

LIQUID PHASE OXIDATION OF THIOPHENOL AND OLEFINS
BY OXYGEN AND t-BUTYL HYDROPEROXIDE

By

George W. Mushrush, John M. Watkins^a, Robert N. Hazlett,
Dennis R. Hardy and Harold G. Eaton
The Naval Research Laboratory Code 6180
Washington, D.C. 20375-5000 and
^aGEO-CENTERS, Inc. Suitland, MD 20746

INTRODUCTION

In supersonic Navy aircraft, aerodynamic heating can cause metal skin temperature to rise to high levels. At mach 2.7, it has been estimated that the fuel in an uninsulated wing tank could reach 430F (1). Hydrocarbon fuels subjected to such temperatures have been shown to undergo considerable degradation. This observed degradation can be manifested by the formation of deposits on filters, in nozzles and on combustor surfaces (2-5). These deposits are the consequence of free radical autoxidation reactions. Trace levels of sulfur compounds have been found to influence the deposit formation process. It has been shown that jet fuels low in sulfur content are relatively stable and that fuels of high sulfur content are fairly unstable (6,7). Presently, it is not possible to relate the observed instability to specific sulfur species. Heteroatoms (oxygen, nitrogen and sulfur) and ash have been found to comprise 40 percent of such deposits (8). The sulfur content of these deposits has been found to vary from 1 to 9% (9). Sulfur (0.4%) is the most abundant heteroatom present in the fuel itself.

Deposits formed in jet fuel in the presence of oxygen contained a greater percentage of sulfur than that present in the fuel itself (10). In previous work in our laboratory, it was observed that thiols, sulfides and aldehydes could be readily oxidized by hydroperoxides (11-13).

The rates of the reactions in autoxidation schemes are dependent on structure, oxygen concentration and temperature (14-16). Catalysts, free radical initiators and inhibitors can materially alter both the rate and the oxidation pathways (17,18).

Although slight thermal deterioration of fuel is known to occur in non-oxidizing atmospheres, the presence of elemental oxygen will greatly

accelerate the deterioration of fuel properties as well as significantly lower the temperature at which undesirable products are formed. Thus the stability of jet fuels is frequently dependent upon the nature of potential autoxidation pathways which can take place under aircraft operating conditions.

If sufficient oxygen is present, the hydroperoxide concentration will reach a high level. If the available oxygen is low, but the temperature is raised, the hydroperoxide level will be limited by free radical decomposition. This regimen, low oxygen and increasing temperature, is similar to the environment in an aircraft fuel system. In this situation fuel degradation can be associated with the reaction of hydroperoxides with the other moieties in the fuel.

This paper is concerned with the reaction between a primary autoxidation product, a hydroperoxide, with thiophenol in the presence of the active olefins indene and styrene. The reactions were carried out in deaerated benzene with *t*-butyl hydroperoxide or in benzene with an oxygen overpressure.

EXPERIMENTAL

Reagents. *tert*-Butyl hydroperoxide, tBHP, (90%), thiophenol, indene and styrene were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity. Benzene (Aldrich Gold Label) was refluxed and distilled from calcium hydride.

Method. The reactions were carried out in sealed borosilicate glass tubes. The reagents (typically $3\text{-}9 \times 10^{-4}$ mol of tBHP and 6×10^{-4} mol of both thiophenol and olefin in 0.6ml of solvent) were weighed into 6 in. long, 1/4-in. o.d. borosilicate glass 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. For those runs in oxygen, the solution was bubbled extensively with oxygen, a 40 - 45 psi over pressure of oxygen was then added. 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 was controlled by a Leeds and Northrup Electromax III temperature controller. The total pressure during each run was estimated to be 5.1 atm for the runs in benzene solvent. After the reaction period (15, 30, 60 min) the sealed tube was quenched to 77K and opened.

The samples were analyzed by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5710 GC, a H-P Model 5982A mass spectrometer, and a Ribermag SADR GC/MS data system. An all glass GC inlet system was used in conjunction with a 0.31 mm x 50 m SP-2100 fused silica capillary column.

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. In this mode, the column was operated at 55C. The chromatogram was recorded and integrated on a Hewlett-Packard Model 3390A reporting integrator. An external standard was used for calibration. A gauge measured the pressure in the sample loop at the time of analysis.

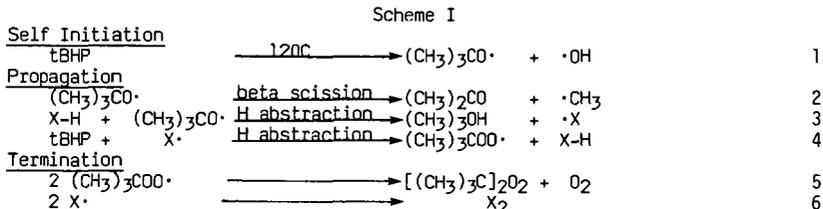
RESULTS AND DISCUSSION

At temperatures of 120C or greater, tBHP decomposes rapidly by an autoinitiated pathway (19,20). The major reaction pathway in the 120C decomposition of tBHP involves attack by free radicals present in the solution. The detailed mechanism is complicated since free radicals are sensitive to structural, solvent and stereoelectronic effects.

The results in Tables 1 and 2 illustrate the product distribution for the tBHP, styrene, indene and thiophenol derived products. The quantities in the tables are expressed in terms of mole percent conversion from the moles of reactant originally present. Products derived solely from tBHP (for example acetone) are calculated based on the starting amount of tBHP. The same is true for products from the thiophenol (i.e., phenyl disulfide). Oxidation products are calculated based on the moles of olefin originally present.

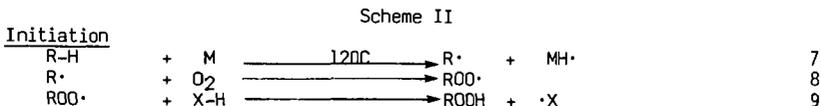
From tBHP, the major product was t-butanol. Small amounts of acetone, methane, isobutylene and the tBHP radical termination product, di-t-butyl peroxide, were also observed.

tBHP products The mechanism of autoinitiated tBHP decomposition can be depicted in Scheme I.



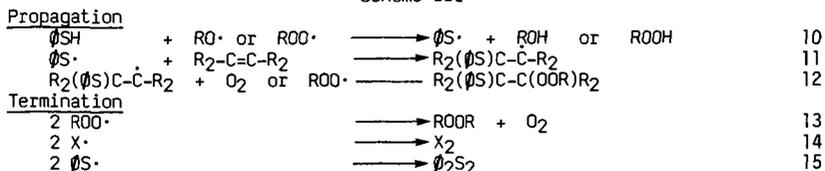
The greater yield of t-butanol compared to acetone, Tables 1 and 2, definitively show that hydrogen abstraction was favored over scission under the conditions of this study. Solvent participation was noted by the formation of trace quantities of toluene and other substituted benzenes from benzene.

The reaction mechanism, initiation step, in the presence of molecular oxygen can be depicted by Scheme II.



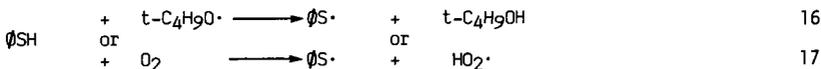
The reaction of the hydroperoxide, step 9, would then follow the same pathways as indicated for steps 1-6 in Scheme I. The reaction of thiophenol and active olefins with oxygen provides a useful co-variant of thiol chemistry termed "co-oxidation" (21). The radicals that result from either Schemes I or II could subsequently react with either the thiophenol and/or olefins that are present in the reaction mixture. This process can be described by Scheme III.

Scheme III

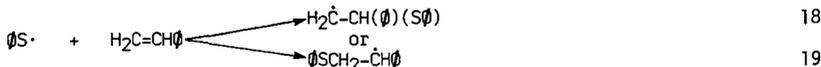


Styrene - thiophenol reaction products The major product, Table 1, observed was the addition product 1-phenyl-2-phenylthiyl ethane. Its yield at 15 min was 41.3% increasing to 71.2% at 30 min and decreasing to 68.3% at 60 min. Other products included: the 1-phenyl-1-phenylthiyl ethane isomer, 0.5% at 15 min increasing to 3.5% at 60 min; the dimer of styrene, 1,4-diphenyl butane, 0.2% at 60 min; 1-phenyl-2-phenylethyl sulfoxide, 1.7% at 15 min increasing to 5.8% at 60 min; 1-phenyl-2-phenylthiyl butane, 1.1% at 15 min decreasing to 0.9% at 60 min and phenyl thiosulfonate, 0.3% at 60 min. Trace products (< 0.1% yield) included: phenyl disulfide, 1-phenyl-2-phenylethyl sulfone, styrene oxide, phenyl methyl sulfide and 2-ethyl toluene. The product slate was the same for both oxygen and tBHP, but the yields of individual components varied significantly. In general, the tBHP reaction was faster as would be expected, than the reaction starting with elemental oxygen. In the presence of tBHP, the major product, 1-phenyl-2-phenylthiyl ethane, increased to 62.4% at 15 min and the sulfoxide product was more than doubled at 3.9% for the same time period.

The reaction of molecular oxygen or tBHP with thiophenol can proceed by the following chain mechanism (steps 16-17). The t-butoxy radical is more reactive than the t-butyl peroxy radical and consequently is a more probable reactant in such a mechanism (11).



The thiyl radical once formed can then react by several different pathways. In a solution with a high molar concentration of an active olefin, the reaction would proceed as shown in steps 18-19.



Equation 19 was the preferred pathway since it resulted in the more thermodynamically stable radical. The major product, 1-phenyl-2-phenyl thiyl ethane, then results by hydrogen abstraction. The other radical generated, equation 18, leads to one of the observed minor products, 1-phenyl-1-phenyl thiyl ethane. Other pathways could involve the reaction of radicals generated in steps 11 or 12 with additional olefin to give products of high molecular weight.

The sulfoxide product, phenyl-2-phenylethyl sulfoxide, could result from

several mechanisms. The most likely mechanism however, would be the reaction of the hydroperoxide with the sulfide formed in step 19. Expansion of the sulfur valence shell is probable in the processes involved in this step. The resulting sulfoxide once formed is quite stable, as can be seen from the gradual increase in yield, Table 1, at extended reaction time.

Table 1

Mole % Conversion for the Reaction of Styrene with Thiophenol and Oxygen or t-Butyl Hydroperoxide at 120°C

	CONVERSION (MOLE%)			
	Reaction Time (Min)			tBHP
	Oxygen			
	15	30	60	15
<u>Addition Products^a</u>				
1-phenyl-2-phenylthiyl ethane	41.3	71.2	68.3	62.4
1-phenyl-1-phenylthiyl ethane	0.5	1.5	3.5	1.4
phenyl-2-phenylethyl sulfoxide	1.7	4.9	5.8	3.9
phenyl disulfide	1.1	1.7	2.3	1.7
1,4-diphenyl-2-phenylthiyl butane	1.1	0.9	0.9	1.9
phenyl thiosulfonate	---	0.2	0.3	1.1
1,4-diphenyl butane	---	---	0.2	0.2
<u>Unreacted</u>				
styrene	34.7	2.0	1.6	13.2
thiophenol	33.2	7.1	5.8	25.2
<u>tBHP Products</u>				
acetone	---	---	---	0.9
t-butanol	---	---	---	57.1
di-t-butyl peroxide	---	---	---	0.1
isobutylene	---	---	---	2.3
<u>Trace Products^b</u>				
	2.2	4.3	6.6	3.2

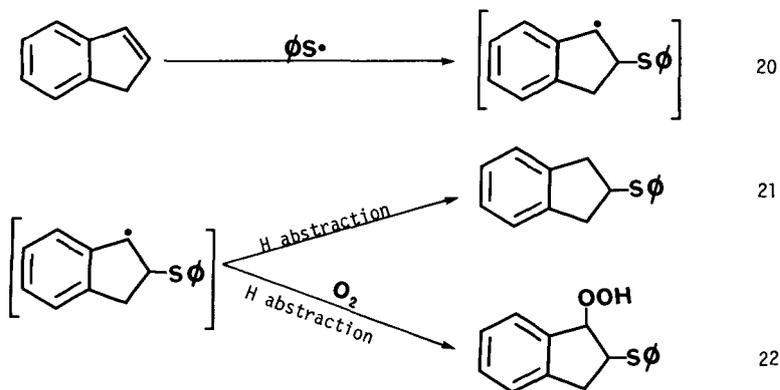
a. based on the starting moles of styrene

b. summation of small peaks

Indene - thiophenol reaction products The products from this co-oxidation reaction can be conveniently divided into primary and secondary reaction products. As shown in Table 2, the major primary reaction product was 2-phenylthiyl indan, 39.4 mole % at 15 min increasing to 58.2% at 30 min and then decreasing to 55.8% at 60 min. The secondary products were formed

by the spontaneous rearrangement of either 2-phenylthiyl-1-indanyl or 1-phenylthiyl-2-indanyl hydroperoxide. Neither hydroperoxide isomer was detected by GC/MS. The observed products from this rearrangement were: 2-phenylthiyl-1-indanol, 0.8% at 15 min increasing to 2.1% at 60 min; 2-phenylthiyl-1-indanone, 0.4% at 15 min increasing to 0.8% at 60 min; and 1-phenylthiyl-2-indanol, 0.2% at 15 min increasing to 0.4% at 60 min. Other products included: from the thiophenol, phenyl disulfide, 2.1% at 15 min increasing to 6.1% at 60 min and phenyl thiosulfonate, 0.1% at 15 min increasing to 0.5% at 60 min. From the 15 min run employing tBHP, products formed were: acetone, 0.7%; t-butanol, 54.3%; di-t-butyl peroxide, 0.5% and isobutylene, 3.2%. As shown in Table 2, many trace products (<0.1% yield) were formed. They were the result of oxidation of the indene, scission of the indene double bond or the more extensive oxidation of other products.

The processes for the reaction of oxygen or tBHP with thiophenol and indene proceeds as shown in Schemes I - III. The most probable step for the formation of the indanyl radical and its subsequent reactions are shown in steps 20-22. The thiyl radical can also undergo a dimerization reaction to produce the disulfide, step 15, and subsequently more extensive oxidation to yield the thiosulfonate product.



The 2-phenylthiyl indanyl radical, step 20, can react by several pathways. Hydrogen abstraction, step 21, would lead to the major observed product 2-phenylthiyl indan. Step 22, the reaction with oxygen would lead to the secondary product, 2-phenylthiyl-1-indanyl hydroperoxide. This secondary product was not detected by GC/MS, but the alcohols and ketones from its decomposition were found. Based on other hydroperoxide studies, it was not surprising that this hydroperoxide compound was not observed (11,12).

A comparison of the amounts of olefin and thiophenol remaining at different reaction times, Tables 1 and 2 indicates that the indene system is less reactive than styrene. The results at 15 min with tBHP also show that the indene system is less reactive. In the indene system, sulfoxides and

sulfones were only observed as minor products.

Table 2

Mole % Conversion for the Reaction of Indene with Thiophenol
and Oxygen or t-Butyl Hydroperoxide at 120C

CONVERSION (MOLE %)

	Reaction Time (Min)			tBHP
	Oxygen			
	15	30	60	
<u>Addition Products^a</u>				
2-phenylthiyl indan	39.4	58.2	55.8	48.3
2-phenylthiyl-1-indanol	0.8	1.7	2.1	1.6
1-phenylthiyl-2-indanol	0.2	0.4	0.4	0.4
2-phenylthiyl-1-indanone	0.4	0.8	0.8	0.6
phenyl disulfide	2.1	3.8	6.1	2.7
phenyl thiosulfonate	0.1	0.2	0.5	0.3
<u>Unreacted</u>				
indene	49.2	34.9	26.2	43.4
thiophenol	44.3	31.1	20.7	39.7
<u>tBHP Products</u>				
acetone	----	----	----	0.7
t-butanol	----	----	----	54.3
isobutylene	----	----	----	3.2
di-t-butyl peroxide	----	----	----	0.5
<u>Minor Products (0.1% or less)</u>				
1-indanone		2-indanone		
1-indanol		2-indanol		
toluene		1-methyl,2-ethyl benzene		
2-phenylsulphinyl-1-indanol				
1-phenylsulphinyl-2-indanol				
2-phenylsulphonyl-1-indanol				
1-phenylsulphonyl-2-indanol				
Trace Products ^b	3.2	3.1	4.6	2.9

a. based on the starting moles of indene.

b. summation of small peaks

CONCLUSION

There are similarities and differences in the styrene and indene systems. The major product in both systems was an addition product; Styrene and thiophenol in the presence of oxygen or tBHP at 120C formed 1-phenyl-2-phenylthiyl ethane while indene under the same conditions formed 2-phenylthiyl indan. The styrene system formed sulfoxides in appreciable yield while these compounds were not observed with the indene system. Indene formed alcohol and ketone products that were not observed with the styrene indicating a different mechanism for these products. Styrene was more reactive than the indene under the conditions of this study.

LITERATURE CITED

1. Chemical Week, 21, (Jan. 14, 1967).
2. Hazlett, R. N. and Hall J. M., "Chemistry of Engine Combustion Deposits"; Plenum Press: New York, 1985, page 245.
3. Taylor, W. F. and Wallace, T. J. Ind. Eng. Chem. Prod. Res. Dev. 6, 258 (1967).
4. Scott, G., "Atmospheric Oxidation and Antioxidants"; Elsevier: Amsterdam, 1965; Chapter 3.
5. Taylor, W. F., Ind. Eng. Chem. Prod. Res. Dev., 13, 133 (1974).
6. Taylor, W. F., Ind. Eng. Chem. Prod. Res. Dev., 15, 64 (1976).
7. Daniel, S. R. and Heneman, F. C., Fuel, 62, 1265 (1983).
8. Nixon, A. C., "Autoxidation and Antioxidants of Petroleum"; Wiley Interscience: New York, 1962.
9. Coordinating Research Council, "CRC Literature Survey on the Thermal Oxidation Stability of Jet Fuel"; CRC Report No. 509; CRC, Inc: Atlanta, GA, 1979.
10. Wallace, T. J., "Adv. Petroleum Chem. and Refining"; Wiley-Interscience: New York, 1964; Chapter 8.
11. Mushrush, G. W. and Hazlett, R. N., J. Org. Chem., 50, 2387 (1985).
12. Mushrush, G. W., Hazlett, R. N. and Eaton, H. G., Ind. Eng. Chem. Prod. Res. Dev., 24, 290 (1985).
13. Mushrush, G. W., Watkins, J. W., Hazlett, R. N. and Hardy, D. R., Ind. Eng. Chem. Prod. Res. Dev., In Review.
14. Morse, B. K., J. Am. Chem. Soc., 87, 3375 (1957).
15. Hiatt, R. R. and Irwin, K. C., J. Org. Chem., 33, 1436 (1968).
16. Denisov, E. T., "liquid Phase Reaction Rate Constants"; IFI/Plenum: New York, 1974.
17. Benson, S. W. and Shaw R., Organic Peroxides"; Wiley-Interscience: New York, 1970; Chapter 2.
18. Howard, J. A. and Ingold, K. U., Can. J. Chem., 47, 3797 (1969).
19. Mosher, H. S. and Durham, L. J., J. Am. Chem. Soc., 82, 4537 (1960).
20. Hiatt, R. R., "Frontiers of Free Radical Chemistry"; Academic Press: New York, 1980.
21. Kharasch, M. S., Nudenberg, W. and Mantell, C. J., J. Org. Chem. 16, 524 (1951).