Mechanisms of Antioxidant Action: Esters of Thiodipropionic Acid

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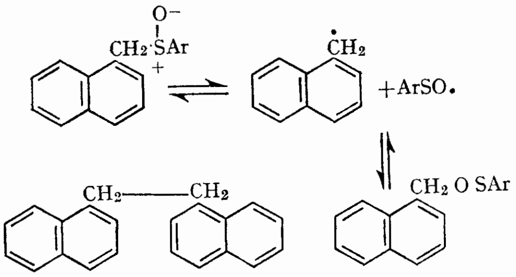
MANY sulphur compounds are effective antioxidants in both liquid hydrocarbons and hydrocarbon polymers.[1,2] Esters of thiodipropionic acid (I; R = H) in particular are important stabilisers for polyolefins and are used as synergistic mixtures with phenolic antioxidants whose ability to remove chain-propagating free radicals is now well established.[1,3]

$$RO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2R \quad (I)$$

Unlike phenolic antioxidants which normally produce a pronounced induction period in liquid hydrocarbons, sulphides show autoretarding characteristics,[2,4] suggesting that the effective antioxidants are not themselves sulphides but a product or products formed from them during oxidation.



A study of the degradation of polypropene at 165° has shown a parallel situation, in that increasing amounts of a thiodipropionate ester decrease the oxidative stability of the polymer during the early stages of processing, but a reversal of this situation occurs as oxidation is continued.[5]

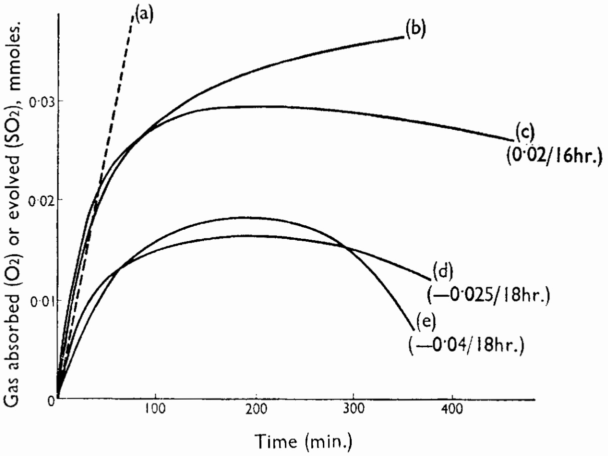


FIGURE 1. *Effect of didodecyl thiodipropionate (DLTP) on the oxidation of tetralin containing* 1 *mmoles of tetralin hydroperoxide (in* 4 *cc) at* 50°*:*

(*a*) *no DLTP.*
(*b*) 2 *m moles DLTP.*
(*c*) 1 *m mole DLTP.*
(*d*) 0·5 *m. moles DLTP.*
(*e*) 0·05 *m moles DLTP.*

Oxygen-absorption studies of simple hydrocarbons have shown that, in common with other sulphur compounds, didodecyl thiodipropionate (I; R = $C_{12}H_{25}$), is oxidised to an effective antioxidant which acts by catalytic destruction of hydroperoxides in a process which does not involve the formation of free radicals.[6] In the early stages of the autoxidation of tetralin in the presence of didodecyl thiodipropionate catalysed by tetralin hydroperoxide, it is found that over a limited range of concentration ratios of tetralin hydroperoxide to sulphide the latter is an effective pro-oxidant (see Figure 1). The effect is most pronounced at molar ratios of hydroperoxide to sulphide in the region of 1 and as the ratio is increased the sulphide becomes increasingly antioxidant with a pronounced evidence of gas evolution at ratios above 2 : 1. The evolved gas was identified as sulphur dioxide by mass-spectrographic examination. Previous work has shown that SO_2 is a powerful antioxidant due to its ability to act as a Lewis-acid catalyst for the decomposition of hydroperoxide.[6] An interesting feature of this phenomenon is the evidence for two distinct phases of pro-oxidant activity at lower hydroperoxide concentrations (Figure 2). This effect is quite reproducible and suggests that two free-radical generating steps precede the formation of SO_2. Didodecyl sulphinyldipropionate (II) which is almost certainly the first product formed by oxidation of didodecyl thiodipropionate

$$C_{12}H_{25}O_2C{\cdot}CH_2{\cdot}S{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2C_{12}H_{23} \qquad (II)$$

with hydroperoxides[7] is an even more effective initial pro-oxidant than didodecyl thiodipropionate

(Figure 3). This fact is not consistent with the assumption that sulphoxides may themselves be the effective antioxidants formed from sulphides.[8]

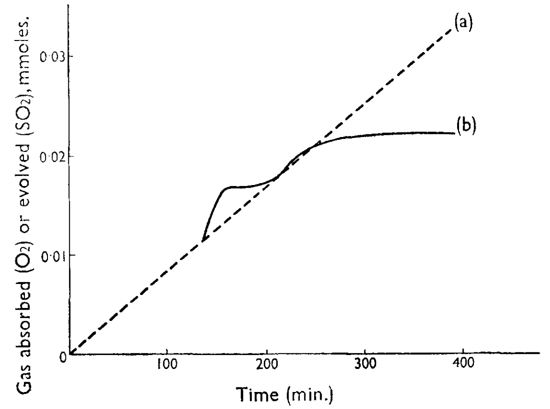


FIGURE 2. *Pro-oxidant effect of didodecyl thiodipropionate on the oxidation of tetralin at* 50°:

(*a*) *tetralin* (4 *c.c.*) *containing tetralin hydroperoxide* (0·5 *mmoles*)

(*b*) *tetralin* (4 *c.c.*) *containing tetralin hydroperoxide* (0·5 *mmoles*) *and didodecyl thiodipropionate* (0·5 *mmoles*).

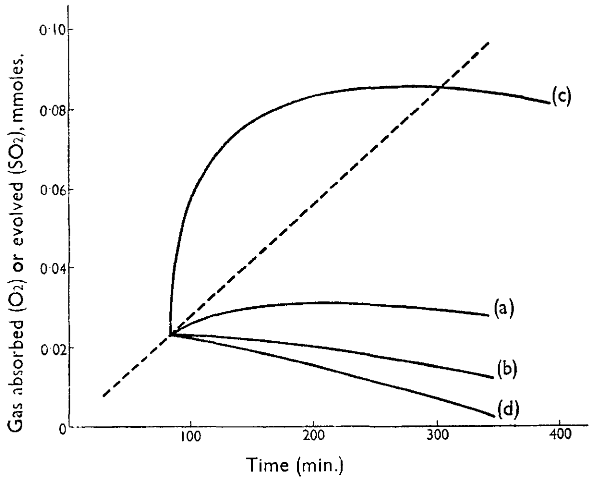


FIGURE 3. *Effects of antioxidants in tetralin at* 50°; 025 *mmoles of antioxidants in* 4 *c.c. tetralin containing* 0·5 *mmoles of tetralin hydroperoxide*:

(*a*) *didodecyl thiodipropionate* (*DLTP*) *in oxygen.*
(*b*) *DLTP in nitrogen.*
(*c*) *didodecyl sulphinyldipropionate* (*DLSP*) *in oxygen*
(*d*) *DDSP in nitrogen.*

Again there is evidence at certain concentrations of two separate stages of free radical formation. The pro-oxidant effect can be explained on the basis of an initial dissociation of the sulphoxide to two free radicals. Similar dissociations have been suggested by Cram[9] to explain some of the features of the inversion of optically active sulphoxides and by Stirling[10] to account for the formation of free radical coupled by-products in the rearrangement of 1-naphthylmethyl *p*-tolyl sulphoxide to the corresponding sulphenate ester.

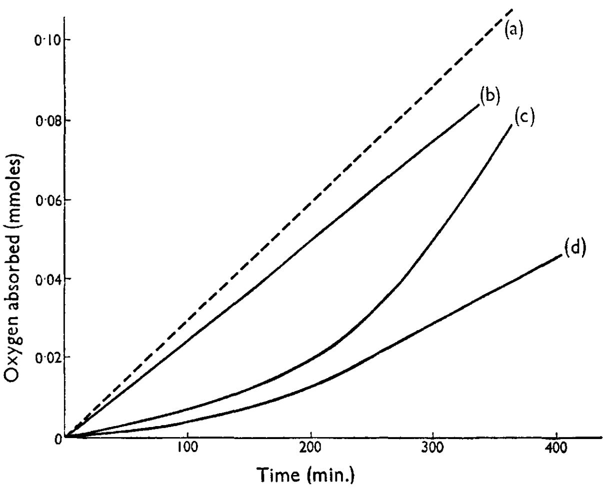


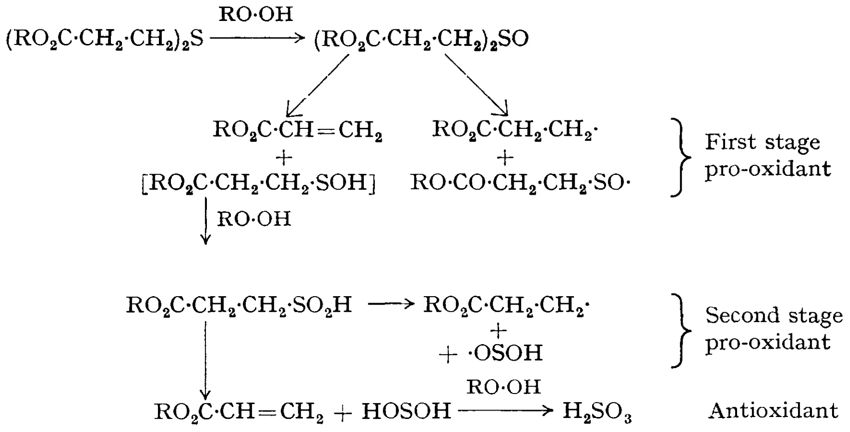
FIGURE 4. *Synergism between didodecyl thiodipropionate* (*DDTP*) *and* 2,6-*di-t-butyl*-p-*cresol* (*DBPC*) *in tetralin* (4 *cc.*) *containing tetralin hydroperoxide* (10 *mmoles*):

(*a*) *No antioxidant.*
(*b*) 0·01 *mmoles DLTP.*
(*c*) 0·0001 *mmoles DBPC.*
(*d*) 0·01 *mmoles DDTP* + 0·0001 *mmoles DLBC.*

The detailed chemistry of the relative contributions of homolytic and heterolytic eliminations to the overall process is at present under investigation but the main features of the process are capable of interpretation on the basis of the following alternative dissociation pathways. Olefin formation has been observed with a number of other sulphoxides.[9,11–13]

In the absence of oxygen the formation of sulphurous acid from both didodecyl thiodipropionate and didodecylsulphinyl dipropionate appears to be auto-accelerating (Figure 3). This is consistent with the length of the above reaction sequence. Moreover this provides an explanation for the autocatalytic decomposition of hydroperoxides by didodecyl thiodipropionate[6] since sulphur dioxide reacts very much faster with cumene hydroperoxide than does the sulphide itself.[6]

The importance of the radical deactivating phenolic component of commercial melt stabilisers



for polypropene receives some explanation on the basis of the above mechanism. In tetralin a relatively small concentration of an effective phenolic antioxidant is capable of eliminating almost completely the effects of the initial radical generating stage of the sulphide oxidation (Figure 4). This has also been confirmed in technological media[5] and results will be published elsewhere.

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