Oxidation of Basic Zinc Dibutyl Dithiophosphate by Cumyl Hydroperoxide at 25 °C: Kinetic Studies by H.P.L.C.

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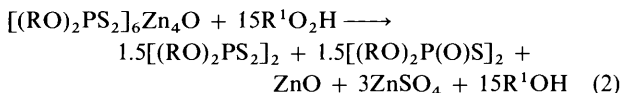[b] Department of Chemistry, Brunel University, Uxbridge, Middlesex, UB8 3PH

Over an 11 h reaction period in cyclohexane at 25 °C, $[(BuO)_2PS_2]_6Zn_4O$ (0.01 mol dm⁻³) induces solely the homolytic decomposition of 0.12 mol dm⁻³ cumyl hydroperoxide. Cumyloxy radicals may abstract hydrogen atoms to form the major aromatic product cumyl alcohol; they may combine to produce dicumyl peroxide; or they may be scavenged by a Zn(SPS) unit which reduces the cumyloxy radicals to 2-phenylpropene. The formation of this last species by the reduction of cumyloxy radicals occurs in contrast with the mechanism usually proposed, viz., by acid-catalysed dehydration of cumyl alcohol. Organothiophosphate oxidation products of $[(BuO)_2PS_2]_6Zn_4O$ include $[(BuO)_2PS_2]_2$, $[(BuO)_2PS_2]_2S$, $[(BuO)_2PS]_2S$, and a monothiophosphate provisionally characterised as $[(BuO)_2P(S)O]_2Zn$.

For the past 45 years, zinc dialkyl dithiophosphates $[(RO)_2PS_2]_2Zn$ have been widely used as lubricating oil additives. They exhibit synergistic properties combining an antioxidant capacity with an ability to act as corrosion inhibitors and antiwear agents. Two types of antioxidant have been recognised: chain-breaking agents which intercept chain-propagating free radicals, and preventative antioxidants which reduce the initiation rate of autoxidation. It is generally accepted that zinc dialkyl dithiophosphates (ZDDPs) act as both chain-breaking antioxidants (radical scavengers)[1-6] and preventative antioxidants (hydroperoxide decomposers).[4,7-11]

The mechanism of hydroperoxide decomposition induced by ZDDPs is complex. Burn et al.[9] and Rossi and Imparato[11] describe a three-stage reaction profile: there is an initial rapid hydroperoxide decomposition followed by an induction period which precedes a further rapid hydroperoxide reduction. It is well established[2,9,11,12] that ZDDPs are oxidised [equation (1)], to basic ZDDP $[(RO)_2PS_2]_6Zn_4O$ and bis(dialkoxy-thiophosphinoyl) disulphide $[(RO)_2PS_2]_2$.

$$4[(RO)_2PS_2]_2Zn + R^1O_2H \longrightarrow$$
$$[(RO)_2PS_2]_6Zn_4O + [(RO)_2PS_2]_2 + R^1OH \quad (1)$$
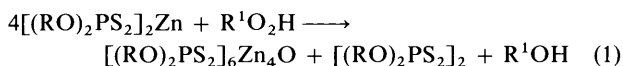
However, little work is reported on the oxidation of basic ZDDPs. Rossi and Imparato[11] proposed that the oxidation of basic isopropyl ZDDP may be represented by equation (2).

$$[(RO)_2PS_2]_6Zn_4O + 15R^1O_2H \longrightarrow$$
$$1.5[(RO)_2PS_2]_2 + 1.5[(RO)_2P(O)S]_2 +$$
$$ZnO + 3ZnSO_4 + 15R^1OH \quad (2)$$

The kinetics of oxidation of 0.04 mol dm⁻³ octyl ZDDP by 0.12 mol dm⁻³ cumyl hydroperoxide in cyclohexane at 30 °C has recently been followed by ³¹P n.m.r. spectroscopy.[13] During a 3 h reaction period two reactions were observed: firstly a rapid oxidation of ZDDP to basic ZDDP and bis(dioctoxy-thiophosphinoyl) disulphide, in accordance with equation (1) (first-order rate constant $k_1 = 0.017$ min⁻¹), followed by a slower oxidation of the basic salt ($k_1 = 0.0021$ min⁻¹). A further increase in the disulphide ³¹P n.m.r. signal at 85.5 ppm (relative to tributyl phosphate, TBP) and the growth of three new signals at 84.4, 79, and 49 ppm were associated with the depletion of the basic ZDDP salt. These observations are only partly explained by the scheme represented by equation (2).

It is commonly assumed that the products formed from the reduction of cumyl hydroperoxide enable a distinction to be drawn between free-radical and ionic decomposition mechanisms. Generally it is considered that phenol is a product of a heterolytic (ionic) mechanism, and 2-phenylpropene, aceto-phenone, and cumyl alcohol result from a homolytic decomposition mechanism.[6,14,15]

This work describes the use of preparative normal-phase h.p.l.c. with u.v. diode-array detection to monitor the kinetics of decomposition of 0.12 mol dm⁻³ cumyl hydroperoxide, induced by 0.01 mol dm⁻³ basic butyl ZDDP in cyclohexane at 25 °C, and to characterise the aromatic and organothio-phosphate reaction products.

Experimental

Apparatus.—The chromatographic separations were performed using a modular system comprising a LKB 2150 h.p.l.c. pump, a LKB 2140 rapid spectral detector and a Rheodyne 7125 injector. All analyses were carried out using two 250 × 4.6 mm Spherisorb S5CN columns in series.

Mass spectra were recorded with a VG 7070 HS double focusing mass spectrometer [electron-impact ionization 70 eV, mass range 10–650 at 3 s decade⁻¹, and resolution (10% valley) 1000].

³¹P N.m.r. spectra were recorded, using deuteriated chloroform as the solvent, at 121.49 MHz on a Bruker MSL 300 instrument operating under the following conditions: chemical shift range −5 to 120 ppm with TBP as the reference, a 90° ³¹P pulse angle, wide-band proton decoupling, and a scan time of 3 s. Transients were collected until an adequate signal-to-noise ratio was obtained.

Reagents and Solvents.—Cumyl hydroperoxide (80%), cumyl alcohol (99%), 2-phenylpropene, and phenol (99%) were purchased from Aldrich Chemicals. Cumyl hydroperoxide was purified via the sodium salt[16] to a purity of 98%. Dicumyl peroxide was extracted and purified from Perkadox BC-40 obtained from Akzo Chemie. $[(BuO)_2PS_2]_6Zn_4O$, bZDDP (97% determined by ³¹P n.m.r. spectroscopy), was prepared by the oxidation of $[(BuO)_2PS_2]_2Zn$ by cumyl hydroperoxide[13] in tetradecane solution. The hexane and diethyl ether h.p.l.c.-grade solvents were supplied by Romil Chemicals.
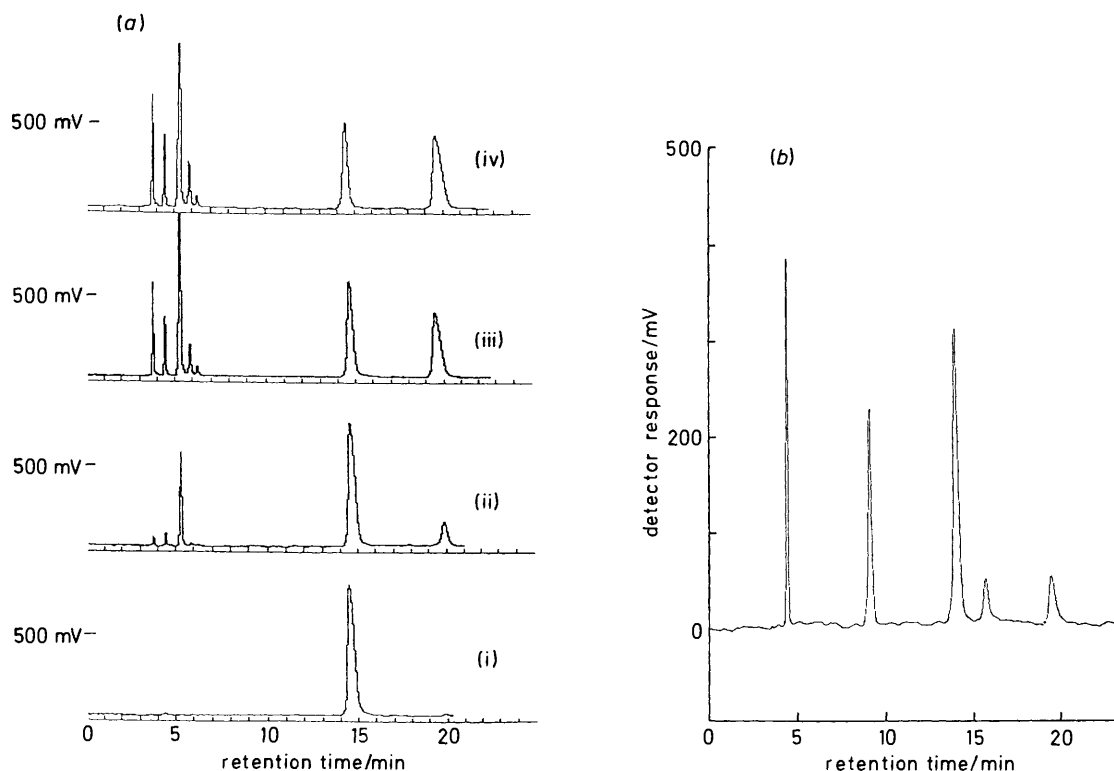
Figure 1. (*a*) Chromatograms, recorded at a wavelength 210 nm using 5% diethyl ether in hexane as the mobile phase, prior to the addition of basic butyl ZDDP (i) and after reaction periods of 45 min (ii), 200 min (iii) and 660 min (iv) at 25 °C. For peak assignments see Table 1. (*b*) Chromatogram, recorded at a wavelength of 210 nm using hexane as the mobile phase, after a reaction period of 680 min at 25 °C. For peak assignments see Table 1.

Procedure.—(i) *Kinetic study.* The solution of 0.12 mol dm^{-3} cumyl hydroperoxide and 0.01 mol dm^{-3} basic butyl ZDDP in cyclohexane was placed in a vessel capped with a self-sealing septum and maintained at 25 °C for 11 h. Prior to capping the vessel the 0.1 cm^3 air space was flushed with nitrogen. 30 mm^3 of solution was sampled through the septum every 30 min for the first 5 h, then after 7.5 h, and finally at 11 h. The portions were promptly diluted tenfold with hexane. The u.v. diode array detector was zeroed whilst pumping the mobile phase, 5% diethyl ether in hexane, at 2 cm^3 min^{-1}, prior to injecting 20 mm^3 of the diluted solutions. U.v. spectra were recorded by the diode-array detector on the eluting material at intervals of 1 s. Reference solutions of 2-phenylpropene, cumyl alcohol, phenol, acetophenone, and cumyl hydroperoxide were run to assign the aromatic species involved in the reaction and to calibrate the peak integration of chromatograms displayed at a wavelength of 210 nm.

(ii) *Preparative h.p.l.c. analysis.* Analytical h.p.l.c. performed on the diluted solution (sampled after the kinetic study) using hexane as a mobile phase, produced a good separation of the compounds exhibiting dissimilar retention times to the reference materials and proved to be sufficient for preparative work. Six aliquots (60 mm^3) were removed from the reaction mixture after the kinetic study and were individually injected onto the column. The uncharacterised fractions were collected and the corresponding fractions from each run were combined. Throughout the course of the fraction collection the chromatograms did not vary appreciably. A rotary evaporator was used to remove the hexane from the combined fractions. ^{31}P N.m.r. analysis was conducted on fractions giving u.v. spectra characteristic of an organothiophosphate. After evaporation of the n.m.r. solvent, the organothiophosphates and other unidentified compounds were analysed by mass spectrometry. H.p.l.c. runs were performed on standard 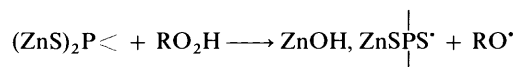solutions of any non-reference aromatics characterised by m.s. analysis, using 5% diethyl ether in hexane as a mobile phase, thereby calibrating the peak integrations of the kinetic study.
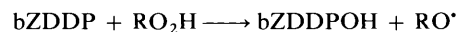
Results and Discussion

The time evolution of the chromatogram, from spectra recorded at 210 nm with 5% diethyl ether in hexane as the mobile phase, is shown in Figure 1(*a*) whilst the chromatogram monitored using hexane as a mobile phase after an interval of 680 min is shown in Figure 1(*b*). The retention times and identities of the eluted reaction species are given in the Table. The retention times of reference aromatics, phenol, and acetophenone are also listed. ^{31}P N.m.r. and mass spectrometric data are tabulated for compounds isolated by preparative h.p.l.c.

Figure 2 shows plots of the concentrations of cumyl hydroperoxide, cumyl alcohol, 2-phenylpropene, and dicumyl peroxide *versus* time and indicates that over the duration of the analysis basic butyl ZDDP promotes the decomposition of half the cumyl hydroperoxide. Cumyl alcohol is the main aromatic product but smaller quantities of 2-phenylpropene and dicumyl peroxide are also formed.

The formation of dicumyl peroxide implies that homolytic cleavage of the hydroperoxide O–O bond occurs to generate cumyloxy radicals, which may then combine to give dicumyl peroxide. The reaction is outlined in the following scheme, where the unit ZnSPSZn represents a portion of the basic salt structure:[17]

$$(ZnS)_2P< + RO_2H \longrightarrow ZnOH, ZnS\overset{|}{\underset{|}{P}}S^{\cdot} + RO^{\cdot}$$

or, more compactly,

$$bZDDP + RO_2H \longrightarrow bZDDPOH + RO^{\cdot}$$

Table. Retention times and identities of eluted compounds.

Eluted fraction	Retention time/min		m/z (major fragments)	^{31}P N.m.r.^{a}	Identity
	5% ether–hexane	hexane			
1	3.7	4.5	—	—	2-phenyl-propene
2	4.2	9.0	270, 135, 119	—	dicumyl peroxide
3	b	14.0	482, 241, 187, 131	86.3	[(BuO)$_2$PS$_2$]$_2$
4	b	16.0	514, 273, 241, 187, 131	85.2	[(BuO)$_2$PS$_2$]$_2$S
5	b	19.5	450, 209, 187, 131	80.0	[(BuO)$_2$PS]$_2$S
6	15.0	>30	—	—	cumyl hydroperoxide
7	20.0	>30	—	—	cumyl alcohol
Reference aromatics					
Acetophenone	9.0	>30	—	—	—
Phenol	16.5	>30	—	—	—

^{a} δ/(ppm) in CDCl$_3$; relative to TBP. ^{b} Fractions 3, 4, and 5: 5.2–6.2 min, not well resolved.
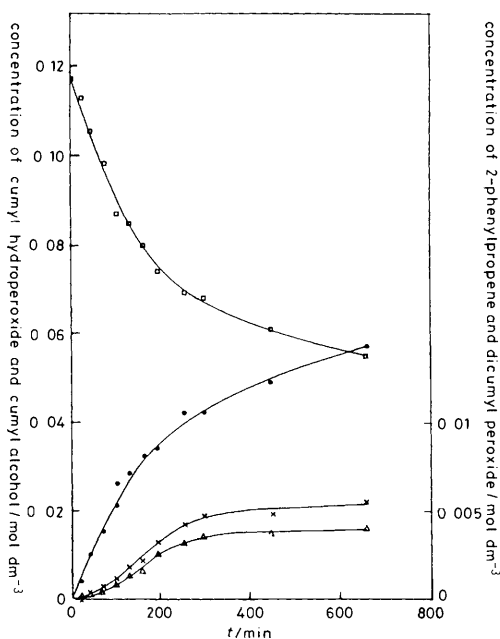

Figure 2. Plot of cumyl hydroperoxide (□), cumyl alcohol (●), 2-phenylpropene (×), and dicumyl peroxide (△) concentrations *versus* time for the reaction of 0.01 mol dm^{-3} basic butyl ZDDP with 0.117 mol dm^{-3} cumyl hydroperoxide at 25 °C in cyclohexane.

followed by,

$$2\,RO^{\bullet} \longrightarrow ROOR \qquad (R = PhC(CH_3)_2^{-})$$

Previous authors[4,6] have suggested that acetophenone is derived from cumyloxy radicals produced in the homolytic decomposition of cumyl hydroperoxide, as described by the following reaction:
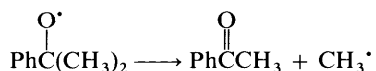

H.p.l.c. analyses[18] conducted on solutions of dicumyl peroxide in squalane exposed to different temperatures have indicated that at 90 °C and above, dicumyl peroxide decomposes producing acetophenone, as follows:
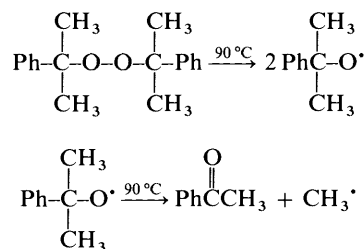
This may explain why acetophenone is detected in kinetic studies involving the homolytic decomposition of cumyl hydroperoxide at temperatures >90 °C,[10,19] or at lower temperatures but using g.c. (with a heated injector) as a technique to characterise the aromatic products.[4] Since the work described here was carried out at 25 °C, acetophenone was not observed.
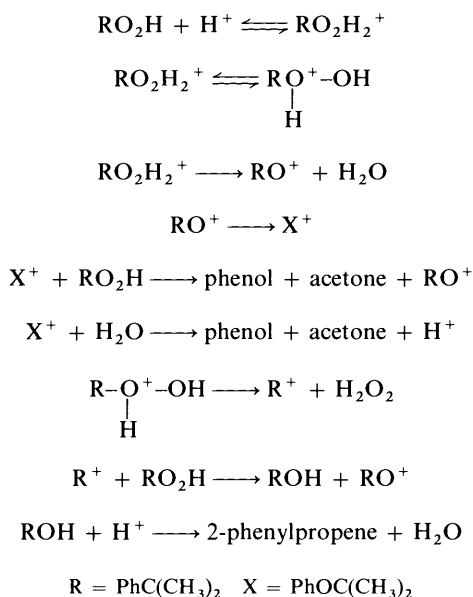
Phenol is considered to be a product from the heterolytic acid-catalysed decomposition of cumyl hydroperoxide.[1,6,10,14,19,20] However, this work indicates that no phenol is produced during the analysis period at ambient temperature. Therefore under these conditions, it is unlikely that significant quantities of an acidic compound arise to catalyse an heterolytic hydroperoxide decomposition.

It has been generally accepted[6,11,14,15] that 2-phenylpropene results from the acid-catalysed dehydration of cumyl alcohol. We believe that a Lewis acid capable of dehydrating cumyl alcohol would also induce the heterolytic decomposition of cumyl hydroperoxide to give phenol, hence we suggest that, as phenol is absent from the reaction, 2-phenylpropene is derived *via* the following pathway:
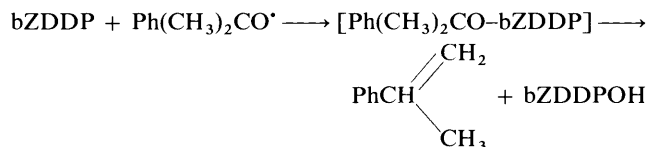
This is consistent with the conclusion of Korcek *et al.*[21] that basic ZDDP acts as a radical scavenger, reacting with cumyloxy radicals.

Bridgewater *et al.*[10] followed the decomposition of 7 × 10^{-2} mol dm^{-3} cumyl hydroperoxide by 7 × 10^{-6} mol dm^{-3} basic butyl ZDDP at 110 °C and suggested that cumyl alcohol and 2-phenylpropene were not formed from the free-radical mechanism usually accepted but by the following ionic acid-catalysed decomposition mechanism:

$$RO_2H + H^+ \rightleftharpoons RO_2H_2^+$$

$$RO_2H_2^+ \rightleftharpoons R\underset{\underset{H}{|}}{O}^+\text{-OH}$$

$$RO_2H_2^+ \longrightarrow RO^+ + H_2O$$

$$RO^+ \longrightarrow X^+$$

$$X^+ + RO_2H \longrightarrow phenol + acetone + RO^+$$

$$X^+ + H_2O \longrightarrow phenol + acetone + H^+$$

$$R\text{-}\underset{\underset{H}{|}}{O}^+\text{-OH} \longrightarrow R^+ + H_2O_2$$

$$R^+ + RO_2H \longrightarrow ROH + RO^+$$

$$ROH + H^+ \longrightarrow 2\text{-phenylpropene} + H_2O$$

$$R = PhC(CH_3)_2 \quad X = PhOC(CH_3)_2$$

However, in the present study, where the reaction is conducted using a much higher mole ratio of cumene hydroperoxide to basic ZDDP, and much lower temperatures, the absence of phenol as a decomposition product indicates that cumyl alcohol derives from hydrogen abstraction by cumyloxy radicals. The origin of the hydrogen source is unclear; a solvent molecule or cumyl hydroperoxide are, however, possible candidates.

The reaction products of $[(RO)_2PS_2]_2Zn$ and peroxy radicals in a mixed heptane–hexadecane solution at 80 °C, reported by Willermet and Kandah[22] include $[(RO)_2PS_2]_2$ as a major product with smaller quantities of $[(RO)_2PS]_2S$ and $[(RO)_2PS_2]_2S$. Mass spectrometric and [31]P n.m.r. analyses performed here on the eluted organothiophosphates using hexane as the mobile phase indicate that $[(BuO)_2PS_2]_2$, $[(BuO)_2PS]_2S$, and $[(BuO)_2PS_2]_2S$ result from the oxidation of basic butyl ZDDP by cumyl hydroperoxide, and confirm Willermet's and Kandah's [31]P n.m.r. assignments for these compounds. It is possible therefore that the oxidation of ZDDP by peroxy radicals, studied by Willermet and Kandah, proceeds via the basic salt.

Recent kinetic studies[13] by [31]P n.m.r. of the oxidation of basic butyl ZDDP by cumyl hydroperoxide indicate that, accompanying the reduction of the [31]P n.m.r. basic butyl ZDDP signal, there occurs the development of a 'fine structure' or splitting of the basic butyl ZDDP signal. This was interpreted in terms of the break-up by progressive oxidation of the $[(BuO)_2PS_2]_6Zn_4O$ cluster species, whose structure is that of a tetrahedron of zinc atoms surrounding a central oxygen, with linking $(BuO)_2PS_2$ ligands along each edge of the tetrahedron.[17] We concur with Howard et al.[3] that oxidation proceeds via oxidant attack at a zinc atom with concomitant breakage of a Zn–S bond at the atom of attack. We suggested[13] that, as long as the number of bond breakages is not too large, the tetrahedral framework is not disrupted so that many closely related species are formed, differing in number, ligation number, and arrangement of $(BuO)_2PS_2$ groups. Other organothiophosphates produced by this process gave [31]P n.m.r. signals of 85.5, 84.4, 79, and 49 ppm in cyclohexane, using TBP as a

reference. These compounds produce ^{31}P signals higher by approximately 1 ppm in chloroform.

The chromatographic conditions used in this work do not detect any zinc-containing species derived from the oxidation of basic butyl ZDDP. The n.m.r. signal at 49 ppm is likely to be a zinc-containing species and we have provisionally assigned this as $[(BuO)_2P(S)O]_2Zn$.[13]

In conclusion, throughout the period of analysis (11 h) at ambient temperature, basic butyl ZDDP induces the homolytic decomposition of cumyl hydroperoxide, to produce cumyloxy radicals which may also participate in the basic ZDDP oxidation. The formation of cumyloxy radicals implies that basic butyl ZDDP exhibits a pro-oxidant capacity, as well as being a radical scavenger and hydroperoxide decomposer. The antioxidant function of basic butyl ZDDP is thus to be interpreted as the net result of these properties. Under the conditions used, the concentration of any Lewis acid produced is insufficient to initiate heterolytic decomposition of cumyl hydroperoxide.

Acknowledgements

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