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13. ABSTRACT (Maximum 200 words)

In this project it is assumed that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. Consequently, it is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited. It is believed that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain suffi thermal stability to function as "JP-900" fuels. In addition, it is postulat that the successful development of thermally activated oxygen scavengers will provide the sub-critical thermal stability necessary for future development of endothermic fuels.

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First Year Annual Report

Development of Oxygen Scavenger Additives for Jet Fuels

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Proposal Abstract

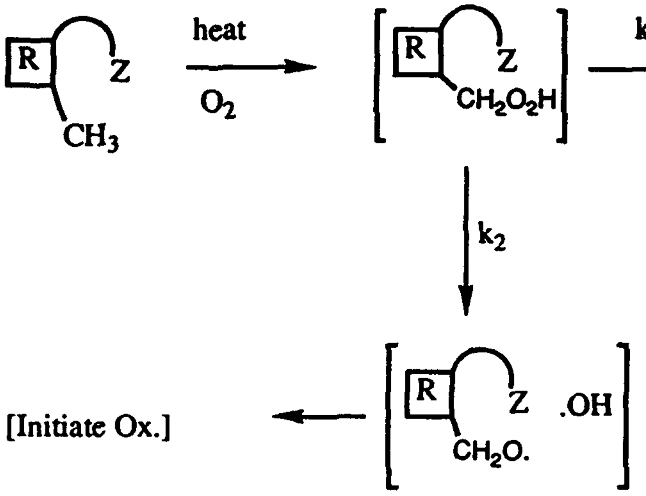
This project is in response to the Air Force's FY93 New Initiative entitled "Advanced Fuel Composition and Use." The critical goal of this initiative is to develop aircraft fuels which can operate at supercritical conditions. This is a vital objective since future aircraft designs will transfer much higher heat loads into the fuel (as compared with current heat loads).

In this project it is assumed that the thermal stability of most jet fuels would be dramatically improved by the efficient removal of a fuel's dissolved oxygen (in flight). It is proposed herein to stabilize the bulk fuel by the addition of an additive which will be judiciously designed and programmed to react with oxygen and produce an innocuous product. Consequently, it is envisioned that a thermally activated reaction between the oxygen scavenging additive and dissolved oxygen will occur, in a controlled and directed manner, such that formation of insoluble thermal degradation products will be limited. It is believed that successful completion of this project will result in the development of a new type of jet fuel additive which will enable current conventional jet fuels to obtain sufficient thermal stability to function as " JP-900" fuels. In addition, it is postulated that the successful development of thermally activated oxygen scavengers will also provide the sub-critical thermal stability necessary for future development of endothermic fuels.

Idea Conceptualization

In Scheme 1 is articulated a logical formulation of how an oxygen scavenger additive would perform its function. The sequence of events begins with the thermally promoted reaction between a portion of the additive molecule [R] and dissolved oxygen to form the initial REDOX product (i.e. on a gross level, the additive is oxidized while oxygen is reduced to produce the "generic hydroperoxide" shown in Scheme 1. The actual details of these events are complex, and currently are speculative, *Vide infra*. However, it is here postulated that the best mechanism for additive oxidation would not be a peroxyl radical chain pathway. This postulation is necessary since operation of a peroxyl radical chain would most likely disperse the dissolved oxygen through out the fuel matrix. Consequently, the additive would be ineffective in sequestering the oxygen and limiting its damage.

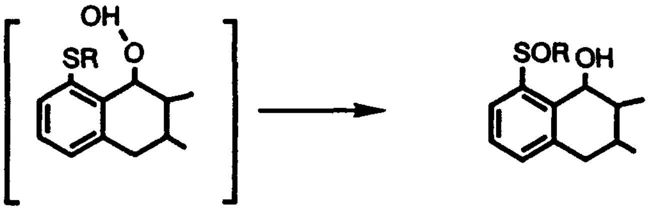
Scheme 1



As indicated in Scheme 1 the fate of the "generic hydroperoxide" is dependent on the relative magnitude of the rate constants k_1 and k_2. Ideally a pendent nucleophile (Z) is appropriately poised for facile intramolecular hydroperoxide reduction (k_1) to produce the corresponding secondary REDOX product. In Scheme 1 it is assumed that all REDOX products are soluble in the liquid fuel. Competitive with the "k_1" process is the thermally promoted homolysis of the weak O-O peroxide bond to produce the reactive hydroxyl and alkoxyl radicals. The rate constant for this process is designated k_2 and to the extent that k_2 is competitive with k_1, the fuel will be subjected to general autoxidative degradation (by these radicals initiating peroxyl radical chains). To limit this scenario at least two criteria will be employed to maximize the "k_1" process at the expense of the "k_2" process:

> (i) the molecular structure of the primary REDOX product needs to promote the facile intramolecular formation of the appropriate transition state for its rapid conversion into a stable secondary REDOX product. This can be accomplished by positioning the Z atom exactly five or six atoms removed from the terminal oxygen of the hydroperoxide (see Scheme 2).

Scheme 2



(ii) for certain additive molecular designs, the molecular structure of the primary REDOX product will be so unstable, that spontaneous conversion into secondary REDOX products will occur(consequently the presence of a Z group is not necessary).

In order to realize the development of oxygen sacavenger additives the following objective has been set:

Objective- Year 1

The rate law for the oxidation of various commercially available substituted aromatic derivatives and aryl phosphines will be measured at 100-165° C in various solvents. Rate laws will be determined both in the presence and absence of a hindered phenol antioxidant(i.e. BHT). **It is proposed that a successful additive candidate will exhibit a first order dependency in both oxygen and the substrate, and exhibit an oxidation rate which is not inhibited by the presence of phenolic antioxidants.** It is envisioned that an additive that meets this criteria would sequester oxygen rather than disperse it through out the fuel matrix.

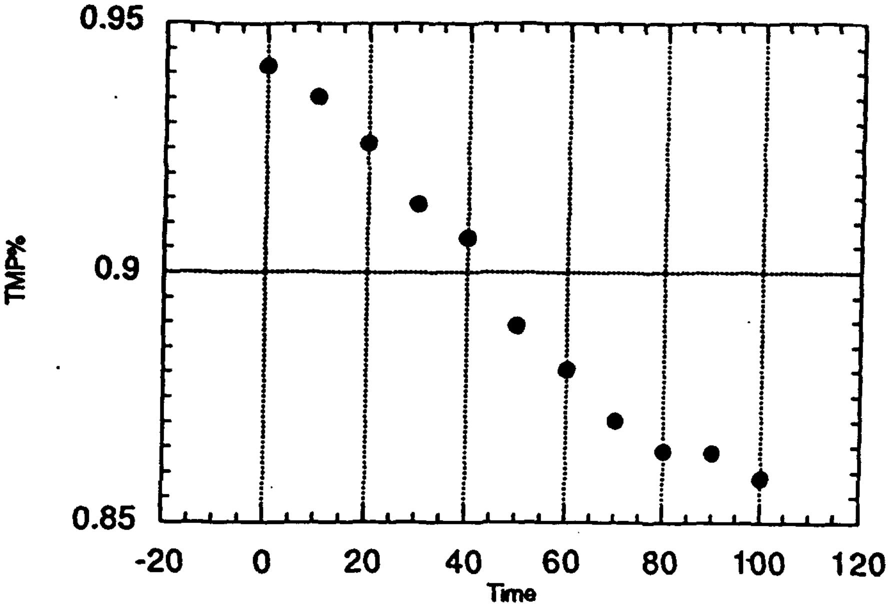
Preliminary Data Analysis

In table 1 is presented a compilation of current rate law data extant. The rate laws were derived by measuring the initial rate of substrate consumption. Usually substrate consumption is monitored with gas chromatography, however, monitoring resorcinol necessitated the development of a UV method. Below is shown a representative decay curve for 1,2,5-trimethylpyrrole (TMP) consumption. With such linear decays rate determinations are straight forward. Examination of table 1 reveals that the compounds can be divided into two groups; those that do or those that do not satistfy our objective. When fluorene, TMP and 2,5-dimethylpyrrole (DMP), are oxidized in the non -polar solvent dodecane, they are found not to satisfy objective stated above. Specifically, the oxidation of these compounds in dodecane was found to exhibit experimental characteristics consistent with operation of a peroxyl radical chain.

Table 1

Rate Laws from Initial Rate Measurments

Substrate	additives (1eq.)	solvent	Temp. °C	Substrate order	O_2 order
fluorene	none	dodecane	165	N.D.	0.8
fluorene	BHT	dodecane	165	no Rx.	no Rx.
resorcinol	none	3/1 tol./dodec	100	-	-
DMP	amine	dodecane	120	1.1	0.8
DMP	amine/BHT	dodecane	120	N.D.	approx. 0
TMP	none	chlorobenz.	131	1.9	0.9
TMP	amine/BHT	chlorobenz.	131	0.95	0.86
TMP	none	dodecane	100	N.D.	approx. 0



This assertion is based upon the observation that the rate law for their oxidation either exhibited a zero order dependency in oxygen or was inhibited by the presence of BHT. More interestingly, however, is that there are two compounds that meet the preliminary criteria of the above objective. Both resorcinol (in toluene/dodecane) and TMP (in chlorobenzene) exhibit the requisite rate law and antioxidant requirements. The resorcinol oxidation has yet to be extensively studied and will be reported in due course. Although chlorobenzene is not a model solvent for jet fuel it was deemed important to pursue limited studies in this system to enhance our limited understanding of the oxidation process. Therefore, TMP oxidation in polar solvents was subjected to a more extensive study which is reported in Table 2 (exp.#3-8).

Table 2
Preliminary Data for Substrate Oxygenation

Exp. #	substrate	solvent (temp. C)	additives (1eq.)	initial rate M/min
1	TPP	dodecane (150)	BHT	1.39×10^{-5}
2	TPP	trichlorobenz. (150)	BHT	3.81×10^{-5}
3	TMP	chlorobenz. (131)	none	$3.18\ (\pm 0.29) \times 10^{-5}$
4	TMP	same	BHT/amine	$1.56\ (\pm 0.41) \times 10^{-5}$
5	TMP	same	TPP	7.60×10^{-5}
6	TMP	same	TPP/BHT/ amine	4.46×10^{-5}
7	TMP	same	TPP/BHT/ amine/MDA	4.82×10^{-5}
8	TMP	same	2xBHT/amine /TPP	1.64×10^{-5}

Examination of Table 1, and Table 2 experiments # 3 and #4, reveal that different oxidation mechanisms are operative for TMP oxidation in the presence or absence of BHT. With out BHT there seems to be a component of the TMP oxidation that has a peroxyl radical intermediate. This assertion is based upon the different rate laws observed in each case (Table 1) and the fact that the presence of BHT decreases the rate of oxidation by approximately 50% (exp. #3 and 4). To further probe the TMP oxidation mechanism, to this system was added several different types of antioxidants (exp. #5-8). In experiment #5 TPP is add as a peroxide destroying antioxidant. The result of epx.#5 is consistent with the existence of the peroxyl radical postulated above. This interpretation assumes that the phosphine rapidly converts the peroxyl radical into a more reactive alkoxyl radical as shown below. This reactive radical then

$$\text{TMP-OO.} + \text{P(Ph)}_3 \text{ ———————— } \text{TMPO.} + \text{OP(Ph)}_3$$

continues the chain by abstracting hydrogen from TMP with a concomitant increase in the rate of oxidation. This hypothesis is supported in exp. #8 in which a doubling in the BHT effectively suppresses this chain oxidation. It is important to note that the oxidation mechanism operating in exp. # 4 is not stopped by any of the antioxidants examined. In addition, exp. #7 suggests that trace metal ions are not involved in the oxidation since the presence of a common petroleum metal deactivator has no effect.

In Table 3 is presented preliminary results of the oxidation of two different phosphines, triphenylphosphine (TPP) and diphenylpyridylphosphine (DPP).

Table 3

Rate Laws from Initial Rate Measurments

Exp.#	Substrate	solvent (temp.) ^{o} C	additive (1eq.)	Substrate order	O_2 order
1	TPP	dodecane (150)	BHT	1.1	1.2
2	TPP	decalin (150)	BHT	0.5	1.3
3	DPP	dodecane (150)	BHT	2.1	0.96
4	TPP	dodecane (120)	none	not determ.	1.5
5	DPP	dodecane (120)	none	not determ.	approx. 0

Experiment #1 reveals that this system meets the previously specified objective in a model jet fuel solvent. The first two experiments reported in Table 2 suggest that the transition state for this oxidation is polar. Consistent with this is the mechanism proposed below:

TPP + O_2 ---------- [TPP.+ O_2 .-] ----- [+TPPOO-] + TPP------- 2TPPO

In this electron transfer mechanism the first step is the rate limiting step. In this manner the above cited experimental data is accounted for. The initial oxidation product is postulated to be a triphenylphosphine oxygen zitterion which is rapidly reduced by unreacted phosphine to yield the phosphine oxide. Consistent with this proposal we observe that the rate of phosphine oxide formation is equivalent with the rate of phosphine loss. Experiments #2-5 suggest operation of a different mechanism than that extant in experiment #1. Although we can not yet speculate on the nature of the mechanism for DPP oxidation (exp.#3), it does meet the previously stated objective and will be subject to further study.

Conclusion

The objective of the first year of this project was to find several different compounds which show promise as potential oxygen scavenger additives for jet fuels. We have assumed that a good potential additive candidate would be a molecule that literally reacts directly with molecular oxygen at a specified temperature. Such an additive candidate would be expected to exhibit two important experimental characteristics as preliminary requirements; a rate law which exhibits a first order dependency in both oxygen and additive, and also the rate of oxidation would not be effected by common antioxidants (namely, BHT). In order to achieve this goal we have screened six compounds. Of the six compounds screened, three [resorcinol, triphenylphosphine (TPP), and diphenylpyridylphosphine (DPP)] were found to meet our preliminary requirements with model jet fuel solvents.

Soon the next phase of this project will begin with a more detailed mechanism study of the reaction of these compounds with oxygen in model jet fuels. Those candidates showing promise will then be synthetically modified such that when oxidized, the oxidized additive (presumably containing oxygen) will remain in solution. At that juncture the additive candidates would be ready for more elaborate testing.