

OXIDATION AND FORMATION OF DEPOSIT PRECURSORS IN HYDROCARBON FUELS

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The object of this research is to determine the mechanism of deposit formation in hydrocarbon fuels, and thus to predict and to prevent deposit formation (1). The deposits cause clogging of filters and hot fuel lines. Our premise is that such deposits, insoluble in hydrocarbons, arise from further condensation of soluble deposit precursors (2). The precursors are the oxidation products of the fuels and condensation products of these, formed in stepwise reactions. When their molecular weights and oxygen contents become high enough, they precipitate from solution (3) either on long storage or quick heating. The problems are: what oxidation products are most likely to condense; is the condensation a radical or nonradical reaction, or both; what fuels or fuel components are most likely to form precursors; and how can the reactions be prevented?

This paper describes our progress in applying field ionization mass spectrometry (FIMS) to these problems. We started with a No. 2 home heating oil (Fuel C) to represent an unstable jet turbine fuel, then used n-dodecane as a simple and common fuel component.

EXPERIMENTAL

As received, Fuel C was brown and contained so much material of high molecular weight and low solubility that it could not be used to follow the development of additional fuel precursors. It was therefore distilled at 2.3 kPa (17 torr) in a Claisen flask with a Vigreux neck. Aliquots of the distillate (10 mL) were oxidized by shaking them with air in 100-mL flasks in a bath at 130°C. Gas samples of 70 μ L were withdrawn through a septum and analyzed for O₂/N₂ by gas chromatography on a 183 x 0.32-cm stainless steel column at 0°C and 30 mL/min He flow rate. The column was packed with 13X molecular sieve.

Pure 99% n-dodecane was obtained from Phillips Chemical Company and distilled at 2.3 kPa. The first and last tenths were rejected.

Two mass spectrometers were used. In one, the whole 5- μ L fuel sample was injected through a septum into an evacuated 0.5-L glass expansion bulb of the batch inlet system. The sample vaporizes immediately and enters the field ionization source through a glass leak. Field ionization of this mixture produces molecular ions from each fuel component and gives a molecular profile of the fuel sample. A second FIMS system was used to analyze deposit precursors. A 0.5-mL sample of Fuel C was spiked with an internal standard, 10 μ g of decacyclene (molecular weight 450), then vacuum-evaporated to <100 μ L. A 5- μ L sample of the concentrate was placed in a standard mass spectrometer sample holder in the solids probe of the mass spectrometer. The probe was cooled to -50°C, introduced into the mass spectrometer vacuum system, and then warmed to 30° with continuous pumping to remove most of the remaining volatile components. The probe was then mated to the ion source. The field ionization spectrum of the residue, including deposit precursors and decacyclene internal standard, was collected with the PDP 11/10 computer system. The resulting FIMS spectra represent the composition of the least volatile components of the fuel sample including impurities. The concentrations of individual deposit precursors are calculated by comparing their intensities in the FI spectrum with that of the decacyclene standard.

Samples of oxidized dodecane were analyzed similarly, except that the internal standard was perylene (molecular weight 252). In general, the oxidation products con-

tained unoxidized fuel, which could not be entirely removed without loss of some oxidation products.

RESULTS

Fuel C. The molecular weight profile of Fuel C shows that the major components are alkanes with 10 to 14 C atoms, with a preponderance of alkylbenzenes with 3 to 5 side-chain C atoms at the low molecular weight end, alicyclics up to C₁₆ at the high end, and small proportions of a wide variety of hydrocarbons over the whole range.

Table 1 summarizes the results of one oxidation of distilled Fuel C; they show steady increases in rate of oxygen absorption (autocatalysis) and in concentration of less volatile materials.

TABLE 1. OXIDATION OF VACUUM-DISTILLED FUEL C AT 130°C

Time at 130°C (min.)	0	255	430	701
O ₂ consumed (mmol/liter)	0	6.55	13.1	32.2
Per minute ^a x 10 ²		2.6	3.7	7.0
Deposit Precursor Properties				
Concentration (ppm) ^b	74	132	2450	2600
Number Av. Mol. Wt., \bar{M}_n	435	388	355	318
Weight Av. Mol. Wt., \bar{M}_n	496	440	419	381

^aDuring preceding interval.

^bBased on total materials found by FIMS.

Figures 1 and 2 summarize FIMS data after the first two oxidation periods in Table 1. The ordinate and the numbers in the upper left corners of the figures are the percentage of the summed ion intensities. Most of the material of molecular weight ~ 250 corresponds to incorporation of one to four atoms of oxygen into fuel molecules (precursor monomers), retained because they are much less volatile than the fuel. Most of the material with molecular weights between 300 and 450 represents combinations of monomer precursors (dimers). Material of intermediate molecular weight presumably represents condensation of monomer precursors and their fragments formed by cleavage of alkoxy radicals. The figures show that the development of monomer precursors and dimer precursors, like the rate of oxygen absorption, is autocatalytic. Development of trimers can also be seen.

During the last oxidation period, the solution became lighter and a dark brown precipitate formed on the reactor walls. During this period, the concentration of precursor monomers increased sharply (these may be the oxidation products that don't condense easily), and the concentrations of dimers and trimers appear to decrease perceptibly (compared with the decacyclene standard), perhaps because they have grown and separated from the fuel mixture.

The precipitate that formed, after washing with hexane and drying, weighed about 3 mg/g of initial fuel. Acetone extraction of this residue gave 0.137 mg of extract/g initial fuel; its \bar{M}_n in N-dimethylformamide was ~ 600. It therefore appears that the deposits precipitated more because of their oxygen and heteroatom contents than because of their high molecular weights.

Although the research described above provides excellent evidence for the deposit formation by stepwise condensation of deposit precursors, the data give us little

indication of the chemical structures or mechanisms involved. However, there is an indication in Figure 2 of a problem that becomes much more obvious with n-dodecane. All the principal components should have even mass numbers, as will all compounds of C, H, and O (but not N). However, 1.1% of natural C is ^{13}C , and so for any C_{12} compound, about 13% of the molecules will contain one ^{13}C . Therefore, all the major peaks will have an obvious satellite with mass number one unit greater. Figure 2 shows that the oxidized products have more than the expected 12 to 20% of materials with odd mass numbers (in the spaces between the peaks with even mass numbers). Odd mass numbers in C, H, and O compounds, except that due to ^{13}C , mean that fragmentation of parent molecules has occurred in the FIMS.

n-Dodecane. To eliminate the multicomponent problem with Fuel C, we investigated the oxidation of n-dodecane. Because the extents of evaporation varied before taking FIMS data, the absolute concentrations of products vary considerably in the three spectra. Dodecane (mass number 170 and its satellite at 171) predominated in the FIMS concentrates but are irrelevant and neglected in this discussion. Table 2 therefore lists the 12 strongest other peaks for each spectrum in order of their relative intensities.

Table 2-A shows that with the untreated oxidation product, the three strongest peaks, and 7 of the 12 strongest, have odd mass numbers. These must represent molecule fragments, uncommon from hydrocarbons, and so we examined the FIMS of known 3-dodecanol and 2-dodecanone. The dodecanol shows little of the parent ion (186), but it decomposes in the FIMS to give six principal significant products: 50 mol % is dodecyl (169 by loss of OH); 20% is decyloxy (157 by loss of ethyl); 18% is dodecene (168 by loss of water); 13% is dodecanone (184 by loss of H_2); 5% is dodecyloxy (185 by loss of H); and 4% is undecyloxy (171 by loss of methyl). The second and last products are probably specific for 3-dodecanol, leaving dodecyl as the principal product from mixed dodecanols. 2-Dodecanone is relatively stable. The parent peak (184) and its ^{13}C satellite (185) comprise >90% of the observed ions. An effort was made to avoid fragmentation by acetylating, methylating, or benzoylating pure higher alcohols but only 6-tridecyl benzoate gave mostly the parent peak.

In the first oxidation of dodecane in Table 2, 120.6 mmol of dodecane absorbed 1.35 mmole oxygen, 1.12 mol %, in 22.3 h at 130° . Part of the product was subjected to FIMS directly, part was heated for one hour at 180°C in the absence of oxygen to destroy peroxides. A major portion was treated with aqueous KI and acetic acid to decompose peroxides; the liberated iodine corresponded to 34% yield of hydroperoxide on the oxygen absorbed. Part of the KI-treated products was then heated for one hour at 180° in the absence of air, and another was benzoylated with 20% excess benzoyl chloride in pyridine. Even after purification, benzoic acid, benzoic anhydride and benzoyl ions gave major FIMS peaks, which are neglected.

In the oxidation products, the 182 and 183 peaks are probably fragments from dodecyl hydroperoxides because their proportions decrease upon heating and are succeeded by alcohol-derived peaks at 169 and 185. The 184 parent peak for dodecanone is little changed on heating. The 169 peak is associated with both alcohol and hydroperoxide but must come only from alcohol in the heated product. The new 203 peak in the heated sample arises from peroxides with >2 oxygen atoms. Mass numbers 194 to 203 and 213 to 217 are closely related products corresponding to gain or loss of H atoms by alcohols and ketones; the borderline between the parent compounds is fuzzy. Volatility considerations must favor the higher oxygen compounds in the data observed for C_{12} products.

Table 2-A shows other effects of heating; the appearance of butyl, pentyl and hexyl radicals (57, 71, 85) in the FIMS of the heated sample and the displacement of the 196, 197, and 217 peaks from the 12 most prominent products after heating. The small radicals can come from cleavage in the FIMS of alcohols or hydroperoxides in the unheated oxidation products,

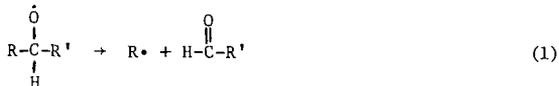


TABLE 2

PRINCIPAL IONS FROM 3-DCDECANOL, 2-DODECANONE, AND OXIDATION PRODUCTS OF n-DODECANE

Ranking	No oxidation		First oxidation				benzoylated	Second oxidn. ^e Ph ₃ P
	3-Do-decanol	2-Do-decanone	Un-treated	Heated to 180°C	KI + AcOH	KI + heating		
A. Ranking for all mass numbers								
1	169	184	183	169	182	182 _c	290 ^d	169
2	157 ^a	185	169	183	183	264 _c	98 ^d	184
3	168	182	199	184	169 _b	296 _c	184	168
4	131	122	184	185	311 _b	183 _c	182	182
5	184	183	182	203	370 _b	328 _c	198 ^d	185
6	185	150	185	198	256 _b	256 _b	194 ^d	157
7	171 ^a	155	197	57	184	184	370 _d	143
8	373	170	198	182	185	169 _c	189 ^d	129
9	186	186	217	199	198 _b	256 _c	203 ^d	
10	183	136	370	85	297 _b	266 _c	302 ^d	
11	182	156	196	71	283 _b	213 _c	185	
12	198	108	99	58	371 _b	196	183	
B. Ranking for mass numbers ≥ 337 only.								
1			370	337 ^f	370	450 ^g		
2			385	385	371	466		
3			399	399	385	436		
4			371	353	399	366		
5			337	367	337	385		
6			367	371	469	337		
7			369	355	355	340		
8			353	366	353	338		
9			355	370	339	365		
10			450	338	367	399		
11			436	351	338	451		
12			366	369	366	367		

Suggested identifications of ions above:

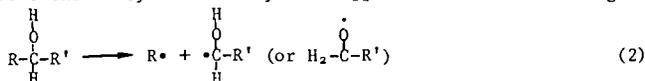
171 and below, C ₁₁ H ₂₃ O and smaller fragments	185 Dodecyl-O 186 Dodecanol	338 Dimer, C ₂₄ H ₅₀
168 Dodecene	194 to 232, mostly C ₁₂ compounds containing	350 to 466, dimer + 0 + fragments
169 Dodecyl	2 to 4 O atoms	
182 Dodecenone		
184 Dodecanone		506 Trimer, C ₃₆ H ₇₄

^a Specific products from 3-dodecanol. ^b Specific for KI.^c Appear or persist after heating KI product. ^d Peculiar to benzoilation product.

^e In 20 hours at 130°C, 7.25 g, 42.6 mmol, of n-dodecane absorbed 0.903 mmol O₂, 2.12 mol %. Hydroperoxide corresponding to 24.8% of the O₂ absorbed was found. The remainder of the product was then treated with 20% excess Ph₃P for 6 hours at 25° and then distilled at 1.7 kPa (13 torr) to remove Ph₃P and its oxide. Therefore, this sample should not contain high-boiling products.

^f Would rank 13 in Part A. ^g Peak height was 2/3 of that of the 196 peak.

but Table 2-A indicates that they come mostly from C₁₂ alcohols formed during heating:



Thus, 3-dodecanol apparently gave methyl and ethyl radicals. The short radicals probably do not come from short alcohols, which would be lost during concentration.

The KI treatment of the oxidation products was expected to decompose hydroperoxides to alcohols without forming free radicals or byproducts. However, the results indicate many byproducts, perhaps traces exaggerated by FIMS.

In comparison with the KI reduction, the triphenylphosphine reduction of the second oxidation products gives more products that are more typical of dodecanols (168, 169, 185) and thus may be a cleaner reduction. However, the absence of peaks above 190 in the triphenylphosphine products is probably due to distillation before FIMS.

The 370-371 peaks appear in several mixtures in Table 2-A and are prominent in all the mixtures in Table 2-B, except in the KI + heat group. They do not survive heating after KI treatment, but they survive benzylation and so are not associated with hydroxyl groups, even though mass number 370 corresponds to a dimer glycol.

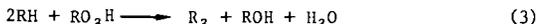
The heated products are similar to the KI products, containing considerable material of mass numbers 169, 182-185, and 198-199. However, the heated products contain more low mass number fragments and the KI products give more ions with mass number >256. Heating the KI products results in appearance or disappearance in Table 2-A of all products of mass number >256. Thus, substantial changes occur upon heating the KI product, even though there are no peroxides left, and hence nonradical reactions as well as radical reactions may lead to polymeric precursors.

Interposing the KI treatment before heating makes the dodecanone peak (182) most important, weakens or eliminates several peaks (57, 58, 71, 85, 185, 199, and 203) and forms several new ones, mostly >250.

The benzyolated KI-treated product contains more dodecyl benzoate (290) than anything else, and establishes hydroperoxide and alcohol as the major primary products. The absence of the 168 and 169 peaks shows that benzyolation of alcohol was essentially complete. The 182, 184, and 185 peaks that persist probably come from dodecanones, but in the KI-treated product, they and the 183 peak may also come from dodecanols.

Table 2-B show the relative ions concentrations from dimeric products. The most prominent also appear in Table 2-A. These products appear in groups corresponding to the dimer (338) and products containing 1, 2, and 3 additional oxygen atoms (near 354, 370, 386, and maybe 402) minus a few hydrogen atoms for formation of ketones or alkoxy radicals instead of alcohols. Starting at about mass number 399, most of the higher mass numbers must represent two dodecane residues plus oxygen plus additional carbon-containing fragments. No trimeric fragments (506 or above) have been observed, probably because of precipitation or volatility limitations. However, their absence may also be caused by low yields with dodecane, because trimers were observed with Fuel C.

We now consider the mechanism by which monomers are converted into dimeric products. The simplest condensation of dodecane by heating with a hydroperoxide would be:



The molecular weight of the C₂₄ dimer is 338, but none of this was found in an oxidation containing sufficient air. Instead, the C₂₄ products found had 2 to 4 oxygen atoms and mass numbers close to 370, 385, and 399. Thus, the dodecane oxidation products have

condensed during oxidation (whatever the mechanism) even though the parent dodecane concentration is 50 times greater than that of the oxidation products. However, the 337 ion, formed by loss of a hydrogen atom from the dimer, becomes a minor product when this oxidation product is heated and a major product in the heated portion of the oxidation in Table 2-B.

In the untreated oxidation products, the four most prominent peaks in Table 2-B correspond to a dimer plus two or three oxygen atoms and either a fourth oxygen atom or an additional carbon atom. The oxidation in Table 2, which absorbed less oxygen in more time, may have been depleted in oxygen, and tends to contain dimer units with fewer oxygen atoms and more fragments containing additional carbon atoms (436, 450).

Comparing the last two columns of Table 2-B shows that heating peroxide-free mixtures to 180° formed more compounds of molecular weight >400. Thus, there is a condensation or coupling reaction that does not depend on hydroperoxides, but probably involves other functional groups.

SUMMARY AND CONCLUSIONS

Our experimental results will now be used to formulate a general picture of deposit formation. Oxygen is required to produce deposits from hydrocarbon fuels, except at pyrolysis temperatures. For a given hydrocarbon, the process goes mainly through monomer oxidation, and coupling of these oxidation products to dimeric products. All of these are at first soluble in fuel, but as oxidation and condensation continue, the products become insoluble at molecular weights around 600. The insoluble products formed in storage probably remain soluble in good solvents (e.g., acetone), but when fuel containing soluble deposit precursors is heated, especially with a little oxygen, oxidation and condensation become rapid and precipitates form on the walls. These precipitates may at first be soluble in acetone but eventually become intractable. The oxidations are almost certainly conventional free radical chain reactions; the coupling of monomer units probably involves both a free radical coupling mechanism like Reaction 3, and a nonradical condensation (e.g., aldol (4)), in unknown proportions. Nitrogen and sulfur compounds concentrate in the precursors and deposits because they are more reactive in oxidation and condensation, and probably less soluble in fuel (5). Whether the effects of some very reactive fuel components are stoichiometric or catalytic remains to be determined.

Products and fragments between 190 and 338 (dimer) mass number must contain at least two oxygen atoms. Because peroxide links are not expected to survive FIMS, most products in this range contain two or more oxygen-functional groups. Their proportion is difficult to estimate with FIMS because of volatility differences, but the work of Jensen et al. (6) on the liquid-phase oxidation of hexadecane at 120 to 180°C shows that at least a quarter of the hydrocarbon molecules attacked contains two or more oxygen functions. Such products are more reactive than monofunctional compounds in radical-coupling and condensation reactions.

At 130°C in air, dodecane oxidizes much faster than Fuel C; it absorbs about 13.2 mmol of oxygen/mol fuel in 10 hours, compared with about 3.82 mmol for Fuel C in 20 hours. Fuel C oxidizes at a constant rate while the rate for dodecane is autocatalytic. However, by FIMS and observed deposit formation, dodecane produces fewer precursors and no visible deposits. Experiments with several Diesel fuels (to be described elsewhere) show little correlation between oxidation rate and gum formation, as measured by ASTM-D2274 before distillation. Paraffins usually predominate in fuels, but the gum formation apparently depends on the nature and amounts of other hydrocarbons, N and S compounds, and fuel history.

FIMS has been very useful for comparing fuel compositions, and for seeing the development of Fuel C deposit precursors at 130°C. Results with dodecane have been discouraging. The principal C₁₂ oxidation products, alcohols and hydroperoxides, fragment in the mass spectrometer and give similar peaks that overlap ketone peaks, probably in

different proportions, so that the primary products and their subsequent changes have been hard to identify. Yields of dimeric and trimeric precursors have been surprisingly low. Further, the relative concentrations of different compounds in the same mixture and of the same compound in different mixtures depend somewhat on the evaporation before the FIMS is taken.

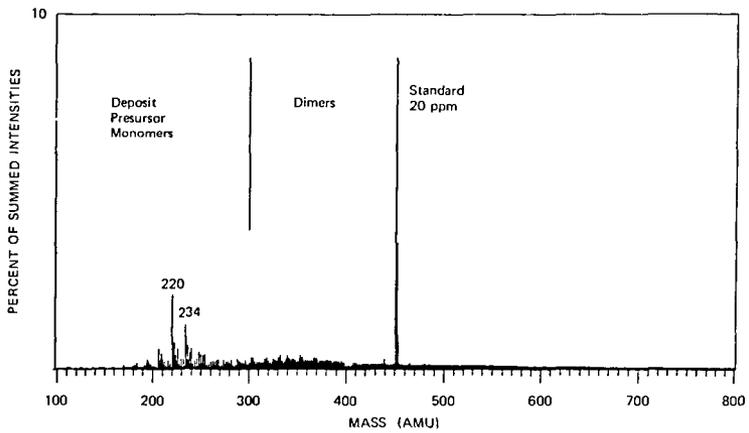
With enough oxygen, the C-C coupling reaction would be inhibited and the product would be unstable R_2O_2 . Hence gum and deposit formation may proceed best near the minimum oxygen concentration that permits oxidation. Some such measurements deserve a high priority.

ACKNOWLEDGMENT

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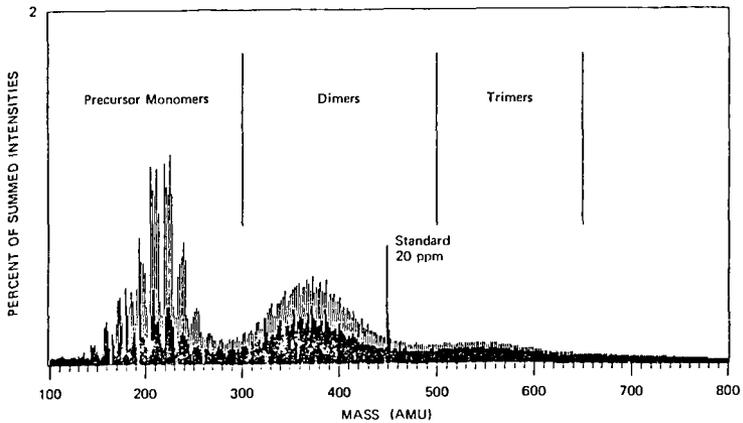
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JA-2115-2A

FIGURE 1 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER OXIDATION FOR 255 MINUTES AT 130°C



JA-2115-4A

FIGURE 2 FI MASS SPECTRUM OF THE DEPOSIT PRECURSORS FORMED IN FUEL C AFTER OXIDATION FOR 430 MINUTES AT 130°C