Mechanisms of Antioxidant Action. Part 3.[1] The Decomposition of 1-Methyl-1-Phenylethyl Hydroperoxide by *OO'*-Dialkyl(aryl)phosphorodithioate Complexes of Cobalt, Nickel, and Copper

Michael D. Sexton
PARAMINS Division, Esso Chemical Ltd., Esso Research Centre, Abingdon, Oxfordshire OX13 6BB

OO'-dialkyl(aryl)phosphorodithioates of cobalt(II), nickel(II), and copper(I) have been used as promoters for the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide). The results have been compared with previous work using zinc bis-[*OO'*-dialkyl(aryl)phosphorodithioates] as promoters for cumene hydroperoxide decomposition. The comparison shows that the product distribution and activation parameters for the reactions promoted by the cobalt, nickel, and copper complexes are identical with the product distribution and activation parameters for the reactions promoted by the corresponding zinc complexes. On this evidence it is proposed that the metal complex promoters form the corresponding *OO'*-dialkyl(aryl) hydrogen phosphorodithioate and it is this acid that is the catalyst for hydroperoxide decomposition. The order of the reaction with respect to the hydroperoxide depends upon the promoter and is second order for all the zinc complexes but first order for all the nickel complexes. This can be explained by assuming that there are two mechanisms for the formation of the acid catalyst. The relative importance of the two mechanisms depends upon the experimental conditions used and this provides an explanation for the three-stage reaction observed in hydroperoxide decompositions carried out at low temperatures in the presence of relatively high concentrations of *OO'*-dialkyl(aryl)phosphorodithioate promoters.

In a previous paper[1] we reported results for the decomposition of 1-methyl-1-phenylethyl hydroperoxide (cumene hydroperoxide) promoted by zinc bis-[*OO'*-dialkyl(aryl)phosphorodithioates][†] (**1**) and related compounds. The results are as follows.

(i) The decomposition of cumene hydroperoxide promoted by the zinc DPPs was second order with respect to the hydroperoxide.

(ii) A small amount of acetophenone was formed from the cumene hydroperoxide and the amount formed was independent of the kind of zinc DDP used to promote the hydroperoxide decomposition.

(iii) The major products formed from the hydroperoxide were phenol, 2-phenylpropene (propene), and 2-phenylpropan-2-ol (alcohol). The amounts of these products formed depended upon the kind of zinc DDP used so that as the % [phenol] increased there was a corresponding decrease in the % [alcohol + propene].

The data was explained as follows.

(a) The acetophenone was formed in a free radical decomposition of the cumene hydroperoxide which was independent of the reactions promoted by the zinc DDP.

(b) The phenol was formed by an ionic mechanism involving a cationic chain reaction.

(c) The (alcohol + propene) were also formed *via* an ionic mechanism and not, as is often assumed,[2-7] a free radical mechanism.

(d) The zinc DDP promoted the decomposition of cumene hydroperoxide by forming the corresponding *OO'*-dialkyl(aryl) hydrogen phosphorodithioate (**2**) which catalysed the decomposition of the hydroperoxide by protonating both oxygen atoms of the hydroperoxide.

It was of interest to see if these ideas could be extended to other metal DDPs and this paper reports the results of a study on the decomposition of cumene hydroperoxide promoted by cobalt(II) bis-[*OO'*-dialkyl(aryl)phosphorodithioates] (**3**),[†] nickel(II) bis-[*OO'*-dialkyl(aryl)phosphorodithioates] (**4**),[†] and copper(I) *OO'*-dialkyl(aryl)phosphorodithioates (**5**).[†]

$[(RO)_2PS_2]_2Zn$ (**1**)
$(RO)_2PS_2H$ (**2**)
$[(RO)_2PS_2]_2Co$ (**3**)
$[(RO)_2PS_2]_2Ni$ (**4**)
$[(RO)_2PS_2]_4Cu_4$ (**5**)
$[(RO)_2PS_2]_2Cu$ (**6**)
$[(RO)_2PS_2]_2$ (**7**)
$[(RO)_2PS_2]_6Zn_4O$ (**8**)
$(RO)_2PS_2^{\bullet}$ (**9**)

a; $R = 4\text{-}MeC_6H_4$
b; $R = Et$
c; $R = Me_3CCH_2$
d; $R = Pr^n$
e; $R = Pr^i$

Experimental

The solvents used in this study were AnalaR grade. The *OO'*-dialkyl(aryl) hydrogen phosphorodithioates and their ammonium salts were prepared by methods outlined in the literature.[8,9] The copper(I) DPPs were prepared from the ammonium salts and copper(II) sulphate and the following preparation is typical of the method used.

Ammonium *OO'*-diethylphosphorodithioate (10.0 g, 4.9×10^{-2} mol) was dissolved in water (100 ml). A solution of copper(II) sulphate pentahydrate (6.4 g, 2.56×10^{-2} mol) in water (30 ml) was added to the solution of the ammonium salt

---

[†] For the sake of brevity *OO'*-dialkyl(aryl)phosphorodithioate will be abbreviated to DDP so that the metal DDPs used as promoters will be referred to as zinc DPPs, cobalt DPPs, nickel DDPs, and copper(I) DDPs.

and a black precipitate was formed immediately. The precipitate was extracted with dichloromethane (3 × 200 ml), the dichloromethane solution was dried, and the solvent was removed. The black residue was treated with methanol (50 ml) to precipitate an off-white crystalline solid. The product was recrystallised twice from dichloromethane–heptane to give the copper(I) DDP (5.3 g, 89%) as a crystalline compound, m.p. 189.5—191 °C (decomp.) (Found: C, 19.3; H, 4.2; S, 25.8. Calc. for $C_{16}H_{40}Cu_4O_8P_4S_8$: C, 19.3; H, 4.1; S, 25.8%).

The cobalt DDPs and nickel DDPs were prepared from the corresponding ammonium compounds by metathetical reactions using aqueous solutions of cobalt(II) chloride and nickel(II) sulphate. All the compounds were characterised by elemental analysis, mass spectroscopy, and i.r. spectroscopy. The diamagnetic copper(I) DDPs were also characterised by n.m.r. spectroscopy.

Cumene hydroperoxide was purified *via* its sodium salt and its purity checked by iodometric titration [10] and h.p.l.c. (> 99%).

Details of the kinetic experiments have been given previously.[1] Briefly the decomposition of cumene hydroperoxide in n-decane is carried out under nitrogen and small samples of the reaction mixture are removed every 30 min for analysis. The samples are analysed using h.p.l.c. to determine the concentration of 2-phenylpropene, acetophenone, cumene hydroperoxide, phenol, and 2-phenylpropan-2-ol. No attempt was made to analyse for propan-2-one because of the high temperatures used. The formulae for calculating the % yield of the products and the distribution of the products are given in the previous paper.

The rate constants were calculated using standard methods of linear regression analysis. The correlation coefficient (*r*) of the regression analysis was used to calculate the Student '*t*' parameter and this parameter was used to test the null hypothesis (H_0; $r = 0$) against the alternate hypothesis (H_0; $r \neq 0$).[11] The null hypothesis was rejected if $P > 99.99\%$. 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 $P > 95\%$. Throughout this paper the errors quoted are standard deviations.

Results and Discussion

(a) *The Existence of Copper*(II) *Bis-*[*OO'-dialkyl*(*aryl*)-*phosphorodithioates*] (**6**).—Before discussing our results in detail we would like to comment on reports about the properties of copper(II) DDPs. It has been shown by Hill [12] that in solution copper(II) DDPs dissociate to form a copper(I) DDP and the disulphide (**7**) [equation (1)] so that Hill was unable to isolate a

$$4[(RO)_2PS_2]_2Cu \rightleftharpoons [(RO)_2PS_2]_4Cu_4 + 2[(RO)_2PS_2]_2 \quad (1)$$

pure copper(II) DDP. Since then the disproportionation reaction has been confirmed [13—16] and Wasson [16] states quite clearly that he, like Hill, was unable to isolate a pure copper(II) DDP. Thus it is surprising that there are references to the thermal decomposition,[9] antiwear properties,[17,18] antioxidant properties,[19—21] and e.s.r. studies [22—25] of copper(II) DDPs. Furthermore, in all these papers the authors claim (or refer to previous work in which it is claimed) that copper(II) DPPs were made by the metathetical reaction of a DDP salt and a copper(II) compound followed by recrystallisation of the crude complex. No comment is made about the disproportionation reaction and its effect upon the synthesis of a copper(II) DDP, and only Rowe and Dickert [9,17,18] support their claim to have made a copper(II) DDP with analytical data and a m.p. Given the obvious problems that exist in trying to synthesise copper(II) DDPs we feel that the results quoted for studies on the properties of copper(II) DDPs should be treated with caution and may be open to reinterpretation. Thus we have studied the copper(I) DDPs and we shall not be discussing previous work on the antioxidant properties of copper(II) DDPs in this paper.

Table 1. The product distribution of the decomposition of cumene hydroperoxide promoted by the metal DDPs. $[\text{metal DDP}]_0 = [P]_0 = 15.0 \times 10^{-6}$ mol dm^{-3}, temperature (383 ± 0.1) K

Promoter	[phenol]/%	[alcohol + propene]/%	[acetophenone]/ %	Yield (%)
(**1a**)	(68.0 ± 3.0)	(27.2 ± 2.2)	(4.78 ± 0.80)	94.1
(**3a**)	(71.4 ± 2.9)	(23.5 ± 2.6)	(4.77 ± 0.49)	87.7
(**4a**)	(70.6 ± 1.6)	(24.7 ± 1.5)	(4.53 ± 0.30)	95.8
(**5a**)	(70.4 ± 1.9)	(25.3 ± 1.8)	(4.29 ± 0.20)	92.5
(**1b**)	(73.1 ± 2.9)	(22.4 ± 2.5)	(4.50 ± 0.49)	97.7
(**3b**)	(73.5 ± 2.1)	(22.4 ± 1.7)	(4.19 ± 0.56)	90.8
(**4b**)	(72.4 ± 2.8)	(22.9 ± 2.8)	(4.75 ± 0.44)	91.6
(**5b**)	(72.4 ± 1.4)	(22.5 ± 1.5)	(4.80 ± 0.51)	95.2
(**1c**)	(72.1 ± 2.2)	(23.5 ± 3.4)	(4.42 ± 0.82)	92.1
(**3c**)	(71.5 ± 1.2)	(23.8 ± 1.2)	(4.69 ± 0.52)	93.8
(**4c**)	(72.2 ± 1.7)	(23.4 ± 1.9)	(4.40 ± 0.54)	97.1
(**5c**)	(72.7 ± 1.6)	(23.0 ± 1.2)	(4.38 ± 0.41)	95.0
(**1d**)	(63.1 ± 3.4)	(32.5 ± 2.9)	(4.27 ± 0.55)	95.5
(**3d**)	(63.0 ± 2.0)	(32.4 ± 1.4)	(4.56 ± 0.59)	96.4
(**4d**)	(64.0 ± 1.4)	(31.5 ± 2.1)	(4.53 ± 0.66)	95.6
(**5d**)	(62.9 ± 1.6)	(32.5 ± 1.2)	(4.64 ± 0.45)	98.6
(**1e**)	(76.4 ± 1.4)	(19.3 ± 2.4)	(4.33 ± 0.31)	91.4
(**3e**)	(76.3 ± 2.6)	(19.2 ± 2.3)	(4.52 ± 0.47)	91.7
(**4e**)	(76.5 ± 2.1)	(19.2 ± 2.4)	(4.31 ± 0.44)	94.6
(**5e**)	(76.5 ± 2.1)	(18.9 ± 2.2)	(4.57 ± 0.40)	99.5

(b) *The Distribution of Products formed from Cumene Hydroperoxide.*—In the temperature range 368—398 K cobalt DDPs, nickel DDPs, and copper(I) DDPs promote the decomposition of cumene hydroperoxide. The reactions are catalytic and the promoter ($[\text{Promoter}]_0 = [P]_0 = 15.0 \times 10^{-6}$ mol dm^{-3}) decomposes >50% of the hydroperoxide ($[\text{ROOH}]_0$ 7.0×10^{-2} mol dm^{-3}) in <6 h. Under comparable conditions the rate of decomposition of the hydroperoxide in the absence of the promoter is significantly slower.

The different promoters were compared at the same concentration of phosphorus ($[P]_0$ 15.0×10^{-6} mol dm^{-3}) and at the same temperature [(383.0 ± 0.1) K] and the distribution of products formed from cumene hydroperoxide was determined. The results are shown in Table 1 together with the results for the comparable zinc DPPs which were obtained in the previous study.[1] Statistical analysis of the results shows the following. (i) The concentration of acetophenone formed is independent of the promoter. (ii) The concentrations of phenol and (alcohol + propene) that are formed depend upon the DDP ligand but are independent of the metal to which the ligand is co-ordinated.

The first conclusion is consistent with the suggestion [1] that, under our experimental conditions, acetophenone is formed *via* a free radical decomposition of the hydroperoxide that is independent of the promoter used. The second conclusion is consistent with the idea that the catalyst formed from the promoter is non-metallic but depends upon the ligand to which the metal is co-ordinated. It has already been shown that the results for reactions promoted by the zinc DDPs are consistent with the formation of the acid (**2**). Thus these results suggest that all the metal DDPs studied in this work decompose hydroperoxides by forming the acid (**2**).

Table 2. The activation parameters for the decomposition of cumene hydroperoxide promoted by the metal DPPs. $[\text{metal DPP}]_0 = [P]_0 = 15.0 \times 10^{-6}$ mol dm^{-3}, $[\text{ROOH}]_0$ 7.0×10^{-2} mol dm^{-3}

Promoter	Order[a]	E^*/kJ mol^{-1}	$\ln(A/h^{-1})$	ΔH^*/kJ mol^{-1}	ΔS^*/J mol^{-1} K^{-1}
(1a)	2	(137.0 ± 4.3)	(41.6 ± 1.3)	(133.8 ± 4.1)	(23 ± 11)
(3a)	2	(141.1 ± 3.8)	(42.4 ± 1.2)	(137.9 ± 3.8)	(29 ± 10)
(4a)	1	(140.6 ± 6.4)	(42.5 ± 2.0)	(137.4 ± 6.4)	(30 ± 17)
(5a)	2	(143.6 ± 8.0)	(43.5 ± 2.5)	(140.4 ± 8.0)	(38 ± 21)
(1b)	2	(143.4 ± 10.3)	(44.2 ± 3.2)	(140.3 ± 10.3)	(45 ± 27)
(3b)	1	(136.9 ± 4.4)	(40.9 ± 1.4)	(133.7 ± 4.4)	(16 ± 11)
(4b)	1	(140.8 ± 5.6)	(43.1 ± 1.8)	(138.3 ± 5.6)	(37 ± 15)
(5b)	1	(147.2 ± 10.0)	(44.5 ± 3.1)	(144.0 ± 10.0)	(47 ± 26)
(1c)	2	(143.4 ± 9.2)	(44.5 ± 2.9)	(141.4 ± 8.7)	(50 ± 23)
(3c)	2	(143.2 ± 10.5)	(44.8 ± 3.0)	(140.0 ± 10.5)	(46 ± 24)
(4c)	1	(145.7 ± 7.5)	(45.3 ± 2.8)	(142.8 ± 7.5)	(54 ± 23)
(5c)	2	(148.1 ± 9.0)	(46.4 ± 2.9)	(144.9 ± 9.0)	(63 ± 24)
(1d)	2	(153.0 ± 8.5)	(45.3 ± 2.6)	(149.7 ± 8.5)	(54 ± 22)
(3d)	1	(153.0 ± 9.0)	(45.3 ± 2.7)	(149.7 ± 9.0)	(54 ± 23)
(4d)	1	(153.8 ± 9.3)	(45.8 ± 2.8)	(150.5 ± 9.3)	(64 ± 23)
(5d)	1	(150.6 ± 7.3)	(45.4 ± 2.3)	(147.4 ± 7.3)	(54 ± 19)
(1e)	2	(196.0 ± 20.6)	(62.4 ± 3.8)	(192.9 ± 20.5)	(196 ± 32)
(3e)	1	(179.1 ± 10.6)	(53.5 ± 3.3)	(175.8 ± 10.6)	(122 ± 27)
(4e)	1	(183.1 ± 14.6)	(52.4 ± 4.2)	(179.9 ± 14.6)	(112 ± 35)
(5e)	1	(180.3 ± 16.8)	(55.3 ± 5.4)	(177.1 ± 16.8)	(136 ± 44)

[a] With respect to the hydroperoxide.

(c) *The Activation Parameters for the Decomposition of Cumene Hydroperoxide.*—The rate constants for the decomposition of cumene hydroperoxide promoted by the cobalt, nickel, and copper(I) DDPs were measured in the temperature range 368—398 K. The activation parameters calculated from these results are shown in Table 2 together with the activation parameters for the corresponding zinc DDPs which were obtained in the previous study. For reactions that were second order with respect to the hydroperoxide the activation parameters shown in Table 2 have been corrected to allow for the difference in dimensions of the rate constant (k_2) and the Eyring equation which is only applicable to first-order rate constants.[26,27]

Two conclusions can be drawn from the results in Table 2. First, the order of the reaction with respect to the hydroperoxide depends upon the promoter. All the zinc DDPs promote a decomposition reaction that is second order with respect to the hydroperoxide. All the nickel DDPs, however, promote reactions that are first order with respect to the hydroperoxide. The cobalt and copper(I) DDPs give results that depend upon the ligand co-ordinated to the metal. When R is 4-methylphenyl or 2,2-dimethylpropyl the reaction is second order with respect to the hydroperoxide but the reaction is first order for the other ligands. Second, once the activation parameters have been corrected for the order of reaction, variance analysis shows that, for a given ligand, the activation parameters are independent of the metal to which the ligand is co-ordinated. We have already shown that the results for the reactions promoted by zinc DDPs are consistent with the formation of the acid (**2**). Thus the results presented here are consistent with the idea that all the metal DDPs studied promote hydroperoxide decomposition *via* the acid (**2**).

(d) *The Activation Parameters for the Formation of the Decomposition Products of Cumene Hydroperoxide.*—The activation parameters for the formation of acetophenone, 2-phenylpropene, and phenol from cumene hydroperoxide in reactions that were promoted by the cobalt, nickel, and copper(I) DDPs have been calculated and compared with the results for the corresponding zinc DDPs.

Variance analysis of the plots of ln k against $1/T$ shows that the activation parameters for the formation of acetophenone do not depend upon the promoter used and are similar to the activation parameters for the formation of acetophenone in the free radical decomposition of cumene hydroperoxide.[28–30] Thus these results are consistent with the suggestion that the acetophenone is formed *via* a free radical reaction that is independent of the promoter.

Variance analysis of the regression lines of ln k against $1/T$ shows that the activation parameters for the formation of 2-phenylpropene are independent of the promoter and are in close agreement with literature values for the dehydration of 2-phenylpropan-2-ol to 2-phenylpropene.[31–33] Also it was found that the concentration of 2-phenylpropan-2-ol in the reaction system was virtually constant throughout a kinetic experiment suggesting that the alcohol is a reactive intermediate that reaches a steady-state concentration. All these observations are consistent with the suggestion[1] that, under the experimental conditions used, it is impossible to measure the activation parameters for the formation of (alcohol + propene) because the kinetics are dominated by a secondary reaction *viz.* the dehydration of the alcohol to the propene.

Variance analysis of the plots of ln k against $1/T$ for the formation of phenol shows that for a given DDP ligand the activation parameters are independent of the metal that is co-ordinated to the ligand. A plot of E^* against ln A for all the data shows that there is an isokinetic relationship between the parameters for the formation of phenol [equation (2)]. There is

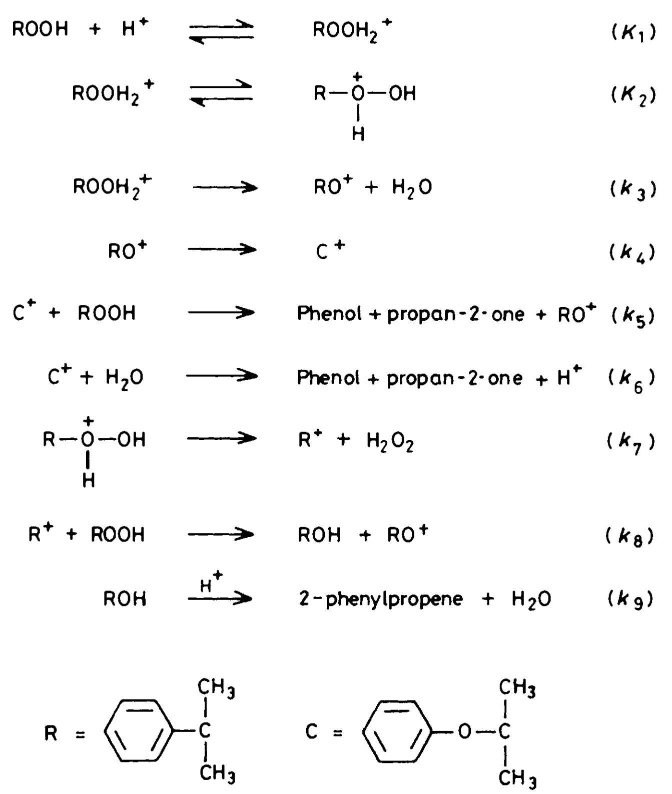
$$E^* = (3.21 \pm 0.02) \times 10^3 \ln A + (7.8 \pm 0.7) \times 10^3 \quad (2)$$

a similar relationship between E^* and ln A for the decomposition of the hydroperoxide [equation (3)] and

$$E^* = (3.12 \pm 0.18) \times 10^3 \ln A + (7.9 \pm 8.4) \times 10^3 \quad (3)$$

variance analysis on the two regression lines shows that they are not significantly different.

Thus, if the existence of an isokinetic relationship is evidence for a common reaction mechanism,[34,35] it follows that the mechanism for the formation of phenol from cumene hydroperoxide is the same as the mechanism for the



Scheme.

decomposition of the hydroperoxide. So if the phenol is formed by an ionic mechanism it follows that, in these experiments, we are measuring the activation parameters for the overall rate of ionic decomposition of the hydroperoxide.

(e) *The Relationship of this Work to Previous Studies.*—The results for the decomposition of cumene hydroperoxide promoted by a range of zinc DDPs were reported in a previous paper.[1] The results were shown to be consistent with a mechanism in which the phenol and (alcohol + propene) were formed *via* an ionic mechanism while the acetophenone was formed *via* a free radical decomposition of the hydroperoxide that was independent of the promoter. Further it was proposed that the zinc DDP promoters form the acid (**2**) and that this acid catalyses the decomposition of the hydroperoxide by protonating both oxygen atoms of the hydroperoxide thereby initiating an ionic chain reaction (Scheme).

The evidence reported in this paper, both product distributions and activation parameters, is consistent with this original reaction scheme, suggesting that all the metal DDPs investigated promote the decomposition of cumene hydroperoxide *via* the formation of the acid (**2**). The only difference between the various metal DDPs is the order of the decomposition with respect to the hydroperoxide, and this difference provides a clue for the mechanism of formation of the acid from the metal DDP.

$$\left[\ln\left(1+\frac{k_6[\mathrm{H_2O}]}{k_5[\mathrm{ROOH}]}\right)\right]_{[\mathrm{ROOH}]_0}^{[\mathrm{ROOH}]_t} \simeq K_1K_2k_7[\mathrm{H^+}]t \qquad (4)$$

$$\frac{1}{[\mathrm{ROOH}]_t}-\frac{1}{[\mathrm{ROOH}]_0} \simeq \frac{K_1K_2k_5k_7[\mathrm{H^+}]t}{k_6[\mathrm{H_2O}]} \qquad (5)$$

$$\ln\frac{[\mathrm{ROOH}]_0}{[\mathrm{ROOH}]_t} \simeq K_1K_2k_7[\mathrm{H^+}]t \qquad (6)$$

The mechanism in the Scheme leads to a complex expression (4) for which there are two extremes. If $k_6[\mathrm{H_2O}]/k_5[\mathrm{ROOH}] \ll 1$ equation (4) reduces to (5) but if $k_6[\mathrm{H_2O}]/k_5[\mathrm{ROOH}] \gg 1$ it reduces to (6). Thus there is a transition from second-order to first-order kinetics if the concentration of water in the system is increased. In the temperature regime 368—398 K the zinc DDPs always promote the second-order decomposition of cumene hydroperoxide. To explain this it was suggested that, in what is essentially an anhydrous system, the acid is formed by partial hydrolysis of the zinc DDP [equation (7)] thus scavenging any remaining traces of water.

$$[(\mathrm{RO})_2\mathrm{PS_2}]_2\mathrm{Zn} + \mathrm{H_2O} \rightleftharpoons [(\mathrm{RO})_2\mathrm{PS_2}]\mathrm{Zn(OH)} + (\mathrm{RO})_2\mathrm{PS_2H} \qquad (7)$$

In the same temperature regime the nickel DDPs always promote the decomposition of cumene hydroperoxide in a reaction that is first order with respect to the hydroperoxide. This can be explained by the reaction sequence (8)—(10) which

$$[(\mathrm{RO})_2\mathrm{PS_2}]_2\mathrm{Ni} + \mathrm{R'OOH} \rightleftharpoons [(\mathrm{RO})_2\mathrm{PS_2}]\mathrm{Ni(OH)} + (\mathrm{RO})_2\mathrm{PS_2}^{\bullet} + \mathrm{R'O}^{\bullet} \qquad (8)$$

$$(\mathrm{RO})_2\mathrm{PS_2}^{\bullet} + \mathrm{R'OOH} \longrightarrow (\mathrm{RO})_2\mathrm{PS_2H} + \mathrm{R'O_2}^{\bullet} \qquad (9)$$

$$[(\mathrm{RO})_2\mathrm{PS_2}]\mathrm{Ni(OH)} + (\mathrm{RO})_2\mathrm{PS_2H} \longrightarrow [(\mathrm{RO})_2\mathrm{PS_2}]_2\mathrm{Ni} + \mathrm{H_2O} \qquad (10)$$

continuously recycles the acid (**2**) in a reaction that generates water. Thus if the metal DDP is susceptible to hydrolysis the acid is generated in a reaction that scavenges water and the result is second-order kinetics. If the metal DDP is not susceptible to hydrolysis the acid is generated in a reaction that forms water and the result is first-order kinetics. It is also probable that the kinetics of the reaction will change as the concentration of the promoter changes. For, in an essentially anhydrous system, the slight traces of water present will only have an effect if the concentration of promoter is relatively small. Thus we might expect a change from second-order to first-order kinetics as the concentration of promoter is increased.

There is evidence for both reaction schemes. First, Luther *et al.*[36–38] have shown that water and acids catalyse the decomposition of zinc DDPs. The first step of this reaction can probably be represented by equation (7). Second, Howard *et al.*[39,40] have demonstrated that the initial reaction of a nickel DDP with hydroperoxide yields free radicals, a reaction that can probably be represented by equation (8). Further, Al-Malaika and Scott[41,42] have shown that the initial reaction of a nickel DDP and cumene hydroperoxide (which is most conveniently investigated by using a [hydroperoxide] : [nickel DDP] ratio of < 10 : 1) produces only acetophenone and 2-phenylpropan-2-ol. The total absence of phenol and 2-phenylpropene indicates that, in this case, both the alcohol and the acetophenone are probably formed *via* a free radical reaction. Once the initial reaction of the nickel DDP and cumene hydroperoxide is complete further hydroperoxide decomposition takes place yielding phenol and 2-phenylpropene,[41–44] products which are consistent with ionic decomposition of the hydroperoxide. Third, Howard and Tang[45] have proposed equation (9) to explain why some oxidation reactions inhibited by metal DDPs are further inhibited by addition of hydroperoxide. It could be argued that the alkoxyl radical produced by reaction (8) would react with the hydroperoxide rather than the *OO'*-dialkylphosporodithioate radical (**9**). There is, however, a very large excess of hydroperoxide sufficient to react with both radicals and reaction (9) will be facilitated by reaction of the acid with the nickel complex [equation (10)].

The two mechanisms for the formation of the acid (**2**) also allow us to rationalise some of the early results for hydroperoxide decomposition promoted by zinc DDPs. This can be done if it is assumed that the mechanism represented by equations (8)—(10) becomes more important than the hydrolysis mechanism [equation (7)] at relatively low temperatures and high metal DDP concentrations. Burn *et al.*[46] in experiments done at 343 K demonstrated the following.

(a) Zinc DDPs promote the decomposition of cumene hydroperoxide in a three-stage reaction. There is a rapid initial reaction followed by an induction period, followed by a final rapid decomposition of the hydroperoxide.

(b) The induction period increases as the concentration of zinc DDP increases.

(c) The products formed from cumene hydroperoxide in the rapid initial reaction are consistent with free radical decomposition of the hydroperoxide.

(d) The disulphide (**7**) was formed during the rapid initial reaction and the yield of this product was *ca.* 50% based upon the zinc DDP.

Since then Rossi and Imparato,[47] Ivanov *et al.*, [48–51] and Okhatsu *et al.*[52] have reported a similar three-stage reaction in hydroperoxide decompositions promoted by zinc DDPs at <363 K. A similar reaction has been observed for the decomposition of hydroperoxides promoted by copper DDPs[19] and nickel DDPs.[41,42] In the experiments with nickel DDPs higher reaction temperatures were used (383 K) and the induction periods were relatively short compared with the induction periods measured by Burn *et al.*[46] Also the induction period increased as the concentration of nickel DDP decreased.

It is known[2,4,47,53–56] that zinc DDPs react with hydroperoxides to form a basic zinc DDP (**8**) and the disulphide (**7**) probably in a reaction that can be represented by equation (11). This reaction can only account for half of the disulphide

$$4[(RO)_2PS_2]_2Zn + R'OOH \longrightarrow [(RO)_2PS_2]_6Zn_4O + [(RO)_2PS_2]_2 + R'OH \quad (11)$$

isolated by Burn *et al.*[46] so it is clear that there is a further reaction taking place that generates more disulphide. It is known[1] that the basic zinc DDP dissociates to form the zinc DDP and zinc oxide [equation (12)] and so it is probable that

$$[(RO)_2PS_2]_6Zn_4O \rightleftharpoons 3[(RO)_2PS_2]_2Zn + ZnO \quad (12)$$

the disulphide is formed by reaction of the zinc DDP with hydroperoxide to form a relatively high concentration of *OO'*-dialkyl(aryl)phosphorodithioate radicals (**9**) [equation (8a)]

$$[(RO)_2PS_2]_2Zn + R'OOH \longrightarrow [(RO)_2PS_2]Zn(OH) + (RO)_2PS_2^{\bullet} + R'O^{\bullet} \quad (8a)$$

most of which will recombine in a reaction [equation (13)] that

$$2(RO)_2PS_2^{\bullet} \longrightarrow [(RO)_2PS_2]_2 \quad (13)$$

is essentially diffusion controlled.[57] It has already been shown[1] that the decomposition of cumene hydroperoxide promoted by disulphides (**7**) is preceded by an induction period. Thus it seems likely that the induction period reported by Burn *et al.*[46] and others[47–52] results from formation of the disulphide (**7**).

As the concentration of the basic zinc DDP (**8**) decreases the concentration of radicals (**9**) decreases and the recombination reaction [equation (13)] ceases to dominate the reaction scheme. Instead the acid (**2**) is formed by reaction of the radical with the hydroperoxide [equation (9)] and the hydroperoxide begins to decompose *via* an ionic mechanism in a reaction that is first order with respect to the hydroperoxide. It follows that the final rapid ionic decomposition of the hydroperoxide will not begin until the concentration of the basic zinc DDP is reduced to a critical level. Hence the induction period increases as the initial concentration of zinc DDP used increases. Also this mechanism predicts that the final rate of decomposition of the hydroperoxide should be a first-order reaction that is independent of the initial concentration of the zinc DDP and this is consistent with observations made by Burn *et al.*[46] If the concentration of zinc DDP is reduced to very low levels the effect of water becomes important and the acid is formed by hydrolysis [equation (7)]. The induction period disappears and the kinetics become second order with respect to the hydroperoxide. Thus the two mechanisms proposed for the formation of the acid (**2**) allow the earlier work of Burn *et al.* to be explained and the differences between that work and more recent observations[1] to be rationalised. Only one result remains unexplained and that is the observation by Al-Malaika and Scott[41,42] that the induction period for cumene hydroperoxide decompositions promoted by nickel DDPs increases as the concentration of nickel DDP decreases.

Finally, a number of alternative suggestions have been made as to the identity of the hydroperoxide decomposition catalyst that is formed from metal DDPs. Shkhiyants *et al.*,[2] Sher *et al.*, [54] and Grishina *et al.*[55,58] have suggested that in hydroperoxide decompositions promoted by zinc DDPs the catalyst is the disulphide (**7**). The differences that we observed[1] between the reactions promoted by the zinc DDPs and reactions promoted by the disulphides show that, under our experimental conditions, the disulphide is not the catalyst. More recently Al-Malaika and Scott[41,42,59] have suggested that, for the decomposition of hydroperoxides promoted by nickel DDPs, the catalyst is SO_2–SO_3–H_2SO_4 formed from the disulphide (**7**) by reactions with the hydroperoxide. A similar idea has been proposed by Okhatsu *et al.*[52,60,61] who have suggested that the catalyst formed from a zinc DDP is sulphuric acid. Examination of the reaction scheme proposed by Okhatsu *et al.* shows the sulphuric acid being formed from sulphurous acid. Since free sulphurous acid probably does not exist[62] Okhatsu *et al.* are, in effect, proposing that the sulphuric acid is formed *via* sulphur dioxide.

This idea, however, appears to be inconsistent with data reported by Al-Malaika and Scott and others as follows.

(i) Al-Malaika and Scott have shown that when a range of promoters are tested at the same sulphur concentration a nickel DDP decomposes cumene hydroperoxide faster than a nickel dithiocarbamate or a nickel xanthate.

(ii) A zinc dithiocarbamate reacted with cumene hydroperoxide evolves sulphur dioxide.[43] It is generally assumed that other metal dithiocarbamates will also evolve sulphur dioxide when reacted with hydroperoxide and that the sulphur dioxide is formed *via* a series of intermediates in which the sulphur atoms in the promoter are oxidised.[42]

(iii) All the evidence on the antioxidant action of metal dithiocarbamates is consistent with the catalyst for hydroperoxide decomposition being derived from the sulphur dioxide formed from the metal complex (see ref. 42 and references therein).

(iv) If sulphur dioxide (or sulphur trioxide–sulphuric acid formed by oxidation of sulphur dioxide[7]) is the catalyst formed from a metal DPP then it follows from (i) that sulphur dioxide will be formed more rapidly from a metal DDP than it is from a metal dithiocarbamate.

(v) Burn *et al.*[46] have shown and we have confirmed[63] that a zinc DDP does not react with a hydroperoxide to form sulphur dioxide. We have also shown[63] that a nickel DDP does not react with a hydroperoxide to form sulphur dioxide. Further, Burn *et al.*[46] demonstrated that benzothiazole-2-sulphonic acid which does decompose at 343 K (the temperature used by Burn *et al.*) to form sulphur dioxide is not as effective a promoter in the decomposition of cumene hydroperoxide as a zinc DDP.

On the basis of the evidence we conclude that the hydroperoxide decomposition catalyst formed from metal DDPs is not sulphur dioxide or sulphur trioxide–sulphuric acid that is formed by oxidation of sulphur dioxide.

The work of Al-Malaika and Scott,[59] reporting the identification of intermediates in the reaction of a disulphide (**7**) with the hydroperoxide, should be treated with caution. It is well known (see, for example, refs. 9, 18, 36—38) that *OO'*-dialkylphosphorodithioate complexes are thermally unstable and decompose to yield mercaptans, alkyl monosulphides, and alkyl disulphides. In the presence of hydroperoxide these compounds will be oxidised to sulphur–oxygen compounds. Hence the compounds identified by Al-Malaika and Scott may result from side reactions that are unrelated to the decomposition of the hydroperoxide promoted by the disulphide (**7**).

Acknowledgements

I thank the management of Esso Chemical Ltd. for permission to publish this paper, and Mr. J. R. Dever for technical assistance.

References

1 Part 2, A. J. Bridgewater, J. R. Dever, and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1006.
2 I. V. Shkhiyants, N. V. Voyevoda, N. I. Komiassarova, L. F. Chenyavskaya, V. V. Sher, and P. I. Sanin, *Neftekhimiya*, 1974, **14**, 312.
3 S. K. Ivanov and I. Kateva, *React. Kinet. Catal. Lett.*, 1977, **6**, 243.
4 P. I. Sanin, I. F. Blagovidov, A. B. Vipper, A. M. Kuliev, S. E. Krein, K. S. Ramaya, G. I. Shor, V. V. Sher, and Yu. S. Zaslavskii, Proceedings of the Eighth World Petroleum Congress, 1971, vol. 5, p. 91.
5 G. Scott, *Rev. Sulfur Chem.*, 1969, **4**, 99.
6 I. V. Shkhiyants, M. A. Dzyubina, N. V. Voyevoda, V. V. Sher, and P. I. Sanin, *Neftekhimiya*, 1973, **13**, 749.
7 G. Scott, in 'Developments in Polymer Stabilisation,' ed. G. Scott, Applied Science, London, 1983, vol. 6, p. 29.
8 V. P. Wystrach, E. O. Hook, and G. L. M. Christopher, *J. Org. Chem.*, 1956, **21**, 707.
9 J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, 1967, **32**, 647.
10 R. D. Mair and A. J. Graupner, *Anal. Chem.*, 1964, **38**, 194.
11 A. Haber and R. P. Runyon, 'General Statistics,' Addison-Wesley, London, 1977, 3rd edn.
12 A. C. Hill, *J. Sci. Food Agric.*, 1969, **20**, 4.
13 W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 69.
14 W. Rudzinski and Q. Fernando, *Anal. Chem.*, 1978, **50**, 472.
15 J. R. Wasson, G. M. Woltermann, and H. J. Stoklosa, *Top. Curr. Chem.*, 1973, **35**, 65.
16 J. R. Wasson, *Inorg. Chem.*, 1971, **10**, 1531.
17 C. N. Rowe and J. J. Dickert, *Am. Chem. Soc., Div. Pet. Chem. (Preprints)*, 1965, **10**, D71.
18 J. J. Dickert and C. N. Rowe, *ASLE Trans.*, 1967, **10**, 85.
19 J. H. B. Chenier, J. A. Howard, and J. C. Tait, *Can. J. Chem.*, 1977, **55**, 1644.
20 J. H. B. Chenier, J. A. Howard, and J. C. Tait, *Can. J. Chem.*, 1978, **56**, 157.
21 J. A. Howard and J. C. Tait, *Can. J. Chem.*, 1978, **56**, 164.
22 D. Shopov and N. D. Yordanov, *Inorg. Chem.*, 1970, **9**, 1943.
23 N. D. Yordanov and D. Shopov, *Chem. Phys. Lett.*, 1972, **16**, 60.
24 N. D. Yordanov and D. Shopov, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 19.
25 N. D. Yordanov and D. Shopov, *J. Chem. Soc., Dalton Trans.*, 1976, 883.
26 R. K. Boyd, *J. Chem. Educ.*, 1978, **55**, 84.
27 P. J. Robinson, *J. Chem. Educ.*, 1978, **55**, 209.
28 J. R. Thomas, *J. Am. Chem. Soc.*, 1955, **77**, 246.
29 G. H. Twigg, G. W. Yodin, H. C. Bailey, and J. Holden, *Erdoel Kohle*, 1962, **15**, 74.
30 V. L. Antonovski, E. T. Denisov, and L. V. Solntseva, *Kinet. Katal.*, 1965, **8**, 815.
31 W. M. Shubert and B. Lamm, *J. Am. Chem. Soc.*, 1966, **88**, 120.
32 J. P. Durand, M. Davidson, M. Hellin, and F. Coussemont, *Bull. Soc. Chim. Fr.*, 1966, **43**, 52.
33 J. L. Jensen and D. J. Carre, *J. Org. Chem.*, 1971, **36**, 3180.
34 O. Exner, *Prog. Phys. Org. Chem.*, 1973, **10**, 411, and references therein.
35 R. R. Krug, W. G. Hunter, and R. G. Greiger, *J. Phys. Chem.*, 1976, **80**, 2335, 2341, and references therein.
36 H. Luther and S. K. Sinha, *Erdoel Kohle*, 1964, **17**, 91.
37 H. Luther, E. Baumgarten, and D. Staeck, *Erdoel Kohle*, 1969, **22**, 530.
38 H. Luther, E. Baumgarten, and K. U. Islam, *Erdoel Kohle*, 1973, **26**, 509.
39 J. A. Howard and J. H. B. Chenier, *Can. J. Chem.*, 1976, **54**, 390.
40 J. A. Howard, in 'Frontiers of Free Radical Chemistry,' ed. W. A. Pryor, Academic Press, London, 1980, p. 237.
41 S. Al-Malaika and G. Scott, *Eur. Polym. J.*, 1980, **16**, 503.
42 S. Al-Malaika, K. B. Chakraborty, and G. Scott, in 'Developments in Polymer Stabilisation,' ed. G. Scott, Applied Science, London, 1983, vol. 6, p. 73.
43 J. D. Holdsworth, G. Scott, and D. Williams, *J. Chem. Soc.*, 1964, 4692.
44 G. Scott, *Br. Polym. J.*, 1971, **3**, 24.
45 J. A. Howard and S.-B. Tang, *Can. J. Chem.*, 1980, **58**, 92.
46 A. J. Burn, R. Cecil, and V. O. Young, *J. Inst. Petroleum*, 1971, **57**, 319.
47 E. Rossi and L. Imparato, *Chim. Ind. (Milan)*, 1971, **53**, 838.
48 S. K. Ivanov, I. Kateva, and D. Shopov, *Neftekhimiya*, 1972, **12**, 606.
49 S. K. Ivanov and I. Kateva, *Erdoel Kohle*, 1973, **26**, 77.
50 S. K. Ivanov and I. Kateva, *J. Polym. Sci., Polym. Symp.*, 1976, **57**, 237.
51 S. K. Ivanov and I. Kateva, *Neftekhimiya*, 1978, **18**, 417.
52 Y. Okhatsu, K. Kikkawa, and T. Osa, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 3606.
53 S. K. Ivanov and I. Kateva, *Neftekhimiya*, 1971, **11**, 290.
54 V. V. Sher, Y. I. Markova, L. G. Khanakova, G. N. Kuzmina, and P. I. Sanin, *Neftekhimiya*, 1973, **13**, 876.
55 O. N. Grishina and V. M. Bashinova, *Neftekhimiya*, 1974, **14**, 142.
56 G. Brunton, B. C. Gilbert, and R. J. Mawby, *J. Chem. Soc., Perkin Trans. 2*, 1976, 650.
57 B. C. Gilbert, P. A. Kelsall, M. D. Sexton, G. D. G. McConnacchie, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1984, 629.
58 O. N. Grishina, N. P. Anoshina, and V. M. Bashinova, *Neftekhimiya*, 1974, **14**, 307.
59 S. Al-Malaika and G. Scott, *Polymer*, 1982, **23**, 1711.
60 Y. Okhatsu, H. Ueda, K. Kikkawa, and T. Osa, *Yukagaku*, 1977, **26**, 296.
61 Y. Okhatsu, *Junkatsu*, 1978, **23**, 606.
62 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, Chichester, 1980, 4th edn., p. 532.
63 M. D. Sexton, unpublished observations.

Received 23rd January 1984; Paper 4/116