

## CHEMICAL BASIS OF INSTABILITY OF SHALE-DERIVED MIDDLE DISTILLATE FUELS

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### ABSTRACT

Fuel deterioration on storage is usually defined in terms of the formation of insoluble deposits and gums. Deposit formation in middle-distillate diesel fuels is a continuing problem. Gravimetric stability tests have been conducted at 80°C using two model nitrogen heterocycles, 2,5-dimethylpyrrole (DMP) and 3-methylindole (3-MI) in an otherwise stable shale-derived diesel fuel. Potential interactive effects for these two model heterocycles in this stable fuel have been described by the presence of co-dopants, hexanoic acid, acetic acid, dodecylbenzene sulfonic acid and p-toluene sulfonic acid. Both nitrogen dopants formed large amounts of insolubles and exhibited positive interactive effects with dodecylbenzene sulfonic acid being the most active sediment promoter co-dopant. Hydroperoxide levels were monitored for each reaction mixture.

### INTRODUCTION

Deterioration of middle distillate fuels with storage continues to be a problem in the utilization of these fuel liquids. With diesel fuels, instability is commonly defined in terms of the formation of sediments, gums and in some cases, the accumulation of hydroperoxides. Gravimetric accelerated storage stability studies conducted with model compounds added as dopants to an other

wise stable fuel have demonstrated that oxidative condensation reactions of polar heterocycles are usually deleterious to stability<sup>1-5</sup>. Correlation of model dopant studies with results obtained from actual fuels have indicated that the autoxidation processes are not isolated reactions, but are sensitive to the presence of other fuel constituents<sup>6-8</sup>. It has been noted that various organo-sulfur and organo-oxygen moieties are readily oxidized to the corresponding sulfonic acid or carboxylic acid by hydroperoxide species under the mild conditions used for accelerated storage testing<sup>9-11</sup>. These same sulfur and oxygen compounds have been found to markedly alter the extent of model nitrogen compound induced storage instability in both model and middle distillate fuels<sup>12</sup>. Little is known about the chemical mechanisms of such interactive effects in fuel instability. Possible explanations include acid catalysis of condensation or oxidation reactions as well as involvement in radical chain processes. Interactive processes between different types of nitrogen moieties have also been studied to a limited extent and may prove to be of great importance in a media as complex as a middle distillate fuel<sup>3,12</sup>.

As part of an effort to gain insight into interactive processes, we have reported on several model systems and interactive studies involving nitrogen heterocycles and hydroperoxide species<sup>2,6,12</sup>. This paper reports on the interactive

studies involving the nitrogen heterocycles 2,5-dimethyl pyrrole and 3-methyl indole in the presence of two different acid species, sulfonic acids and carboxylic acids. The specific acids chosen were: p-toluenesulfonic acid, dodecylbenzene sulfonic acid, acetic acid and hexanoic acid. The acid species were selected on the basis that they were representative of a number of polar species which are conceivably present in shale-derived diesel fuel.

## EXPERIMENTAL

Storage Test Technique. The storage test technique has been described elsewhere<sup>6</sup>. In brief, 300 mL samples of filtered fuel (doped and undoped) were thermally stressed at 80°C in the dark in 500 mL screw cap borosilicate glass bottles with teflon-lined caps. Oxygen was not replenished during the unvented runs. After the 14 day stress period, the test bottles were allowed to cool in the dark to room temperature before the contents were filtered under slight vacuum. The filter consisted of a double Gelman Type A/E, 47 mm glass fiber filter with a pore size of 1.2 microns. The residue from the bottles was rinsed with n-heptane, with additional sediment being collected on the filter. The bottles and filters were heated to 120°C for 12 hr under vacuum, allowed to equilibrate to room temperature for 4 hr, and weighed. Appropriate blank filter corrections were applied. All samples were run in duplicate or triplicate.

Peroxide values were determined in the stressed fuel samples following filtration by a standard iodometric titration procedure (ASTM D-1583-60).

Base Fuel. The base fuel was a diesel fuel marine, DFM, refined from Paraho crude shale oil by SOHIO. This fuel has been well characterized 14-16. It was available with, D-11 and without, D-1, antioxidant added. The antioxidant, AO-30, 2,4-dimethyl-6-tertbutyl phenol, was originally present at the 24 mg/L level in D-11. No other additives were present in either sample.

Reagents. 2,5-Dimethyl pyrrole and 3-methyl indole were National Bureau of Standards reference samples. The purity of each reagent was checked by combined capillary column GC/MS. Acetic Acid was reagent grade, 99.7%, from Fisher Chemical Co. and was used without further purification. Dodecylbenzene sulfonic acid, 99+%, was obtained from Continental Chemical Co. Hexanoic acid gold label, 99.5+%, decanoic acid, 99+% and p-toluene sulfonic acid, 99+% were obtained from Aldrich Chemical Co. and were used without further purification.

## RESULTS AND DISCUSSION

In an extension of the study of interactive effects in the autoxidation of DMP and 3-MI in shale diesel fuel, four organic acids were examined as co-dopants in fuel D-11. This work was intended to determine whether the autoxidation of these unstable nitrogen compounds is subject to acid catalysis and/or if condensation products could form in lieu of true catalysis. To accomplish this goal, a series of experiments were run where the D-11 fuel was doped with the nitrogen compounds 2,5-dimethyl pyrrole, DMP, or 3-methyl indole, 3-MI, together with an organic acid as a co-dopant. The co-dopant could serve as a potential catalyst or as a reactant. Accelerated stor

age stability was assessed for an 80°C/14 day matrix. The results are expressed in terms of gravimetric stability data, peroxide number determinations, and sediment analyses. The nitrogen compound dopant was added at levels of 135 and 450 ppm N (w/v), with the co-dopant at  $3.21 \times 10^{-2}M$  or  $9.64 \times 10^{-3}M$ .

The four potential acid catalysts selected for use as co-dopants in this study: acetic acid (HOAc), hexanoic acid (HA), p-toluenesulfonic acid (p-TsOH) and dodecylbenzenesulfonic acid (DBSA) were selected on the basis that they were representative of a number of polar species which are conceivably present in shale diesel fuel. Straight-chain carboxylic acids are frequently present in middle distillate fuels (represented by HOAc and HA), and sulfonic acids (represented by p-TsOH and DBSA) are believed to form from the oxidation of sulfur species. Thiols, disulfides and sulfides are the most likely precursors to these sulfur acid species in fuels 9,17.

Autoxidation of DMP in the Presence of Organic Acids. The gravimetric results for the organic acid interactive experiments with DMP are given in Table 1. The results in Table 1 show that acetic acid (HOAc) interacts positively with DMP to increase the formation of insoluble material. In general, for a given set of experimental conditions, more insolubles resulted when a high HOAc appears to lead to more sediment in three of four instances, but this observation was not statistically significant.

Results obtained with DMP where hexanoic acid (HA) was the co-dopant are also shown in Table 1. The results indicate that HA interacts with DMP in a positive fashion, forming somewhat more sediment than was observed in the HOAc/DMP

Table 1

Insolubles for DFM (D-11) with Added DMP and Various Co-Dopants at the 80°C/14 Day Stress Matrix

Co-Dopant*	Total Insolubles (mg/100mL fuel)		
	Fuel D-11	Low DMP	High DMP
<u>Hexanoic Acid (HA)</u>			
Fuel D-11	0.3	47.4	171.4
Low HA	0.7	76.7 (81.7)	160.7 (252)
High HA	0.3	94.5 (96.7)	259.3 (282)
<u>Acetic Acid (HOAc)</u>			
Fuel D-11	0.0	47.4	171.4
Low HOAc	0.3	57.4 (72.7)	193.8 (192.7)
High HOAc	0.3	78.2 (86.7)	145.5 (264)
<u>p-Toluene Sulfonic Acid (p-TsOH)</u>			
Fuel D-11	0.4	47.4	171.4
p-TsOH	0.4	51.0 (54.7)	145.6 (164.1)
<u>Dodecylbenzene sulfonic Acid (DBSA)</u>			
Fuel D-11	0.1	47.4	171.4
Low DBSA	0.6	373.5 (382.2)	640.8 (604.4)
High DBSA	0.6	1.5 (6.2)	1323.6 (1338.8)

\*Concentrations: High = 450 ppm N(w/v) = 135 ppm N  
 Low = 135 ppm N = 9.64 x 10<sup>-3</sup>M  
 HA, HOAc, DBSA = 3.21 x 10<sup>-2</sup>M = 9.64 x 10<sup>-3</sup>M  
 pTsOH = Saturated solution in D-11 (limited solubility)  
 ( ) = Vented runs

experimental set. Thus, approximately 280 mg/100 ml of total insolubles resulted in the high HA/high DMP/vented trials, as compared with about 170 mg/100 mL of solids which formed in the absence of the acid. Sediment analysis data indicated that there was a great deal of similarity in the HOAc and HA sediments, so that significant condensation reactions of the carboxylic acids with the DMP did not apparently occur.

As a further probe of carboxylic acid interactive effects with DMP, we examined decanoic acid (DA) as a co-dopant. The results indicated that DA and DMP interacted in a synergistic manner. As

might have been expected from the similarity in  $pK_a$  values, the DA provided results which were comparable to those obtained when HA and HOAc were used as co-dopants with DMP. For all acids, more sediment was normally formed at the higher acid concentration.

Table 1 depicts the results obtained when a sulfonic acid, p-toluenesulfonic acid (p-TsOH), was used as the co-dopant. A saturated, not measured but quite low concentration, solution of p-TsOH in D-11 was used for the test, conducted at 80°C for 14 days. The effects of p-TsOH were found to be small and variable under these test conditions. Thus, the low DMP trials with p-TsOH present formed slightly higher amounts of solids than did the corresponding low DMP blanks, but the opposite seemed to be true for the high DMP trials. In this data set, the presence of p-TsOH may have slightly inhibited the formation of sediment. These results would not seem to support the notion that p-TsOH is an active promoter of sedimentation when DMP is present. Frankenfeld et al. found that p-TsOH did not show synergism with DMP in a No. 2 diesel fuel<sup>2</sup>. However, they did detect a mild degree of synergism, a 20% increase in sedimentation, shown to be statistically significant, when the diluent was decane or a jet fuel. Thus, our results in D-11 diesel fuel are consistent with the observations of these other workers. Other factors may help account for the apparent discrepancy which arises upon changing the diluent to decane or jet fuel. One obvious potential problem is the fact that the p-TsOH is only very sparingly soluble in these hydrocarbon fuels, too low to be readily determined. In addition, Frankenfeld et al. emphasized 43°C/13 weeks storage stability tests, which may not be

directly comparable to the results which we obtained at 80°C for 2 weeks. Another interesting result reported by these workers was that p-TsOH, when added as the sole dopant, was found to be able to induce significant instability behavior in the diesel fuel after protracted periods of storage<sup>2</sup>.

In order to look more closely at a possible temperature effect in the p-TsOH/DMP interactive experiment, we conducted a stability test at 43°C for 52 days in our D-11 fuel. The results confirmed that the presence of a saturated solution of p-TsOH had an insignificant effect upon the amount of sediment generated in the presence of DMP<sup>3</sup>.

In contrast to p-TsOH, dodecylbenzenesulfonic acid (DBSA) was very soluble in the D-11 fuel, so that a 2 x 2 experimental matrix, Table 1, was used for this co-dopant. Table 1 indicated that it was possible for DMP and DBSA to interact strongly in a synergistic manner under favorable conditions. The high DBSA/high DMP trials, vented and unvented, generated the largest quantity of sediment yet observed in any of our stability tests with DMP, about 4 g of sediment formed per flask. However, all four samples consisting of high DBSA/low DMP, vented and unvented, runs formed very little sediment. Thus, the observed interaction of DMP with DBSA is more complex than simple catalysis or synergism.

Peroxide number determinations have been made for one interactive experimental set, the HOAc/DMP set. The data are given in Table 2, the corresponding gravimetric data were given in Table 1. The results indicate that the presence of acetic acid in the "acid blanks" was associated with an elevation in the hydroperoxide levels in the

diesel fuel. However, when DMP was present, the measured peroxide numbers were uniformly zero in the presence of the acid moieties. When DMP was present but HOAc was absent, low but detectable

Table 2

Peroxide Number for DFM (D-11) with Added DMP and Acetic Acid at the 80°C/14 day Stress Matrix

Co-Dopant	Peroxide Number meq active oxygen/kg fuel		
	Fuel D-11	Low DMP	High DMP
Acetic Acid HOAc			
Fuel D-11	3.8	0.4	0.1
Low HOAc	11.6	0.0 (0.0)	0.0 (0.0)
High HOAc	36.7	0.0 (0.0)	0.0 (0.0)

( ) = Vented flasks

levels of hydroperoxide were found. An explanation for this behavior is that the HOAc may have catalyzed the reaction of DMP with any hydroperoxide present.

Analysis of the sediments in Table 1 combined with the fact that the yields of sediment achieved in several instances are in excess of the amount which could be attributed only to DMP participation, indicate that the DBSA or, possibly molecules derived from the base fuel, are condensing directly with the DMP. The reason for the very low yields of sediment found in the high DBSA/low DMP runs, Table 1, (those containing 3.33 equivalents of DBSA/DMP) is obscure, but may indicate substantially different solubility behavior for sediment in the presence of excess strong acid.

Table 3 summarizes elemental analysis results for several samples of DMP-induced sediment. The sediments generated in all of the instances shown were similar in elemental composition to one another and to typical values seen for DMP sedi-

ments generated in the absence of a codopant<sup>3,4</sup>.

Note that results are not shown for the DBSA/DMP set. These results suggest that true catalysis, rather than incorporation of the codopants into the DMP sediment by reaction, is likely

Table 3

Elemental Analysis Data for Sediments Derived from DFM (D-11) with added DMP and Various Co-Dopants at the 80°C/14 day Stress Matrix

Co-Dopant*	Percent by Weight				Empirical Formula
	N	C	H	O	
HA	10.99	61.67	5.50	21.84	C <sub>6.6</sub> H <sub>7.0</sub> N <sub>0.17</sub>
HOAc	11.37	60.35	5.09	23.19	C <sub>6.2</sub> H <sub>6.2</sub> N <sub>0.18</sub>
p-TsOH	11.16	59.55	5.09	24.20	C <sub>6.2</sub> H <sub>6.3</sub> N <sub>0.19</sub>

\*HA, HO Ac = 3.21 X 10<sup>-2</sup>M  
 DMP = 450ppm N (w/v)  
 p-TsOH = Saturated solution (limited solubility)

in those instances when synergism is observed. These sediments provided empirical formulas which were quite consistent with what would be expected for sediment which was comprised overwhelmingly of oxidized pyrrolic oligomers derived almost entirely from the DMP. Thus, any slight elevation in the carbon content of the carboxylic acid/DMP runs is likely due to either a trace incorporation of the acid into the sediment or else is the result of reaction of other components of the D-11 fuel under the test conditions. For all of the sediments derived from DMP in the presence of the four codopants mentioned in Table 1, the (KBr pellet) infrared absorption spectra, as well as the (d<sub>5</sub> pyridine) <sup>1</sup>H-nmr spectra were virtually superimposable with each other and with the spectra for DMP sediments produced in the absence of codo



Significantly, mostly adherent gum formed in the unvented test flasks; corresponding vented flasks were unusually higher in the amount of filterable sediment. In three of four instances, the high HOAc flasks were associated with more total insolubles than the corresponding low HOAc flasks.

Table 4 indicated that, like HOAc, hexanoic acid (HA) interacts in a positive fashion with 3-MI. Again, the maximum yield of total insolubles was ca. 50 mg/100 mL and high HA and high 3-MI trials were both generally higher in solids than were the corresponding low concentration flasks. Venting of test flasks also increased the amount of sediment. For comparison, an experimental set employing decanoic acid (DA) was also examined. It was found that, as anticipated, the results for DA were comparable to those obtained with the other two carboxylic acid co-dopants in the 3-MI/D-11 system. Thus, the gravimetric results would seem to indicate that acid catalysis of the autoxidation of 3-MI is significant.

Sulfonic acids were also examined as co-dopants with 3-MI. Table 4 shows that 3-MI and p-TsOH did not generate significant levels of insolubles after 14 days-80°C stress in fuel D-11. As seen for the DMP/p-TsOH interaction, the effect was very small and of little apparent significance, and is probably a result of the very limited solubility of the p-TsOH in the diesel fuel. With dodecylbenzenesulfonic acid, DBSA, it was possible to generate small quantities of sediment under some conditions, but only one set of conditions (high DBSA/high 3-MI unvented) led to the formation of large amounts of solids (ca. 70 mg/100 mL). Thus, as was the case of DMP, the interactive effects of 3-MI with the sulfonic acids were difficult to interpret.

Table 5 summarizes the elemental analysis results for several samples of 3-MI induced sediment. The sediments generated in all of the instances shown were similar in elemental compo

Table 5

Elemental Analysis Data for Sediments Derived from DFM (D-11) with Added 3-MI and Various Co-Dopants at the 80°C/14 day Stress Matrix.

Co-Dopant*	N	Percent by Weight			Empirical Formula
		C	H	O	
HA	5.65	72.16	5.78	16.41	C <sub>14.9</sub> H <sub>14.2</sub> NO <sub>2.5</sub>
HOAc	5.57	72.74	5.92	15.77	C <sub>15.2</sub> H <sub>14.8</sub> NO <sub>2.5</sub>
None	5.36	72.63	5.88	16.13	C <sub>15.8</sub> H <sub>15.2</sub> NO <sub>2.6</sub>

\*HA, HOAc =  $3.21 \times 10^{-2}M$   
3-MI = 450 ppm N (w/v)

Table 6

Summary of Relative Interactive Effects of DMP or 3-MI with Various Co-Dopants at the 80°C/14 Stress Matrix

Co-Dopant*	Interactive Effect	
	DMP	3-MI
HA	++	++v
HOAc	++	++v
pTsOH	i	i
DBSA	++	++v

\*Key to symbols  
++ = strong synergism  
v = sensitive to venting  
i = indeterminate effect (small and/or variable)

sition to one another and to typical values seen for 3-MI sediments generated in the absence of a co-dopant<sup>3,4</sup>. The sediments generated in the presence of the DBSA co-dopant gave a waxy sediment that did not lend itself to further analysis. These 3-MI induced sediments provided empirical formulas which are quite consistent with what

would be expected for sediment which was comprised of oxidized indole oligomers. These results suggest that like DMP, 3-MI sediments do not show significant incorporation of the co-dopant. Thus, the co-dopant acid species were functioning as catalysts.

#### CONCLUSION

Table 6 summarizes qualitatively the results of both carboxylic and sulfonic acid species interactive experiments with both DMP and 3-MI model compounds. DMP and to a lesser extent 3-MI are themselves deleterious to fuel stability. Interactive studies with these acid species co-dopants show that for the High DMP/High DBSA mixture, the maximum insolubles were 1323.6 mg/100mL fuel and the least insolubles was for Low DMP/Low HOAc, 57.4 mg/100mL fuel experimental set. For 3-MI interactive runs, a similar trend but with much less sediment was observed. For example, with the High 3-MI/High DBSA mixture, the maximum sediment observed was 69.7 mg/100 mL fuel. The results clearly indicate that the acid species function as both a catalyst or radical initiator and in the case of dodecylbenzene sulfonic acid functions in a minor role as a reactant in sediment formation when either DMP or 3-MI is inducing instability in a shale-derived diesel fuel. In an earlier study with tert-butyl hydroperoxide<sup>6</sup>, no incorporation of the oxygen moieties from this dopant was found in the sediment that subsequently formed. In this study employing acids co-dopants MS and IR data indicate that trace amounts of the sulfonic acid were incorporated into the sediment.

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