

PEROXIDE FORMATION IN JET FUELS

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ABSTRACT

This paper reports recent results from an ongoing study of the kinetics of peroxide formation and the development of a method to measure potential peroxides in jet fuels. In the earlier work, rates of peroxide formation in six jet fuels were measured over a temperature range of 43 to 120 °C with oxygen partial pressures ranging from 10 to 1140 kPa. Global rate constants for the peroxide formation were based on a kinetic model of the autoxidation process, which showed that the peroxide concentration increased as the square of the stress duration. The rate of peroxide formation was strongly dependent on temperature, but independent of the partial pressure of oxygen. Recently, rates of peroxide formation have been measured in four more jet fuels at temperatures of 80, 100 and 120 °C with an oxygen partial pressure of 240 kPa. Global Arrhenius rate constants for peroxide formation were determined for the induction and post-induction periods in the new fuels. These results were found to be in good agreement with the earlier work, which encouraged the development of a test method to predict rates of peroxide formation at ambient conditions from rate measurements at elevated temperatures.

INTRODUCTION

The need for a method of predicting the potential formation of peroxides in jet fuels arose from fuel pump failures in jet aircraft. Shertzler (1), Hazlett, et al. (2), and Love, et al. (3) found that peroxides cause significant deterioration of neoprene, nitrile rubber, and Buna-N diaphragms and O-rings used in aircraft engine fuel pumps.

To avoid future problems, a program was initiated to study the kinetics of peroxide formation and ultimately to develop a timely method of predicting the potential peroxide content of jet fuels.(4-7) Several test methods have been developed to determine the oxidative stability of fuels, e.g., ASTM D 2274; they are carried out at elevated temperatures to reduce the test duration to an acceptable level. An accelerated high-temperature test is also desired for the timely determination of potential peroxide formation in jet fuels.

It is well-known that peroxides form in fuels by an oxidation process that is slow at room temperature, but relatively fast at temperatures ranging from 80 to 120 °C.(7-9) Since the objective was to provide a basis for a practical test method, not exceeding about 48 hours, the foremost goal was to determine if the mechanism of peroxide formation at elevated temperatures was the same as that at ambient temperature. If the mechanism is unchanged over a limited temperature range (e.g., 0 to 150 °C), it is possible to predict ambient temperature behavior from a global Arrhenius rate expression that can be determined by making two or more rate measurements at higher temperatures.

Recent results have shown that the reaction mechanism responsible for peroxide formation is the same from ambient temperature conditions to at least 120 °C.(7) In that work, rates of peroxide formation in six jet fuels were measured over a temperature range of 43 to 120 °C with oxygen partial pressures ranging from 10 to 1140 kPa. Experiments in the 80 to 120 °C range were performed in a pure oxygen atmosphere in a stirred pressure reactor. Long-term experiments at 65 and 43 °C were accomplished by bottle storage with fuels exposed to air. Global rate constants for peroxide formation, derived from a kinetic model of the autoxidation process, were strongly dependent on temperature and independent of the partial pressure of oxygen. In the present study, global rates of peroxide formation were measured in four more jet fuels in the temperature range of 43 to 120 °C. Additionally, limited oxidation experiments were also performed on dodecane, ethyl benzene, and tetralin. These results support the conclusions of the earlier work (7) and agree favorably with other reported rate measurements.

EXPERIMENTAL SECTION

To establish baseline data on the long-term stability, a modified version of the ASTM D 4625 method of bottle storage at 43 °C was used. (10) The modified procedure ensured that the autoxidation reactions will not become oxygen concentration limited. In the revised procedure, each fuel sample was purged with "synthetic" air until the fuel became saturated with oxygen, as determined by gas chromatography. Then the fuel samples were stored at 43 °C in sealed amber borosilicate bottles. The oxygen contents were determined periodically in both the liquid and vapor phases. If the oxygen concentration in the vapor phase dropped below 10.0 vol%, the remaining bottles of the same fuel were again aerated.

Accelerated oxidative stressing of the test fuels was carried out in replicate in two nominally identical 600-mL, 316 stainless-steel pressure reactors. Temperature was regulated to ± 0.5 °C, and the oxygen pressure was continuously monitored. For details of the experimental procedure, see Ref. 7.

The test fuels selected for this study are described in Table 1. Since the objective of this paper is to compare the new results with those obtained previously, (7), a description of the fuels 1 through 6 examined in the first study will also be included.

The new test fuels 7 through 10 were hydrocracked kerosenes in the Jet A boiling point range.

All the test fuels were claimed by the suppliers to be free of synthetic antioxidant-type additives. Infrared analysis of the polar fraction of the fuels did not show any substituted phenolic or amine-type compounds in excess of the detection limit, < 5 ppm.

MECHANISM

It is well-known that the autoxidation of hydrocarbons is based on a free-radical mechanism (11), which includes the familiar radical initiation, propagation, and termination reaction steps. While several reaction steps are conceivable in the overall autoxidation of hydrocarbon fuels, the formation of alkyl hydroperoxides, ROOH, water and gums may be described by the mechanism shown in Reactions 1 through 6 in Table 2.

In this mechanism, the alkyl peroxide, ROOH, itself initiates the chain mechanism defined by these reactions. For a truly pristine fuel, a chain propagated autoxidation process can not start unless there is a trace of a radical initiator such as ROOH present. In reality, all fuels contain a trace of ROOH even though the concentration is below the detection limits of current analytical methods. In fact, since free radicals are inevitably formed in fuels by exposure to background radiations such as muons, it is highly probable that traces of ROOH will form by Reactions 4 and 5 in Table 2.

The remaining mechanistic arguments and derivation of the kinetic relationships were discussed earlier. (7) Basically, it was concluded from both theory and experiment that the formation of peroxides in jet fuels is independent of the oxygen concentration and appears to depend only on the hydrocarbon concentration, which is assumed to be constant during the autoxidation process. The final relationship based on Reactions 1 through 6, which was used in the analysis of the data, is

$$[\text{ROOH}]^{1/2} = k_2/(k_1/2k_3)^{1/2} [\text{RH}] t \quad (\text{Equ. 1})$$

where the combination of constants $k_2/(k_1/2k_3)^{1/2} [\text{RH}]$ is the global rate constant for peroxide formation. It is important to note (9), however, that if the partial pressure of oxygen is too low (< 7 kPa), Reaction 4 may become the rate controlling step in the mechanism, and Reaction 7 below would then take the place of Reaction 6.



For the oxygen-starved reaction, it may be shown that

$$[\text{ROOH}]^{1/2} = k_g/(k_p/2k_t)^{1/2} [\text{O}_2] t \quad (\text{Equ. 2})$$

where the peroxide concentration now depends on the oxygen concentration, $[\text{O}_2]$, in the fuel.

RESULTS AND DISCUSSION

The basic goal of this study was to develop a method to predict the slow formation of peroxides in jet fuels at ambient conditions from global rate constants obtained at higher temperatures. In the previous work (7) on fuels 1 through 6, the rates of peroxide formation were measured over the temperature range 43 to 120 °C, and the partial pressure of oxygen was varied from 10 to 1140 kPa. In the continuation, global rate constants for the formation of peroxides were measured in fuels 7 through 13.

Existing methods for the evaluation of the storage stability of distillate fuels include "bottle storage" under an atmosphere of air at 43 and 65 °C (10,12) for extended periods ranging from weeks to months. To establish baseline data, bottle storage tests were performed on fuels 1 through 8. Fuels 1 through 4, 7 and 8 were aged at 43 °C, and fuels 5 and 6 were aged at 65 °C. All the test fuels were stressed in the stirred pressure reactors at temperatures ranging from 80 to 120 °C.

Results of the experiments on the new fuels 7 through 10 are shown in Figures 1 through 7. Figure 1 shows the peroxide concentration time curves for fuels 7 and 8 measured in bottle storage experiments at 43 °C. Figures 2 and 3 show the peroxide concentration versus time curves for fuels 7 and 8 measured in the stirred reactor at 80, 100, and 120 °C. Fuels 7 and 8 each had pronounced induction periods that lengthened as the stress temperature was lowered. The induction periods were substantial considering that synthetic antioxidants were not added to these fuels. Previous studies (13) on the autoxidation of hydrocarbons have shown that similar induction periods appear in autoxidations of hydrocarbons when antioxidants are added.

Figure 4 shows the Arrhenius plots of the global rate constants determined for fuels 7 and 8. Figures 5 and 6 show the peroxide concentration time curves for fuels 9 and 10 measured in the stirred reactor at 80, 100, and 120 °C. Fuels 9 and 10 also exhibited pronounced induction periods that increased as the stress temperature was lowered. Figure 7 shows the Arrhenius correlation of the global rate constants measured in the stirred reactors.

The results given in Table 3 show a favorable correlation of global rate constants over the temperature range of 43 to 120 °C. Except for the induction period of fuel 7, the activation energies were also about the same, ≈ 22 kcal/mol. The activation energy for the induction period for fuel 7 (28.4 kcal/mol) is similar to that (29.4 kcal/mol) obtained earlier for fuel 3. Fuels 3 and 7 represent two instances where the activation energy for the induction period is higher than what has been commonly observed for fuels. It is important to note, however, that an activation energy as high as 29.4 kcal/mol is not unusual for the formation of peroxides in hydrocarbons. Rubio, et al. (14) measured rate constants in basically the same way as the present study and found an activation energy of 31 kcal/mol for peroxide formation in C_{10} to C_{16} normal alkanes. Arrhenius parameters given for fuels 9 and 10, which do not include 43° or 65 °C data, are consistent with those of the other fuels.

Two issues arose from the previous study.(7) First, there was a desire for some confirmation of the results obtained from the stirred reactors. To satisfy that need, rates of peroxide formation were determined in dodecane and compared with data in the literature. A second concern was that there were induction periods observed when the test fuels were known to be free of synthetic antioxidants. The induction periods generally lasted until the peroxide concentration reached about 50 to 100 ppm.

To satisfy the above concerns, some experiments were conducted with model compounds. The global rate constant for dodecane was measured at 120 °C and was found to compare favorably with similar rate constants measured

by Rubio, et al. (14) for peroxide formed in decane, dodecane and hexadecane. The rates of peroxide formation in ethyl benzene and tetralin were measured in the stirred reactor at 80 °C. It is interesting to note that there were no induction periods observed in the oxidations of the model compounds. Because these compounds contained traces of peroxides when procured, they were carefully purified by distillation before they were oxidized. The distillation may have removed trace amounts of antioxidant-type impurities that could have caused an induction period. The fact that the test fuels were reportedly free of antioxidants, but nevertheless exhibited induction periods, suggests that fuels contain natural oxidation inhibitors that appear to be quite alien to synthetic antioxidants.

Table 4 shows that the global rate constants for model compounds decrease in the order tetralin > ethyl benzene >> dodecane. The rate constant for dodecane was calculated using a rate expression developed by Rubio, et al. (14)

If the well-known argument is used, i.e., the rate-controlling step in the autoxidation process is the attack on the C-H bond by the $RO_2\cdot$ radical, then the ease of hydrogen abstraction determines the overall rate of oxidation. (9, 13, 15-17) The results in Table 4 agree with the basic order of free-radical attack on the carbon-hydrogen bond, which is benzylic and allylic H >> aliphatic H.

Since the rate of peroxide formation in alkyl-substituted aromatics is about 100 times faster than in normal alkanes, it would seem that it is the aromatic constituents of the fuel that determine the peroxide potential. This belief seems to concur with the observations in that the rate constants of the test fuels, except for fuel 1, are similar to that of ethyl benzene (3.9×10^6 (mol/L)^{1/2}/s), i.e., they ranged from about 1×10^6 to 4×10^6 (mol/L)^{1/2}/s at 80 °C. The aromatic contents of the fuels ranged from 8.5 to 44.0 percent and the amounts of alkyl groups bonded to the aromatic rings ranged from 4.3 to 17.7 percent. The aromatic alkyl group content was determined as the difference between the total aromatics by FIA and the total aromatic ring carbon measured by UV absorption spectroscopy. It seems reasonable to conclude that the aromatics play a major role in determining the peroxide potential since the concentration of benzylic type C-H bonds appears to be in plentiful supply in all the test fuels.

The above argument seems reasonable except for fuel 1, which formed peroxides at a much slower rate than the other test fuels. In fact, the measured rate of peroxide formation in fuel 1 at 120 °C was somewhat less than that measured in dodecane. There was nothing unusual about the composition of fuel 1. Its total aromatic content was 18.7 percent and the amount of aromatic alkyl groups was 9.3 percent, so there was no obvious reason why the fuel should have oxidized so slowly. Perhaps, because it was a straight run fuel, i.e., not hydrocracked etc., the natural oxidation inhibitors were preserved in the refinement process. A complicating factor is that a later report by the refiner of fuel 1 indicated that this fuel "may have been" Mercox treated. It is interesting that some fuels seem to contain relatively potent natural oxidation inhibitors that are not detectable by the analytical methods used to measure synthetic antioxidants.

CONCLUSION

The new results on fuels 7 through 10 agree with the original observations (7) on fuels 1 through 6. It is evident from the Arrhenius correlations that the mechanism designated by reactions 1 through 6 predominates over the temperature range of 43 to 120 °C.

Potential peroxide formation in jet fuels depends on both the reactivity of the bulk hydrocarbons and the presence of small, possibly undetectable, amounts of (natural) antioxidants.

It is concluded that the peroxide potential of jet fuels at ambient conditions can be predicted from relatively timely measurements at elevated temperatures. However, since the activation energies for peroxide formation in jet fuels range from 19 to 29 kcal/mol, it is concluded that a timely prediction of peroxide potential at ambient conditions would require measurements of global rate constants at two or more elevated temperatures.

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Table 1. Model Fuels

Fuel Code	Fuel Type
1	Straight-run, additive-free, salt-dried, clay-treated kerosene
2	Hydrocracked kerosene, alumina treated
3	Hydrocracked kerosene
4	Fuel 3, alumina treated
5	Hydrofined kerosene
6	Hydrocracked kerosene
7	Hydroprocessed kerosene
8	Hydroprocessed kerosene
9	Hydrocracked kerosene
10	Hydrocracked kerosene
11	Dodecane, distilled
12	Ethyl benzene, distilled
13	Tetralin, distilled and alumina treated

Table 2. Mechanism of Hydrocarbon Oxidation

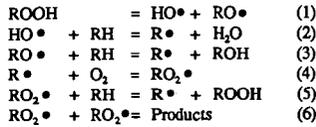


Table 3. Linear Regression Analysis of the Arrhenius Plots Based on $\ln k = \ln A - E_a/RT$

Fuel Code	Period	Range T, °C	E _a kcal/mol	ln A	R ²
1	Unknown	43-120	19.4	23.5	0.963
2	Unknown	43-120	21.6	29.4	0.998
3	Unknown	43-120	29.4	40.3	0.985
4	Unknown	43-120	22.0	30.5	0.998
5	IP	65-120	23.0	30.5	0.999
5	PIP	65-120	21.3	28.8	0.999
6	IP	65-120	21.9	28.2	0.969
6	PIP	65-120	21.5	28.8	0.997
7	IP	43-120	28.4	38.7	0.990
7	PIP	43-120	23.3	32.4	0.988
8	IP	43-120	23.0	30.0	0.994
8	PIP	43-120	23.0	31.9	0.990
9	IP	80-120	22.9	29.3	0.999
9	PIP	80-120	20.7	29.0	0.944
10	IP	80-120	24.4	31.4	0.999
10	PIP	80-120	24.1	32.8	0.984

Notes: IP = Induction Period; PIP = Post-Induction Period.

Table 4. Global Rate Constants for Model Compounds at 80 °C

Compound	Global Rate Constant, (mol/L) ^{1/2} /s × 10 ⁶
Dodecane	0.058
Ethyl benzene	3.9
Tetralin	18.3

Figure 1

PEROXIDE FORMATION
DURING 43 °C BOTTLE STORAGE

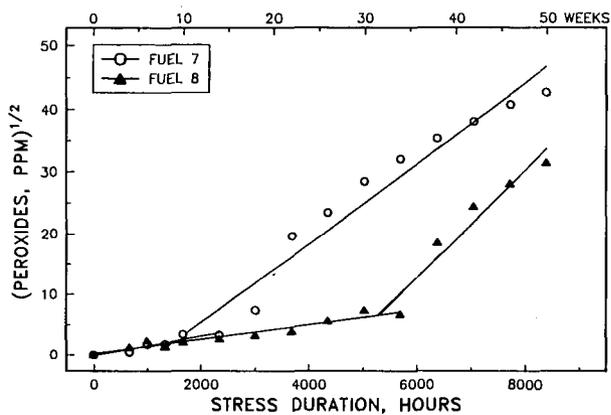


Figure 2

OXIDATION OF FUEL 7
AT 80, 100, AND 120 °C

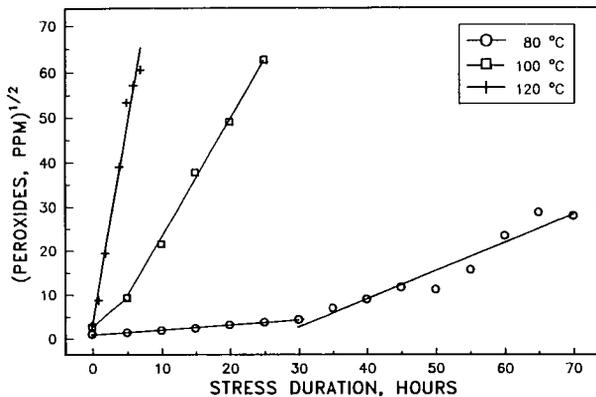


Figure 3

OXIDATION OF FUEL 8
AT 80, 100, AND 120 °C

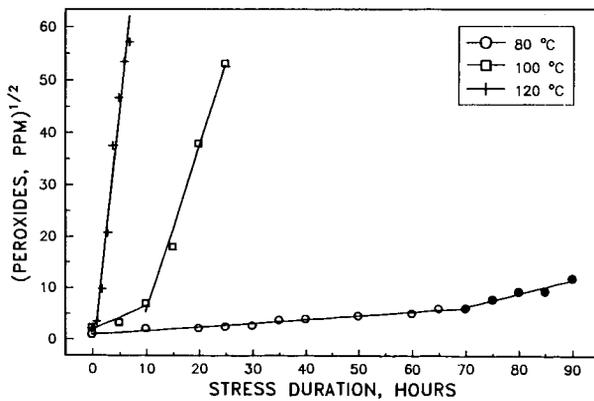


Figure 4
ARRHENIUS PLOT OF OXIDATION
FUELS 7 & 8

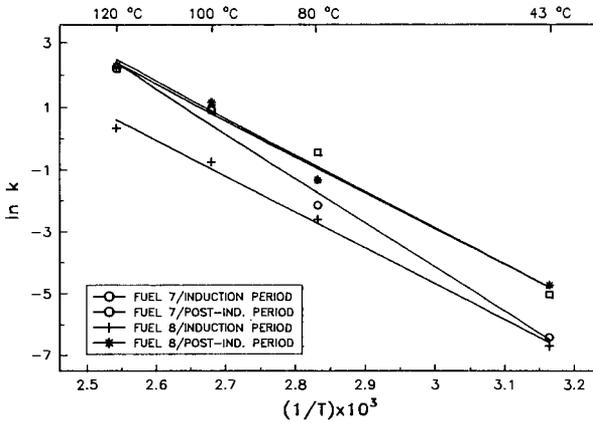


Figure 5
OXIDATION OF FUEL 9
AT 80, 100, AND 120 °C

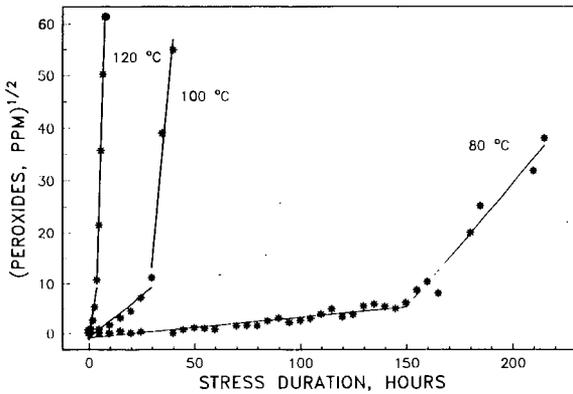


Figure 6
 OXIDATION OF FUEL 10
 AT 80, 100, AND 120 °C

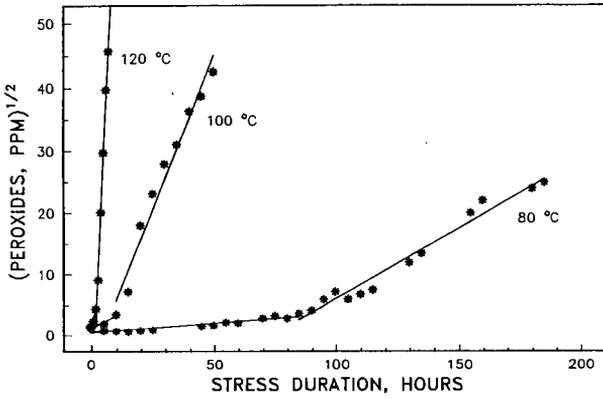


Figure 7
 ARRHENIUS PLOT OF OXIDATION
 FUELS 9 AND 10

