

923. *Oxidation of Organic Sulphides. Part XV.¹ The Antioxidant Action of Phenothiazine, Zinc Isopropylxanthate, Zinc Di-isopropyl-dithiophosphate, and Zinc Dibutyldithiocarbamate, in Squalene.*

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The compounds named in the title inhibit both the heat- and the $\alpha\alpha'$ -azodi-isobutyronitrile-catalysed oxidation of squalene. They also rapidly decompose t-butyl and squalene hydroperoxides. It is suggested that the mechanism of their antioxidant action involves both interference with the propagation of the oxidative chain reaction and decomposition of the olefin hydroperoxide.

SULPHUR compounds inhibit the autoxidation of lubricating oils,² fats,³ polyethylene,⁴ and vulcanized rubber,⁵ and it has been suggested that their inhibitory action arises from their ability to decompose hydroperoxides.^{2a,b,c,e} Detailed studies of the effect of sulphur compounds on the autoxidation of squalene,^{1,6-8} however, have shown that the mechanism of their antioxidant action is complicated. Many sulphur compounds have no effect upon the autoxidation of squalene, and others which are antioxidants can be divided into two types which act in different ways. The first type includes dialkenyl monosulphides, alkyl alkenyl monosulphides, and dialkyl disulphides; these compounds are oxidised by the olefin hydroperoxide to the corresponding sulphoxide or thiolsulphinates which are the actual inhibitors.^{6,8} These inhibitors do not, however, interfere with the propagation step of the oxidative chain reaction; inhibition is due to complex-formation between squalene

¹ Part XIV, Cain and Cunneen, *J.*, 1963, 3323.

² (a) Denison, *Ind. Eng. Chem.*, 1944, **36**, 477; (b) Denison and Condit, *ibid.*, 1945, **37**, 1102; (c) Kennerly and Patterson, *ibid.*, 1956, **48**, 1917; (d) Berry, Toettcher, and Knowles, Div. Petroleum Chem., Amer. Chem. Soc., Symposium on Additives in Lubricants, Atlantic City, N.J., 1956, p. 70; (e) Oberright, Leonardi, and Kozocik, *ibid.*, p. 115; (f) Jezl, Stuart, and Schneider, Div. Petroleum Chem., Amer. Chem. Soc., General Papers, Miami, 1957, p. 27; (g) Leonardi, Oberright, Orkin, and White, *ibid.*, p. 35; (h) Harle, *ibid.*, p. 51.

³ Thompson, *Ind. Eng. Chem.*, 1951, **43**, 1638; Thompson, Chenicek, and Symon, *ibid.*, 1952, **44**, 1659; 1958, **50**, 797.

⁴ Hawkins, Lanza, Loeffler, Matreyek, and Winslow, *J. Polymer Sci.*, 1958, **28**, 439; *J. Appl. Polymer Sci.*, 1959, **1**, 43.

⁵ (a) Barnard, Bateman, and Cunneen, "Organic Sulphur Compounds," Pergamon Press, Oxford, 1961, p. 229; (b) Dunn, *J. Appl. Polymer Sci.*, 1960, **4**, 151; (c) Dunn and Scanlan, *Trans. Inst. Rubber Ind.*, 1958, **34**, 228; (d) Dunn and Scanlan, *J. Polymer Sci.*, 1959, **35**, 267.

⁶ Barnard, Bateman, Cain, Colclough, and Cunneen, *J.*, 1961, 5339.

⁷ Cain and Cunneen, *J.*, 1962, 2959.

⁸ Bateman, Cain, Colclough, and Cunneen, *J.*, 1962, 3570.

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hydroperoxide and the sulphanyl compound.⁸ Dialkenyl disulphides, alkyl alkenyl disulphides, tri- and tetra-sulphides, and elemental sulphur are representatives of the second type. These compounds are weak inhibitors but they resemble conventional inhibitors (phenols and amines) in that they prevent autoxidation by stopping the oxidative chain reaction.¹

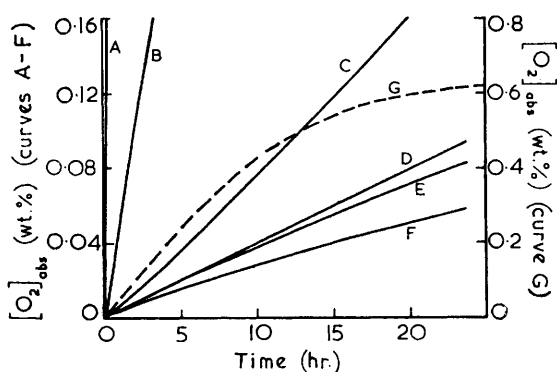


FIG. 1. Autoxidation of squalene in the presence of inhibitors at 75°/760 mm.

- A, No addition.
 B and G, Zinc dibutyldithiocarbamate (0.01M).
 C, 2-Naphthol (0.008M).
 D, Zinc di-isopropylidithiophosphate (0.01M).
 E, Zinc isopropylxanthate (0.01M).
 F, Phenothiazine (0.004M).

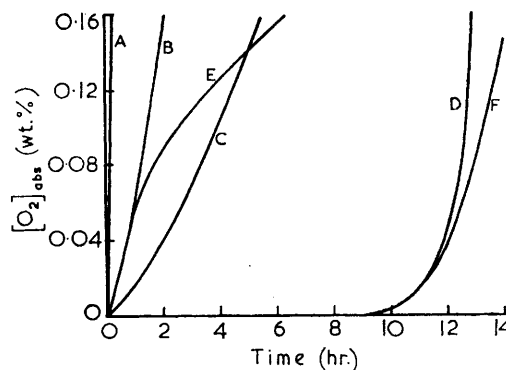


FIG. 2. Effect of inhibitors (0.01M) on the $\alpha\alpha'$ -azodi-isobutyronitrile (0.10M)-catalysed oxidation of squalene at 60°/760 mm.

- A, No addition.
 B, Zinc dibutyldithiocarbamate.
 C, 2-Naphthol.
 D, Zinc di-isopropylidithiophosphate.
 E, Zinc isopropylxanthate.
 F, Phenothiazine.

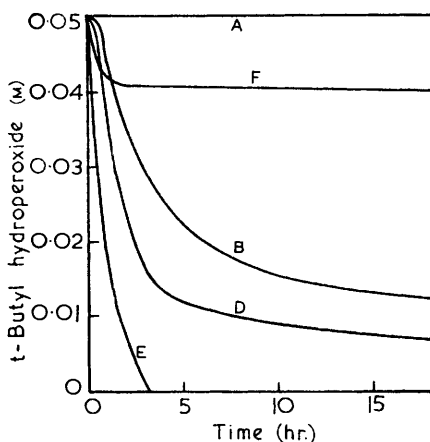


FIG. 3. Decomposition of t-butyl hydroperoxide (0.05M) by oxidation inhibitors (0.05M) in carbon tetrachloride at 20°.

- A, No addition or 2-naphthol.
 B, Zinc dibutyldithiocarbamate.
 D, Zinc di-isopropylidithiophosphate.
 E, Zinc isopropylxanthate.
 F, Phenothiazine.

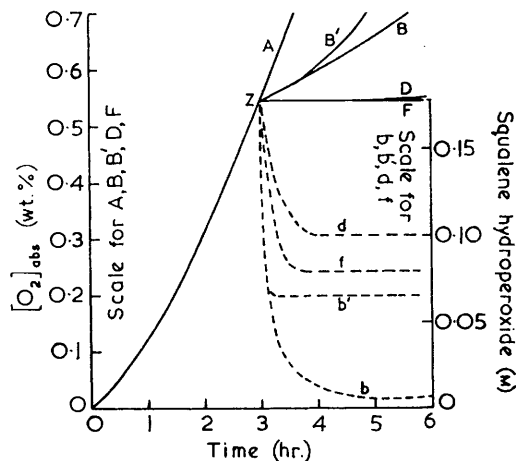


FIG. 4. Effect of inhibitors added at Z on the autoxidation and the hydroperoxide content of squalene (20% by wt.) in chlorobenzene 75°/760 mm. (concentration of the inhibitors in squalene in parentheses).

- A, No addition.
 B and b, Zinc dibutyldithiocarbamate (0.019M).
 B' and b', Zinc dibutyldithiocarbamate (0.009M).
 D and d, Zinc di-isopropylidithiophosphate (0.009M).
 F and f, Phenothiazine (0.084M).

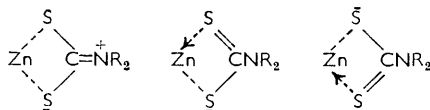
The compounds named in the title are well-known inhibitors which contain either zinc, nitrogen, or phosphorus, as well as sulphur. It has been suggested that, as with the simple sulphur compounds, they prevent oxidation simply by functioning as peroxide decomposers.^{2c,h} In the case of phenothiazine, however, there is some confusion since it has also been reported that this compound stops the oxidative chain reaction and does not decompose hydroperoxides.^{2h}

The results in Fig. 1 show that 2-naphthol and the compounds named in the title suppress the autoxidation of squalene and that their potency as inhibitors follows the order: phenothiazine > zinc isopropylxanthate > zinc di-isopropylthiophosphate > 2-naphthol > zinc dibutylthiocarbamate. If the autoxidation is catalysed by $\alpha\alpha'$ -azodi-isobutyronitrile, again all five compounds function as inhibitors, and their order of activity is: phenothiazine > zinc di-isopropylthiophosphate > 2-naphthol > zinc isopropylxanthate > zinc dibutylthiocarbamate (Fig. 2). Zinc dibutylthiocarbamate is a good protective agent for certain vulcanizates of natural rubber,^{5c} but it is a poor inhibitor for the autoxidation of squalene. Curve G of Fig. 1, however, indicates that zinc dibutylthiocarbamate produces a more effective inhibitor as oxidation proceeds, and presumably in the experiments with natural rubber this more potent inhibitor is formed before measurements of ageing are recorded.

Fig. 3 shows the effect of the five inhibitors on t-butyl hydroperoxide. 2-Naphthol has no effect but the other four compounds decompose the hydroperoxide, the efficiency of decomposition following the order: zinc isopropylxanthate > zinc di-isopropylthiophosphate > zinc dibutylthiocarbamate > phenothiazine.

These results show that the five inhibitors interfere with the propagation of the oxidative chain reaction (Fig. 2), and with the exception of 2-naphthol decompose t-butyl hydroperoxide far more rapidly than the sulphanyl compounds previously described (Fig. 3).⁸ If the inhibitory activity of the four sulphur compounds is confined to reaction with the oxidative chain carriers then the order of potency should be the same in both the catalysed and uncatalysed oxidations of squalene, since the propagating radicals ($R\cdot$ and $RO_2\cdot$) are the same in both cases. This is not so, since in the $\alpha\alpha'$ -azodi-isobutyronitrile-initiated oxidations, where catalysis by squalene hydroperoxide is trivial, zinc di-isopropylthiophosphate and 2-naphthol are better inhibitors than zinc isopropylxanthate. When no catalyst is added and the effective initiator is squalene hydroperoxide, the xanthate is a better inhibitor than the other two. Since the xanthate is the most effective decomposer of t-butyl hydroperoxide this indicates that peroxide decomposition contributes towards its antioxidant action. Similar results were obtained with the other inhibitors, since the addition of phenothiazine, zinc dibutylthiocarbamate, and zinc di-isopropylthiophosphate to autoxidizing squalene showed that they immediately retarded the oxidation and rapidly lowered the squalene hydroperoxide content (Fig. 4).

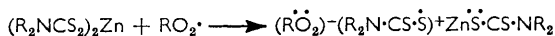
It is therefore concluded that the inhibitors in the title suppress the autoxidation of squalene by acting as peroxide decomposers and by stopping the propagation of the oxidative chain reaction. Furthermore, although the latter process presumably occurs through a hydrogen transfer with phenothiazine it cannot occur in this way with the zinc salts, since no suitably activated hydrogen atom is available. The structure of zinc dialkyldithiocarbamates, $Zn(S_2CNR_2)_2$, is represented by a hybrid of the following canonical forms.⁹



Similar structures have been suggested for zinc isopropylxanthates,⁹ and presumably similar structures are also possible with zinc dialkyldithiophosphates. With all these

⁹ Chatt, Duncanson, and Venanzie, *Nature*, 1956, **177**, 1042.

structures the peroxy-radical can be converted into a peroxy-anion¹⁰ by the abstraction of an electron from the electron-rich sulphur atom:



It is suggested that this type of electron transfer process accounts for the stopping of the oxidative chain reaction by the zinc salts.

EXPERIMENTAL

Oxidations.—Measurements of oxygen absorption were carried out at 760 mm. oxygen pressure in an apparatus previously described.¹¹ The method used for studying the effect of the antioxidants on autoxidising squalene involved interruption of the oxidation. Squalene (ca. 1 g., 20% by wt.) in chlorobenzene was autoxidised for 3 hr. at 75° and then added to a second oxidation vessel containing the additive, and the autoxidation restarted.

Materials.—Squalene was obtained as previously described;⁶ it was chromatographed on alumina immediately before each oxidation experiment. $\alpha\alpha'$ -Azodi-isobutyronitrile and t-butyl hydroperoxide were purified as previously described.⁸ Zinc dibutyldithiocarbamate,^{5c} zinc di-isopropylidithiophosphate,^{5d} and zinc isopropylxanthate^{5b} were purified and supplied by Dr. J. R. Dunn. Phenothiazine (m. p. 178°) was recrystallized from benzene.

Analysis.—t-Butyl hydroperoxide was estimated by the stannous chloride method of Barnard and Hargrave¹² except that iodine was used instead of potassium dichromate to estimate the excess stannous chloride. Squalene hydroperoxide was estimated iodometrically.¹³

Decomposition of Hydroperoxides.—Aliquot parts (5 ml.) were taken from the agitated chlorobenzene and carbon tetrachloride solutions. In the latter system, the hydroperoxide was first separated by aqueous extraction to avoid interference by the sulphur compounds in the analytical method.

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¹⁰ Pedersen, *Ind. Eng. Chem.*, 1956, **48**, 1881; Boozer, Hammond, Hamilton, and Sen, *J. Amer. Chem. Soc.*, 1955, **77**, 3233, 3238; Fueno, Ree, and Eyring, *J. Phys. Chem.*, 1959, **63**, 1940.

¹¹ Bateman and Cunneen, *J.*, 1955, 1596.

¹² Barnard and Hargrave, *Analyt. Chim. Acta*, 1951, **5**, 476.

¹³ Bateman and Hughes, *J.*, 1952, 4594.