

OXIDATION OF SELECTED ORGANOSULFUR COMPOUNDS IN DODECANE
OVER A HEATED METAL SURFACE

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INTRODUCTION

The use of jet fuel as a heat exchange medium imposes significant levels of thermal stress. 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 heat exchanger surfaces, on filters, in nozzles and on combustor surfaces (1,2). Heteroatoms, i.e., oxygen, nitrogen and sulfur and ash have been found to comprise as much as 40 percent of such deposits (3).

Sulfur can constitute the most abundant heteroatom present in military jet fuel (JP-4 and JP-5), since up to 0.4% total sulfur by weight is allowed per MIL-T-5624M. In commercial jet fuels, the ASTM Standard Specification for Aviation Turbine Fuels (4) permits up to 0.3% total sulfur by weight. Trace levels of sulfur, particularly as thiols, have been found to greatly increase the deposit forming tendencies of fuels during thermal stress. For this reason, much more stringent controls over thiol content are generally exercised. Deposits formed in jet fuel over the temperature range of 150 to 650°C in the presence of oxygen have been found to contain a much greater percentage of sulfur, up to a 100-fold increase, than that present in the fuel itself (1,5). The sulfur content of these deposits has been found to vary from 1 to 9% (6). The formation of such deposits has been attributed to the participation of mercaptans, sulfides and disulfides (7). Trace levels of thiols, sulfides and polysulfides were found to increase deposit formation even in deoxygenated jet fuels (7,8,9). In contrast, accelerated storage testing of fuels at 120-135°C indicated that while thiols promoted deposit formation, sulfides and disulfides exhibited inhibitory effects on deposition by decomposing peroxides (10).

Previous work in our laboratory has shown that aldehydes, thiols, sulfides and disulfides could be readily oxidized by hydroperoxides (11,12,13). During accelerated storage testing of a jet fuel at 65°C for four weeks, we have found (14) peroxide levels of 0.1 meq/kg. In the presence of 0.03% (w/w) sulfur from thiophenol, the accumulation of peroxides increased to 1.4 meq/kg. If the oxygen availability is limited but the temperature is sufficiently high, the hydroperoxide level will then be limited by free radical decomposition. In studies of the same jet fuel in our laboratory using a modified JFTOT apparatus, the maximum

hydroperoxide concentration reached after sparging with air for 15 min before stressing was 0.7 meq/kg; sparging with pure oxygen for a similar time before stressing raised the maximum hydroperoxide concentration to 2.8 meq/kg at 280°C.

It is difficult to identify specific reaction pathways from studies of fuels, which are complex mixtures. Model studies have been utilized to determine trace reaction products. These model studies were conducted in sealed borosilicate glass tubes at 120°C for up to 60 min. From the t-butylhydroperoxide (tBHP) initiated oxidation of dodecane thiol and hexyl sulfide (13) the major oxidation products were the dodecyl disulfide and hexyl sulfoxide, respectively. Similar studies revealed the major product of the oxidation of thiophenol by tBHP or oxygen to be phenyl disulfide.

We have utilized our modified JFTOT apparatus as a first step in determining the applicability of the findings from the model studies with changes occurring in aircraft fuel systems. This paper describes studies of the oxidation of thiophenol and hexyl disulfide in dodecane during stress in the JFTOT.

EXPERIMENTAL

Reagents. n-Hexyl disulfide and Thiophenol were obtained from Aldrich Chemical Co. They were distilled in vacuo to 99.9% purity before use. n-Dodecane (99% min.) was obtained from Phillips Petroleum Co. and was used without further purification.

Methods. Samples were thermally stressed in the modified JFTOT apparatus which has been described previously (15). The sulfur compound was blended into the dodecane in a glass vessel and aerated samples with dry air for 15 minutes, where applicable. To increase the heated surface area available and to reduce the steepness of the tube temperature profile, 304 stainless steel JFTOT heater tubes with five-inch heated sections were employed. The modified JFTOT apparatus permits sampling of stressed samples after passing over the heater tube and before returning to the reservoir (15). Procedures for determining the oxygen and hydroperoxide concentrations in the stressed dodecane have been described earlier (16). Product identification was obtained by combined GC/MS (EI mode). The GC/MS unit consisted of a Hewlett-Packard Model 5980 GC coupled to a Finnigan MAT ion trap detector. An all glass GC inlet system was used in combination with a 0.2mm x 50m OV-101 fused silica capillary column. A carrier gas flow of 1mL/min was used with an inlet split ratio of 60:1. A temperature program with an initial hold at 70°C for 2 min, increasing at 6°C/min, with a final temperature of 240°C.

RESULTS AND DISCUSSION

The influence exerted by sulfur compounds in controlled testing is affected not only by the structure of the organosulfur compound but also by the stress regimen employed. In the JFTOT, the liquid

flows at a rate of approximately 3 ml/min. With the non-standard length JFTOT heater tubes employed in this study, the sample passes over the tube in approximately 28 sec. While the JFTOT does not simulate turbulent flow conditions such as those in the heat exchangers, it does however provide a relatively short reaction time under conditions of limiting oxygen availability.

As the dodecane comes in contact with the hot metal surface of the heater tube, reaction with oxygen leads to autoxidation and the formation of peroxy radicals. The ensuing propagation mechanism continues as long as the temperature is sufficient to produce more free radicals. In the JFTOT where the reaction time is relatively short, the available dissolved oxygen is not fully depleted until the tube temperature approaches 300°C. This is evident in the temperature profiles of oxygen (Fig. 1) and hydroperoxide concentrations (Fig. 2) measured in neat dodecane. The profiles indicate a correspondence between oxygen consumption and hydroperoxide concentrations. While some peroxidation occurs below 220°C, rapid oxidation ensues above that temperature. At temperatures exceeding approximately 280°C, the dodecyl hydroperoxide undergoes decomposition (15), which accounts for the decrease in concentration above that temperature.

The addition of 0.4% (w/w) sulfur from n-hexyl disulfide (HDS) suppressed peroxidation (Table I) by about 46% of the level attained in the neat fuel. Additions of 0.2% (w/w) sulfur from HDS resulted in suppression to approximately 68% that of the neat dodecane.

Table I. Hydroperoxide Concentrations Measured in Dodecane Containing Organosulfur Compounds as a Function of JFTOT Maximum Heater Tube Temperature

Maximum Tube Temp., °C		Hydroperoxides, meq/kg			
		Hexyl Disulfide		Thiophenol	
	neat	0.2% S	0.4% S	0.005% S	0.03% S
21-120	nd ^a	nd	nd	nd	nd
200	0.11	0.01	nd	nd	nd
240	2.15	1.09	1.50	0.13	nd
280	2.25	1.03	1.52	1.02	nd
320	1.60	0.36	nd	0.69	nd

^anot detected, less than 0.01 meq/kg.

While a proportional response between HDS concentration and suppression of peroxidation was observed, it was far from quantitative, given the great excess of sulfur over the quantity of hydroperoxide formed in the neat dodecane. This is probably a consequence of the limitations imposed by the relatively short reaction time. The oxidation of disulfides in non-aqueous media has been reported (17) to proceed via successive coordination of oxygen

to the sulfur centers to produce the α -disulfone which cleaves to yield the sulfonic acid. Comparison of oxygen consumption profiles shown as a function of temperature in Fig. 1 reveal that direct oxidation by dissolved oxygen did not play a role in peroxide reduction. Therefore, the disulfide was reacting with dodecane autoxidation products to block the formation of hydroperoxides. Attempts to identify the oxidation products of hexyl disulfide in the JFTOT effluent were complicated by the low concentration of products and the difficulties experienced in detection. Future studies directed towards model studies of hexyl disulfide oxidation by t-butyl hydroperoxide are expected to provide information concerning product distributions and allow for optimization of detection procedures.

Thiophenol was much more reactive and completely suppressed peroxidation when added at 0.03% (w/w) Sulfur (Table I). By reducing the amount of sulfur from thiophenol to 0.005% (w/w), a detectable amount of hydroperoxides accumulated at temperatures between 240 and 280°C. Previous model studies in our laboratory (13), have shown that the oxidation of thiophenol by t-BHP results in the formation of the corresponding disulfide, phenyl disulfide. The oxidation of thiols classically occurs through the formation of the thiyl radical, which in the case of thiophenol, would be favored by resonance stabilization through the phenyl group. Thus, it is not surprising that thiophenol would be such an effective radical trap, terminating the chain reactions early in the propagation step. Examination of the oxygen consumption profiles generated from dodecane containing 0.03% and 0.005% (w/w) sulfur from thiophenol confirm that the free radical chain reactions were being terminated very quickly before significant autoxidation could ensue. In the presence of thiophenol, the oxygen consumption was reduced with respect to that of the neat dodecane.

Examination of the reaction products of thiophenol oxidation in the JFTOT by combined GC/MS confirmed the presence of phenyl disulfide. Examination of JFTOT effluent taken over a range of temperatures by GC/MS (Fig. 2) revealed that the formation of the disulfide corresponded to the temperature at which dodecane autoxidation proceeded and the hydroperoxide concentration in the neat dodecane reached a maximum. Thus thiophenol was being oxidized to the phenyl disulfide by dodecane autoxidation products, most likely by dodecoxy radicals, which suppressed the formation of hydroperoxides. The conversion to phenyl disulfide reached a maximum at temperatures above 300°C, which corresponds to the temperature at which all the available oxygen has been consumed and where dodecyl hydroperoxide disproportionates. To determine the contribution of the anaerobic thermal decomposition of the thiophenol to thiyl radicals and dimerization to phenyl disulfide, deoxygenated dodecane containing 0.03% (w/w) sulfur from thiophenol was examined. The corresponding curve (Fig. 2) for disulfide/thiol ratios indicated that thermal decomposition was significant only at temperatures above 320°C and would not account for the magnitude of phenyl disulfide conversion observed.

CONCLUSIONS

The principal products arising from the liquid phase oxidation of thiophenol by peroxides formed in situ by reaction of the dodecane with dissolved oxygen at elevated temperatures were identical to those identified in the model studies. Thus, these data indicate that the findings of the model studies can be applicable to aircraft fuel systems. The major route of oxidation of thiophenol most likely involved the donation of a hydrogen radical to the dodecoxy radical. While the resultant alcohol was not detected, interaction with dodecylperoxy radical would result in the formation of dodecyl hydroperoxide. However this is ruled out since hydroperoxides were not detected. While in the model studies, the disproportionation of tBHP was responsible for providing the alkoxy radicals, in the JFTOT, dodecane autoxidation provided the source of free radicals. Due to the ease of formation of the thiylphenyl radical, free radical chains were effectively terminated thus suppressing formation of dodecyl hydroperoxide. Although oxidation of thiophenol by dissolved oxygen in the JFTOT was not significant, thermal decomposition of thiophenol was observed to occur above 280°C to form the disulfide.

The behavior of hexyl disulfide in the JFTOT was consistent with an oxidation mechanism which involves coordination of oxygen to the sulfur centers. Since disulfides cannot act as peroxide reducers, by donating hydrogen radicals, minimal effects were realized on peroxidation during short reaction times in the JFTOT. There was no evidence of direct oxidation of the disulfide by dissolved oxygen.

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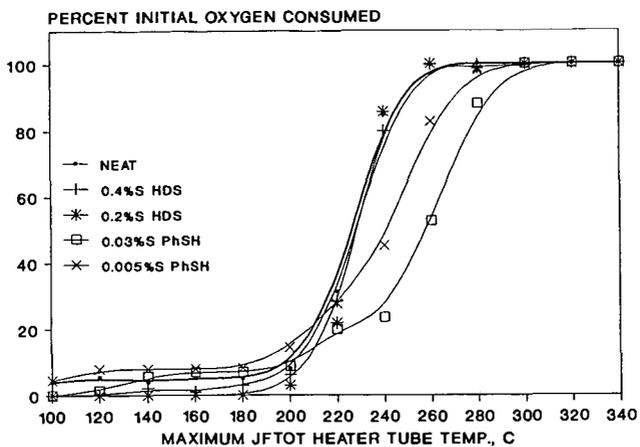


Figure 1. Temperature Dependence of Oxygen Consumption by neat and Doped Dodecane During Stress in the JFTOT.

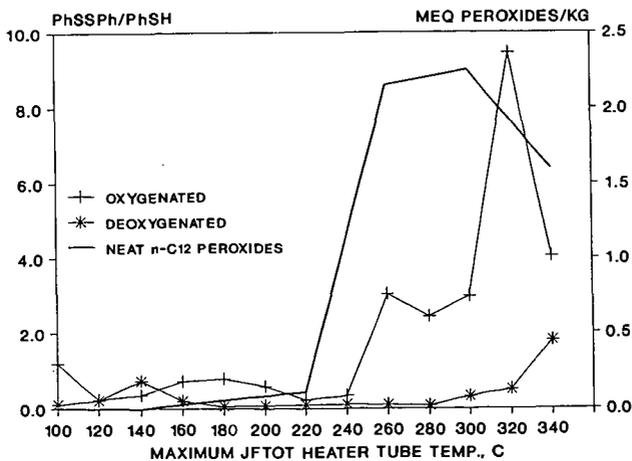


Figure 2. Phenyl Disulfide/Thiophenol Conversion Ratios by GC/MS (left ordinate scale) and Peroxidation of Neat Dodecane (right ordinate scale).