

## LIQUID PHASE OXIDATION OF ALKYL SULFIDES AND THIOLS BY HYDROPEROXIDES

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### INTRODUCTION

In general, jet fuels deteriorate in quality with time. One of the significant undesirable changes is the formation of insoluble material which can plug nozzles and filters and coat heat exchanger surfaces. Deposit formation in fuels is triggered by autoxidation reactions and is closely associated with hydroperoxide concentration (1-3). If the available oxygen is low and the temperature raised, the hydroperoxide concentration will be limited by free radical decomposition (2). This regimen (low oxygen and increasing temperature) is similar to the environment found in an aircraft fuel system.

The composition of deposits affords clues to the molecular species involved in deposit formation and the mechanism of formation. Hetero-atoms (oxygen, nitrogen and sulfur) and ash have been found to comprise up to 40% of such deposits (4-6). The sulfur content of these deposits has been found to vary from 1 to 9%. Sulfur (0.4% max. allowed) is the most abundant hetero-atom present in jet fuels.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, and organo sulfides and thiols. Specifically, we examine the tert-butyl hydroperoxide oxidation of hexyl sulfide and dodecyl thiol in deaerated benzene at 120°C. The reactions were studied for time periods from 15 min to 180 min. Additionally, we have developed reaction conditions and an analytical method of high reproducibility which may be applicable to the study of other hydroperoxide oxidative processes.

### EXPERIMENTAL

Reagents tert-Butyl hydroperoxide, tBHP, (90%), hexyl sulfide and dodecyl thiol were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. Benzene (Aldrich Gold Label) was refluxed and distilled from  $\text{CaH}_2$ .

**Method.** The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically  $3\text{-}9 \times 10^{-4}$  mol of tBHP and  $6 \times 20^{-4}$  mole of hexyl sulfide or  $6 \times 10^{-4}$  mole of dodecyl thiol in 3.6 m mol of solvent) were weighed into 6 in. long, 1/4-in. o.d. Pyrex tubes closed at one end and fitted at the other with a stainless steel valve via a Swagelok (Teflon ferrules) fitting. The tube was attached to a vacuum system, cooled to 77K and subjected to several freeze-pump-thaw cycles. The tube was then subsequently flame-sealed below the valve. The ullage volume (0.30 ml) was kept constant for all runs. The deaerated samples were warmed to room temperature and immersed in a Cole-Parmer fluidized sand bath. The temperature (120°C) was controlled by a Leeds and Northrop Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm for the runs in benzene. After the reaction period the sealed tube was quenched to 77K and opened. The tube was capped, warmed to room temperature and the internal standards added. The solution was transferred to a screw cap vial (Teflon cap-liner) and stored at 0°C until analysis. Since a typical chromatogram required 90 min, two internal standards were added. One, p-xylene, afforded quantitation for peaks with short retention times, and a second, 1-phenyltridecane, for the peaks with longer retention times.

Samples were heated for time periods of 15, 30, 60, 120 and 180 min except for those runs with the more reactive mercaptan (60 min max). All tubes were subjected to the same cleaning procedure. They were filled with toluene, cleaned with a nylon brush, rinsed with toluene twice, then with methylene chloride, and dried in air at 150°C for 8 h. A search of the literature gives a few examples of catalytic behavior with glass systems (7,8); however, when a glass tube was filled with crushed Pyrex, thus increasing the surface area, the results at 120°C for the above time periods were not substantially altered.

The samples were analyzed by two techniques, both based on gas chromatography. Peak identification for both techniques was based on retention time matching with standards and mass spectrometry. In the first, a Varian gas chromatograph Model 3700 with flame ionization detector (F.I.D.) and equipped with a 50-m 0.20-mm i.d. wall-coated open tubular (OV-101) fused silica capillary column gave the necessary resolution to distinctly separate the individual components. A carrier gas flow of 1 ml/min was combined with an inlet split ratio of 60:1, a temperature program with an initial hold at 50°C for 8 min and a ramp of 4°/min to a final temperature of 260°C.

In the second technique, gases formed during the reaction were analyzed using a Perkin-Elmer Model Sigma 2 gas chromatograph equipped with a 6-ft 5A Molecular Sieve column or a 4-ft Porapak/S column. For the gas analysis, the column was operated at 55°C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. For this procedure, the valve was left on the reaction tube and after the appropriate reaction period, the tube valve was connected directly to a GC gas sampling valve via a Swagelok connection. An external standard was used for calibration. A pressure gauge measured the pressure in the sample loop at the time of analysis.

A material balance was assessed for each compound. The principal peaks of the chromatogram accounted for approximately 90% of the original compounds.

The very small peaks account for another 5-10%. The product distribution was repeatable to within 2-3% for each component.

## RESULTS AND DISCUSSION

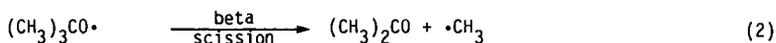
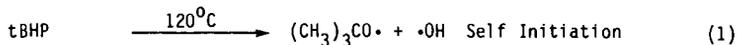
The thermal decomposition of an alkyl hydroperoxide is complex. At temperatures of 120°C or greater, tBHP decomposes by an autoinitiated pathway.<sup>9</sup> The major reaction pathway in the 120°C decomposition of tBHP, however, involves its attack by free radicals in the solution. The detailed mechanism of tBHP decomposition is highly dependent upon the specific reaction conditions employed since radical behavior is sensitive to structural, solvent and stereoelectronic effects.

The results in Table 1 illustrate that the product distribution from the reaction of tBHP with hexyl sulfide in deaerated benzene solvent can be conveniently divided into lower and higher molecular weight products. The quantities in Table 1 are based on per cent conversion from the moles of reactants originally present. Products derived solely from hexyl sulfide are calculated on the basis of the starting amount of hexyl sulfide. The tBHP derived products (for example, t-butanol) are similarly calculated based on the starting amount of tBHP. Mixed condensation products (i.e., tBHP + hexyl sulfide) are calculated on the basis of moles of hexyl sulfide. The values in Table 2 were likewise calculated using dodecyl thiol.

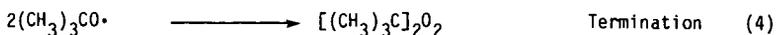
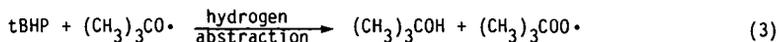
From tBHP, the major product was t-butanol. A small amount of acetone, methane, isobutylene and the tBHP radical termination product di-t-butylperoxide were also observed. From hexyl sulfide, lower molecular weight products included hexane, hexene and hexanal; higher molecular weight condensation products included the major product hexyl sulfoxide along with hexyl sulfone and hexyl disulfide. From dodecyl thiol, Table 2, lower molecular weight products included dodecane and dodecanol; higher molecular weight condensation products included the major product dodecyl disulfide along with dodecyl sulfoxide, dodecyl sulfide and dodecyl sulfone.

Solvent participation was noted by the formation of trace quantities of toluene and other substituted benzenes.

tBHP products The mechanism of autoinitiated tBHP decomposition can be depicted as follows:



Propagation



In aliphatic hydrocarbon solvent, it has been shown that beta-scission is favored over hydrogen abstraction at temperatures of 100°C or less. In the benzene solvent of this study, beta-scission was found to be less than competitive with hydrogen abstraction at 120°C. Small amounts of acetone were formed ranging from 1.5% for hexyl sulfide to 4.7% for dodecyl thiol at 60 min. By contrast, t-butanol was 75.4% for hexylsulfide and 76.7% for dodecyl thiol at 60 min. The greater yield of t-butanol compared to acetone definitively shows that hydrogen abstraction was favored over cleavage in benzene solvent under the conditions of this study. The increasing yield of acetone indicated, however, that at long reaction times beta-scission was a viable competing process.

Gaseous products The gaseous products formed included isobutylene, methane and a trace amount (0.1%) of ethane. No free oxygen was observed in any of the runs. As indicated in Table 1, isobutylene was 4.2% initially and decreased to 2.7% at 180 min. Methane increased from 0.8% at 15 min to 1.6% at 180 min. For dodecyl thiol, Table 2, isobutylene was 3.6% initially and decreased to 3.0% at 60 min. Methane increased from 0.9% at 15 min to 1.4% at 60 min.

Isobutylene probably resulted from the acid catalyzed dehydration of t-butanol. The decreasing yield was not surprising in light of the many pathways open to a reactive olefin in a radical environment.

The yield of methane was similar to that of acetone. This was an expected result since they both form via beta scission of the alkoxy radical (reaction 2). The reactive methyl radical easily abstracts hydrogen to yield methane rather than reacting with other radicals present in the system. This accounted for the low yield of methyl radical derived products.

The lack of measured oxygen does not mean that it was not formed. It could form from a non-terminating reaction of two t-butyl peroxy radicals and then be consumed immediately by any of several pathways.

Hexyl sulfide products The cleavage of a C-S bond in sulfides is known to occur in thermal and photochemical reactions.<sup>10</sup> The most direct means of generating a sulfur centered radical is the homolysis of a bond to sulfur. However, most simple alkyl sulfides are thermally quite stable (C-S bond dissociation energies are ca. 74 kcal/mol) and quite unreactive toward oxygen.<sup>11</sup> In the presence of t-butyl hydroperoxide, the t-butoxy radical generated was found to abstract the hydrogen alpha to the sulfur. Thus for hexyl sulfide, observed products were the thiyl radical and hexene. An alternate pathway would involve the attack of an alkoxy by a S<sub>H</sub>2 mechanism to yield both a thiyl radical and hexyl radical. That these processes were minor pathways can be seen from the results in Table 1. Hexane and hexene were present in low yields at all reaction times (hexane ca. 0.3% at 180 min and hexene 0.2%). Combination of thiyl radicals to form the disulfide was also a minor termination pathway (0.6% yield at 180 min).

Table 1

Mole % Conversion for the Reaction of Hexyl Sulfide with t-Butyl Hydroperoxide in Benzene Solvent at 120°C.

	Conversion (Mole %)				
	Reaction Time (min.)				
	15	30	60	120	180
<u>TBHP Products<sup>a</sup></u>					
Acetone	1.0	1.5	1.5	1.5	2.5
t-Butanol	55.5	59.5	65.9	69.8	75.4
di-t-butyl peroxide	0.5	0.7	0.7	0.7	1.0
<u>Hexyl sulfide Products<sup>b</sup></u>					
Hexene	0.1	0.1	0.1	0.3	0.2
Hexane	0.1	0.1	0.3	0.4	0.3
Hexanal	0.2	0.2	0.3	0.2	---
Hexyl disulfide	0.3	0.5	0.5	0.5	0.6
<u>Condensation Products<sup>b</sup></u>					
Hexyl sulfoxide	74.8	85.9	81.6	81.9	80.7
Hexyl sulfone	1.2	1.4	3.0	3.4	4.0
Hexyl thiosulfinate	0.1	0.1	0.1	0.1	---
<u>Gaseous Products</u>					
Methane	0.8	0.8	1.0	1.4	1.6
Isobutylene	4.2	3.9	3.6	3.1	2.7
<u>Unreacted</u>					
TBHP	28.9	23.9	8.7	3.9	1.8
Hexyl sulfide	22.5	13.9	8.2	3.9	2.9
<u>Trace Products<sup>c</sup></u>					
	6.7	7.8	9.7	10.1	8.1

a. based on the starting moles of TBHP

b. based on the starting moles of hexyl sulfide

c. summation of small peaks

The observed hexanal can be formed by several reaction pathways. Among these are the thermal rearrangement of the hexyl sulfoxide,<sup>12</sup> or more likely, the coupling of a t-butylperoxy radical with a thioacetal radical. Based on bond dissociation energy considerations alone, the t-butylperoxy radical was probably the least reactive and most plentiful radical present in the system.<sup>13</sup> This would favor a termination step involving this radical over a termination involving the very reactive alkoxy radical which would be expected to propagate the chain.

The major higher molecular weight product observed from the oxidation of hexyl sulfide by tBHP was hexyl sulfoxide. Its yield varied from 74.8% at 15 min. to 85.9% at 30 min., gradually decreasing to 80.7% at 180 min. of reaction. Other products included: hexyl sulfone (1.2% at 15 min. gradually increasing to 4.0% at 180 min.), hexyl disulfide (0.3 to 0.6%) and a trace amount of dihexyl thioisulfinate (0.1%).

Table 2

Mole % Conversion for the Reaction of Dodecyl Thiol with t-Butyl Hydroperoxide in Benzene Solvent at 120°C

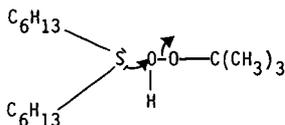
	Conversion (Mole %)		
	Reaction Time (min.)		
	15	30	60
<u>TBHP Products<sup>a</sup></u>			
Acetone	4.7	4.4	4.7
t-Butanol	59.2	65.4	76.7
di-t-butyl peroxid	1.6	1.6	1.9
<u>Dodecyl thiol Products<sup>b</sup></u>			
Dodecane	0.1	0.3	0.4
Dodecanal	0.6	0.7	1.1
Dodecyl sulfide	1.9	1.8	1.4
Dodecyl disulfide	74.4	78.8	74.1
<u>Condensation Products<sup>b</sup></u>			
Dodecyl sulfoxide	2.3	2.1	2.1
Dodecyl sulfone	0.9	1.5	1.7
<u>Gaseous Products</u>			
Methane	0.9	1.3	1.4
Isobutylene	3.6	3.3	3.0
<u>Unreacted</u>			
TBHP	19.7	12.6	1.3
Dodecylthiol	15.6	7.3	3.4
Trace Products <sup>c</sup>	4.6	6.7	9.4

a. based on the starting moles of TBHP

b. based on the starting moles of dodecyl thiol

c. summation of small peaks

The major product hexyl sulfoxide could result from at least two mechanisms: attack of oxygen-centered radicals (i.e., alkoxy) on sulfur followed by a beta scission;<sup>14</sup> or alternatively, the sulfoxide may arise from the reaction of t-butyl hydroperoxide with the hexyl sulfide.



The resulting sulfoxide once formed is quite stable, as can be seen from the slight lowering of the yield at extended reaction times.

The hexyl sulfone yield in the present work varied from an initial 1.2% at 15 min. to 4.0% at 180 min of reaction. This very slight increase compared to the yield of hexyl sulfoxide at 180 min. (80.7%) definitively illustrates the stability of the alkyl sulfoxide in the presence of tBHP.

The further oxidation of a sulfide or a sulfoxide to a sulfone is believed to proceed by a mechanism similar to that for sulfoxide formation from an alkyl sulfide.<sup>15</sup> The formation of an alkyl sulfone is a facile reaction only in the presence of a strong oxidant or when the reaction is catalyzed by transition metal ions.<sup>16</sup>

The hexyl disulfide product was a consequence of a self annihilation by dimerization of the thiyl radical. The thiyl radical was in low concentration at all reaction times (see hexyl termination products in the Table). As a result, the termination product hexyl disulfide was a minor product at all reaction times (1% at 180 min.). The other minor observed product forms as a direct result of the disulfide. The trace amounts of hexyl thiosulfinate observed (0.1% at all reaction times) resulted from the peroxidation of the disulfide.

**Dodecyl thiol products.** When thiols are oxidized by air or peroxides, disulfides are the major product regardless of the presence or absence of a catalyst.<sup>17</sup> The mechanism of thiol oxidation has been the subject of discussion for many years. Some reports support ionic mechanisms while others support radical processes.<sup>18</sup> The results in the present work, Table 2, support a radical mechanism. The t-butoxy radical generated from tBHP was found to abstract the thiol hydrogen. By contrast, hydrogen abstraction by the thiyl radical to yield a thiol is only observed in cases involving very stable thiyl radicals with active hydrogen donors.<sup>19</sup> Actually, the problem with this hydrogen abstraction is not that the process is slow, but that abstraction of a hydrogen from a thiol is thermodynamically favorable. Likewise, the thiyl radical has not been observed to undergo a beta scission to yield a thione and a methyl radical.<sup>20</sup> In the present work, thiones and thiols were not detected, even in trace amounts, in the product mix.

The observed secondary reaction products dodecane, dodecanal and dodecyl sulfide were present in low concentration for all reaction time periods. Dodecyl sulfide, 1.9% at 15 min decreasing to 1.4% to 60 min, was probably formed by the reaction of dodecyl thiol with the condensation product dodecyl sulfoxide. The products of such a reaction would be dodecyl disulfide and dodecyl sulfide. Dodecyl sulfide once formed could then undergo other side reactions. The observed dodecane was the result of such a reaction scheme: an  $S_H2$  reaction between the t-butoxy radical and dodecyl sulfide would result in both the dodecyl radical and a thiyl radical. The dodecanal product, 0.6% at 15 min increasing to 1.1% at 60 min, could result from several mechanisms. Among these are the thermal rearrangement of the sulfoxide or the coupling of the t-butyl peroxy radical with a thioacetal radical.

The major higher molecular weight product observed from the oxidation of dodecyl thiol by tBHP was dodecyl disulfide. Other products included dodecyl sulfoxide, dodecyl sulfone and trace but unreported amounts of dodecyl thiosulfinate.

Dodecyl disulfide, 74.4% at 15 min increasing to 78.8% at 30 min and then decreasing to 74.1% at 60 min, was formed by the direct oxidation of dodecyl thiol and subsequent dimerization of the thiyl radicals. An alternative side reaction for its formation would be the reaction of the

starting thiol with dodecyl sulfoxide to generate additional dodecyl disulfide.

The dodecyl sulfoxide, 2.3% at 15 min decreasing to 2.1% at 60 min, probably resulted from the same two pathways mentioned for hexyl sulfoxide.<sup>14</sup> The dodecyl sulfoxide yield was not observed to increase significantly due to further oxidation to dodecyl sulfone or for example its reaction with the starting thiol. The latter reaction would produce both dodecyl disulfide and dodecyl sulfide.

The low yield of dodecyl sulfone, 0.9% at 15 min increasing to 1.7% at 60 min, indicated the stability of alkyl sulfoxides toward further oxidation by tBHP in the liquid phase at 120°C.

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