Mechanisms of Antioxidant Action. Part 2.[1] Reactions of Zinc Bis-[*OO*-dialkyl(aryl)phosphorodithioates] and Related Compounds with Hydroperoxides

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Zinc bis-[*OO*-dialkyl(aryl)phosphorodithioates] (1), hexakis-[*OO*-dialkyl(aryl)phosphorodithioate]-μ_4-tetraoxozincs (2), and *OOOO*-tetra-alkyl(aryl) thioperoxydiphosphates (3) promote the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide). The reaction is second-order with respect to the hydroperoxide when it is promoted by the zinc complexes (1) and (2), but first-order with respect to the hydroperoxide when promoted by the diphosphate (3). The results that we have obtained are not consistent with the accepted reaction mechanisms for the decomposition of cumene hydroperoxide. Our results lead us to propose that, under our experimental conditions, (i) acetophenone (10) is formed from cumene hydroperoxide by a free-radical reaction that is independent of the promoter used, (ii) 2-phenylpropan-2-ol (11) and 2-phenylpropene (12) are formed by an ionic deomposition of the hydroperoxide and not by the free-radical mechanism normally accepted, (iii) the ionic decomposition of cumene hydroperoxide takes place by a cationic chain reaction, and (iv) the catalyst formed from the promoters (1)—(3) may be the *OO*-dialkyl(aryl) hydrogendithiophosphate (4). We have proposed a mechanism for the ionic decomposition of cumene hydroperoxide, and suggest possible schemes for the formation of the acid (4) from the promoters (1)—(3) which are consistent with the observed kinetics and our proposed mechanism.

FOR the past 40 years bis-[*OO*-dialkyl(aryl)phosphorodithoates] of zinc (1) † have been used as antioxidants in lubricating oils. An early paper by Kennerley and Patterson[2] established that these complexes promote the decomposition of hydroperoxides. This observation has been confirmed in many subsequent papers,[3—19] but in our opinion no satisfactory explanation for the mechanism of this reaction has been proposed. We attribute this lack of success to the complexity of the reaction profile. Burn *et al.*,[8] Rossi and Imparato,[9] and Ivanov *et al.*[11,12,18,19] all describe a three-stage reaction. There is an initial rapid reaction, followed by an ' induction period ', when the rate of decomposition of the hydroperoxide is very slow. This is followed by a final rapid decomposition of the hydroperoxide. Such a complex reaction profile makes it difficult to measure accurate rate constants. Consequently it is difficult to compare different neutral ZDDPs (1) and determine the factors that affect their performance as hydroperoxide decomposers.

$[(RO)_2PS_2]_2Zn$ (1)

$[(RO)_2PS_2]_6Zn_4O$ (2)

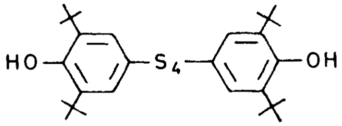
$[(RO)_2PS_2]_2$ (3)

$(RO)_2PS_2H$ (4)

a; R = 4-MeC_6H_4
b; R = Et
c; R = Me_3CCH_2
d; R = Me_2CHCH_2
e; R = Pr^n
f; R = Bu^n
g; R = Pr^i

$[(EtO)_2PSO]_2Zn$ (5)

$(EtO)_2PSOH$ (6)



(7)

We have found that this reaction profile can be simplified by using a large excess of hydroperoxide ([ROOH] : [ZDDP] *ca.* 10^4) at relatively high temperatures (>368 K). Using these reaction conditions we have compared a wide range of neutral ZDDPs (1) as promoters for the decomposition of cumene hydroperoxide.

Previous work[8-10,13,14,16,20-22] has established that a zinc bis-[*OO*-dialkyl(aryl)phosphorodithioate] is oxidised by a hydroperoxide to hexakis-[*OO*-dialkyl(aryl)phosphorodithioate]-μ_4-tetraoxozinc (2) † and *OOOO*-tetra-alkyl(aryl) thioperoxydiphosphate (3) † [equation (1)].

If we assume that this reaction also takes place at the

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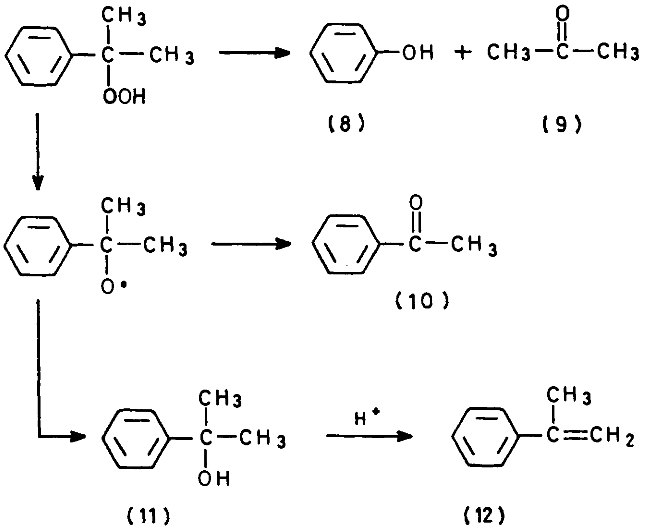
† For the sake of brevity compounds (1) will be called neutral ZDDPs, compounds (2) basic ZDDPs, and compounds (3) disulphides.

higher temperatures used in this work it is clear that any study of a neutral ZDDP (1) as the promoter for hydroperoxide decomposition should also include a study of the corresponding basic ZDDP (2) and the corresponding disulphide (3). So we have included some basic ZDDPs and disulphides in this study. We have also tested as hydroperoxide decomposers an *OO*-dialkyl hydrogendithiophosphate (4), zinc bis-[*OO*-diethylphosphoromonothioate] (5), and 4,4′-dihydroxy-3,3′,5,5′-tetra-t-butyldiphenyl tetrasulphide (7). The latter compound allowed us to compare the results of this study with our previous work.[1]



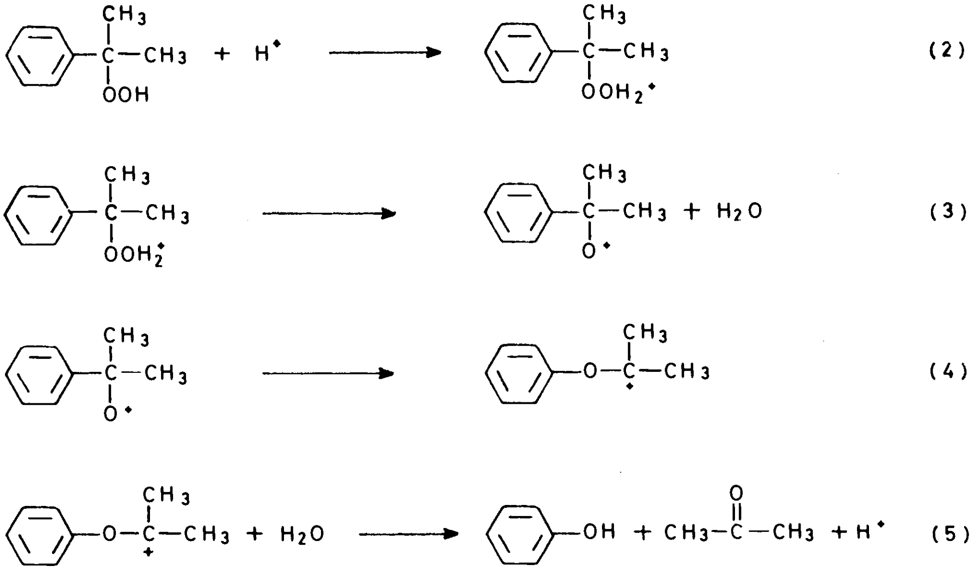
SCHEME 1 Ionic *versus* free-radical decomposition of cumene hydroperoxide

In most studies of antioxidant mechanisms it is assumed that ionic decomposition of the hydroperoxide is desirable to prevent free-radical chain-branching reactions (see for example ref. 4). It is also a common assumption that the products formed from cumene hydroperoxide distinguish between free-radical and ionic decomposition of the hydroperoxide [1,16,17,22] (Scheme 1).

$$4\ \underset{(1)}{[(RO)_2PS_2]_2Zn} + R'OOH \longrightarrow \underset{(2)}{[(RO)_2PS_2]_6Zn_4O} + \underset{(3)}{[(RO)_2PS_2]_2} + R'OH \quad (1)$$

Some of our results, however, lead us to believe that this assumption may be incorrect for the promoters that we have studied under the experimental conditions we have used. Also, we have had great difficulty trying to fit some of our kinetic data to the reaction mechanisms that have been proposed for the ionic decomposition of cumene hydroperoxide (*e.g.* Scheme 2).

Our results and the problems we have encountered lead us to propose that under our experimental conditions (i) acetophenone (10) is formed from the hydroperoxide by a free-radical mechanism that is independent of the promoter used, (ii) 2-phenylpropan-2-ol (11) and 2-phenylpropene (12) are formed from cumene hydroperoxide by an ionic mechanism and not a free-radical mechanism, (iii) the ionic decomposition of the hydroperoxide takes place *via* a cationic chain reaction, and (iv) the catalyst formed from the promoters (1)—(3) may be the *OO*-dialkyl(aryl) hydrogendithiophosphate (4).



SCHEME 2 A simple mechanism for the ionic decomposition of cumene hydroperoxide

EXPERIMENTAL

The solvents used in this study were AnalaR grade. The *OO*-dialkyl hydrogenphosphorodithioates and their ammonium salts were prepared by methods described in the literature.[23,24] The neutral ZDDPs (1) were prepared from the ammonium salts by metathetical reactions using aqueous solutions of zinc sulphate.[24] The basic ZDDPs (2) were prepared by oxidation of the neutral ZDDPs with 2,2-dimethylethyl hydroperoxide.[21] The disulphides (3) were prepared from the ammonium salts by oxidation with an aqueous solution of iodine–potassium iodide. Zinc bis-[*OO*-diethylphosphoromonothioate] was prepared by the method of Pesin and Khaletskii [25] and recrystallised from absolute ethanol. All the compounds were characterised by elemental analysis, mass spectroscopy, i.r. spectroscopy, and n.m.r. spectroscopy. A more detailed analysis of some of the n.m.r. spectra will be published elsewhere.[26]

Cumene hydroperoxide was purified *via* its sodium salt and its purity was checked by iodometric titration [27] and h.p.l.c. (>99%).

In a typical experiment a solution of cumene hydroperoxide (7.0×10^{-2} mol dm^{-3}) and a neutral ZDDP (7.5×10^{-6} mol dm^{-3}) in n-decane was placed in a reaction flask equipped with a stirrer, reflux condenser, and nitrogen inlet. The mixture was kept under nitrogen at 383.0 ± 0.1 K for 6 h and samples [$(2.00 \pm 0.01) \times 10^{-6}$ dm^3] were removed every 30 min for analysis. The samples were analysed by h.p.l.c. using a 250-mm × 4-mm column packed with Partisil 10. The mobile phase was ethyl acetate–n-heptane (10 : 90 v/v). The column was connected to a Pye–Unicam L.C.-3 chromatograph fitted with a fixed wavelength (254 nm) u.v. detector, and the detector was connected to a Pye–Unicam DP 101 computer–integrator. The computer–integrator was calibrated prior to each kinetic run, using a standard solution of 2-phenylpropene, acetophenone, cumene hydroperoxide, phenol, and 2-phenylpropan-2-ol in n-decane. No attempt was made to analyse for propan-2-one because of the high temperatures used. No other products were detected in the h.p.l.c chromatogram and the overall yield of products was high (see, for example, Table 4). Reaction yields were calculated using equation (6). The %[phenol] was calculated for every reading using equation (7).

$$\%\ \text{Yield} = \frac{[(8)]_f + [(10)]_f + [(11)]_f + [(12)]_f}{[\text{ROOH}]_0 - [\text{ROOH}]_f} \times 100 \qquad (6)$$

$$\%[\text{phenol}] = \frac{[(8)]_t}{[(8)]_t + [(10)]_t + [(11)]_t + [(12)]_t} \times 100 \qquad (7)$$

Similar equations were used to calculate %[acetophenone] and %[alcohol + propene]. The values quoted in Table 4 are the mean and standard deviation for the entire run.

The rate constants were calculated using standard methods of linear regression analysis. The correlation coefficient was used to calculate *t* (the parameter of the student *t* test) from formula (8) where *r* is the correlation

$$t = [r(n-2)^{1/2}]/(1-r^2)^{1/2} \qquad (8)$$

coefficient and *n* is the number of points in the line. The parameter *t* was used to test the null hypothesis ($H_0 : r = 0$) against the alternate hypothesis ($H_1 : r \neq 0$) and the null hypothesis was rejected if $P > 99.9\%$. Reactions followed to *ca.* 3 half-lives showed no significant deviation from linearity and duplicate experiments showed that the rate constants were reproducible to *ca.* ±(6—10)%. Product distributions were compared using a two-tailed student *t* test or variance analysis, and the null hypothesis ($H_0 : \mu_1 = \mu_2 =$ *etc.*) was rejected if $P > 95\%$.[28]

RESULTS AND DISCUSSION

(a) *The Kinetics of Hydroperoxide Decomposition.*—In the temperature range 368—398 K the neutral ZDDPs (1a—g) and the basic ZDDPs (2b and f) promote the decomposition of cumene hydroperoxide. The reactions are catalytic: the promoter ($[\text{ZDDP}]_0 = 2$—20×10^{-6} mol dm^{-3}) decomposes >50% of the hydroperoxide ($[\text{ROOH}]_0 = 7.0 \times 10^{-2}$ mol dm^{-3}) in <6 h. Under comparable reaction conditions the rate of decomposition of the hydroperoxide in the absence of the promoter is significantly slower. The catalysed hydroperoxide decompositions are second-order with respect to the hydroperoxide. The magnitude of the second-order rate constant (k_2), however, depends upon the initial concentration of the promoter and is related to $[\text{ZDDP}]_0$ by

$$k_2 = A_2 + B_2[\text{ZDDP}]_0 \qquad (9)$$

equation (9) where A_2 and B_2 are constants. Values of A_2 and B_2 for some of the ZDDPs are shown in Table 1.

TABLE 1

The values of *A* and *B*. Temperature = (393 ± 0.1) K, $[\text{ROOH}]_0 = 7.0 \times 10^{-2}$ mol dm^{-3}

Promoter	A_1/h^{-1}	$10^{-5}B_1$/ h^{-1} mol^{-1} dm^3	$10^{-6}B_1$(corrected)/ h^{-1} mol^{-2} dm^6	A_2/ h^{-1} mol^{-1} dm^3	$10^{-6}B_2$/ h^{-1} mol^{-2} dm^6
(1a)				$-(6.32 \pm 4.35)$ [a]	(1.03 ± 0.38)
(1b)				$-(6.97 \pm 3.37)$	(1.84 ± 0.26)
(1c)				$-(0.39 \pm 0.92)$	(0.26 ± 0.08)
(3c)	(0.02 ± 0.01)	(0.17 ± 0.01)	(0.25 ± 0.01)		
(1f)				$-(5.68 \pm 1.95)$	(2.39 ± 0.29)
(2f)				$-(10.82 \pm 2.17)$	(7.15 ± 0.19)
(3f)	$-(0.34 \pm 0.09)$	(1.84 ± 0.22)	(2.62 ± 0.32)		
(4f)	$-(0.20 \pm 0.04)$	(0.91 ± 0.07)	(1.30 ± 0.10)		

[a] Errors are standard errors.

Zinc *OO*-diethylphosphoromonothioate (5) also promotes the decomposition of cumene hydroperoxide in a reaction which is second-order with respect to the hydroperoxide, but significantly higher temperatures (>393 K) are necessary to obtain a measurable rate of reaction.

The disulphides (3c, f, and g) and the acid (4f) also promote the decomposition of cumene hydroperoxide, but there are significant differences when we compare these compounds as promoters with the corresponding ZDDPs. First, higher temperatures (398—413 K) are required to obtain measurable rates of reaction. Secondly, the reaction profile for the kinetic runs (0—6 h) cannot be fitted to a simple rate equation. If it is assumed that there is an induction period (0—2 h), when the decomposition of the hydroperoxide is very slow, the remainder of the kinetic run (2—6 h) is first-order with respect to the hydroperoxide.

The first-order rate constant (k_1) depends upon the initial concentration of the promoter [equation (10)] where A_1 and B_1 are constants and $[\text{P–S}]_0$ is the initial concentration of the promoter. Values of A_1 and B_1 are shown in Table 1.

$$k_1 = A_1 + B_1[\text{P–S}]_0 \qquad (10)$$

The constants B_1 and B_2 have different dimensions but we can correct for this difference by dividing B_1 by the initial concentration of hydroperoxide. Then a plot of B for the promoters (1f)—(4f) against x (where x is the number of *OO*-bis-n-butylphosphorodithioate ligands in each molecule of the promoter) is a straight line [equation (11)]. Similarly if the same correction is applied to the

$$10^{-6}B = (1.17 \pm 0.03)x + (0.16 \pm 0.10) \qquad (11)$$

value of B_1 for the disulphide (3c) the values of B for the promoters (1c) and (3c) are not significantly different.

These results suggest that the concentration of catalyst formed from the promoters (1)—(4) is proportional to the number of ligands in the molecule. Therefore the activation parameters for the decomposition of cumene hydroperoxide promoted by the neutral ZDDPs (1a—g), the basic ZDDPs (2b and f), the disulphides (3c, f, and g), the acid (4f), and the phosphoromonothioate (5) were measured using the promoters at a constant concentration of phosphorus. The results are shown in Table 2.

TABLE 2

The activation parameters for the decomposition of cumene hydroperoxide. [Promoter] $\equiv$ [P] = 15.0×10^{-6} mol dm^{-3}

Promoter	E^*/kJ mol^{-1}	ln (A/h^{-1})	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(1a)	(137.0 ± 4.3) [a]	(41.6 ± 1.3)	(133.8 ± 4.1)	(22.5 ± 10.8)
(1b)	(143.4 ± 10.3)	(44.2 ± 3.2)	(140.3 ± 10.3)	(44.8 ± 26.9)
(2b)	(139.8 ± 14.1)	(44.2 ± 4.6)	(136.7 ± 4.1)	(44.8 ± 38.2)
(1c)	(143.4 ± 9.2)	(44.5 ± 2.9)	(141.4 ± 8.7)	(50.1 ± 22.8)
(3c)	(144.5 ± 12.9)	(41.9 ± 3.8)	(141.1 ± 12.9)	(60.6 ± 31.6)
(1d)	(151.4 ± 7.9)	(47.0 ± 2.5)	(148.2 ± 7.8)	(67.8 ± 20.5)
(1e)	(153.0 ± 8.5)	(45.3 ± 2.6)	(149.7 ± 8.5)	(53.7 ± 21.6)
(1f)	(193.3 ± 5.7)	(59.3 ± 1.8)	(190.1 ± 5.8)	(169.7 ± 14.8)
(2f)	(205.7 ± 10.8)	(62.9 ± 3.3)	(202.6 ± 10.7)	(199.7 ± 27.4)
(3f)	(193.8 ± 10.9)	(57.0 ± 3.4)	(190.5 ± 10.9)	(220.0 ± 27.7)
(4f)	(190.0 ± 13.6)	(55.9 ± 4.1)	(186.7 ± 13.6)	(208.9 ± 34.5)
(1g)	(196.0 ± 20.6)	(62.4 ± 3.8)	(192.9 ± 20.5)	(195.7 ± 31.6)
(3g)	(193.2 ± 19.7)	(56.0 ± 4.8)	(189.9 ± 19.6)	(199.8 ± 39.9)
(5)	(258.1 ± 13.6)	(75.0 ± 4.0)	(254.7 ± 13.6)	(299.9 ± 33.6)

[a] Errors are standard errors.

The values of ln A and ΔS^* for the reactions promoted by the ZDDPs and the phosphoromonothioate have been corrected to allow for the difference in dimensions between the second-order rate constant (k_2) and the Eyring equation, which is only applicable to first-order rate constants.[29,30]

Analysis of the results in Table 2 using variance analysis to compare the regression lines of ln k against $1/T$, shows that for the promoters (1b) and (2b), (1c) and (3c), (1f)—(4f), and (1g) and (3g), the activation parameters are not significantly different when R is constant. From this we conclude that the compounds (1)—(4) probably promote the decomposition of the hydroperoxide *via* the same catalyst.

If this conclusion is correct then clearly the catalyst is non-metallic. Sher *et al.*,[13] Grishina *et al.*,[14,15] and Shkhiyants *et al.*,[16] have all suggested that the disulphide (3), formed from the neutral ZDDP by oxidation [equation (1)], is the catalyst. The differences, however, that we observe between the ZDDP-promoted reactions and the disulphide-promoted reactions show that, under our experimental conditions, reaction (12) is not the

$$\text{ZDDP} \longrightarrow \text{disulphide} \qquad (12)$$

rate-determining step in the decomposition of cumene hydroperoxide promoted by neutral ZDDPs.

Inspection of the results in Table 2 for the reactions promoted by the neutral ZDDPs (1a—g) and the phosphoromonothioate (5), shows that there is an isokinetic relationship between E^* and ln A and also between ΔH^* and ΔS^*. The activation parameters are related by equations (13) and (14). Exner[31a] and Krug *et al.*[31b]

$$E^* = (3.472 \pm 0.194) \times 10^3 \ln A - (1.004 \pm 1.041) \times 10^4 \qquad (13)$$

$$\Delta H^* = (418.1 \pm 23.3)\Delta S^* + (121 \pm 3.4) \times 10^3 \qquad (14)$$

have shown that an uncritical acceptance of an isokinetic relationship will often lead to error because the activation parameters are inter-related. We have shown that there is an extra-thermodynamic effect in our results by plotting ln k_2 (398 K) against ln k_2 (368 K) [equation (15); see ref. 31*a*] and by testing and rejecting the null hypothesis $H_0 : \gamma = 1$ (see ref. 31*b*).

$$\ln k_2\,(398\text{ K}) = (3.89 \pm 0.29) + (0.685 \pm 0.113) \ln k_2\,(368\text{ K}) \qquad (15)$$

The significance of isokinetic relationships for homogeneous reactions is uncertain. The relationship predicts that the reactions under examination will all have the same rate constant at the isokinetic temperature [in this example (418 ± 23) K; equation (14)]. Further, the order of the rates of reaction should be inverted as the reaction system passes through the isokinetic temperature. A few examples of such an inversion have been documented by Hall *et al.*,[32,33] but the consensus of opinion[31] is that an isokinetic relationship demonstrates only that a series of reactions have a common mechanism. It follows that the neutral ZDDPs (1) and the zinc phosphoromonothioate (5) probably decompose cumene hydroperoxide by the same mechanism.

Kabachnik *et al.*[34] have measured the pK_a values of *OO*-dialkyl(aryl) hydrogenphosphorodithioates and *OO*-dialkyl(aryl) hydrogenphosphoromonothioates at 293 K. We have used the activation parameters shown in Table 2 to calculate log k_2 (293 K) for the decomposition of cumene hydroperoxide promoted by the ZDDPs (1b and e—g) and the zinc phosphoromonothioate (5). The calculated values of log k_2 (293 K) and the pK_a values for the acids from which the promoters are derived are shown in Table 3.

TABLE 3

Values of log k_2 (293 K) and pK_a

Promoter	log k_2 [a]	Acid	pK_a [b]
(1b)	−5.20	(4b)	2.56
(1e)	−6.43	(4e)	2.57
(1f)	−7.54	(4f)	2.64
(1g)	−6.67	(4g)	2.65
(5)	−12.27	(6)	2.84

[a] Calculated from the activation parameters in Table 2. [b] In 80% EtOH–20% H_2O (from ref. 34).

A plot of log k_2 (293 K) against pK_a is linear [equation (16)]. The linear relationship between log k_2 and the

$$\log k_2 = (55.0 \pm 8.4) - (23.6 \pm 3.2)\, \mathrm{p}K_a \quad (16)$$

pK_a of the acid is consistent with an acid-catalysed reaction.[35] This leads us to suggest that the promoters (1) and (5) may catalyse the decomposition of cumene hydroperoxide by forming small concentrations of the acids (4) and (6), respectively. This idea is very difficult to test directly because the acids react stoicheiometrically with hydroperoxides, irrespective of any catalytic reactions that might take place. Thus, for example, the acid (4) is oxidised by hydroperoxides to form the disulphide (3) [reaction (17)] [14] so that if we use

$$2\ (RO)_2PS_2H + R'OOH \longrightarrow [(RO)_2PS_2]_2 + R'OH + H_2O \quad (17)$$

the acid (4f) as a promoter for the decomposition of cumene hydroperoxide we obtain kinetics that are characteristic of the disulphide (3f).

Although the linear relationship between log k_2 (293 K) and pK_a is consistent with an acid-catalysed reaction, the slope of the line (the Bronsted α coefficient) is very large. Normally, for a series of acid-catalysed reactions, where the catalysts are structurally similar, α has a value between 0 and 1.[35] A possible reason for the very large value of α will become apparent later in the discussion [see section (c)].

(b) *The Distribution of Products formed from Cumene Hydroperoxide.*—Table 4 shows the distribution of products formed from cumene hydroperoxide in a series of reactions promoted by the neutral ZDDPs (1a—g) and the basic ZDDPs (2b and f).

The reactions were carried out at a constant temperature [(383.0 ± 0.1) K] and the promoters were used at a constant concentration of phosphorus ([P] = 15.0 × 10^{-6} mol dm^{-3}). For comparison the tetrasulphide (7) was also tested under the same reaction conditions; the concentration of the tetrasulphide used was equal to the concentration of the neutral ZDDP so that both promoters were tested at the same concentration of sulphur ([S] = 30.0 × 10^{-6} mol dm^{-3}).

Analysis of the results in Table 4 for the reactions promoted by the neutral ZDDPs (1b and f) and the basic ZDDPs (2b and f) shows that the product distribution for a reaction promoted by a neutral ZDDP is not significantly different from the product distribution for the reaction promoted by the corresponding basic ZDDP. This supports the hypothesis outlined above that neutral and basic ZDDPs probably promote the decomposition of the hydroperoxide *via* the same catalyst.

TABLE 4

The product distribution for the decomposition of cumene hydroperoxide catalysed by ZDDPs and the tetrasulphide (7). $[ZDDP]_0 \equiv [P] = 15.0 \times 10^{-6}$ mol dm^{-3}. Temperature = (383 ± 0.1) K

Promoter	ln k_2 [a]	%[(8)]	%[(11) + (12)]	%[(10)]	% Yield
(1a)	1.28	(68.03 ± 2.96) [b]	(27.19 ± 2.17)	(4.78 ± 0.80)	94.1
(1b)	1.87	(73.05 ± 2.88)	(22.96 ± 2.53)	(4.00 ± 0.49)	97.7
(2b)		(74.40 ± 1.58)	(21.84 ± 2.08)	(4.05 ± 0.42)	93.4
(1c)	2.17	(72.10 ± 2.21)	(23.48 ± 3.42)	(4.42 ± 0.82)	92.1
(1d)	2.15	(74.31 ± 1.47)	(21.60 ± 1.05)	(4.09 ± 0.44)	96.0
(1e)	−0.05	(63.11 ± 3.36)	(32.52 ± 2.94)	(4.37 ± 0.55)	95.5
(1f)	1.30	(69.01 ± 1.33)	(26.37 ± 2.55)	(4.71 ± 0.38)	95.6
(2f)		(69.98 ± 1.54)	(25.74 ± 2.33)	(4.28 ± 0.40)	93.2
(1g)	3.55	(76.35 ± 1.44)	(19.32 ± 2.42)	(4.33 ± 0.31)	91.4
(7) [c]		(57.63 ± 2.07)	(35.31 ± 2.46)	(7.07 ± 0.64)	94.5

[a] Calculated from the activation parameters of Table 2. [b] Errors are standard deviations. [c] Concentration 7.5 × 10^{-6} mol dm^{-3}.

Further analysis of the results in Table 4 shows that (i) there is no significant variation in the concentration of acetophenone formed in the reactions promoted by the ZDDPs, (ii) there is a linear relationship between %[phenol] and ln k_2 (383 K) represented by equation (18),

$$\%[\text{phenol}] = (64.1 \pm 1.1) + (3.88 \pm 0.54) \ln k_2\ (383\ \text{K}) \quad (18)$$

(iii) there is a linear relationship between %[alcohol + propene] and ln k_2 (383 K) represented by equation (19),

$$\%[\text{alcohol} + \text{propene}] = (31.5 \pm 0.9) - (3.81 \pm 0.46) \ln k_2\ (383\ \text{K}) \quad (19)$$

and (iv) there is a significant difference between the product distribution for the reaction promoted by the tetrasulphide (7) and the product distributions for reactions promoted by the ZDDPs (note in particular the difference in %[acetophenone]). This last result is inconsistent with the mechanism suggested by Ivanov and Kateva.[17,19] They propose that sulphur dioxide, formed as the final product of ZDDP oxidation, is the catalyst for hydroperoxide decomposition. We have previously shown [1] that the tetrasulphide (7) decomposes hydroperoxides by forming sulphur dioxide. We would expect the tetrasulphide and the neutral ZDDP to give identical product distributions if they decompose cumene hydroperoxide *via* the same catalyst.

We consider that the linear relationships represented by equations (18) and (19) are inconsistent with the accepted mechanism for the formation of the products (8)—(12) from cumene hydroperoxide. Kharasch *et al.*[36] demonstrated that, at low temperatures, strong acids catalyse the decomposition of cumene hydroperoxide to phenol (8) and propan-2-one (9), while at high temperatures, in the absence of an acid, the hydroperoxide decomposes to acetophenone (10) and 2-phenylpropan-2-ol (11). The acid-catalysed reaction is thought to be an ionic reaction while the high-temperature decomposition is thought to be a free-radical reaction. As a result many authors [1,16,17,22,37,38] have assumed that the products from cumene hydroperoxide differentiate between ionic and free-radical decomposition of the hydroperoxide (Scheme 1).

If the mechanism of Scheme 1 is correct for our reaction conditions we would find it difficult to explain why the %[alcohol + propene] depends upon the promoter used while the %[acetophenone] is apparently independent of the promoter used. Also it would be difficult to explain the relationship between equations (18) and (19) which shows that, within experimental error equation (20) applies. These results are readily explained if we

$$\frac{\mathrm{d}\ \%[\text{phenol}]}{\mathrm{d}\ (\ln k_2)} = - \frac{\mathrm{d}\ \%[\text{alcohol} + \text{styrene}]}{\mathrm{d}\ (\ln k_2)} \qquad (20)$$

assume that, under our reaction conditions and with our promoters, both the (phenol + propan-2-one) and the (alcohol + propene) are formed by an ionic mechanism that is dependent upon the promoter used, while the acetophenone is formed by a free-radical mechanism that is independent of the promoter used. We have attempted to confirm these ideas by calculating the activation parameters for the rates of formation of the products formed from cumene hydroperoxide.

TABLE 5

The activation parameters for the formation of acetophenone from cumene hydroperoxide. [Promoter] $\equiv$ [P] = 15.0×10^{-6} mol dm^{-3}

Promoter	E^*/kJ mol^{-1}	ln (A/h^{-1})	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(1a)	(118.5 ± 18.0) [a]	(31.3 ± 5.6)	(115.3 ± 18.0)	(−63.1 ± 46.9)
(1b)	(121.2 ± 12.1)	(32.4 ± 3.8)	(118.0 ± 12.1)	(−53.4 ± 31.6)
(2b)	(124.6 ± 10.3)	(32.8 ± 3.6)	(121.4 ± 10.3)	(−48.6 ± 29.9)
(1c)	(122.1 ± 13.6)	(32.9 ± 4.3)	(118.9 ± 13.6)	(−49.6 ± 35.8)
(1d)	(118.3 ± 16.8)	(31.6 ± 5.3)	(115.1 ± 16.8)	(−60.1 ± 44.1)
(1e)	(120.1 ± 11.7)	(31.3 ± 3.6)	(116.9 ± 11.7)	(−63.4 ± 29.7)
(1f)	(129.0 ± 20.0)	(34.5 ± 6.2)	(125.8 ± 20 0)	(−36.1 ± 52.0)
(2f)	(121.4 ± 12.3)	(31.9 ± 3.6)	(118.1 ± 12.3)	(−57.8 ± 37.2)
(1g)	(119.7 ± 15.9)	(32.4 ± 4.7)	(116.6 ± 15.9)	(−53.3 ± 32.3)
(5)	(121.6 ± 17.5)	(31.3 ± 5.1)	(118.2 ± 17.5)	(−63.0 ± 42.7)

[a] Errors are standard errors.

The activation parameters in Table 5 are for the formation of acetophenone from cumene hydroperoxide in reactions promoted by the neutral ZDDPs (1a—g), the basic ZDDPs (2b and f), and the monothiophosphate (5). The rate of formation of the acetophenone is second-order with respect to the hydroperoxide and the parameters in Table 5 have been corrected. Variance analysis of the regression lines of ln k against $1/T$ shows that the activation parameters in Table 5 are not significantly different from each other. Further, the values of the pre-exponential factor A and the activation energy E^* are in close agreement with literature values for the free radical decomposition of cumene hydroperoxide.[39-41] Thus our results are consistent with our proposal that acetophenone, produced in the decomposition of cumene hydroperoxide promoted by neutral and basic ZDDPs, is formed by a free-radical reaction that is independent of the promoter.

The formation of phenol, in the reactions promoted by the neutral ZDDPs (1a—g), the basic ZDDPs (2b and f) and the zinc phosphoromonothioate (5), is second-order with respect to the hydroperoxide. The corrected activation parameters are shown in Table 6.

There is an isokinetic relationship between these activation parameters represented by equations (21) and (22). A plot of ln k_2 (398 K) against ln k_2 (368 K) [equation (23)] and rejection of the null hypothesis

$$E^* = (3.45 \pm 0.29) \times 10^3 \ln A + (0.26 \pm 9.67) \times 10^3 \qquad (21)$$

$$\Delta H^* = (406.0 \pm 36.2)\Delta S^* + (131.5 \pm 2.5) \times 10^3 \qquad (22)$$

$$\ln k_2\ (398\ \text{K}) = (2.47 \pm 0.24) + (0.783 \pm 0.103) \ln k_2\ (368\ \text{K}) \qquad (23)$$

$H_0 : \gamma = 1$ shows that there is an extra-thermodynamic effect in these results. Comparison of equations (14) and (22), coupled with variance analysis, shows that the two regression lines represented by these equations are not significantly different. The two lines can be combined, therefore, to give the regression line of equation (24). If we assume that the consensus of opinion is correct, *viz.* an isokinetic relationship is indicative of a common

$$\Delta H^* = (381.7 \pm 14.5)\Delta S^* + (128.0 \pm 1.7) \times 10^3 \quad (24)$$

reaction mechanism, it follows that the mechanism for the formation of phenol from cumene hydroperoxide is the same as the mechanism for the decomposition of the hydroperoxide. So if phenol is formed from cumene hydroperoxide by an ionic mechanism it follows that in our experiments we are measuring the rate of ionic decomposition of the hydroperoxide.

TABLE 6

The activation parameters for the formation of phenol from cumene hydroperoxide. [Promoter] ≡ [P] = 15.0 × 10^{-6} mol dm^{-3}

Promoter	E^*/kJ mol^{-1}	ln (A/h^{-1})	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(1a)	(94.60 ± 5.99) [a]	(26.7 ± 1.9)	(91.38 ± 5.98)	(−101.2 ± 15.5)
(1b)	(93.38 ± 8.49)	(26.9 ± 2.7)	(90.20 ± 8.49)	(−99.5 ± 22.2)
(2b)	(95.13 ± 7.30)	(27.4 ± 2.5)	(91.95 ± 7.30)	(−95.4 ± 20.8)
(1c)	(105.2 ± 10.2)	(30.8 ± 3.2)	(102.0 ± 10.2)	(−67.6 ± 26.6)
(1d)	(110.2 ± 4.3)	(32.3 ± 1.3)	(107.0 ± 4.3)	(−54.8 ± 11.2)
(1e)	(100.9 ± 2.7)	(28.7 ± 0.8)	(97.68 ± 2.74)	(−93.7 ± 7.0)
(1f)	(132.6 ± 12.0)	(38.8 ± 3.7)	(129.4 ± 12.0)	(−1.2 ± 30.8)
(2f)	(130.4 ± 10.8)	(37.1 ± 3.0)	(127.2 ± 10.8)	(5.8 ± 24.9)
(1g)	(132.1 ± 18.7)	(40.2 ± 6.0)	(129.0 ± 18.7)	(11.4 ± 49.9)
(5)	(154.7 ± 4.7)	(42.3 ± 1.4)	(151.3 ± 4.7)	(28.0 ± 11.5)

[a] Errors are standard errors.

Our attempts to find a similar relationship between the activation parameters for the rates of formation of the (alcohol + propene) and the rates of decomposition of the hydroperoxide were not successful. The concentration of 2-phenylpropan-2-ol in the reaction system is constant throughout the entire kinetic run (suggesting possibly that the alcohol is a reactive intermediate that reaches a steady-state concentration). Table 7 shows the activation parameters for the formation of 2-phenylpropene in the decomposition of cumene hydroperoxide promoted by the neutral ZDDPs (1a—g). The reaction is second-order with respect to the hydroperoxide and the results in Table 7 have been corrected. Analysis of the results shows that the activation parameters in Table 7 are not significantly different from each other. Further, the values of the pre-exponential factor A, and the activation energy E^*, are in close agreement with the literature values for the dehydration of 2-phenylpropan-2-ol to 2-phenylpropene.[42-44] We conclude that, under our experimental conditions, we are unable to measure activation parameters for the rate of formation of the (alcohol + propene) from cumene hydroperoxide because the kinetics are dominated by a secondary reaction, the dehydration of the alcohol to propene.

TABLE 7

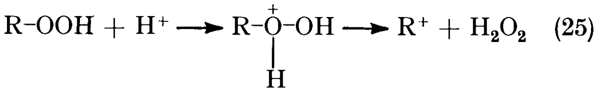
The activation parameters for the formation of 2-phenylpropene from cumene hydroperoxide. [Promoter] ≡ [P] = 15.0 × 10^{-6} mol dm^{-3}

Promoter	E^*/kJ mol^{-1}	ln (A/h^{-1})	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(1a)	(102.9 ± 3.3) [a]	(27.7 ± 1.0)	(99.7 ± 3.3)	(−92.9 ± 8.5)
(1b)	(103.7 ± 3.2)	(28.4 ± 1.0)	(100.5 ± 3.2)	(−86.7 ± 7.3)
(1c)	(109.1 ± 9.4)	(30.4 ± 3.0)	(106.0 ± 9.4)	(−70.0 ± 25.0)
(1d)	(99.6 ± 2.8)	(27.2 ± 0.9)	(96.4 ± 2.8)	(−97.0 ± 6.4)
(1e)	(95.2 ± 7.3)	(24.7 ± 2.2)	(91.9 ± 7.3)	(−118.0 ± 18.5)
(1f)	(101.3 ± 8.8)	(27.2 ± 2.8)	(98.1 ± 8.8)	(−97.2 ± 22.9)
(1g)	(109.8 ± 9.9)	(31.2 ± 4.0)	(106.7 ± 9.9)	(−63.7 ± 31.1)

[a] Errors are standard errors.

(c) *The Ionic Decomposition of Cumene Hydroperoxide.*—Although we cannot obtain direct evidence for the formation of 2-phenylpropan-2-ol and 2-phenylpropene from cumene hydroperoxide by an ionic mechanism' there is evidence in the literature that is consistent with our proposal.

Product studies have shown that some hydroperoxides can undergo ionic decomposition *via* acid attack at the β-oxygen atom of the hydroperoxide and loss of a molecule of hydrogen peroxide [equation (25)]. This



$$R\text{-}OOH + H^+ \longrightarrow R\text{-}\underset{\overset{|}{H}}{\overset{+}{O}}\text{-}OH \longrightarrow R^+ + H_2O_2 \quad (25)$$

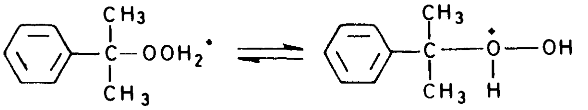
reaction predominates if the carbenium ion (R^+) is very stable or if the Criegee rearrangement of the oxenium ion (RO^+) is slow. Thus Bissing *et al.*[45] were able to demonstrate that in the acid-catalysed decomposition of triarylmethyl hydroperoxides, a complete equilibrium is established between the hydroperoxide and water, and the triarylmethyl alcohol and hydrogen peroxide [equation (26; R = Ar_3C)]. The formation of t-butyl

$$ROOH + H_2O \overset{H^+}{\rightleftharpoons} ROH + H_2O_2 \quad (26)$$

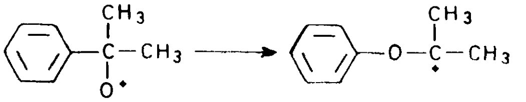
hydroperoxide from 2-methylpropan-2-ol and hydrogen peroxide [equation (26); R = Bu^t] is also well known.

These reactions are favoured by the high stability of the triarylmethyl carbenium ion [46] and the slow rate of migration of the methyl group in the Criegee rearrangement.[47] By contrast the ionic decomposition of cumene hydroperoxide is dominated by acid attack at the α-oxygen atom [45] and rapid phenyl-group migration in the 1-methyl-1-phenylethyl oxenium ion.[47] There is evidence, however, for acid attack at the β-oxygen atom in the ionic decomposition of cumene hydroperoxide.

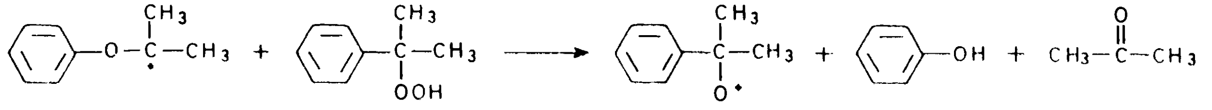
Kharasch *et al.*[36a,48] have shown that 2-phenylpropan-2-ol and 2-phenylpropene react with hydrogen peroxide in aqueous acids to give a quantitative yield of phenol and propan-2-one. More recently, Olah *et al.*[47] have reacted 2-phenylpropan-2-ol with hydrogen peroxide–magic acid and obtained products consistent with the formation of phenol and propan-2-one. Hock and Lang [49] and van Steveninck and Kooyman [50] have obtained products from the acid-catalysed decomposition of cumene hydroperoxide that are consistent with protonation of the hydroperoxide at the β-oxygen atom.


(27)

Clearly there is good evidence to support our suggestion that the ionic decomposition of cumene hydroperoxide can lead to the formation of 2-phenylpropan-2-ol and 2-phenylpropene as well as phenol and propan-2-one. Further, if we assume that the two conjugate acids, formed from the hydroperoxide, are in equilibrium [reaction (27)] we have a simple explanation of why equations (18) and (19) are related by equation (20). We can also explain the abnormal Brønsted coefficient [equation (16)]. For if our ideas are correct the ionic decomposition of cumene hydroperoxide involves attack by the catalyst at two chemically dissimilar sites. Thus the Brønsted coefficient that we measure is the *ratio* of the Brønsted coefficients for the two reactions.


(28)

(13) (14)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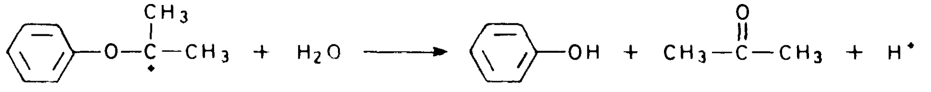

(30)

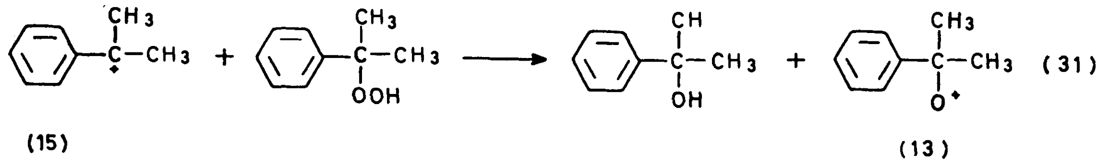
A number of papers [45,50-65] have been published on the kinetics of the ionic decomposition of hydroperoxides. Without exception, these papers describe a reaction that is first-order with respect to the hydroperoxide. Only Chien and Boss [66] describe a catalytic decomposition that is second-order with respect to the hydroperoxide. A careful reading of the literature shows, however, that some authors may have missed a significant point in the treatment of their results.

The ionic decomposition of hydroperoxides is solvent-dependent. In protic solvents the reaction is first-order with respect to the hydroperoxide and first-order with respect to the catalyst.[50-57,59,60,65] Addition of an aprotic solvent increases the rate of reaction [59,60] while addition of water to a non-aqueous reaction solvent retards the rate of reaction.[53-57,62,63] It is claimed that the reaction in an aprotic solvent is also first-order with respect to the hydroperoxide.[58,61,64] In these papers, however, the authors report that the hydroperoxide decomposes in two stages; there is an initial rapid reaction followed by a slower reaction that follows good first-order kinetics. Significantly, if we plot $\ln [\mathrm{ROOH}]_t$ against time for the decomposition of cumene hydroperoxide promoted by the ZDDPs we obtain results similar to those reported. We suggest that by forcing their results into first-order kinetics, previous workers may have missed a significant point, *i.e.* that in aprotic solvents the ionic decomposition of hydroperoxides is second-order with respect to the hydroperoxide.

The simple mechanism proposed by Seubold and Vaughan [51] and Wichterle and Cefelin [52] (Scheme 2) cannot explain all the facets of the ionic decomposition of hydroperoxides that we have observed. We can explain the second-order dependence in hydroperoxide if we assume that the decomposition of the hydroperoxide is a *cationic chain-reaction* in which the oxenium ion (13) and the carbenium ion (14) are chain carriers and the chain reaction is terminated by water [equations (28)—(30)]. This idea was first proposed by Kharasch *et al.*[36b,67-69] who assumed that the cationic chain reaction proceeded *via* the formation of a peroxyester. Shushunov and Yablokov [70] demonstrated that addition of a peroxy ester does not promote the decomposition of a hydroperoxide. As a result both Shushunov and Yablokov, and Farrissey [71] have criticised the concept of a cationic chain-reaction.

The criticisms are based upon the mechanism for the decomposition of peroxyesters. For the hydroperoxide to decompose by a cationic chain-reaction the oxenium ion (13) and the carbenium ion (14) must be discrete ions. All the evidence shows that the ionic decomposition of peroxyesters, *via* the Criegee rearrangement, is a concerted reaction that does not form discrete ions.[72-76] We believe, however, that it is probably a mistake to equate the ionic decomposition of a hydroperoxide with the ionic decomposition of a peroxyester. Firstly, we do not have to assume that, for example, an *OO*-dialkyl hydrogenphosphorodithioate (4) reacts with a hydroperoxide to form a peroxyester.

Second, the formation of an oxenium ion in the decomposition of a peroxyester involves the formation of an 'ion-pair' so that the anion will always be close to the cation, thus facilitating the concerted reaction; in contrast, if a hydroperoxide reacts with an acid without forming a peroxyester the formation of an oxenium ion involves the removal of a neutral molecule (water) from the hydroperoxide. The resulting oxenium ion and the anion of the catalyst will be independent of each other and the conditions required for a cationic chain-reaction are satisfied.



$$ROOH + H^+ \rightleftharpoons ROOH_2^+ \qquad (K_1)$$

$$ROOH_2^+ \rightleftharpoons R{-}\underset{H}{\overset{+}{O}}{-}OH \qquad (K_2)$$

$$ROOH_2^+ \longrightarrow RO^+ + H_2O \qquad (k_3)$$

$$RO^+ \longrightarrow C^+ \qquad (k_4)$$

$$C^+ + ROOH \longrightarrow \text{Phenol} + \text{acetone} + RO^+ \qquad (k_5)$$

$$C^+ + H_2O \longrightarrow \text{Phenol} + \text{acetone} + H^+ \qquad (k_6)$$

$$R{-}\underset{H}{\overset{+}{O}}{-}OH \longrightarrow R^+ + H_2O_2 \qquad (k_7)$$

$$R^+ + ROOH \longrightarrow ROH + RO^+ \qquad (k_8)$$

$$ROH + H^+ \longrightarrow \text{2-phenylpropene} + H_2O \qquad (k_9)$$

SCHEME 3 Proposed mechanism for the acid-catalysed decomposition of cumene hydroperoxide

When the acid reacts at the β-oxygen atom of the hydroperoxide loss of hydrogen peroxide leads to the formation of the carbenium ion (15). In an anhydrous aprotic reaction medium the carbenium ion can undergo two possible reactions, (i) loss of a proton to form 2-phenylpropene and (ii) reaction with a molecule of hydroperoxide to form 2-phenylpropan-2-ol and the oxenium ion (13) [reaction (31)]. The alcohol will be dehydrated to 2-phenylpropene and the oxenium ion (13) will react with hydroperoxide in the cationic chain reaction [equations (28)—(30)] to form phenol and propan-2-one.

The low concentration of the alcohol that is present throughout the entire kinetic run and the activation parameters for the formation of 2-phenylpropene are consistent with (ii), in which the 2-phenylpropan-2-ol is formed directly from the hydroperoxide and then dehydrated to 2-phenylpropene.

From the above discussion we would like to propose the mechanism shown in Scheme 3 for the ionic decomposition of cumene hydroperoxide.

The decomposition of the hydroperoxide can be represented by equation (32). This can be solved if we

$$-\,d[\mathrm{ROOH}]/dt \simeq k_5[\mathrm{C^+}][\mathrm{ROOH}] + k_8[\mathrm{R^+}][\mathrm{ROOH}] \qquad (32)$$

make the normal steady state approximations and assume that $K_2 \gg 1$ to give equation (33) which integrates to (34). There are two extremes for equation (34).

$$-\,d[\mathrm{ROOH}]/dt \simeq K_1K_2k_7[\mathrm{H^+}]\frac{k_5[\mathrm{ROOH}]^2}{k_6[\mathrm{H_2O}]} + [\mathrm{ROOH}] \qquad (33)$$

$$\left\{\ln\left(1 + \frac{k_6[\mathrm{H_2O}]}{k_5[\mathrm{ROOH}]}\right)\right\}_{[\mathrm{ROOH}]_0}^{[\mathrm{ROOH}]_t} \simeq K_1K_2k_7[\mathrm{H^+}]t \qquad (34)$$

(a) If $k_6[\mathrm{H_2O}]/k_5[\mathrm{ROOH}] \ll 1$ then equation (35) obtains. (b) If $k_6[\mathrm{H_2O}]/k_5[\mathrm{ROOH}] \gg 1$ then equation (36) holds. It is clear from equations (35) and (36) that

$$\frac{1}{[\mathrm{ROOH}]_t} - \frac{1}{[\mathrm{ROOH}]_0} \simeq \frac{K_1K_2k_5k_7[\mathrm{H^+}]t}{k_6[\mathrm{H_2O}]} \qquad (35)$$

$$\ln\frac{[\mathrm{ROOH}]_0}{[\mathrm{ROOH}]_t} \simeq K_1K_2k_7[\mathrm{H^+}]t \qquad (36)$$

there will be a transition from second-order to first-order kinetics as the concentration of water in the system is increased. Thus we can explain the second-order kinetics for the decomposition of cumene hydroperoxide promoted by the neutral ZDDPs (1) if there is an efficient method for scavenging the water formed during the reaction.

Luther *et al.*,[77-79] in their studies on the thermal stability of neutral ZDDPs (1) demonstrated that the decomposition of a neutral ZDDP is catalysed by water and by acids formed from hydrolysis reactions. The first step in this reaction is probably (37). Our results

$$[(\mathrm{RO})_2\mathrm{PS}_2]_2\mathrm{Zn} + \mathrm{H_2O} \rightleftharpoons [(\mathrm{RO})_2\mathrm{PS}_2]\mathrm{ZnOH} + (\mathrm{RO})_2\mathrm{PS}_2\mathrm{H} \qquad (37)$$

suggest that *OO*-dialkyl(aryl) hydrogendithiophosphate (4) may be the catalyst, for the ionic decomposition of cumene hydroperoxide, that is formed from the neutral ZDDPs (1). If this is correct, and the first step in the decomposition of a neutral ZDDP is represented by equation (37) then the formation of the acid scavenges water from the reaction system and we have a simple explanation for the second order kinetics. The explanation can be extended to the basic ZDDPs (2), for we have shown that, at the temperatures used in this study, basic ZDDPs are unstable and decompose to the corresponding neutral ZDDP and zinc oxide [equation (38)].[80]

Our results suggest that the disulphide (3) also promotes the decomposition of cumene hydroperoxide by virtue of forming the acid (4). The temperatures required for the reaction are significantly higher than the temperatures required for the ZDDP-promoted reactions.

$$[(\mathrm{RO})_2\mathrm{PS}_2]_6\mathrm{Zn}_4\mathrm{O} \rightleftharpoons 3\,[(\mathrm{RO})_2\mathrm{PS}_2]\mathrm{Zn} + \mathrm{ZnO} \qquad (38)$$

Also the kinetics for the decomposition reactions promoted by the disulphides are first-order with respect to the hydroperoxide. One possible explanation consistent with these observations is that the acid (4) is formed by reactions (39) and (40) and removed from the system by

$$[(\mathrm{RO})_2\mathrm{PS}_2]_2 \longrightarrow 2(\mathrm{RO})_2\mathrm{PS}_2\cdot \qquad (39)$$

$$(\mathrm{RO})_2\mathrm{PS}_2\cdot + \mathrm{R'OOH} \longrightarrow (\mathrm{RO})_2\mathrm{PS}_2\mathrm{H} + \mathrm{R'O}_2\cdot \qquad (40)$$

the oxidation reaction represented by equation (17). Thus a steady-state concentration of acid is formed by a cyclic reaction scheme that generates water, and so the kinetics of decomposition of the hydroperoxide will be first-order with respect to the hydroperoxide.

We thank the management of Esso Chemical Ltd. for permission to publish this paper, Professor D. L. Trimm for useful discussions, and Dr. R. J. Kelly for his detailed and critical appraisal of the manuscript. We are also indebted to Mr. R. Amos for his help with the h.p.l.c. system, and to Mr. S. F. W. Noel and Dr. H. Spedding for m.s. and n.m.r. measurements.

[9/1353 *Received, 23rd August*, 1979]

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