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## Journal of Sulfur Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926081>

### Organosulfur Antioxidants in Hydrocarbon Oils

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**To cite this Article** Harpp, David N. , Robertson, John , Laycock, Kim and Butler, David(1985) 'Organosulfur Antioxidants in Hydrocarbon Oils', *Journal of Sulfur Chemistry*, 4: 6, 195 – 219

**To link to this Article:** DOI: 10.1080/01961778508082477

**URL:** <http://dx.doi.org/10.1080/01961778508082477>

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# ORGANOSULFUR ANTIOXIDANTS IN HYDROCARBON OILS

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*(Received November 22, 1984)*

The literature for this review was searched by CAS-On-Line procedures so as to provide the most up-to-date references for this somewhat focussed review. The decision as to include a reference or not was somewhat arbitrary, however, it was based on whether or not the article addressed itself to the antioxidant activity in hydrocarbon oils. For instance, articles on jet fuel antioxidants were generally not included. Nomenclature may appear inconsistent e.g. the use of episulfide vs thiirane. Insofar as possible names were used as they appeared in the original articles so that references made to that article would hopefully be less confusing to the reader.

## INTRODUCTION

Although organosulfur components in petroleum oils can be deleterious in a number of ways<sup>1</sup> (catalyst poisoning, metal corrosion, undesirable color, deposit formation in engines) these materials are also recognized as very efficient “natural” anti-oxidants for oil hydrocarbons.<sup>2</sup> The useful life of such oils in a wide variety of products (e.g. electrical insulating oils, engine oils, heat transfer oils, gear lubricants, hydraulic oils, greases) can be greatly extended when these components are present. This results in lower costs for chemical additives and more economical operation for product users. The role of sulfur in anti-oxidant mechanisms has been widely studied<sup>3a,b,c</sup> but a unified description has not yet been achieved, mainly because these systems are highly complex mixtures of organosulfur and hydrocarbon compounds which are difficult to separate and identify. The purpose of this review is to consolidate the available literature in this complex and economically important area.

Three fundamental approaches can be taken to study the effect of sulfur on oxidation of organic compounds. The most complex is to use natural hydrocarbons, including their sulfur components, in kinetic studies and elucidate mechanisms by identifying and measuring the concentrations of reactant and product sulfur species. Alternatively, a pure organosulfur compound can be added to a hydrocarbon oil, and the effect on oxidation stability observed. The simplest and most common approach has been to use model systems in which a limited number of model compounds (including potential synergists) are mixed, experimental conditions varied systematically, and products analyzed. Conclusions from these latter experiments should be applied with considerable caution to working systems in order that interactions among the many chemical types present are not overlooked.

## COMPOSITION OF CRUDE AND REFINED OILS

Several detailed studies of the sulfur compound composition of crude oils have been reported (Ref. [9], and references therein). Sulfur is the third most abundant atomic constituent of crude petroleum after carbon and hydrogen. The types and relative amounts of sulfur compounds vary enormously between crudes, depending on conditions of deposition, temperature and pressure, host rock, and extensive microbial reworking.

Sulfur is often present in concentrations too high to be accounted for by the natural sulfur content of biological tissue from which petroleum eventually formed.<sup>4a</sup> Therefore, the major part of the sulfur found in petroleum is believed to be derived from biogenic reduction of sulfates obtained from surrounding rock.<sup>5</sup> Elemental sulfur, if present, is produced by a non-biogenic process, the reaction of H<sub>2</sub>S with sulfates<sup>6</sup> (Fig. 1).



FIGURE 1

Sulfur and H<sub>2</sub>S may then react with hydrocarbon components of crude oil to produce organic sulfur compounds. It has been postulated that the absence of olefins in crude is due to reaction with H<sub>2</sub>S to yield thiols, and ultimately, sulfides.<sup>4a</sup> Elemental sulfur may also act as an aromatization agent.

Crude oil sulfur distribution is bimodal, the high and low sulfur types being separated by a minimum at 1% S. Sulfur concentrations of 13.95% have been reported,<sup>7</sup> but it appears that such high levels require a source other than that of petroleum hydrocarbons.<sup>4a</sup> The average sulfur concentration in a wide variety of crudes has been calculated at 0.65%.<sup>8</sup>

The wide variability of sulfur content in crudes can be related to the geochemical characteristics of the deposits.<sup>9a,c</sup> The average sulfur content of crudes from clay/carbonate sources (0.86%) is significantly higher than that of crudes from sand/shale sources (0.51%). Sulfur content also gradually decreases with the depth and age of the crude deposits.<sup>9b,d,4b</sup>

In the early 1900's, German workers were active in analyzing petroleum and coal liquids for sulfur compounds.<sup>10</sup> Benzothiophenes<sup>11</sup> and dibenzothiophenes<sup>12</sup> were shown to be present in petroleum oils. In addition, thiols, sulfides and thiophenes were isolated from coal tar<sup>13</sup> via hydrogen peroxide oxidation. By 1947, only 25 sulfur compounds had been identified in petroleum. At that time, a 20 year study of the organic sulfur compounds in Wasson, Texas crude was initiated by the U.S. Bureau of Mines.<sup>4a</sup> As a result of this exhaustive study, elemental sulfur, the existence of which was expected on biogenic grounds, was identified for the first time. Elemental sulfur, thiols, sulfides, disulfides, and thiophene derivatives were found in the light and medium fractions of crudes. The content of thiols and disulfides decreases with increasing boiling point, since most of these compounds have low molecular weights. In the heaviest fractions (resins and asphaltenes), sulfur is usually incorporated in large polycyclic molecules containing oxygen and nitrogen as well.

Almost all distillates contain sulfides and thiophenes as the major part of the total sulfur content. In the lower boiling fractions, sulfides predominate whereas the concentration of thiophenic sulfur increases in cuts above 200°C.<sup>14</sup> Nonthiophenic sulfur compounds are generally more abundant in immature crudes, whereas thiophenic sulfur content increases with maturation.<sup>15</sup> Terpenoid and steroid skeletons which reflect the biological origin of the petroleum have been identified. In Athabasca bitumen, 17-thiasteroids (**1**) and 8-thia-9-nordecalins (**2**) were found,<sup>16</sup> and other studies have revealed a variety of organosulfur compounds which presumably have their origins in the terpene compound classes (**3-5**).<sup>17</sup>

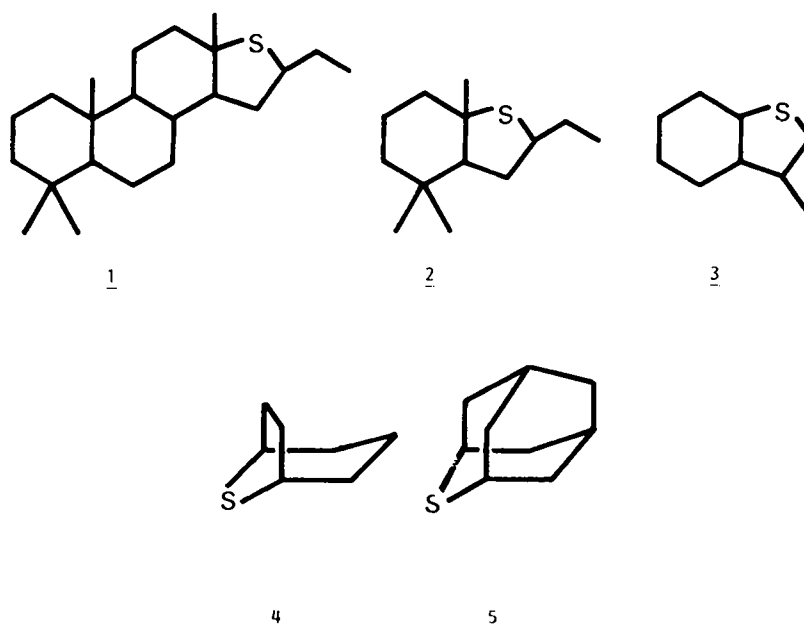


FIGURE 2

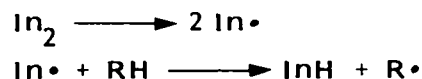
Although a wide variety of inorganic and organic sulfur structural types are found in crude oils, the processing of refined hydrocarbon oils removes many of them. Elemental sulfur, for example, is destroyed during processing, as are thiols, disulfides, and oxidized sulfur compounds. However, a large number of structural variations are possible for the remaining organosulfur classes (sulfide and thiophene derivatives). The problems of discovering oxidation mechanisms for such a multiplicity of components are simplified to some extent by broad similarities for closely related structural types although subtle differences will still exist.

For refined oils, the technique of controlled oxidation followed by chromatography has been used to isolate sulfur compounds.<sup>18</sup> Other procedures include ion and ligand exchange<sup>19</sup> as well as related metal salt extraction.<sup>20</sup> This area is one of active interest and current studies will benefit from computer-aided spectroscopy (FT-IR, FT-NMR, high resolution mass spectrometry), combination techniques (GC/MS, HPLC/MS, GC/IR), and separations (capillary GC, HPLC) with highly specific detectors which have become generally available only in the last decade.

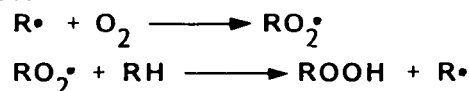
## OUTLINE OF CHEMISTRY

With few exceptions, the liquid phase oxidation of hydrocarbons proceeds *via* a free radical chain mechanism<sup>21</sup> represented as follows (Fig. 3):

### INITIATION



### PROPAGATION



### TERMINATION

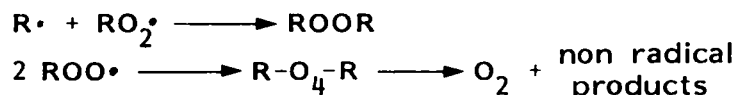


FIGURE 3

In the absence of added initiator, free radical oxidation is triggered by peroxide or hydroperoxide type impurities. The alkoxy radical formed attacks hydrocarbon, forming an alkyl radical. The reaction between alkyl radical and oxygen is exothermic and rapid enough to be considered diffusion controlled. The rate controlling step is hydrogen transfer from substrate hydrocarbon to peroxy radical. The alkyl peroxy radical is relatively stable and initially attacks the most weakly bonded hydrogen atom. The rate of propagation depends on both reactivity of the substrate and the nature of the attacking peroxy radical.

Chain termination results from reaction of an alkyl radical with a peroxy radical, or by mutual reaction of two peroxy radicals. Under oxidation conditions, there are no alkyl radicals present so termination occurs exclusively by self-reaction of two peroxy radicals to yield an intermediate tetroxide. The tetroxide ultimately decomposes exclusively to non-radical products and oxygen in the case of primary and secondary radicals. Tertiary radicals yield tetroxides which decompose to either dialkyl peroxides, *via* a non-radical mechanism, or alcohols, *via* the alkoxy radical. It is generally assumed that the oxidation of hydrocarbon oils proceeds by the same mechanism as that of pure hydrocarbons, with the obvious qualification that the mixture of alkyl aromatic and polynuclear aromatic species, alkanes, and low concentrations of various heteroatom-containing compounds leads to very complicated kinetics.

Antioxidants can act at two sites in the oxidation chain. Compounds with labile hydrogen atoms which yield stable radicals are known as chain breaking antioxidants. By reaction with peroxy radicals they interrupt propagation. Compounds which decompose hydroperoxides to stable products *via* a non-radical mechanism, thereby interrupting the source of initiators, are known as preventive antioxidants.

It is worth noting that various hydrocarbons have been used as substrates for oxidation tests. In early work, the rate of uptake of oxygen by mixtures of antioxidants in 'white paraffin oil' was measured.<sup>37,38</sup> In recent years most workers

have chosen a pure mono-substituted benzene derivative since the benzylic site is particularly reactive and only a limited number of oxidation products are formed. The most popular hydrocarbon is cumene (isopropylbenzene). Not only is this hydrocarbon smoothly oxidized but the resulting hydroperoxide is stable under many conditions. Further, the hydroperoxide is commercially available and a common means of assessing an antioxidant's potential is to measure the rate at which it decomposes solutions of cumene hydroperoxide (CHP). The relative amounts of the products obtained from the decomposition of CHP (mostly phenol, acetone, 2-phenylpropan-2-ol, 2-phenylpropene and acetophenone) from the decomposition of CHP give valuable clues to the mechanisms of the reaction.<sup>23a,b,c,d,e</sup>

A variety of organic sulfur compounds are important antioxidants in oil, rubbers, polyolefins and foodstuffs. Sulfur compounds appear to function as antioxidants in two ways, either as peroxy radical scavengers<sup>23d,e</sup> or hydroperoxide decomposers.<sup>3a</sup> Scott<sup>3b</sup> reviewed the mechanisms of action of sulfur compounds in autoxidation. It should be noted that in some circumstances sulfur species may be pro-oxidants<sup>3b</sup> because of their ability to form free radicals and thus initiate oxidation.

Early investigations established<sup>2a</sup> that the unoxidized sulfur compounds were not themselves the active antioxidants. The kinetics of an oxidation often reveal an induction period during which the sulfur compound reacts with the oxidizing system. This is usually followed by a rapid decrease in the rate of oxidation of the hydrocarbon or increase in the rate of decomposition of hydroperoxide. The real antioxidants are concluded to be the various oxidation products.

The stoichiometric reaction between a sulfide and a hydroperoxide results in heterolytic hydroperoxide decomposition, but the most effective antioxidants of this type are compounds which decompose hydroperoxides rapidly and catalytically. Sulfur compounds such as SO<sub>2</sub>, SO<sub>3</sub>, and alkyl or aryl sulfonic acids have been invoked as catalytic antioxidants derived from the oxidation and thermal degradation of various organosulfur compounds.<sup>22a,b</sup> This is not surprising, since sulfur dioxide and related oxysulfur compounds have been recognised as antioxidants in, for example, foods for a long time.<sup>22c</sup>

Husbands and Scott<sup>22a</sup> report that sulfonic acids show essentially no antioxidant activity. On the other hand, Shelton and co-workers<sup>27</sup> consider them to play at least some role as a source of acid for the catalytic decomposition of hydroperoxides. Sulfinic acids, while not themselves effective peroxide decomposers, are antioxidants because of their ability to readily condense to give thiosulfinates and release SO<sub>2</sub>.

Husbands and Scott<sup>22a</sup> also showed that SO<sub>2</sub> has both chain breaking and hydroperoxide decomposing functions in autoxidizing systems. In a hydroperoxide initiated oxidation it shows a pro-oxidant effect at high mole ratios. The reaction of SO<sub>2</sub> with hydroperoxides results in the formation of sulfur trioxide which was shown to be the actual catalyst for peroxide decomposition by the following experiments. The addition of pyridine or zinc oxide to an SO<sub>2</sub> inhibited system destroyed the antioxidant action, and the addition of 5Å molecular sieves (which trap SO<sub>2</sub>), substantially reduced it. However, if the SO<sub>2</sub> inhibited autoxidation was allowed to proceed approximately 30 min before the addition of the sieves, incomplete attenuation of the antioxidant effect was observed. This was attributed to the formation of SO<sub>3</sub> which combined with water produced in the reaction to give sulfuric acid.

Due to the lower solubility of  $\text{SO}_3$  in the organic medium, the later stages of the reaction are slowed.

The  $\text{HOSO}_2$ ,  $\text{MeSO}_2$ , and  $t\text{-BuOSO}_2$  radicals have been observed by e.s.r.<sup>27</sup> as intermediates in the reactions between hydroperoxides and sulfur dioxide (Fig. 4).

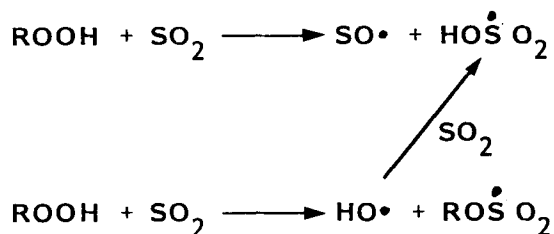


FIGURE 4

Sulfur dioxide is a particularly powerful Lewis acid catalyst for hydroperoxide decomposition. Bridgewater and Sexton<sup>23a</sup> showed that one equivalent of  $\text{SO}_2$  was able to decompose up to 20,000 equivalents of cumene hydroperoxide.

The peroxide radical scavenging of some organosulfur compounds has been attributed to the transient sulfenic acid species ( $\text{RSOH}$ ), of which few stable examples are known.<sup>24</sup> Although sulfenic acids have been postulated as intermediates in the thermolytic decomposition of various sulfoxides,<sup>26</sup> it is only recently that the existence of an aliphatic sulfenic acid has been demonstrated. Shelton and Davis<sup>25</sup> described the preparation of *t*-butylsulfenic acid from di-*t*-butyl sulfoxide in various solvents. Sulfenic acids will in most cases quickly condense to thiosulfinates (cf. Fig. 10). Various other alkyl and aryl sulfenic acids generated by the decomposition of sulfoxides undergo facile additions to alkenes and alkynes.

Koelewijn and Berger<sup>28,29</sup> investigated the reactivity of sulfenic acids as antioxidants and showed that both *t*-butyl and anthraquinon-1-sulfenic acid (one of the few sulfenic acids that can be prepared in pure form) were very efficient radical chain breakers. It was also noted that tertiary sulfenic acids are less effective than the primary analogs.

In conclusion, it is generally accepted that oxidation products of organosulfur compounds are antioxidants. The specific chemistry of these oxidation products is discussed in the next section.

## ORGANIC SULFUR COMPOUNDS AS ANTIOXIDANTS

The following compounds have been identified, or can be reasonably expected to be found in petroleum.

- a. Elemental sulfur
- b. Thiols
- c. Organic sulfides
- d. Organic disulfides
- e. Organic polysulfides

- f. Thiophenes  
g. Other synergistic substances

The relevant chemistry of each material will be summarized in separate sections below; some overlap of sections is inevitable.

## ELEMENTAL SULFUR

The long disputed presence of elemental sulfur in crude oils was clearly established by the American Petroleum Institute Research Project 48.<sup>4a,d</sup> It has been shown to be an efficient antioxidant even at low (<0.1%)<sup>30</sup> concentrations; but it is extremely corrosive to refinery equipment and metal engine parts. In any event, sulfur is present only in lower boiling (<2000°C) fractions of crudes<sup>14</sup> and would not normally survive the refining procedures to which high boiling petroleum products are subjected.

The direct reaction of elemental sulfur with hydrocarbons has been extensively investigated.<sup>32</sup> At high temperatures, sulfur is known to act as a dehydrogenating agent, yielding aromatic or olefinic hydrocarbons and thiols;<sup>31</sup> but the details of these reactions are not within the scope of this review (Fig. 5).

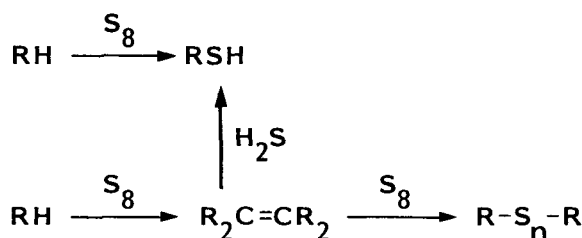


FIGURE 5

## THIOLS

Normal, isoalkyl, cyclopentyl, and cyclohexyl thiols have been found in crude petroleum,<sup>34</sup> but aromatic thiols have not been reported. Most are of low molecular weight<sup>4a</sup> and their concentration decreases with increasing boiling point of distillate cuts, becoming insignificant in residues boiling above 300°C.<sup>4b</sup>

Thiols are readily oxidized under a variety of conditions and their most likely reaction would seem to be the initial formation of sulfenic acids (Fig. 6).

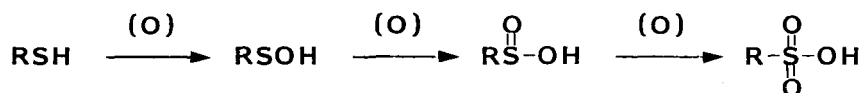


FIGURE 6

Davis<sup>33</sup> gave the first direct evidence for the involvement of sulfenic acids in the oxidation of thiols to higher sulfur oxides. The addition of 1 equivalent of



2-(benzenesulfonyl)-3-phenyl-oxaziridine (**6**) to 2 equivalents of *t*-butane thiol in a NMR tube reaction gave sulfoximine (**7**) (>90%), *t*-butyl sulfinic acid (**8**), and *t*-butylbutanesulfinate (**9**) (6%); the thiosulfinate must have come from the intermediate sulfinic acid.

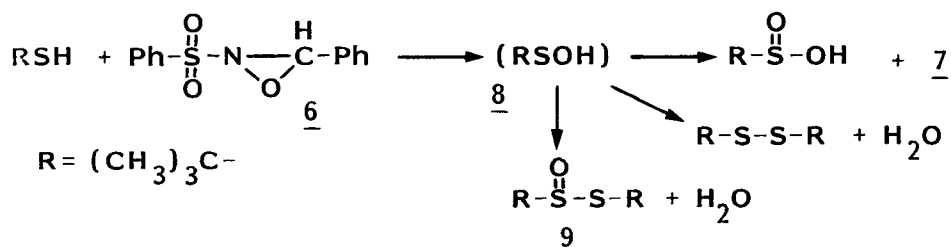


FIGURE 7

Although alkyl sulfinic acids are unstable to self-condensation, their transitory presence can be invoked to explain some of the oxidation inhibition observed for thiols both as free radical scavengers and as acid catalysts for the decomposition of hydroperoxides (see below the discussion of sulfinic acids derived from sulfoxides). Thiols can also oxidize to give disulfides or add to alkenes yielding sulfides (Fig. 8).

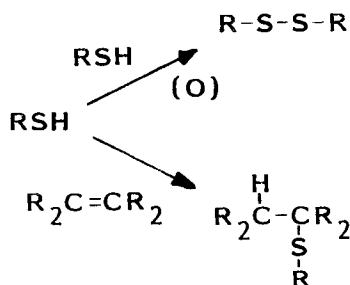


FIGURE 8

## ORGANIC SULFIDES

Sulfides occur widely in all crude oils,<sup>3c,35</sup> especially in middle distillate fractions where they can account for 50% or more of the total sulfur.<sup>4a,36</sup> Although sulfides are generally less abundant than thiophenes in middle and high-boiling fractions, they were the first organic sulfur compounds to be investigated as antioxidants.<sup>2a,37</sup>

The autoxidation of sulfides and the effects of sulfides on the autoxidation of hydrocarbons have been studied. Bateman and Cunneen<sup>38</sup> undertook the first study of the reactivity of a variety of organic monosulfides toward molecular oxygen. It was determined that saturated sulfides did not react spontaneously with oxygen at temperatures below 100°C. However, allylic and vinylic sulfides absorbed oxygen autocatalytically at first, but the rate slowed and sometimes ceased before 0.1 mole of oxygen per mole of sulfide was absorbed.<sup>38</sup> Oxygen absorption was promoted by light,

the free radical initiator azoisobutyronitrile, and certain metallic compounds, but not by peroxides. A more recent study of organic sulfide autoxidation by Howard and Korcek<sup>39a</sup> confirmed many of Bateman's results, but discounted the lack of reactivity of sulfides toward *t*-butylperoxy radicals. More recent work has for the most part completely confirmed these early observations.<sup>39b,c</sup>

In their studies on the inhibiting effect of oxygenated sulfide products on the autoxidation of squalene, Bateman<sup>40</sup> demonstrated that the most important antioxidant effect of dialkyl sulfides came from the derived sulfoxides. However, sulfoxides were ineffective if autoxidation was initiated by methods other than the homolytic decomposition of hydroperoxide. The antioxidant action was attributed to formation of a molecular complex between the sulfoxide and hydroperoxide, preventing the latter from dissociating into free radicals. Koelewijn and Berger noted a serious objection to the mechanism namely, the improbability that sulfoxide at a concentration of 0.005M should be capable of preventing the decomposition of 0.1M squalene hydroperoxide by complex formation.<sup>29</sup> They further observed that the level of initiation by hydroperoxides in Bateman's work was much lower than that of the other initiators studied. Repetition of the experiments at equal levels of oxidation initiation showed that sulfoxides were excellent inhibitors of free radical initiated oxidations in general.

The mechanism of antioxidant activity of sulfoxides depends on two factors. The first is their ability to undergo a thermal  $\alpha$ -cleavage<sup>41</sup> to give a sulfinyl radical (**10**) and a carbon radical.<sup>42</sup> Both species are efficient free radical traps but might also behave as pro-oxidant free radical initiators.<sup>22</sup> Sulfinyl radicals also dimerize head-to-tail to give sulfinyl sulfenates which rearrange to thiosulfonates<sup>43</sup> (Fig. 9).

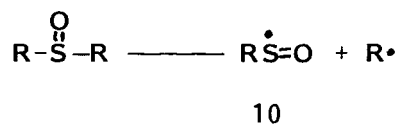


FIGURE 9

The second, more favored mechanism is the generation of sulfenic acids *via* an endo-cyclic rearrangement. Cram and Kingsbury<sup>44</sup> studied the thermolysis of the four diastereomers of 1,2-diphenyl-1-propyl phenyl sulfoxide at 80°C, and found that the reaction proceeded *via* a concerted elimination of the  $\beta$ -hydrogen. They postulated that at higher temperatures (120°C) the preferred route is formation of a radical pair produced within the solvent cage which disproportionates by hydrogen transfer in the second stage. By a combination of NMR and IR spectral techniques Shelton and Davis<sup>25</sup> established that the thermolysis of di-*t*-butyl sulfoxide (**11**) at 80°C in benzene gave *t*-butyl sulfenic acid (**12**) and isobutene (**13**) as initial products. Various sulfenic acids were prepared by flash vacuum pyrolysis.<sup>25c</sup> The simple sulfenic acids primarily underwent dehydration to thiosulfonates, but *t*-butyl sulfenic acid was apparently prevented by steric hindrance (Fig. 10).

On the other hand, 2,4,6, tri-*t*-butylbenzenesulfenic acid appears to be destabilized as a consequence of interaction between the SOH and adjacent *t*-butyl groups; on pyrolysis it decomposes to phenol and the aryl radical which reacts further.<sup>25c</sup>

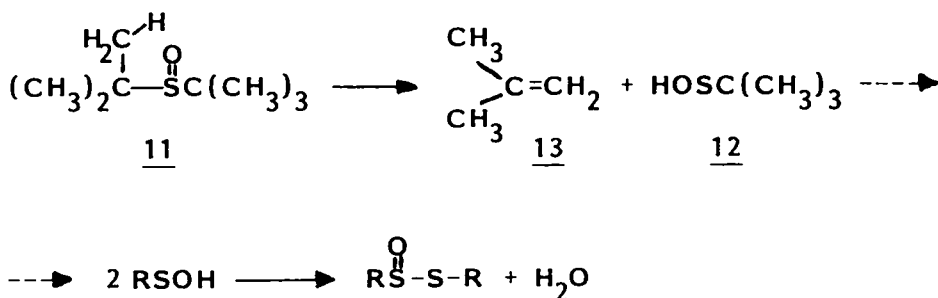


FIGURE 10

It is interesting to note that whereas diverse sulfenic acids are known to be stable,<sup>24</sup> close analogs are not. 1-Antraquinonesulfenic acid (**14**) was prepared by Fries in 1912 but the closely related 9-oxofluorene-1-sulfenic acid (**15**) could not be isolated.



FIGURE 11

The same thermal reaction of sulfoxides to give sulfinyl radicals and/or sulfenic acids can be expected from the oxidation of cyclic sulfides. An interesting rearrangement which proceeds *via* a sulfenic acid is possible with alkyl substituted cyclic sulfoxides. The reaction requires a hydrogen  $\beta$  to the sulfoxide group and approximately co-planar with it. This type of rearrangement was first found in penicillin chemistry<sup>48</sup> but is now considered a general reaction<sup>49-53</sup> (Fig. 12).

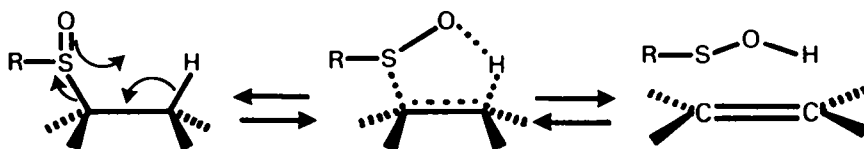


FIGURE 12

Jones<sup>54</sup> studied the intramolecular addition of sulfenic acids to alkenes to give cyclic and bicyclic sulfoxides. Alkyl sulfenic acids (**16**) generated by the thermolysis of (*t*-butyl sulfinyl) alkenes cyclized regio- and stereospecifically to *cis*-2-methylthiacycloalkane 1-oxides (**17**).

The reverse reaction, thermolysis of cyclic sulfoxides, has also been studied.<sup>53</sup> At 140°C, in xylene, conditions under which acyclic sulfoxides readily decompose,<sup>25c</sup> thian-1-oxide (**18**) was essentially inert whereas thiepan-1-oxide (**19**) rearranged with a half life of *ca.* 28 h to give *cis*-2-methylthian-1-oxide (**20**) (40%). Under the same conditions, *cis*-2-methylthiepan-1-oxide (**21**) decomposed even more readily with a

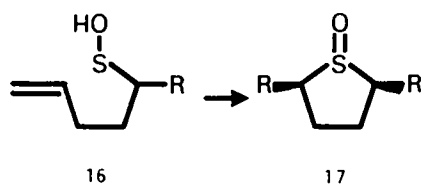


FIGURE 13

half life of 6h to give *cis*-2-ethylthian-1-oxide (**22**) (35%) and 3-thiolen (**23**) (32%). The 3-thiolen was presumably obtained by cyclization of the thioaldehyde (**24**) formed *via* thermolysis of the intermediate thiosulfinate (**25**) derived from the sulfenic acid.

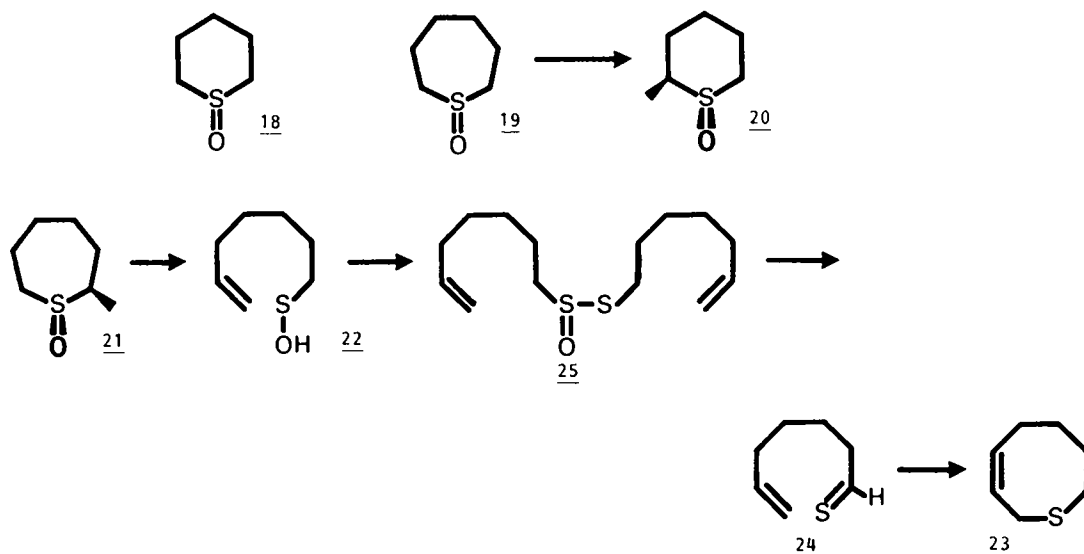


FIGURE 14

Although the incorporation of the sulfoxide in a six-membered ring normally precludes the reaction, the geometric requirement can sometimes be circumvented by increasing the acidity of the migrating hydrogen with an activating group. Baxter and Stoodley<sup>55</sup> showed that a 4-azapentamethylene sulfoxide (**26**) rearranged at 20°C to the sulfenic acid (**27**) by abstracting a ring  $\beta$ -hydrogen without going through the

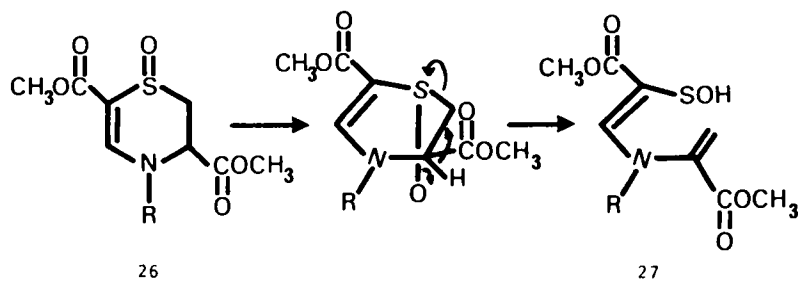


FIGURE 15

usual coplanar transition state. A ring contraction analogous to those reported by Jones was involved.

Koelwijin and Berger<sup>29a</sup> determined that the antioxidant action of dialkyl sulfoxides in the autoxidation of hydrocarbons derived from the ability of the sulfoxides to form sulfenic acids on thermal decomposition. Sulfenic acids appear to be almost as active in scavenging peroxy radicals as a hindered phenoxy radical.<sup>45</sup>

In most cases, one peroxy radical is destroyed per molecule of sulfenic acid. However, the inhibitor is less efficient if sulfoxides yielding tertiary or possibly secondary alkyl sulfenic acids are used in hydrocarbons which oxidize *via* tertiary peroxy radicals.<sup>28</sup> This was attributed to the generation of alkyl radicals from the sulfenic acid perester (28) formed in the inhibition reaction (Fig. 16).

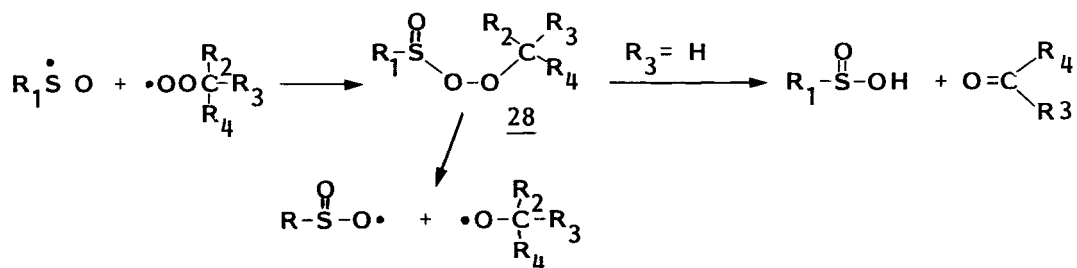


FIGURE 16

The ionic decomposition of hydroperoxide by strong acid formed from the sulfoxides was observed in later stages of autoxidation. Addition of calcium carbonate to the oxidation reaction greatly reduced the antioxidant ability of the sulfoxide (see also Ref. [29b]). No specific structure for the acidic species was proposed.

Bridgewater and Sexton<sup>46</sup> concluded that both aryl and alkyl sulfides and disulfides catalyze the decomposition of cumene hydroperoxide by forming sulfur dioxide, a strong Lewis acid. The SO<sub>2</sub> is formed by the thermolysis of thermally unstable sulfur-oxygen compounds. It was noted that certain sulfides do not undergo this decomposition. For example, dibenzyl sulfide did not decompose CHP under the experimental conditions. The study concentrated on the reactions of 3,3',5,5'-tetra-*t*-butyl-4,4'-dihydroxydiphenyl mono-, di-, tri-, and tetrasulfides (29). These analogs of butylated hydroxytoluene (BHT) (30) were being tested as free radical inhibitors. Similar BHT analogs investigated by Scott<sup>47</sup> were very good melt stabilizers in polypropylene processing.

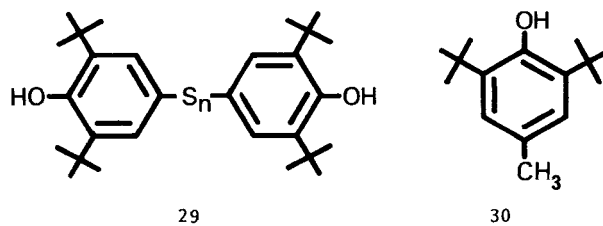


FIGURE 17

To reiterate, sulfides can oxidize to sulfoxides which undergo thermolysis to alkylsulfenic acids. Alkylsulfenic acids are short lived free radical scavengers which condense to give alkylthiosulfinate esters. The thermal decomposition of dialkyl thiosulfinate esters is a very complex process, yielding thiosulfonates, disulfides, or alkyl sulfinyl or alkyl sulfonyl disulfides *via* the Pummerer rearrangement. Block<sup>56-59</sup> has demonstrated that the alkyl thiosulfinate esters, which have particularly weak S—S bonds, undergo elimination under mild conditions to again generate alkylsulfenic acids (Fig. 18).

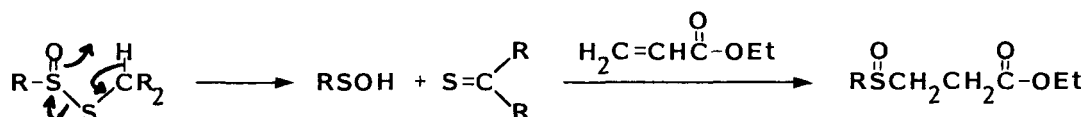


FIGURE 18

This was demonstrated by trapping the intermediate with a reactive alkene or alkyne. In addition, it was shown that a rapid equilibrium is established on mixing two different thiosulfinate esters, resulting in complete scrambling of the sulfinyl fragments.

Block<sup>57</sup> also showed that the pyrolysis of *t*-butyl thiosulfinate affords alkane thiosulfoxylic acids (R-SSOH) by a closely related mechanism to that of the generation of sulfenic acids. It was suggested that sulfenic and thiosulfoxylic acids, thermally produced from alkyl thiosulfonates, are the effective inhibitors of the reaction of squalene with oxygen and certain other autoxidation processes,<sup>40</sup> rather than the thiosulfonates themselves.

Kulich and Shelton<sup>60</sup> consider thiosulfoxylic acids to be important antioxidants derived from thiosulfonates under mild conditions (<100°C). The thiosulfoxylic acids may be expected to undergo oxidation to thiosulfurous and thiosulfuric acids (Fig. 19).

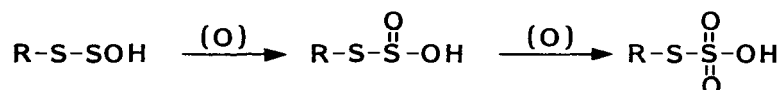


FIGURE 19

Thiosulfuric acids are unstable; acidified solutions of their salts undergo oxidation to the corresponding disulfide and sulfuric acid<sup>61</sup> which is a particularly effective antioxidant.

Generally sulfones have remarkable thermal stability.<sup>62</sup> Certain cyclic sulfones, however, will generate SO<sub>2</sub> on heating to moderate temperatures. Gipstein<sup>63</sup> investigated the effect of varying numbers of  $\beta$ -hydrogen atoms in the hydrocarbon structure on the thermal stability of 12 alkyl and aryl sulfones having from 0 to 18  $\beta$ -hydrogens. This was determined by measuring the volume of gas generated during pyrolysis at 275°C for 1 hour; unfortunately, no products were identified. They found that thermal stability was inversely proportional to the number of  $\beta$ -hydrogen atoms and that phenyl rings  $\alpha$  to the sulfone group acted as electron withdrawing groups and had a stabilizing effect. To further test their observations, sulfone polymers were prepared

and their stabilities studied. With the exception of the methylene polymer which decomposed extensively to a large number of products [ $\text{SO}_2$ ,  $\text{CS}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{H}_2\text{S}$ ,  $\text{CH}_3\text{-S-CH}_3$ ,  $\text{CH}_3\text{-S-S-CH}_3$  and ethylene episulfide, (most of these would be excellent antioxidants)] the results were in accord with those for monomeric sulfones. Dae<sup>31</sup> gives a good review of catalyzed and uncatalyzed sulfone eliminations.

Under basic conditions, it is possible for sulfones to eliminate  $\text{SO}_2$  at relatively low temperatures.<sup>64</sup> For example, this has been used in the synthesis of vitamin A derivatives.<sup>65</sup>

It has also been observed<sup>28</sup> that sulfoxides catalyze the radical decomposition of hydroperoxide *via* the formation of complexes of sulfoxide and hydroperoxide. This pro-oxidant effect becomes more important as the concentrations of sulfoxide and hydroperoxide increase.

The complexity of behavior of sulfide derived sulfoxides and their various decomposition products is the main reason why the action of sulfides in autoxidizing systems has often seemed to be erratic, resulting in conflicting views.<sup>28</sup>

## ORGANIC DISULFIDES

Disulfides are present in lower boiling (<250°C) fractions of some crude oils,<sup>14,4a,b</sup> but the concentration decreases to negligible levels in higher boiling cuts.

Disulfide oxidation has been widely studied.<sup>66</sup> The ultimate product is the corresponding sulfonic acid, which arises from S—S bond fission.<sup>67</sup> A number of intermediate oxidation products, as well as products from side reactions have been identified by isolation under carefully controlled oxidation conditions.

As was the case for sulfides, it is not disulfides which are the effective antioxidants but rather their oxidation products.<sup>68a,b</sup> Hawkins and Sautter<sup>68c</sup> showed that the ability of diaryl disulfides to inhibit polyethylene oxidation results from the formation of active antioxidants *in situ* as demonstrated by their ineffectiveness until substantial oxidation had occurred. They proposed that a thiosulfinate (31), which is the first oxidation product of a disulfide, was the active species.<sup>60</sup> Other workers<sup>60</sup> have reached similar conclusions. The thermal degradation of thiosulfonates to thiosulfoxylic acids or sulfenic acids was outlined above (Fig. 20).

The existence of  $\alpha$ -disulfoxides in the oxidative pathway of disulfides to thiosulfonates has been postulated for some time. Using low temperature NMR techniques

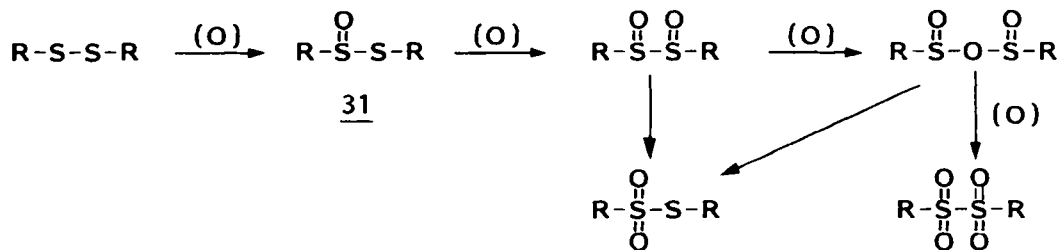


FIGURE 20

Freeman and Angeletakis<sup>69</sup> were able to identify a number of  $\alpha$ -disulfoxides as intermediate species in the metachloroperbenzoic acid oxidation of thiosulfinates. The results indicated that direct attack of oxidant on the sulfinyl sulfur was not a major reaction pathway, and various rearrangement mechanisms to give the observed reaction products from the  $\alpha$ -disulfoxide were proposed (Fig. 21).

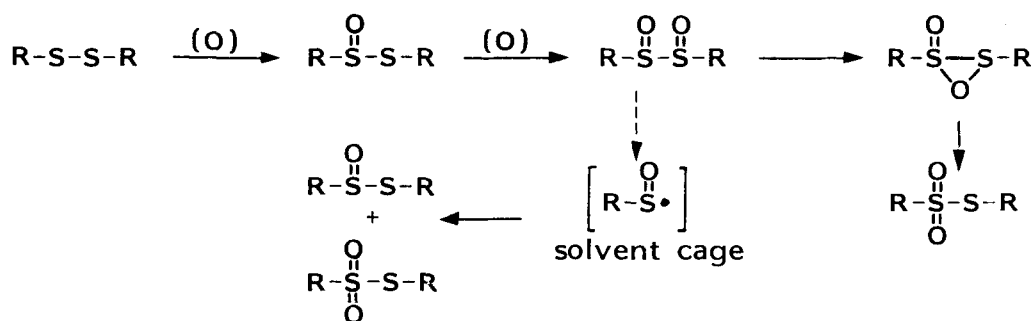


FIGURE 21

Thiosulfonates of the type  $\text{R-SO}_2\text{SCH}_2\text{Ar}$  (where  $\text{R} = \text{ArCH}_2\text{-}$  or  $\text{Ar}_2\text{CH-}$ ) undergo thermal decomposition<sup>70,71,73</sup> in inert solvents in the temperature range 130–200°C, with essentially quantitative evolution of sulfur dioxide and the formation of varying amounts of  $\text{R-S-CH}_2\text{Ar}$ ,  $\text{RH}$ , stilbene,  $\text{R-R}$ , and dibenzyl disulfide. The rate of decomposition is strongly dependent on the nature of the  $\text{R}$  groups and is fastest where  $\text{R}$  is aryl. The mechanism is thought to involve heterolytic cleavage of both the  $\text{C-SO}_2$  and  $\text{C-S}$  bonds in the rate determining step (Fig. 22).

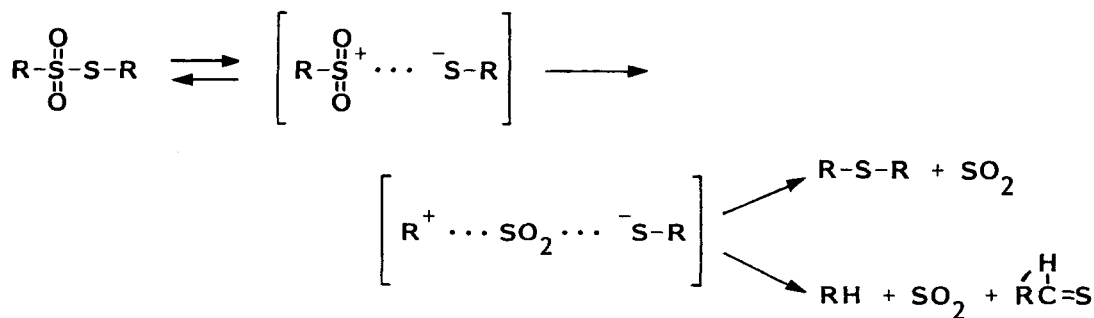


FIGURE 22

The stereochemistry of the thermal decomposition of thiosulfonates was also investigated.<sup>71</sup> Thermolysis of  $\text{R-phenyl-}\alpha\text{-toluenethiosulfonate}$  was remarkably non-stereospecific, yielding racemic phenylbenzyl sulfide. It was concluded that the mechanism involved a four-membered transition state which yielded a carbene/thiol pair and led to the extrusion of  $\text{SO}_2$ . The pair then recombined to give the racemic sulfide (Fig. 23).

In an early study of the disproportionation of sulfinic acids, Kice<sup>71,72,74</sup> determined the rate and equilibrium constants for the sulfinic acid/sulfinyl sulfone equilibrium in aqueous acetic acid (Fig. 24).



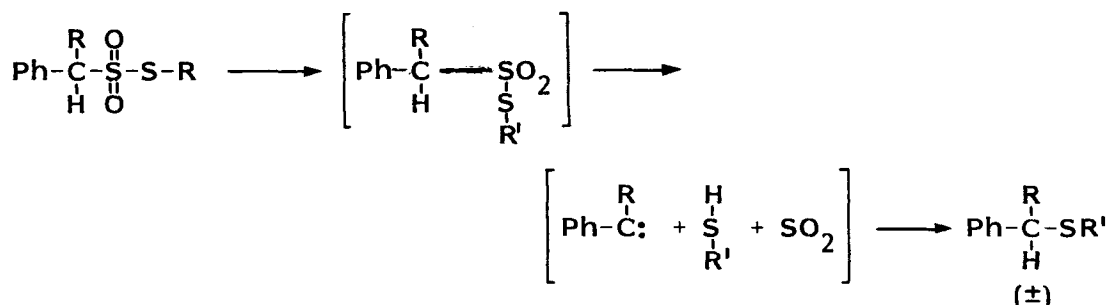


FIGURE 23

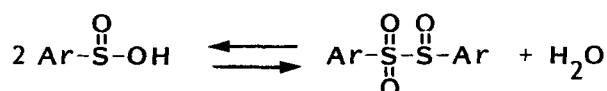


FIGURE 24

Sulfenic acids are moderately stable at room temperature, decomposing slowly to give sulfinyl sulfonates. However, if the carbanion ( $\text{R}^-$ ), generated by loss of  $\text{SO}_2$  from  $\text{R}-\text{SO}_2^-$  is stabilized,<sup>75</sup> then the reaction is relatively facile (Fig. 25).

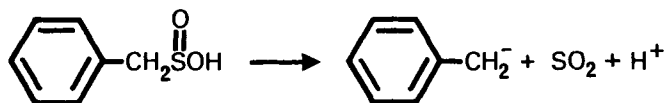


FIGURE 25

A detailed discussion of the reactions of sulfenic acids is contained in Oae's book (Ref. [31], and references therein).

$\alpha$ -Disulfones derived from disulfides are not considered effective antioxidants since the intermediates are relatively less stable and would probably decompose before reaching this oxidation state. However, once formed, aryl  $\alpha$ -disulfones undergo thermal decomposition at 145–165°C *via* homolytic cleavage of the S—S bond.<sup>76</sup> The arylsulfonate radicals then react further to yield a variety of recombination products and a small amount of sulfur dioxide (*ca.* 20%) (Fig. 26).



FIGURE 26

Kice and Farn<sup>77</sup> also investigated the thermal decomposition of benzyl, 3-phenylpropyl, and methyl  $\alpha$ -disulfones. The products from 1 mmol of the benzyl compound were bibenzyl (.41 mmol), benzyl sulfone (.12 mmol) and  $\text{SO}_2$  (1.6 mmol). The other two compounds were much slower to react and gave lower yields. The higher reactivity of the benzyl disulfone was attributed to formation of a stable benzyl radical from the sulfonyl radical in an unexpected two-bond cleavage (Fig. 27).

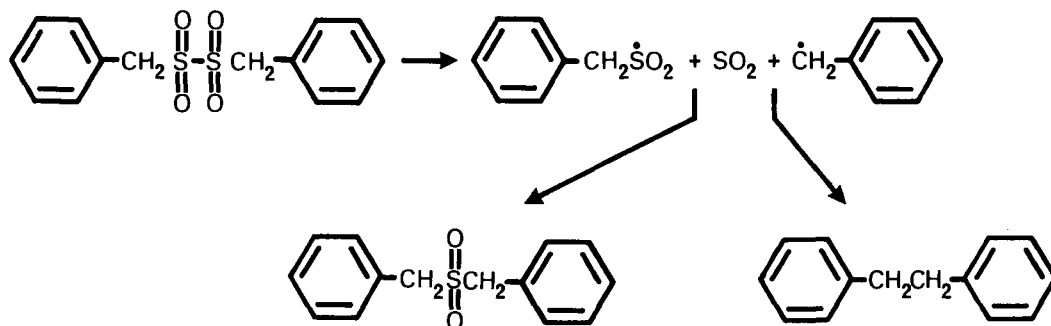


FIGURE 27

Hydrolysis of  $\alpha$ -disulfones gave sulfonic and sulfenic acids,<sup>78,79</sup> both of which are potential antioxidants.<sup>79b</sup> In hydrocarbon oils, water is present from many reactions, hence aqueous chemistry should be considered.

### ORGANIC POLYSULFIDES AND OTHER ORGANIC SULFUR COMPOUNDS

Polysulfides have not been reported as natural constituents of crude or refined oils. However, polysulfides have been investigated as antioxidant additives.<sup>23a,b</sup> In general, their chemistry is similar to that of the disulfides, except that the presence of a chain of sulfur atoms results in a more complex series of decomposition reactions including elemental sulfur extrusion.

The presence of alkenes<sup>2</sup> and hydrogen sulfide, either from the reactions of elemental sulfur with hydrocarbon or from other sources, could lead to the formation of small quantities of episulfides. On oxidation, these give products which readily decompose yielding  $\text{SO}_2$ .

Baldwin<sup>80</sup> studied the thermal decomposition of *cis*- and *trans*-2,3-dimethyl-episulfoxide (**32**, **33**). At higher temperatures ( $150^\circ\text{C}$ ), both isomers decomposed to  $\text{SO}$  and alkene. At lower temperatures ( $35^\circ\text{C}$ ), the *cis* isomer was stable but the *trans* isomer underwent a cyclic rearrangement giving an unsaturated sulfenic acid in equilibrium with a thiosulfoxylate and a thiosulfinate (Fig. 28).

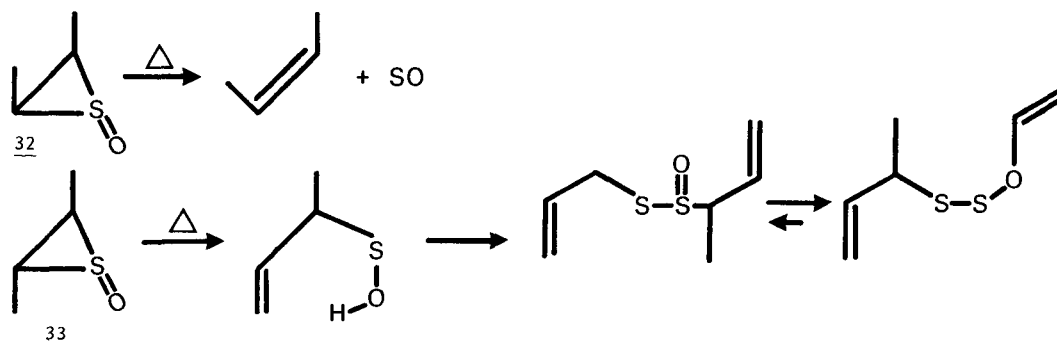


FIGURE 28

## THIOPHENES

Thiophenes are one of the most important groups of organosulfur types found in crude oils, constituting 45–84% of the sulfur in middle and high boiling fractions.<sup>4b</sup> Benzo- and dibenzothiophenes are predominant; alkyl and cycloalkyl thiophenes constitute only a small proportion of the total. Polyarene thiophenes containing up to five fused rings have been found in higher boiling petroleum fractions, but the tetra and penta-arene content is low even in heavy petroleum residues. Despite their relatively high concentrations, the importance of thiophenes as natural antioxidants has not been investigated extensively.

In early studies, dibenzothiophenes were found to have no stabilizing effect on hydrocarbon oil oxidation.<sup>2a</sup> Recently, van Tilborg and Smael<sup>81,82</sup> studied a series of thiophenes and benzothiophenes as autoxidation inhibitors. The hydroperoxides formed during autoxidation were efficiently decomposed in the presence of thiophenic compounds, suppressing hydroperoxide-initiated chain branching. Benzothiophenes displayed a moderate inhibitory effect and thiophenes were the most active.

The activity of a thiophene is greatly influenced by the type and position of the substituents.<sup>81</sup> Thiophenes can be divided into three classes in order of decreasing activity; those with strong electron releasing groups, those with weaker electron releasing groups, and least active, those with electron withdrawing substituents. The mechanisms of antioxidant activity are as yet unclear but several possibilities have been investigated.

1. Diels-Alder dimerization
2. Thermal decomposition
3. Acid catalyzed decomposition of thiophene 1,1-dioxides
4. Direct attack of hydroperoxide on thiophenes
5. Attack of hydroxy or peroxy radicals on thiophenes
6. Reaction of thiophenes with singlet oxygen

### 1. Diels-Alder Dimerization

Diels-Alder dimerization of thiophene 1,1-dioxides results in the evolution of SO<sub>2</sub>. However, at low thiophene concentrations, the dimerization is too slow to account for the formation of SO<sub>2</sub> in the required amounts.

When sterically unhindered thiophenes are oxidized at room temperature, the major product is a 'sesquioxide' formed from the mono- and dioxides. The autoxidation of the thiophene to the oxide is much slower than the subsequent oxidation to the dioxide. Under autoxidation conditions, the concentration of the thiophene 1-oxide is even lower than that of the dioxide, so the rate of this type of Diels-Alder reaction will also be extremely low.

Davies and James<sup>83</sup> were the first to assign a structure to the dimer (**34**) and the trimer (**35**) subsequently produced during the oxidation of thiophene by hydroperoxide in acetic acid (Fig. 29).

Thiophene is quite unreactive as a Diels-Alder diene. Recently however, Kotsuki<sup>84</sup> showed that the Diels-Alder addition of thiophene to maleic anhydride can be accomplished at 100°C and 15 kbar.

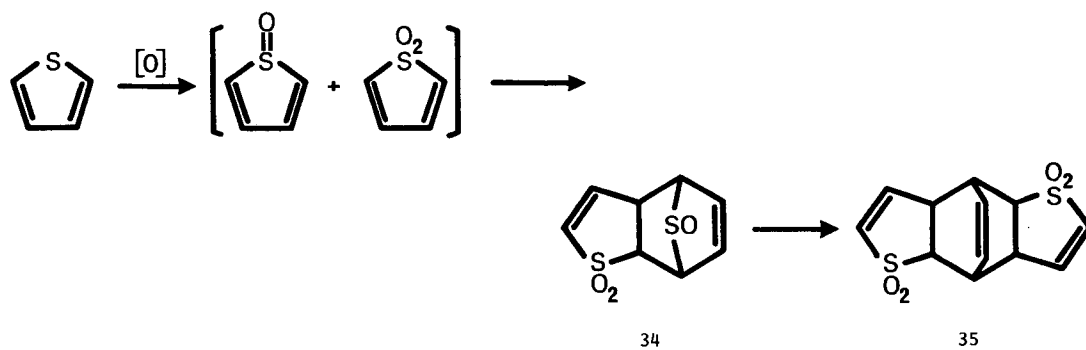


FIGURE 29

## 2. Thermal Decomposition

Flash vacuum pyrolysis of thiophene 1,1-dioxides showed that the temperatures required to thermally decompose alkyl and benzothiophenes are much too high (>800°C) to explain the evolution of SO<sub>2</sub> under autoxidation conditions.

## 3. Acid Catalyzed Decomposition of Thiophene 1,1-Dioxides

Thiophene 1,1-dioxides are extremely stable to desulfurization in the presence of strong acids, so this mechanism was also discounted.

## 4. Direct Attack of Hydroperoxide on Thiophenes

Van Tilborg and Smael<sup>81</sup> noted very little reaction between hydroperoxides and thiophenes in the presence of phenolic antioxidants, but no explanation of the significance of this observation with respect to mechanism was given.

## 5. Attack of Hydroxy or Peroxy Radicals on Thiophenes

*t*-Butyl peroxy radicals react with 2,5,-dimethyl thiophene to give the 5-carboxylic acid, which was found to be a poorer antioxidant than the starting material.<sup>81</sup> It was concluded that a reaction of this type could not be responsible for hydroperoxide-decomposing antioxidant activity of thiophenes. Hydroxyl radicals are virtually unreactive towards thiophenes.

## 6. Reaction of Thiophenes with Singlet Oxygen

Singlet oxygen can react with thiophenes<sup>85</sup> to give sulfines and sulfur. Sulfines are thermally unstable, decomposing to give SO<sub>2</sub>.<sup>85a</sup> Howard and Ingold<sup>86</sup> investigated the self-reaction of *sec*-butylperoxy radicals to give singlet oxygen *via* the Russell mechanism. Two *sec*-peroxy radicals dimerize to form a linear tetroxide which decomposes in a cyclic manner to give an alcohol, a ketone, and singlet oxygen.

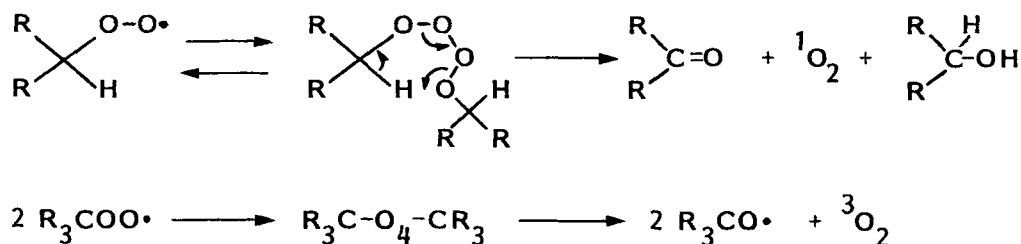


FIGURE 30

Tertiary peroxy radicals yield two alkoxy radicals (Fig. 30).

Skold and Schlessinger<sup>87</sup> showed that singlet oxygen undergoes a facile Diels-Alder reaction with 2,5-dimethylthiophene (**36**) to give an adduct which decomposes to an

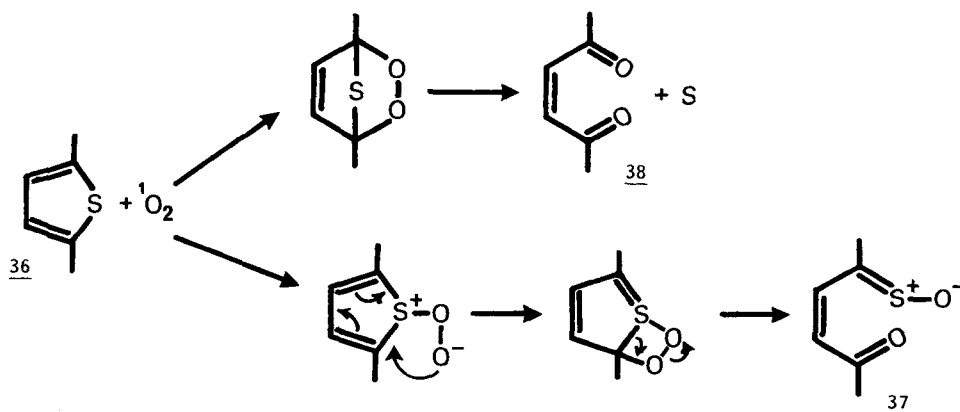


FIGURE 31

unsaturated keto-sulfine (**37**) and an enedione (**38**) (Fig. 31).

Van Tilborg<sup>88</sup> investigated the reaction of singlet oxygen with alkyl and aryl substituted thiophenes. A comparison of the products indicated that singlet oxygen plays an insignificant role in the desulfurization of thiophenes under autoxidative conditions. The relative reactivities towards singlet oxygen of a number of thiophenes compared with their previously reported antioxidant behavior confirmed these conclusions.

No satisfactory explanation of the observed antioxidant behavior of thiophenes has been formulated at present. The evidence suggests that free radicals are necessary to initiate the antioxidant action. A possible mechanism may involve the formation of a thiophene radical which is subsequently oxidized.<sup>89</sup>

## OTHER SYNERGISTIC SUBSTANCES

Hawkins and Worthington<sup>90a</sup> noted a synergistic effect between some sulfur species and apparently unreactive compounds such as carbon black, alkylated diphenoquinones and their corresponding diphenols. The effect is documented but the

mechanism is uncertain (see also Donnet and Voet<sup>91</sup>). Synergistic effects between phenolic compounds and organic sulfur compounds are well documented.<sup>90b,c,d,e,f,g,h</sup>

### ANTIOXIDANT SYSTEMS OF RELATED INTEREST

The mechanism of action of synthetic sulfur containing antioxidant additives was reviewed by Scott.<sup>3a</sup> Important industrial antioxidants include; zinc dialkyl-dithiocarbamates (**39**) and dialkylthiophosphates (**40**) in lubricating oils and rubbers, dialkyldithiopropionates (**41**) in foodstuffs and polyolefins, 4,4'-dihydroxydiphenylsulfides (**42**) in polyolefins and mercaptobenzimidazole (**43**) (Fig. 32) in rubbers and polyolefins.

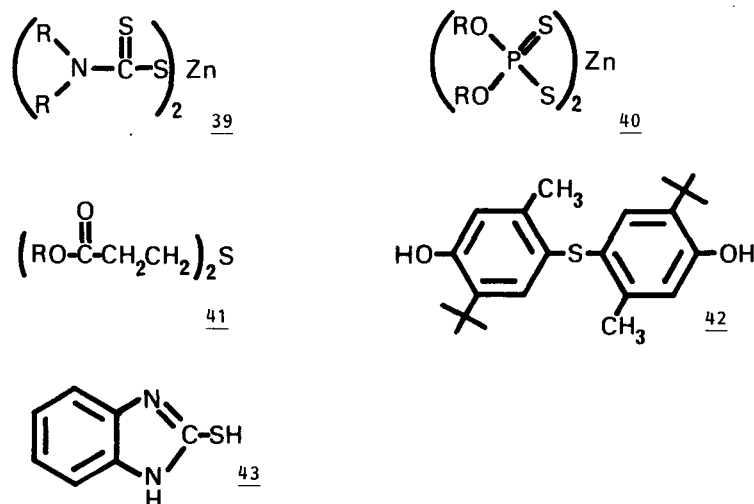


FIGURE 32

Some products of the decomposition of dimethyl disulfinyldipropionate (DMDS), a polymer antioxidant, were identified and found effective as antioxidants.<sup>92</sup> The only compounds capable of destroying hydroperoxides as rapidly as DMDS were  $SO_2$  and methyl  $\beta$ -sulfinopropionate (MSP, a sulfinic acid) which extrudes  $SO_2$  at elevated temperatures during polymer processing (Fig. 33).

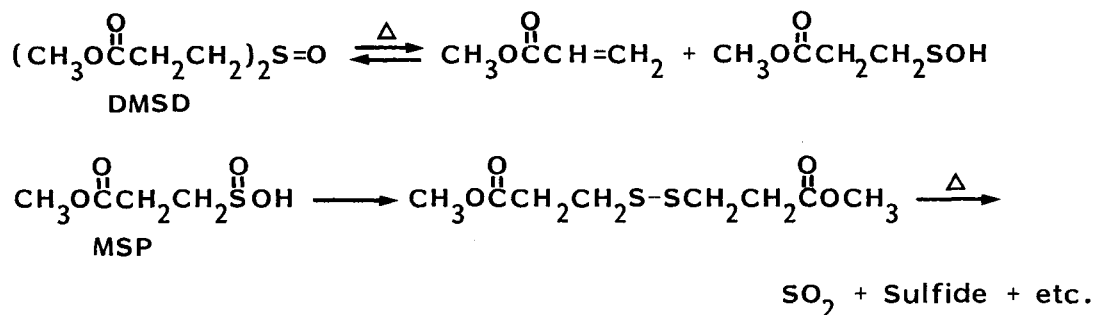


FIGURE 33

DMDS decomposes to a thiosulfinate in the presence and absence of *t*-butyl hydroperoxide. The stable end-product under all conditions was the thiosulfonate. This and the corresponding disulfide were low activity peroxide decomposers by comparison with the thiosulfinate.

Although this work was aimed at polymer antioxidants, the reaction sequence: sulfoxide  $\rightarrow$  sulfenic acid  $\rightarrow$  thiosulfinate  $\rightarrow$  thiosulfonate  $\rightarrow$  sulfinylsulfonate  $\rightarrow$  sulfonylsulfonic acid  $\rightarrow$  sulfonic acid appears to be applicable. The sulfonylsulfonic acid decomposes to  $\text{SO}_3$  and alkene in the presence of hydroperoxide.

An interesting study by Scott<sup>3a</sup> supports the general observations concerning strong acid as hydroperoxide decomposers. The reaction of dry HCl gas with cumene hydroperoxide (CHP) results in predominantly ionic decomposition at high CHP/HCl ratios, while free-radical decomposition is favored at low ratios. The latter conditions can also lead to a pro-oxidant effect.

## CONCLUSIONS

A number of general conclusions can be drawn concerning the antioxidant properties of organic sulfur compounds.

1. It is not organosulfur compounds, but their subsequent oxidation and decomposition products that act as antioxidants.
2. The most effective break-down product appears to be sulfur dioxide (or subsequently) sulfur trioxide.  
Sulfenic acids have also been shown to be effective antioxidants as both free radical traps and eventual sources of  $\text{SO}_2$ .
3. Because of their complex and facile reactions to give both sulfur dioxide and sulfenic acids, disulfides appear to be the most effective antioxidant precursors.

It should be noted that rapid action alone is not necessarily a desirable feature. The slower onset of oxidation inhibition by thiophenes may be one of the important features in the long-term stability of uninhibited lubricating oil.

This review is directed at deriving an understanding of the effect of organosulfur compounds on the autoxidation of refined, high-boiling hydrocarbon oils. There is also a large body of literature concerning the influence of sulfur compounds in fuels where an antioxidant effect is not necessarily desirable and where the presence of organic sulfur compounds leads to unacceptably high levels of sulfur dioxide in the combustion products. Clearly, the chemistry is related whereas fuel combustion involves large quantities of oxygen at  $>1000^\circ\text{C}$ , the oxidation of lubricating oils takes place with a more limited oxygen supply at much lower temperatures.

A better understanding of the complex reactions of these organic sulfur compounds in autoxidizing oils is clearly desirable hopefully leading to more accurately designed antioxidants with predictable lifetimes and efficacies.

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