Mechanism of Antioxidant Action: Reactions of Alkyl and Aryl Sulphides with Hydroperoxides

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The aryl sulphides 3,3',5,5'-tetra-t-butyl-4,4'-dihydroxydiphenyl sulphide (1), the corresponding disulphide (2), trisulphide (3), and tetrasulphide (4), and the alkyl sulphides di-t-butyl sulphide (7) and dibenzyl disulphide (10) have been used to catalyse the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide) at 393 K. The decompositions are catalytic pseudo-first-order reactions. The kinetic data and product studies demonstrate that the catalyst for hydroperoxide decomposition is sulphur dioxide. The mechanism for formation of the sulphur dioxide has been demonstrated to involve oxidation of the sulphides and decomposition of the resulting thermally unstable sulphur–oxygen compounds. The results demonstrate that the thermal chemistry of sulphur–oxygen compounds (sulphoxides, thiolsulphinates, *etc.*) formed from the sulphides determines whether or not the sulphide will catalyse hydroperoxide decomposition.

It has been known for some time that certain alkyl and aryl mono-, di-, and poly-sulphides act as antioxidants and prevent the free radical oxidation of hydrocarbons.[1,2] The antioxidant mechanism of these compounds has been the focus of considerable research which has shown that sulphides can act both as free radical scavengers,[3-7] and hydroperoxide decomposers.[4-14] The sulphide will be a free radical scavenger if the sulphur–oxygen compound that is formed by oxidation can decompose to form a sulphenic acid.[3,7] Thus, for example, di-t-butyl sulphide acts as a free radical scavenger by forming t-butylsulphenic acid [reactions (1)—(3)].

$$(CH_3)_3C{\cdot}S{\cdot}C(CH_3)_3 \longrightarrow (CH_3)_3C{\cdot}S(O){\cdot}C(CH_3)_3 \quad (1)$$

$$(CH_3)_3C{\cdot}S(O){\cdot}C(CH_3)_3 \longrightarrow (CH_3)_3CSOH + (CH_3)_2C{=}CH_2 \quad (2)$$

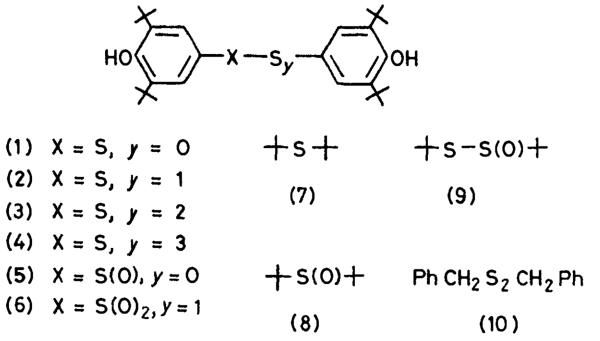
$$(CH_3)_3CSOH + ROO^{\cdot} \longrightarrow (CH_3)_3CSO^{\cdot} + ROOH \quad (3)$$

The mechanism for hydroperoxide decomposition is less certain. Previous work has established that (i) the effect of the sulphide is catalytic and (ii) the catalyst that decomposes the hydroperoxide is not the sulphide but a product that is formed from the sulphide. Circumstantial evidence has indicated that the catalyst is sulphur dioxide.[2,5,6,8-10] This compound is known to be a very effective catalyst for hydroperoxide decomposition [8-10,14,15] and is thought to act as a Lewis acid.[15]

In this paper we demonstrate that at elevated temperatures sulphur dioxide is the catalyst which is formed from sulphides that act as hydroperoxide decomposers. Also we shall show that sulphur dioxide is formed by oxidation of the sulphides and pyrolysis of the resulting thermally unstable sulphur–oxygen compounds.

RESULTS AND DISCUSSION

At 393 K the aryl sulphides (1)—(4), the sulphoxide (5), the thiolsulphonate (6), di-t-butyl sulphide (7), di-t-butyl sulphoxide (8), t-butyl 1,1-dimethylethanethiolsulphinate (9), and dibenzyl disulphide (10) decomposed cumene hydroperoxide.



The effect of the sulphur compounds was catalytic. In all the experiments the sulphur compound (5—60×10^{-6} mol dm^{-3}) decomposed $>50\%$ of the cumene hydroperoxide (0.2 mol dm^{-3}) over a period of 6 h. All the decompositions followed the same pattern. There was a rapid initial reaction that was complete in *ca.* 0.25 h. After this the reaction slowed down and from 2.00 to 6.00 h the decomposition followed good first-order kinetics. However, we found that the first-order rate constant for the hydroperoxide decomposition was dependent upon the initial concentration of the sulphur compound. Thus the rate constant was related to the concentration of the sulphur compound by equation (4)

$$k_n = A_n + B_n[S] \qquad (4)$$

where k_n is the first-order rate constant, A_n and B_n are constants, and [S] is the concentration of the sulphur compound expressed as a concentration of sulphur

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[2] G. Scott, *Mechanisms of Reactions of Sulphur Compounds*, 1969, **4**, 99.

[3] P. Koelewijn and H. Berger, *Rec. Trav. chim.*, 1972, **91**, 1275.

[4] G. Scott, *Pure Appl. Chem.*, 1972, **30**, 267.

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[6] C. Armstrong, M. A. Plant, and G. Scott, *European Polymer J.*, 1975, **11**, 161.

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[8] J. D. Holdsworth, G. Scott, and D. Williams *J. Chem. Soc.*, 1964, 4692.

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[12] G. Scott and P. A. Shearn, *J. Appl. Polymer Sci.*, 1969, **13**, 1329.

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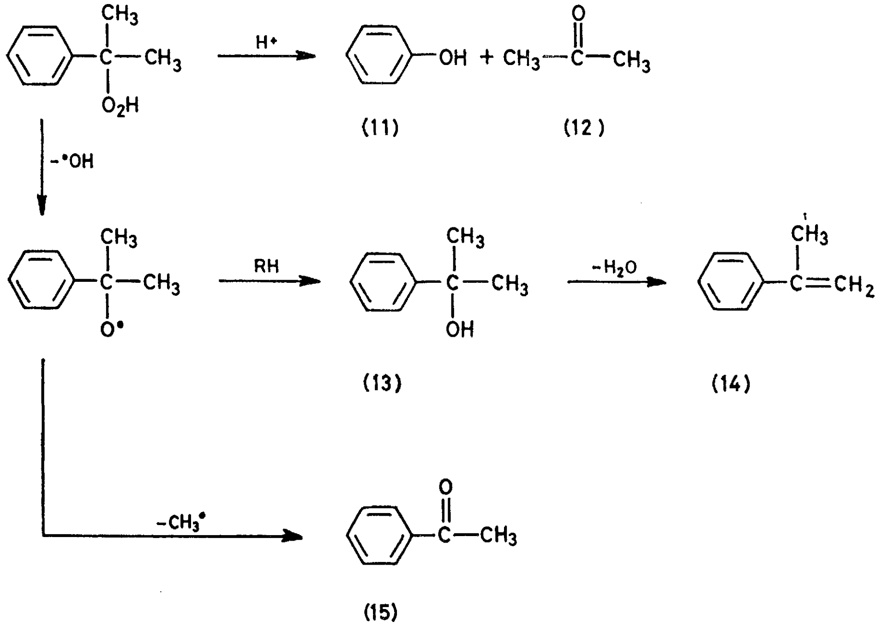
(S_1, mol dm^{-3}). This allows us to compare mono- and di-sulphides at the same sulphur level.

TABLE 1

Values of A_n and B_n for the compounds (1)—(10)

Compound	$10^2 A_n$/h^{-1}	$10^{-3} B_n$/h^{-1} mol^{-1} dm^3
(1)	(3.71 ± 0.62)	(1.36 ± 0.15)
(2)	(4.48 ± 1.17)	(1.83 ± 0.26)
(3)	(0.98 ± 1.28)	(2.06 ± 0.33)
(4)	(0.38 ± 0.34)	(2.11 ± 0.11)
(5)	(3.92 ± 0.55)	(0.98 ± 0.13)
(6)	(4.43 ± 0.04)	(1.86 ± 0.10)
(7)	(1.77 ± 1.14)	(1.23 ± 0.18)
(8)	(0.20 ± 0.78)	(1.14 ± 0.12)
(9)	−(0.51 ± 1.08)	(1.16 ± 0.18)
(10)	−(0.21 ± 1.06)	(2.19 ± 0.16)

The values of A_n and B_n were calculated for each sulphur compound using linear regression analysis. The results are shown in Table 1. The errors quoted represent 95% confidence limits on each result.



From Table 1 it is clear that (i) the rate of change of k_n with respect to [S] is not significantly different for the disulphide (2), the trisulphide (3), and the tetrasulphide (4), (ii) the value of B for the sulphide (1) is significantly less than the value for compounds (2)—(4), and (iii) the values of B for di-t-butyl sulphide (7), di-t-butyl sulphoxide (8), and t-butyl 1,1-dimethylethanethiolsulphinate (9) are not significantly different.

Kharasch *et al.*[16] have demonstrated that the major products obtained from the decomposition of cumene hydroperoxide are phenol (11), acetone (12), 2-phenylpropan-2-ol (13), 2-phenylpropene (14), and acetophenone (15).

In a series of experiments using the sulphides (1)—(4), the sulphoxide (8), and the thiolsulphinate (9) at a fixed concentration of sulphur the hydroperoxide decomposition products were analysed using h.p.l.c. The results are shown in Table 2 expressed as a percentage of the hydroperoxide decomposed. No attempt was made to analyse for acetone because it is not easily detected at the u.v. wavelength used (see Experimental section) and also the high reaction temperatures would make quantitative estimation very difficult.

TABLE 2

Product analysis of cumene hydroperoxide decompositions catalysed by sulphur compounds. [S_1] 44.6 × 10^{-6} mol dm^{-3}; T 393 K

Compound	(11)(%)	[(13) + (14)] (%)[a]	(15)(%)
(1)	48.5 ± 3.6[b]	23.5 ± 4.3	18.0 ± 3.0
(2)	53.5 ± 2.5	26.5 ± 1.1	16.8 ± 2.1
(3)	51.0 ± 2.2	25.6 ± 1.3	19.1 ± 2.1
(4)	52.0 ± 1.8	23.2 ± 2.2	15.3 ± 1.9
(8)	44.8 ± 1.8	24.5 ± 1.6	15.6 ± 2.3
(9)	46.2 ± 4.9	24.2 ± 4.6	15.0 ± 1.3
SO_2[c]	45.1 ± 5.1	28.0 ± 10.4	15.0 ± 4.3

[a] Concentrations of (13) and (14) are added together since the products are formed by the same mechanism. [b] Errors quoted are standard deviations. [c] 12 p.p.m. v/v in nitrogen; flow rate 0.05 dm^3 min^{-1}.

The results in Table 2 were analysed using variance analysis. This analysis demonstrated that at the 95% confidence level, there was no significant difference between the product distributions. Thus compounds (1)—(4), (8), and (9) all decompose cumene hydroperoxide *via* the same catalyst. This implies that the catalyst is an inorganic sulphur compound.

To determine the catalyst we analysed the products obtained from the reaction of the disulphide (2) with cumene hydroperoxide at 393 K. The products formed were 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybiphenyl (16), 2,6-di-t-butylphenol (17), and sulphur dioxide [reaction (5)].

Sulphur dioxide decomposes cumene hydroperoxide very rapidly at 393 K. Kinetic analysis shows that at

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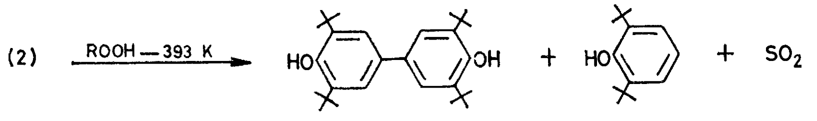
[16] M. S. Kharasch, A. Kono, and W. Nudenberg, *J. Org. Chem.*, 1950, **15**, 748, 753, 763.

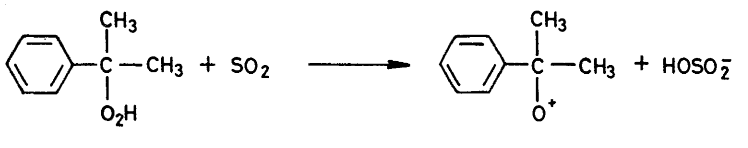
this temperature 1 mole of sulphur dioxide will decompose *ca.* 2×10^5 moles of cumene hydroperoxide. The distribution of the decomposition products is shown in Table 2. (The relatively high standard deviations are a result of the rapid rate of the reaction. The figures are based on a small number of measurements of relatively low concentrations of hydroperoxide.) Variance analysis of this product distribution shows that, at the 95% confidence level, it is not significantly different from the other results shown in Table 2.



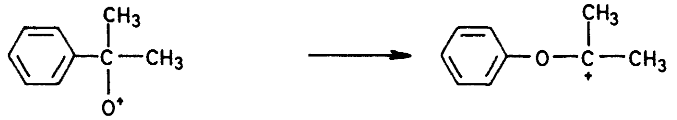
(5)

(16) (17)

3·8 x 10⁻² mol 2·58 x 10⁻² mol 0·83 x 10⁻² mol



(6)



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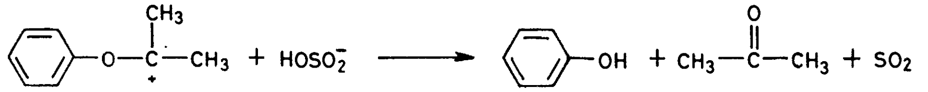

(8)

Thus it is sulphur dioxide generated from the sulphur compounds (1)—(10) that catalyses the decomposition of cumene hydroperoxide. It is also apparent that sulphur dioxide catalyses both ionic and free radical decomposition. This is consistent with previous work. The ionic decomposition of cumene hydroperoxide by sulphur dioxide is well known and a mechanism [reactions (6)—(8)] for the reaction has been proposed by Hawkins and Sautter.[15]

Also Lewis acids, including sulphur dioxide, are known to catalyse the free radical decomposition of hydroperoxides,[17,18] and the $HOSO_2^{\bullet}$ radical can be detected in the e.s.r. spectrum of hydroperoxides treated with sulphur dioxide.[19]

Previous work [20-42] has demonstrated that sulphoxides, thiolsulphinates, and thiolsulphonates are thermally unstable in the temperature range 373—423 K. Based upon this work we can propose Scheme 1 for the formation of sulphur dioxide from the sulphide (1) and the disulphide (2). Also we can propose the mechanism

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[17] V. M. Solyanikov, L. V. Petrov, and K. E. Kharlampidi, *Doklady Akad. Nauk S.S.S.R.*, 1975, **223**, 1412.

[18] W. J. M. van Tilborg and P. Smael, *Rec. Trav. chim.*, 1976, **95**, 138.

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[27] J. L. Kice and F. M. Parham, *J. Amer. Chem. Soc.*, 1960, **82**, 6168.

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[29] J. L. Kice, R. H. Engebrecht, and N. E. Pawlowski, *J. Amer. Chem. Soc.*, 1965, **87**, 4131.

[30] J. L. Kice and N. E. Pawlowski, *J. Amer. Chem. Soc.*, 1964, **86**, 4898.

[31] J. R. Shelton and K. E. Davis, *Internat. J. Sulphur Chem.*, 1973, **8**, 197 and references therein.

[32] D. H. R. Barton, F. Comer, and P. G. Sammes, *J. Amer. Chem. Soc.*, 1969, **91**, 1529.

[33] J. R. Shelton and K. E. Davis, *J. Amer. Chem. Soc.*, 1967, **89**, 718.

[34] J. R. Shelton and K. E. Davis, *Internat. J. Sulphur Chem.*, 1973, **8**, 205.

[35] D. H. R. Barton, F. Comer, D. G. T. Greig, G. Lucente, P. G. Sammes, and W. G. E. Underwood, *Chem. Comm.*, 1970, 1059.

[36] D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *Chem. Comm.*, 1970, 1683.

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[38] D. H. R. Barton, F. Comer, D. G. T. Greig, P. G. Sammes, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *J. Chem. Soc.* (*C*), 1971, 3540.

[39] I. Ager, D. H. R. Barton, D. G. T. Greig, G. Lucente, P. G. Sammes, M. V. Taylor, G. H. Hewitt, B. E. Looker, A. Mowatt, C. A. Robson, and W. G. E. Underwood, *J.C.S. Perkin I*, 1973, 1187.

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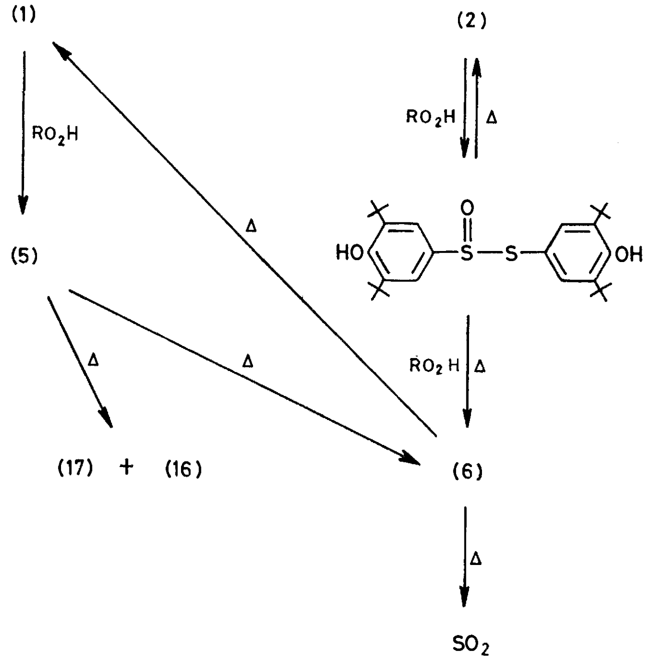
[41] H. Tanida, R. Muneyuki, and T. Tsushima, *Tetrahedron Letters*, 1975 3063.

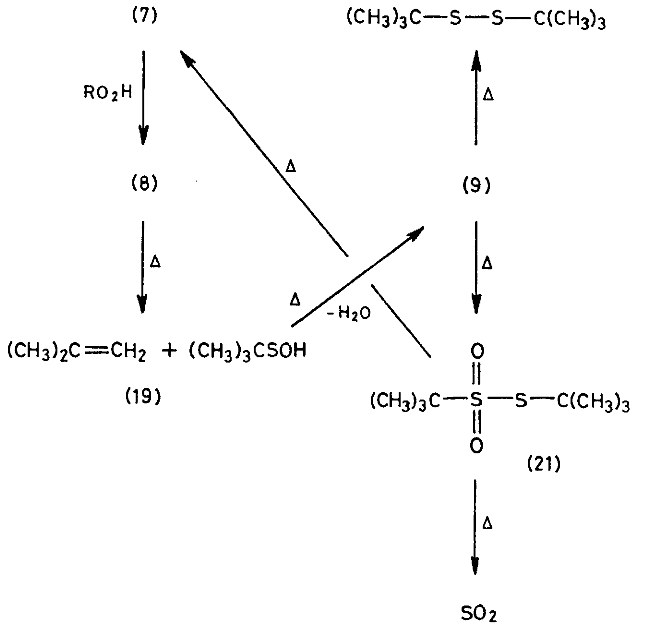
[42] (*a*) E. Block, *J. Amer. Chem. Soc.*, 1972, **94**, 642; (*b*) E. Block, *ibid.*, p. 644; (*c*) E. Block and S. W. Weidman, *ibid.*, 1973, **95**, 5046; E. Block and J. O'Connor, *ibid.*, 1974, **96**, (*d*) 3921; (*e*) 3929.

in Scheme 2 for the formation of sulphur dioxide from di-t-butyl sulphide (7).

The mechanism in Scheme 1 explains why the slope of k_1 against [S] is less than the slope of k_2 against [S]. The



SCHEME 1 Formation of sulphur dioxide from sulphide (1) and disulphide (2)



SCHEME 2 Formation of sulphur dioxide from di-t-butyl sulphide (7)

disulphide (2) can form the thiolsulphonate (6) *via* direct oxidation or by ready cleavage of a sulphur–sulphur bond in the thiolsulphinate [dissociation energy of the S(O)–S bond is 144.3 kJ mol^{-1} [24]]. By comparison the sulphide (1) can only form the thiolsulphonate (6) *via* homolytic fission of a carbon–sulphur bond in the sulphoxide (5) [dissociation energy of the S(O)–C bond is 234—289 kJ mol^{-1} [43]].

The mechanisms shown in Schemes 1 and 2 have been verified by a number of experiments including (i) the determination of the values of A_n and B_n for the sulphur–oxygen compounds postulated as intermediates, (ii) pyrolysis of the sulphur–oxygen compounds in an inert solvent and, (iii) determination of the activation parameters for hydroperoxide decomposition catalysed by the sulphur–oxygen compounds.

(i) *Determination of* A_n *and* B_n.—Reference to Table 1 shows that the values of A_5 and B_5 for the sulphoxide (5) are not significantly different from the values of A_1 and B_1 for the sulphide (1). Similarly the values A_6 and B_6 for the thiolsulphonate (6) are not significantly different from the values of A_2 and B_2 for the disulphide (2). This implies that the sulphide and sulphoxide generate sulphur dioxide by the same mechanism, and that the disulphide and thiolsulphonate generate sulphur dioxide by the same mechanism. These results are consistent with the mechanism in Scheme 1. The results in Table 1 also show that the values of A and B are not significantly different for di-t-butyl sulphide, di-t-butyl sulphoxide, and t-butyl 1,1-dimethylethanethiolsulphinate. These findings are consistent with the mechanism in Scheme 2.

(ii) *Pyrolysis Experiments*.—The sulphoxide (5) and the thiolsulphonate (6) when heated to 393 K in an inert solvent decompose to form sulphur dioxide, the bisphenol (16), and the sulphides (1)—(4) (Table 3). The sulphoxide (8) and the thiolsulphinate (9) decompose at 393 K to form sulphur dioxide, di-t-butyl sulphide (7), di-t-butyl disulphide (18), and 2-methylprop-1-ene (19) (Table 3).

TABLE 3

Thermal decomposition of the sulphur–oxygen compounds

Compound	Conditions	Products
(5)	393 K–6 h	(16) + (1) + (2) + SO_2 [a]
(6)	393 K–6 h	(16) + (1) + (2) + (3) + (4) + SO_2 [a]
(8)	393 K–6 h	(7) + (18) + (19) + SO_2 [a]
(9)	393 K–6 h	(7) + (18) + (19) + SO_2 [a]

[a] Detected by g.l.c.

The pyrolysis reactions were followed very easily by n.m.r. spectroscopy. All the compounds have very simple ^{1}H n.m.r. spectra and the chemical shift in compounds of the type $R-S_x-R$ depends upon the value of x.[44-46] Thus the aromatic protons of the compounds (1)—(6) give rise to singlets at δ 7.0—7.5 and the protons of the t-butyl groups in compounds (7)—(9) yield singlets at δ 1.2—1.5 (Table 4).

A more detailed examination of the decomposition of di-t-butyl sulphoxide (8) shows that (*a*) the sulphoxide decomposes very rapidly in a reaction that is first order with respect to the sulphoxide, (*b*) the thiolsulphinate

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[43] D. B. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, **90**, 4854.

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[46] T. L. Pickering, K. J. Saunders, and A. V. Tobolsky, *J. Amer. Chem. Soc.*, 1967, **89**, 2364.

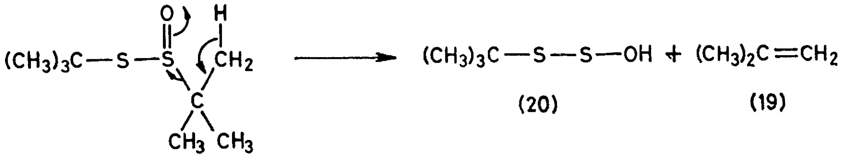
(9) is a reactive intermediate in the decomposition of the sulphoxide; it is formed early in the decomposition, reaches a maximum concentration when all the sulphoxide has decomposed, and is then itself decomposed. Also in the decomposition of the sulphoxide (8) we found no evidence for 1,1-dimethylethanesulphenic acid. This apparently contradicts the observations of Shelton and Davis,[34] but our pyrolysis temperature was much higher than that used in previous work. Thus our failure to detect the acid may simply reflect its thermal stability.

TABLE 4

^{1}H N.m.r. data for the sulphides and related compounds

Compound	Chemical shift [a]
(1)	7.02(s) [b]
(2)	7.20(s) [b]
(3)	7.31(s) [b]
(4)	7.39(s) [b]
(5)	7.54(s) [b]
(6)	7.20(s), 7.48(s) [b]
(7)	1.35(s) [c]
(8)	1.31(s) [c]
(9)	1.28(s), 1.48(s)[c]
(16)	7.13(s) [b]
(18)	1.38(s) [c]
(19)	1.63(CH_3), 4.57(CH_2)

[a] Values relative to tetramethylsilane. [b] Aromatic protons. [c] t-Butyl protons.


$$(CH_3)_3C-S-S(O)CH_2C(CH_3)_2H \longrightarrow (CH_3)_3C-S-S-OH + (CH_3)_2C=CH_2 \qquad (9)$$

(20) (19)

In the decomposition of the thiolsulphinate (9) the yield of acid (20) [reaction (9)] is $<30\%$ as measured by the amount of 2-methylprop-1-ene (19) formed. Neither acid (20) nor t-butyl 1,1-dimethylethanethiolsulphonate (21) could be detected. The failure to detect the thiolsulphonate, presumably because of its thermal instability, is in agreement with previous work. Block [42d,e] does not report the formation of the thiolsulphonate (21) from the thiolsulphinate (9) although other alkyl thiolsulphinates readily disproportionate to the thiolsulphonate and the disulphide.[4,42d,e]

(iii) *Activation Parameters.*—The sulphoxide (5), thiolsulphonate (6), sulphoxide (8), and thiolsulphinate (9) have been used to catalyse the decomposition of cumene hydroperoxide over the temperature range 383—408 K. From the results the activation parameters shown in *Table 5* were calculated.

TABLE 5

Activation parameters for the decomposition of hydroperoxide catalysed by the sulphur–oxygen compounds

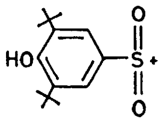
Compound	E/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
(5)	67.3 ± 5.6 [a]	64.0 ± 5.6	−(104 ± 14)
(6)	50.3 ± 6.7	47.0 ± 6.7	−(144 ± 17)
(8)	100.0 ± 4.9	96.7 ± 4.9	−(23.7 ± 12.4
(9)	106.4 ± 14.6	103.0 ± 14.6	−(7.9 ± 36.2)

[a] Errors are standard deviations.

The results are consistent with the mechanisms in Schemes 1 and 2. Thus the activation energy for the hydroperoxide decomposition catalysed by the sulphoxide (5) is significantly larger than the activation energy for the decomposition catalysed by the thiolsulphonate (6). Also the activation parameters for the hydroperoxide decomposition catalysed by the sulphoxide (8) and the thiolsulphinate (9) are not significantly different.

The mechanism shown in Scheme 1 for the sulphide (1), and the disulphide (2) may be extended to include the trisulphide (3) and tetrasulphide (4). It has been shown [47,48] that the oxidation of polysulphides takes place preferentially at terminal sulphur atoms. Also Kice *et al.*[26-29] have shown that thiolsulphonates decompose *via* the heterolytic fission of a sulphur–sulphur bond. So the di-, tri-, and tetra-sulphides will each form sulphur dioxide *via* the sulphonyl cation (22) and therefore the variation of k_n with [S] for compounds (2)—(4) will be the same, in agreement with experiment.

It is clear that sulphides which catalytically decompose hydroperoxides do so by forming sulphur dioxide. Also sulphur dioxide is formed by pyrolysis of thermally unstable sulphur–oxygen compounds. Thus the mechanism of decomposition of the sulphur–oxygen compound(s) that can be formed by oxidation of the sulphide assumes critical importance in assessing the potential of a sulphide as a hydroperoxide decomposer. This is neatly illustrated by the compounds dibenzyl sulphide (23) and dibenzyl disulphide (10).



(22)

Under our conditions dibenzyl sulphide does not catalyse the decomposition of cumene hydroperoxide, whereas dibenzyl disulphide is a very effective catalyst (Table 1). The reason for this difference is that dibenzyl disulphide can form the thiolsulphonate (24) which decomposes to form sulphur dioxide [reaction (10)].[26]

By contrast dibenzyl sulphoxide decomposes to form benzaldehyde and benzyl mercaptan in a reaction that is similar to the pyrolysis of benzyl methyl sulphoxide.[48] In a sealed tube the mercaptan is oxidised to the disulphide by the benzyl sulphoxide so that the overall stoicheiometry of the reaction becomes (11).

Conclusions.—In this paper we have shown that both aryl and alkyl sulphides catalyse the decomposition of cumene hydroperoxide by forming the Lewis acid

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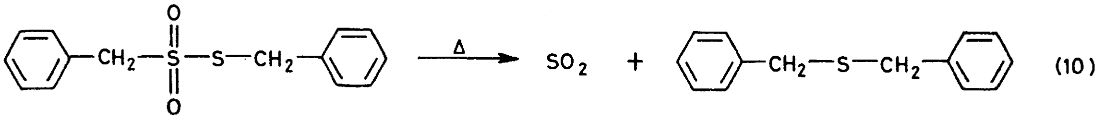
[47] F. Feher, K. H. Schafer, and W. Becher, *Z. Naturforsch*, 1962, **17b**, 847.

[48] R. Steudel and J. Lutte, *Chem. Ber.*, 1977, **110**, 423.

sulphur dioxide. Further, the sulphur dioxide is formed by thermolysis of thermally unstable sulphur–oxygen compounds. Sulphides which form sulphur–oxygen compounds that do not decompose to form sulphur dioxide do not catalyse hydroperoxide decomposition. We feel that this paper illustrates the importance of the thermal chemistry of sulphur–oxygen compounds in determining the antioxidant activity of sulphides.


(24)·

$$3C_6H_5CH_2\cdot S(O)\cdot CH_2C_6H_5 \longrightarrow 2C_6H_5CHO + (C_6H_5CH_2)_2S + (C_6H_5CH_2)_2S_2 + H_2O \quad (11)$$

EXPERIMENTAL

N.m.r. spectra were recorded with a Varian A-60 spectrometer and mass spectra were recorded on an A.E.I. MS-30 instrument. Sulphides (1)—(4) were prepared by literature methods.[49–51]

Bis-(4*-hydroxy-*3,5*-di-t-butylphenyl*) *Sulphoxide* (5).—This was prepared by oxidation of 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxydiphenyl sulphide (1) using *m*-chloroperbenzoic acid in dichloromethane. The sulphoxide was very insoluble in all common organic solvents and could not be recrystallised. The compound had m.p. 457 K (lit.,[52] 454 K) (Found: C, 69.2; H, 8.8; S, 6.4. Calc. for $C_{28}H_{42}O_3S$: C, 73.4; H, 9.2; S, 7.0%), δ (DMF) 1.40 (36 H, s, t-butyl) and 7.54 (4 H, s, ArH).

4*-Hydroxy-*3,5*-di-t-butylphenyl* 4*-Hydroxy-*3,5*-di-t-butylbenzenethiolsulphonate* (6).—This was prepared by the oxidation of 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxydiphenyl disulphide (2) using *m*-chloroperbenzoic acid in dichloromethane. Recrystallisation from methanol yielded crystals of (6), m.p. 442—443 K (decomp.) (Found: C, 66.6; H, 8.2; S, 12.5. Calc. for $C_{28}H_{42}O_4S_2$: C, 66.4; H, 8.3; S, 12.6%), δ($CDCl_3$) 1.35 (36 H, s), 7.20 (2 H, s), and 7.48 (2 H, s, ArH).

Di-t-butyl sulphide (7) (Emanuel) was used without further purification.

Di-t-butyl Sulphoxide (8).—This was prepared by the oxidation of di-t-butyl sulphide using *m*-chloroperbenzoic acid in dichloromethane. Recrystallisation from heptane gave hygroscopic needles of the sulphoxide, m.p. 328—330 K (lit.,[31] 334.7—335.2 K) (Found: C, 57.7; H, 10.6; S, 18.0. Calc. for C_8H_8OS: C, 59.3; H, 11.1; S, 19.8%).

t-Butyl 1,1*-Dimethylethanethiolsulphinate* (9).—This was prepared by oxidising di-t-butyl disulphide with *m*-chloroperbenzoic acid in dichloromethane. The crude product was purified by chromatography on silica gel, using heptane–chloroform (25 : 75) to elute *m*-chlorobenzoic acid, and chloroform to elute the thiolsulphinate. The product was a clear viscous liquid, *m*/*e* 192, δ($CDCl_3$) 1.28 and 1.48.

Pyrolysis of (5) *and* (6).—This was carried out in tetrachloromethane at 393 K in sealed n.m.r. tubes. The reactions were monitored using n.m.r. Involatile products were separated and identified by h.p.l.c. and mass spectroscopy.

Pyrolysis of Dibenzyl Sulphoxide.—A sample of dibenzyl sulphoxide (Aldrich) was suspended in tetrachloromethane in a sealed n.m.r. tube. The tube was heated to 393 K for 6 h and 403 K for 3 h. The decomposition of the sulphoxide was followed to completion using n.m.r., and the spectrum of the final clear solution showed the presence of benzaldehyde, δ 10.00 (s), dibenzyl monosulphide, and dibenzyl disulphide, δ 3.41(s) and 3.47(s). The presence of the two benzyl sulphides was confirmed by ' spiking ' the solution with samples of the pure compounds.

Integration of the spectrum gave a product ratio benzaldehyde : dibenzyl sulphide : dibenzyl disulphide of 2 : 1 : 1 consistent with equation (11). A small quantity of a secondary phase that separated out above the tetrachloromethane solution was analysed by g.l.c. and shown to be water.

Pyrolysis of Di-t-butyl Sulphoxide and t-Butyl 1,1*-Dimethylethanethiolsulphinate.*—These reactions were carried out at 393 K in sealed n.m.r. tubes using tetrachloromethane as a solvent and hexamethyldisiloxane as internal reference. The reactions were followed by n.m.r., g.l.c., and mass spectroscopy.

Reaction of (2) *with Cumene Hydroperoxide.*—Compound (2) (3.0 g, 6.33×10^{-2} mol) and cumene hydroperoxide (8.6 g, 4.24×10^{-2} mol) were dissolved in 1,2-dichlorobenzene (100 cm^3). The solution was heated to 393 K and sulphur dioxide (detected by g.l.c.–m.s.) was evolved very rapidly. When the evolution of gas was complete the solution was analysed by h.p.l.c. The products detected were 2-phenylpropene (19.5%; based on cumene hydroperoxide), acetophenone (7.3%), phenol (68.3%), 2-phenylpropan-2-ol (4.9%), unchanged disulphide (2.53×10^{-2} mol), 2,6-di-t-butylphenol (0.83×10^{-2} mol), and 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butyldiphenyl (2.58×10^{-2} mol).

Cumene hydroperoxide (Koch–Light; 70% cumene hydroperoxide in cumene) was washed with water (2 × 150 cm^3), dried (Na_2SO_4), and stored over molecular sieves. The hydroperoxide was used without further purification and we could not detect any significant variation between different batches of the hydroperoxide. Cumene (B.D.H.) was stored over molecular sieves and filtered immediately before use. 1,2-Dichlorobenzene (B.D.H.) was used without further purification.

The kinetic studies were carried out in a simple apparatus that allowed a stream of nitrogen (100 cm^3 min^{-1}) to be passed through the solution. In a typical run a solution of cumene hydroperoxide (2×10^{-1} mol dm^{-3}), cumene (1.0 mol dm^{-3}), and the tetrasulphide (4) (5.0×10^{-6} mol dm^{-3})

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[49] T. Fujisawa and G. Tsuchihashi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3615.

[50] T. Fujisawa, M. Yamamoto, and G. Tsuchihashi, *Synthesis*, 1972, 3615.

[51] T. Fujisawa, K. Hata, and T. Kogima, *Synthesis*, 1972, 38.

[52] G. Brunton, D. Phil. Thesis, University of York, 1974.

in 1,2-dichlorobenzene was kept at 393 K for 6 h. Samples were withdrawn from the solution every 30 min and the concentration of hydroperoxide determined iodometrically.[53] The kinetic data were analysed using standard methods of linear regression analysis.

The cumene hydroperoxide decomposition products were analysed using h.p.l.c. Phenol, acetophenone, and 2-phenylpropan-2-ol were separated by adsorption chromatography in a 1 m × 3 mm stainless steel column with silica coated glass beads (Perisorb A). The mobile phase was ethyl acetate–heptane (5 : 95 v/v). 2-Phenylpropene was separated by reverse phase partition chromatography in a similar column packed with hydrocarbon bonded silica coated glass beads (Octadecyl Corasil). The mobile phase was water–methanol (40 : 60 v/v).

Both columns were operated below 500 lb in^{-2} using an Orlita diaphragm pump. The separated compounds were detected by a u.v. monitor set at 254 nm (Cecil). The repeatability of the analysis was better than ±2% of the amount present. Variance analysis of the results was carried out using standard computer programs.

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[7/908 *Received, 26th May, 1977*]

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[53] R. D. Mair and A. J. Graupner, *Analyt. Chem.*, 1964, **36**, 194.