearance of the peroxide, summarized in Table 3, are correlated by

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[1] R. Curci and G. Modena, *Tetrahedron*, 1963, 1947; 1965, 863.

[2] C. A. Bunton, 'Peroxide Reaction Mechanisms,' ed. J. O. Edwards, Interscience, New York, 1962, p. 11.

[3] R. Curci and G. Modena, *Tetrahedron*, 1966, **22**, 1227, 1235.

[4] Y. Ogata and S. Suyama, *Chem. and Ind.*, 1971, 707.

equation (4). Here, $k_{2,\mathrm{obs}}$, k, and $-n$ are the pseudo-

$$k_{2,\mathrm{obs}} = k[\mathrm{R^2OH}]^{-n} \qquad (4)$$

second-order rate constant, the overall rate constant, and the order with respect to alcohol, respectively. The plot of log $k_{2,\mathrm{obs}}$ against log [$\mathrm{R^2OH}$] for equation (4) gives n from the slope. The order with respect to alcohol is negative for the alcohols used and decreases with increasing acidity of alcohol in a mixture of benzene and alcohol; *i.e.*, t-butyl alcohol (pK_a 19 [5]) > isopropyl alcohol (pK_a 18 [5]) > n-butyl alcohol.[5] Hence the overall rate equation is expressed as (5).

$$v = k[\mathrm{Me_2SO}][\mathrm{R^1O{\cdot}ONa}][\mathrm{R^2OH}]^{-n} \qquad (5)$$

TABLE 2

Effect of substituent in sulphoxide on the first-order rate constants [a] in benzene–isopropyl alcohol (9 : 1) [b]

Reactant	$10^4k_{1,\mathrm{obs}}/\mathrm{s^{-1}}$ 2 °C	20 °C	30 °C	E_a/kcal mol^{-1}	Relative rate at 20 °C
$\mathrm{Me_2SO}$	0·184	0·166	20·0	22·2	4·50
$\mathrm{Et_2SO}$	0·056	0·603	5·80	21·9	1·60
$\mathrm{Pr_2SO}$	0·035	0·384	4·35	22·8	1·00
Tetrahydrothiophen oxide	0·148	1·23	16·1	22·2	3·26

[a] Pseudo-first-order rate constants, $v = k_{1,\mathrm{obs}}[\mathrm{RO{\cdot}ONa}]$. [b] Initial concentration: $\mathrm{PhCMe_2{\cdot}OOH}$, 0·05M; sulphoxide, 0·20M; sodium isopropoxide, 0·025M.

TABLE 3

Second-order rate constants [a] and the order with respect to alcohols for the oxidation of dimethyl sulphoxide (0·80M) with the sodium salt of 1-methyl-1-phenylethyl hydroperoxide (0·08M) in benzene–alcohol at 25 °C

[Isopropyl alcohol] [b]/M	$10^2k_{2,\mathrm{obs}}$/l mol^{-1} s^{-1}	Order in alcohol
0·66	7·90	
0·99	3·62	−1·80
1·32	1·67	
1·65	1·50	
[n-Butyl alcohol] [b]/M		
0·55	7·30	
1·09	1·45	−3·47
1·63	0·39	
2·18	0·14	
[t-Butyl alcohol] [b]/M		
0·53	12·5	
1·05	8·80	−1·62
1·32	6·00	
1·58	4·45	
2·10	2·92	
[$\mathrm{PhCMe_2{\cdot}O{\cdot}OH}$] [c]/M		
0·04	14·2	
0·09	10·8	−1·75
0·14	5·70	
0·23	1·80	
0·42	0·79	

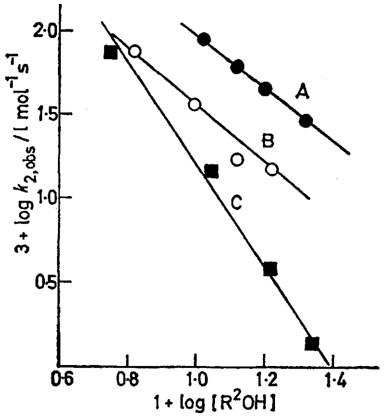
[a] $v = k_{2,\mathrm{obs}}[\mathrm{RO{\cdot}ONa}][\mathrm{Me_2SO}]$. [b] Dielectric constants of these alcohols are: $\mathrm{Bu^nOH}$, 17·1 at 25 °C; $\mathrm{Pr^iOH}$, 18·3 at 25 °C; $\mathrm{Bu^tOH}$, 10·9 at 30 °C [5] (A. A. Maryott and E. A. Smith, 'Tables of Dielectric Constants of Pure Liquids,' NBS Circular 514, 1951). [c] Solvent: benzene–isopropyl alcohol (9 : 1).

Effect of Radical Inhibitors.—The g.l.c. analysis of gas emitted from the reaction mixture shows that neither evolution nor absorption of oxygen occurs. The addition of a small amount of diphenylpicrylhydrazyl (DPPH), a radical trapper, had no effect on the rate in benzene–isopropyl alcohol (9 : 1) at 20 °C; *i.e.*, in the presence of 0·025M-DPPH, $k_{2,\mathrm{obs}} = 1{\cdot}10 \times 10^{-4}$ l mol^{-1} s^{-1}; in its absence, $k_{2,\mathrm{obs}} = 1{\cdot}25 \times 10^{-4}$ l mol^{-1} s^{-1}.

DISCUSSION

The mechanism for the peroxyacid anion oxidation [3] of sulphoxides might be applied to the present hydroperoxide oxidation. But these two reactions differ in the following features. The peroxyacid anion oxidation affords sulphones in aqueous media, while the hydroperoxide anion oxidation afford sulphones only in non-aqueous media and gives a poor yield in aqueous media.[4]

Active Species.—The rate-dependence on solvent acidity (Table 3), and the reactivity of the sodium salt of hydroperoxide,[4] suggest that an electrophilic attack of undissociated hydroperoxide on the sulphur atom is unimportant, while nucleophilic attack of 1-methyl-1-phenylethyl peroxide anion on the sulphur atom is favoured.



Dependence of the second-order rate constant on alcohol concentration for the oxidation of $\mathrm{Me_2SO}$ with the sodium salt of cumene hydroperoxide in benzene–alcohol at 25 °C: A, $\mathrm{Bu^tOH}$; B, $\mathrm{Bu^nOH}$; C, $\mathrm{Pr^iOH}$

Kinetics.—The hydroperoxide oxidation of dimethyl sulphoxide is expressed kinetically as equation (5). The first-order dependence on both the sodium salt of the hydroperoxide and sulphoxide is consistent with a mechanism involving an intermediate as shown in equations (1) and (2). A stationary concentration of the intermediate being assumed, equations (1) and (2) lead to the rate expression (6) where the subscripts now

$$\mathrm{d[product]}/\mathrm{d}t = k_1k_2[\mathrm{Me_2SO}][\mathrm{RO{\cdot}O^-}]/(k_{-1} + k_2) \qquad (6)$$

refer to equations (1) and (2).

As will be discussed, the intermediate adduct in reactions under basic conditions in a non-aqueous solvent may release peroxide anion much more easily than it collapses to sulphone and alkoxide ion, *i.e.*,

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[5] The pK_a values of alcohols in benzene were reported to be $\mathrm{Bu^tOH}$, 19 and $\mathrm{Pr^iOH}$, 18 (W. K. McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124). Further, it is said that n-butyl alcohol is more acidic than isopropyl or t-butyl alcohol (J. D. Roberts and M. C. Caserio, 'Basic Principles of Organic Chemistry,' Benjamin, New York, 1964, p. 384).

$k_2 \ll k_{-1}$. Therefore, the observed rate constant k_{obs} [equation (3)] should be equal to k_1k_2, where K_1 is k_1/k_{-1}, *i.e.*, the equilibrium constant of equation (1).

The anion in protic solvents is solvated by the molecules of solvent through hydrogen bonding;[6] the observed decrease of anion reactivity by protic solvents may be ascribed to the enhancement of their solvation. The rate-retarding effect of protic component in the oxidation may also be explained by similar hydrogen bonding. Then the overall rate equation for the oxidation with the peroxide anion can be expressed as (7). The observed linear dependence of v on $[R^2OH]^{-n}$

$$v = k[R^1O{\cdot}ONa][Me_2SO][R^2OH]^{-n} \qquad (7)$$

means that the extent of retardation of reaction is small at low alcohol concentration. The order in alcohol is explained by the tendency of solvation, where n is the number of molecules of alcohol in a solvated shell [equation (8)].

$$R^1O{\cdot}O^- + nR^2OH \rightleftharpoons [R^1O{\cdot}O^-(HOR^2)_n] \qquad (8)$$

The nucleophilic reactivity of desolvated ion $R^1O{\cdot}O^-$ should be much higher than that of solvated hydrogen-bonded forms, $R^1O{\cdot}O^-(HOR^2)_n$. The lower rate at higher alcohol concentration may be due to a decrease in concentration of free hydroperoxide ion.

Equation (8) gives the expression (9). The concen-

$$[R^1O{\cdot}O^-] = [R^1O{\cdot}O^-(HOR^2)_n]/(K_8[R^2OH]_{free}{}^n) \qquad (9)$$

tration of free alcohol in equation (9) is practically the same as the total concentration of alcohol, since the concentration of alcohol is much larger than that of peroxide ion; *i.e.*, equation (10) holds. Introduction

$$[R^2OH]_{free} \simeq [R^2OH]_{total} \qquad (10)$$

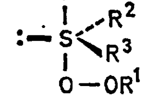
of $[R^1O{\cdot}O^-]$ in equation (6) gives equation (11). Here,

$$v = k'[R^1O{\cdot}O^-(HOR^2)_n][Me_2SO][R^2OH]_{total}{}^{-n} \qquad (11)$$

$k' = k_1k_2/K_8(k_{-1} + k_2)$. This is practically identical with the experimentally observed rate equation (5), because $[R^1O{\cdot}O^-(HOR^2)] \simeq [R^1O{\cdot}O^-]_{total}$. The values of n decreased in the order t-butyl alcohol > isopropyl alcohol > n-butyl alcohol. The marked dependence of rate on alcohol acidity shows that the hydrogen bonding between peroxy-anion and alcohol is important. The low yield of sulphones observed in aqueous media[4] is probably caused by the solvation of peroxide ion with water and the base-catalysed decomposition of the hydroperoxide to αα-dimethylbenzyl alcohol and oxygen.

The reactive peroxide ion should also be solvated by hydroperoxide itself. The order n for hydroperoxide was expected to be higher, since the acidity of cumene hydroperoxide ($pK_a = 12{\cdot}6$)[7] is lower than that of the above alcohols, but the observed n value was similar to those for isopropyl or t-butyl alcohol. This may be ascribed to the formation of a stable equimolar complex with free hydroperoxide and the peroxide ion or sodium salt of hydroperoxide.[8,9] The further hydrogen bonding to the equimolar complex may be difficult because of the steric hindrance between 1-methyl-1-phenylethyl groups.

Substituent Effects.—The effect of alkyl substituents (Table 2) shows that the alkyl substitution on the S=O group causes only a slight change in the rate. The ρ^* value in the Taft equation in benzene–isopropyl alcohol at 20 °C is *ca.* $+2{\cdot}8$, which is similar to the value reported for the perbenzoate ion oxidation of dialkyl sulphoxides ($+2{\cdot}04$).[3] Hence, the activated complex in the cumene hydroperoxide anion oxidation of sulphoxide has probably an analogous configuration (I),[3] formed by overlapping of the oxygen *p* orbital of peroxide ion with the *d* orbital of the sulphur atom of the sulphoxide.



(I)

The rate-determining step for the peroxide anion oxidation of sulphoxide to sulphone may be a cleavage of the O–O bond in (I) rather than a nucleophilic attack of peroxide ion on the SO group, as postulated for the perbenzoic acid oxidation of sulphoxides on examination of the effect of substituents.[3] The hydroperoxide ion is more nucleophilic than the perbenzoate ion; on the other hand, alkoxide ion as a leaving group is less effective than benzoate ion. Hence, the formation of (I) is faster than its collapse *via* O–O bond scission.

As to the possibility of induced decomposition of peroxide ion, there was neither evolution nor absorption of oxygen; hence the autoxidation with hydroperoxide as a carrier, as reported for the hydroperoxide oxidation of cyclohexyl methyl sulphide,[10] can be ruled out.

Another scheme may be a radical-chain mechanism, *e.g.*, the decomposition of 1-methyl-1-phenylethyl hydroperoxide and of its complex with the sodium salt[8] giving radicals, which can act as reactive species, the mechanism leading eventually to acetophenone as a main product.[8] However, the radical mechanism is improbable, since (i) the addition of a small amount of diphenylpicrylhydrazyl has no effect on the rate and (ii) the main product is αα-dimethylbenzyl alcohol.

EXPERIMENTAL

Materials.—Dialkyl sulphoxides were of reagent grade and distilled under reduced nitrogen pressure; dimethyl sulphoxide, b.p. 80 °C at 23 mmHg (lit.,[3] 87 °C at 18 mmHg), diethyl sulphoxide, b.p. 98—100 °C at 25 mmHg (lit.,[11]

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[6] B. A. Feit and Z. Bigon, *J. Org. Chem.*, 1969, **34**, 3942.

[7] J. M. Kolthoff and A. I. Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3789.

[8] V. A. Belyaev and M. S. Nemtsov, *Zhur. obshchei Khim.*, 1962, **32**, 3483.

[9] W. Waters, 'Mechanism of Oxidation of Organic Compounds,' Methuen, London, 1964, p. 46.

[10] D. Barnard, *J. Chem. Soc.*, 1956, 2845.

[11] D. Barnard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, 1949, 2442.

88—90 °C at 12 mmHg), di-n-propyl sulphoxide, m.p. 15 °C (lit.,[12] 18 °C), tetrahydrothiophen oxide, b.p. 124 °C at 21 mmHg (lit.,[13] 106 °C at 12 mmHg). 1-Methyl-1-phenylethyl hydroperoxide, 83% pure, was supplied by Nippon Oils and Fats Co. Ltd., the impurity being mainly cumene. Alcohols and benzene of reagent grade were dried (Na) and distilled.

Preparation of Reagents.—Kharasch's method [14] was applied for the preparation of the sodium salt of 1-methyl-1-phenylethyl hydroperoxide. Metallic sodium was dissolved with stirring in a mixture of the hydroperoxide and benzene. The filtered solution is comparatively unstable at room temperature and is reduced to αα-dimethylbenzyl alcohol even after 2 h. Hence a fresh solution was used in kinetic runs.

Products.—The products were detected by g.l.c. with a Yanagimoto GCG-550 programmed gas chromatograph. G.l.c. columns used were 1·0 m PEG 20M 2% on Chamelite.

Kinetics.—A typical experiment for the rate measurements was as follows. A solution (10 ml) of 0·72M-dimethyl sulphoxide in isopropyl alcohol and a solution (90 ml) of 0·08M-sodium salt of 1-methyl-1-phenylethyl hydroperoxide in benzene, which had previously come to thermal equilibrium (25 ± 0·2 °C), were mixed to start the reaction. Aliquot portions (1 ml) were pipetted out at regular intervals and the content of hydroperoxide was evaluated by iodometry. The base-catalysed decomposition of the sodium salt was negligible within 1 h under these conditions.

Gas Analysis.—The evolved gas was collected in a flask over water. The collected gas was transferred into a gas sampler and analysed by g.l.c. by use of a column of molecular sieve 13X. It was thus found that the gas collected with t-butyl alcohol contained only a small amount of ethane besides the gas of atmospheric composition, *i.e.*, $N_2 : O_2 = 79 : 21$ (v/v).

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[12] W. Strecker, *Ber.*, 1926, **59**, 1765.

[13] D. S. Tarbell and S. Weaver, *J. Amer. Chem. Soc.*, 1941, **63**, 2941.

[14] M. S. Kharasch, A. Fono, W. Nudenberg, and B. Bischof, *J. Org. Chem.*, 1952, **17**, 212.