AD-A164 256 OXIDATION AND GUM FORMATION IN DIESEL FUELS(U) SRI 1/1
INTERNATIONAL MENLO PARK CA CHEMISTRY LAB F R MAYO
20 DEC 85 ARO-21165-4-EG DAAG29-84-K-0161
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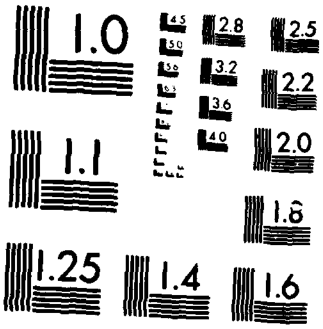

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER ARO 21165.4-EG	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Oxidation and Gum Formation in Diesel Fuels		5. TYPE OF REPORT & PERIOD COVERED Interim Technical May to December 1985
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Frank R. Mayo		8. CONTRACT OR GRANT NUMBER(s) DAAG29-84-K-0161 SRI Project 7753
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International Chemistry Laboratory, Menlo Park, CA 94025		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE December 20, 1985
		13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Diesel fuels, gum, deposits, oxidation, n-dodecane, tetralin, nickel.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This Report describes experiments on oxidation and gum formation from n-dodecane, tetralin, and several Diesel fuels at 43, 60, and 100°C, with and without added initiators, t-butyl peroxide and 2,2'azobis(2-methylpropionitrile) (ABN). Experiments on gum determination and a manuscript for publication, "Gum and Deposit Formation from Jet Turbine and Diesel Fuels at 100°C", are included.

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1. OBJECTIVES

One objective of work on this Contract is to relate oxidations of diesel fuels at 100° and 130°C, where experiments can be performed in hours or days, to standard tests for fuel stability at ambient temperatures and 43.3°C (110°F), which require many weeks. A second objective is to devise a fast test for fuel stability.

2. PROGRESS ON THIS CONTRACT SINCE SEPTEMBER 1984

A manuscript on oxidations of jet turbine and diesel fuels at 130° has been submitted to Ind. Eng. Chem., Product R&D, and then revised at the request of the Editor. Changes were mostly reorganization of the original material, resulting in considerable improvement of the manuscript. Recipients of this Report may request copies of the revised manuscript.

A similar manuscript on oxidations at 100°C, mostly with added t-Bu_2O_2, has been submitted recently to the same Journal. It presents three mechanisms for gum formation. A copy of this manuscript is attached to this Report. In both manuscripts, experiment numbers including K or L have been done on the present Contract. Experiments designated by F, G, H, and J were done by Mr. B. Y. Lan on previous ARO and NASA contracts. These manuscripts contain essentially all of our useful 130° and 100° oxidations.

The present Report describes progress on gum determinations (Section 3); shows that powdered nickel eliminates deposit formation from Fuel 10 at 100°C but increased somewhat the formation of soluble gum (Section 4); describes some preliminary oxidations at 60° with t-Bu_2O_2 and 2,2'-azobis(2-methylpropionitrile)(ABN, Section 5)); and finally presents data on some oxidations at 43-44°C, without initiator for one year, and with 0.1 mM ABN for 40 days (Section 6).

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3. GUM DETERMINATIONS

Section 3 of Interim Report 2 described thermogravimetric analyses of the residue of oxidation of Fuel 14 after aging for 16 weeks at 43-44°C. It was clear that there was no equilibrium or constant weight on heating in a slow stream of nitrogen at either 200° or 292°C. Further TGA experiments have now been carried out with the semicrystalline "dimer" of 2-ethylnaphthalene, made with t-Bu_2O_2 as described on page 9 of the attached 100°C Manuscript. The "dimer" presumably contains small portions of higher oligomers. Results of TGA at 100°C (Figure 1) indicate that most of the monomeric material is lost within 3 hours and that dimeric material is then lost very slowly but steadily on longer heating. On steady heating at 150 or 175°C, dimeric material is lost rapidly enough that loss of monomeric material cannot be distinguished.

TGA of a "dimer" sample at a temperature increase of 5°/min gave no breaks that would be useful in distinguishing monomer from dimer.

Heating in a slow stream of nitrogen for four hours at 100° appears to be the best present measure of gum formation but may be misleading when fuels contain high boiling ends. Heating for 20 hours at 200°C has been the standard procedure but results in loss of considerable gum. In some experiments in this Report gum has been determined after 4 hours at 100° and then after further heating at 200°C. Data in Tables 1 and 3 show that 1.4 to 20 times as much gum is found at 100° as at 200°C. In Table 2, the high-boiling fraction of Fuel 14 complicates the 100°gum (Section 6). With tetralin in Table 3, gum determinations give poor checks at 100°, much better at 200°C. Comparison of gum determinations at 100° and 200°C will be continued.

4. EFFECT OF POWDERED NICKEL ON OXIDATIONS OF FUEL 10 AT 100°C

These experiments, summarized in Table 1, are the beginning of an effort to understand the effects of metal surfaces on gum and deposit formation. Each experiment contained 10.00 mL of Fuel 10 (8.24 g) and 0.0100 M t-Bu_2O_2. Experiments A, B, and D were the same for 312 h (13

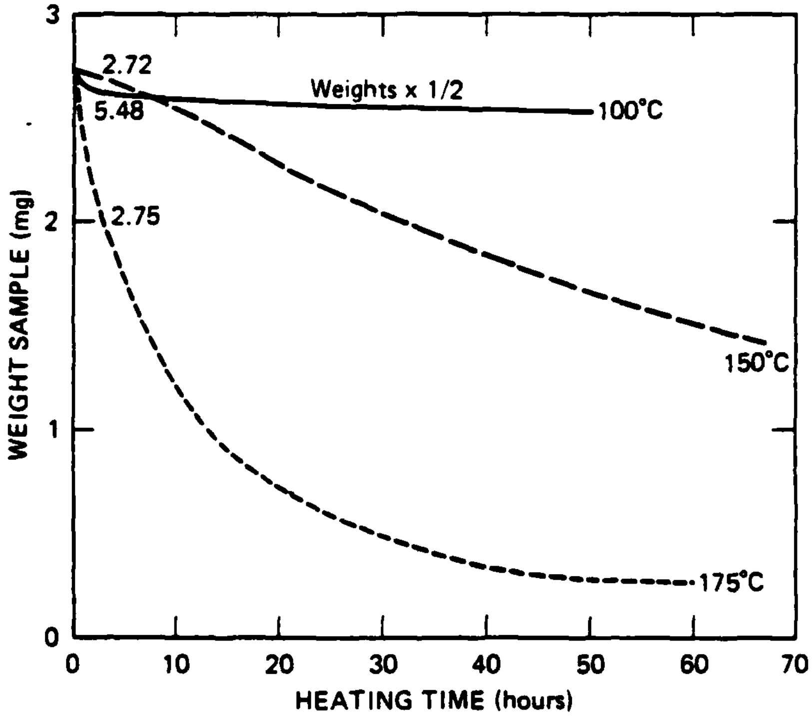

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FIGURE 1 WEIGHT LOSSES FROM SAMPLES OF 2-EtN "DIMER" AT THREE CONSTANT TEMPERATURES

Initial weights of samples in mg are near the left margin.

Table 1

OXIDATIONS OF FUEL 10 AT 100°C

	29A		29B		29C		29D	
Mmoles O_2 Reacted at Indicated Time (R_o for previous interval in µmole O_2(g fuel·h)								
24 h	0.0595	(0.3009)	0.0529	(0.2675)	0.0637	(0.322)	0.0596	(0.3014)
96 h	0.1213	(0.1042)	0.1060	(0.0895)	0.1468	(0.1401)	0.1226	(0.1062)
192 h	0.1842	(0.0795)	0.1714	(0.0827)	0.3205	(0.1968)	0.1889	(0.0838)
312 h	0.2584	(0.0749)	0.2123	(0.0414)	0.5277	(0.2278)	0.2385	(0.0502)
3.12 h av.		(0.1005)		(0.0826)		(0.2053)		(0.928)
Next 7 days after refill with air							0.1589	(0.1148)
46 days			0.3024	(0.0463)				
Weights in mg., 4 h at 100° (additional 20 h at 200°)								
Films	4.120		5.365		0.493		1.893	
Extracts of Ni[a]					0.0141		0.0050	
Soluble Gum	36.6	(1.795)	19.9	(4.215)	16.0	(3.695)	50.8	(3.453)
Total, mg/100 g fuel	494	(72)	307	(57)	200	(51)	640	(65)

[a] By acetone/methanol/benzene mixture after previous rinse with hexane.

[b] Film and Ni extract weights included.

days); Experiment B was then continued for another 33 days. 0.9995 g of powdered nickel (Johnson and Matthey, 3-u spheres, rinsed with reagent acetone) was added to Experiment C, 0.995 g of nickel was added at the beginning.

Table 1 shows that Experiments A, B, and D absorbed oxygen at similar and steadily decreasing rates for 312 h and that this trend continued in Experiment B. Experiment C gave a minimum rate of oxygen absorption in the 24-96 h interval and a steadily increasing rate thereafter, so that it reacted twice as far in 312 h as all the other experiments. Experiments A and B gave dark adherent films on the reactors; Experiment C gave no obvious film except on washing and weighing. Experiment D ultimately gave significantly less film than A or B and I infer that part of the film present at 312 h was dissolved during subsequent oxidation with nickel. Oxidation in this last period was faster than in the three previous intervals. By the 100° test, A gave 2.3 times as much/soluble gum as C in 312 h, but only 43% as much by the 200° test. The 200° tests are the easiest to rationalize: the long-term Experiment B gave the most gum; 29A gave the least, and the runs containing nickel gave intermediate results.

The data in Table 1 say that nickel largely prevents formation of deposits and may even cause partial solution of those aready formed, with a greater than proportionate increase in 200° soluble gum.

5. OXIDATIONS AT 60°C

Oxidations of n-dodecane and Fuels 14 and 14A at 60°C, with and without 0.2 M $t\text{-Bu}_2O_2$, were described in Table 1 of Interim Report 2. Even with this large (for us) concentration of initiator, the oxidations were too slow to be followed conveniently. Further, the R_g/R_o values for Fuel 14 at 60° were only one-half to one-quarter of those found at 100°C (attached manuscript) while those for dodecane at 60° were much higher than at 100°C.

We therefore began oxidations at 60°C with 0.1 mmole of ABN in 10 mL of solution (0.01 M) in benzene (blank), DOD, and Fuel 14A. The data show that the corrections for the oxygen absorbed and nitrogen evolved were too large, about one-third of the changes due to oxidation. The results were also inconsistent. Therefore, these results are not reported here, but experiments with 1% as much ABN at 43.3° are reported in the next section.

6. OXIDATIONS AT 43-44°C

To relate gum formation at 43.3°C (the standard 110°F) to gum formation at higher temperatures, Fuel 14 was oxidized for one year under conditions resembling those in the standard test (Experiment K79). Because of limited supplies of fuel, experiments were carried out with 50-mL samples of fuel in serum bottles with volumes of 75 mL, loosely covered with inverted weighing bottles. The 2- and 4-week tests were run with one bottle, and so on, but the 32-, 40-, and 52-week test were run on the fourth bottle. The bottles were shaken gently and aerated every week. For the first 43 weeks, aging was done in an oven at 43-44°C, then, protected from light, in a 16-oz. bottle in an oil bath at 43.3°C. No deposits were seen and no significant amount of hydroperoxide was found, although the pale yellow color of Fuel 14 made the endpoint uncertain. For aging up to 32 weeks, gum was determined by evaporation of 4-mL samples of fuel in a slow stream of nitrogen at about 200°, as described for oxidations at 130°. Gum in the 40 and 52 week samples was determined by the vacuum distillation method described in Section 3. Results are summarized in Table 2. They show that the rate of gum formation decreases fairly regularly until the last interval. The final increase, 1.6 fold, may reflect the change in determining gum. The very high gum at 52 weeks by the 100° method is probably due to the high-boiling component of Fuel 14 (Fuel 14B, Table 1 of 130° manuscript).

0.001 mmole of ABN was recently used to initiate oxidations of 10 mL of benzene or tetralin. Because several long-term oxidations are eventually to be run, new and simpler reactors were used: 100-mL Pyrex bulbs were fitted with 13-cm lengths of heavy 2-mm ID capillary tubing

Table 2

GUM FORMATION FROM FUEL 14 OVER 52 WEEKS AT 43-44°C

Aging Time (weeks)	mg gum / 100 g fuel	R_g	
0	1.70		
2	2.06	0.0030[a]	0.0010[b]
4	2.40	0.00010	0.00016
8	2.64	0.00070	0.00036
16	2.8	0.00041	0.0012
24	4.7	0.00075	0.0014
32	4.6	0.00054	negative
40	6.7	0.0074	0.0016
52	12.4(2173[c])	0.0012	0.0028

[a,b] R_g in mg/100 g fuel•h, corrected for blank at zero time, (a) since zero time, (b) during previous interval.

[c] 100° method, Section 3.

with rubber plugs (for supporting and shaking the reactors) and also with 3.5-cm necks of 6-mm OD tubing with serum caps (for withdrawing gas samples). Reaction mixtures were shaken in an oil bath at 43.3°C. These reactors appear to be satisfactory for the lower air pressures at 43° and 60°C.

The first two runs are summarized in Table 3. L31A was a blank run in benzene, which was not expected to oxidize. From the DuPont booklet on azo compounds, ABN has a k_d of 0.00260/h at 43.3° and a half-life of 267 h. Therefore 39.3% of the ABN should have decomposed in 192 h (8 days) and 91.8% in 960 h (40 days).

For complete decomposition of 0.001 mmole of ABN in 98-99 mL of air, with evolution of 0.001 mmole of nitrogen and absorption of 0.001 mmole of oxygen, the calculated change in O_2/N_2 is from 0.2682 to 0.2679. This change is less than our other experimental errors, and no corrections are needed.

The gas in the reactors was analyzed by our gc method after 192 and 960 h. In Experiment A, the O_2/N_2 ratio at 960 h was much more than at 192 h and so some air must have leaked into the reactor during this interval. Data for Experiment B for the same period indicate that oxidation was retarded by depletion of oxygen. Table 3 also shows that during the first 192 h 97 and 1700 molecules of oxygen were absorbed in Experiments A and B per ABN molecule decomposed to two radicals. Either these oxidation chains were surprisingly long or initiation is greatly augmented by the hydroperoxides formed. In the tetralin oxidation, 4.4 molecules of hydroperoxide were formed per molecule of oxygen absorbed, an impossible result unless air leaked into the reactor, reducing the apparent oxygen absorption.

The experiments in Table 3 show that ABN can induce oxidation and gum formation in tetralin at 43°C at a low but useful rate. I shall test this approach on other hydrocarbons and fuels and also see if these oxidations can be accelerated usefully by use of more ABN over shorter time periods.

Table 3

OXIDATIONS OF BENZENE AND TETRALIN WITH 0.1 mM ABN AT 43.3°C

L31A in C_6H_6	Experiment Number	L31B in Tetralin
8.71	Wt. 10 mL substrate, g	9.67
	0.001 mmole ABN (0.1 mM)	
	Initial mmoles, Calc.	
4.3760	Air	4.1118
0.9166	O_2	0.8613
3.4170	N_2	3.2107
	Initial O_2/N_2 = 0.2682	
4.15, 0.0380	ΔO_2 at 192 h, %, mmoles	77.6, 0.6684
39.3, 0.000393	ABN dec. (calc.), %, mmoles	39.3, 0.000393
41	$\Delta O_2/\Delta ABN$	1700
Less than at 192 h	ΔO_2 at 40 d, %, mmoles	90.26, 0.7774
91.8, 0.000918	ΔABN, calc., %, mmoles	91.8, 0.000918
---	$\Delta O_2/\Delta ABN$, last internval	208
0.0227	R_o[a], first 192 h	0.360
---	last 768 h	0.0147
---	average 960 h	0.0837
	Gum, mg/100g fuel at 960 h	
1.91	100° Test	644, 112[c]
1.372	200° Test	78, 68[c]
0.0541[d]	R_g[b]$/R_o$	0.91
~0	RO_2H, mmoles in 10 mL	3.39
~0	% of O_2 absorbed	437

[a] In μmoles O_2/g fuel·h

[b] In mg/100 g fuel·h

[c] Duplicate determinations

[d] Calculated O_2 absorbed at 960 h is mmoles absorbed at 197 h x ratio of O_2 absorbed by tetralin at 960 and 192 h = 0.0380 x 0.7774/0.6684 = 0.0442 mmoles R_o for benzene is then 0.0054 μmoles/g benzene·h.

GUM AND DEPOSIT FORMATION FROM JET TURBINE AND DIESEL FUELS AT 100°C

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ABSTRACT

Rates of oxidation and gum formation for six hydrocarbons, three jet turbine fuels, and three diesel fuels have been measured at 100°C in the presence of t-Bu_2O_2 as initiator. Four of the six fuels oxidize faster at 100° than in previous work at 130° without initiator. For any single substrate, the amount of gum produced for the oxygen absorbed tends to be similar at 100 and 130°, even with large changes in rates of oxidation and gum formation and t-Bu_2O_2 concentration. Thus, one mechanism of gum formation is intimately associated with oxidation.

The effects of t-Bu_2O_2 concentration on rates of oxygen absorption and gum formation show that gum formation is associated with chain termination by two peroxy radicals, but that the efficiency of this coupling to dimer and gum varies greatly with the substrate. In general, the pure hydrocarbons have long kinetic chains and give good yields of hydroperoxides. Most of the fuels have short kinetic chain lengths and produce little hydroperoxide but much gum for the oxygen absorbed.

Another mechanism of gum formation is the coupling of substrates by peroxides in the absence of oxygen. This is an efficient mechanism for coupling and the products contain little or no oxygen. This mechanism is replaced by the oxidation termination mechanism when oxygen is present.

A third mechanism, condensation of oxidation products from alkylnaphthalenes, is also proposed.

1. INTRODUCTION

Our previous paper on gum and deposit formation (Mayo, Lan, 1986) described rates of oxidation and gum formation from pure hydrocarbons and fuels in air at 130°. (All temperatures are Centigrade.) The pure hydrocarbons oxidized faster than the fuels but the fuels gave more gum and deposits for the oxygen absorbed. Cooxidations of fuels with additives showed that only those that were most reactive in oxidation had much effect (positive or negative) on the rates of oxidation and that such additives were soon consumed. Evidence with Fuel C showed that soluble oxidation products and gum are the first products formed and that as gum accumulates, it eventually precipitates. However, no precipitate was obtained from oxidation of any pure hydrocarbon. 2-Ethylnapthalene, which gave the most gum of any hydrocarbon, is apparently a good solvent for gum.

The present Paper describes similar experiments at 100° in the presence of di-t-butyl peroxide ($t\text{-}Bu_2O_2$). We had several motives in this work. We want to bring our experimental work closer to the temperature range of practical fuel stability problems; we expect to need chain initiators to obtain convenient rates of oxidation at lower temperatures; and we want to determine the effect of rate of initiation on rates of oxidation and gum formation.

2. EXPERIMENTAL

2.1. Fuels

The fuels used were described previously (Mayo, Lan, 1986). Fuel 14B was the highest boiling 6% of Fuel 14; Fuel 14A was the remainder of 14.

2.2. Oxidation Procedures

Oxidations were run on 10-mL samples of fuels in the presence of about 100 mL of air. Depletion of oxygen was measured by gas chromatography as described earlier. t-Bu_2O_2 (ICN Pharmaceutical, 97% by the HCl method of Mair and Graupner (1964)) was weighed in the reactor for each run.

2.3. Gum Determination

Most of the peroxide survived the oxidations and so we did not use our previous evaporation technique in a nitrogen stream at atmospheric pressure; decomposing peroxide might cause at least some coupling of fuels to dimers. In some runs, the peroxide was removed by adding about 50% of dodecane and distilling at 15 torr. (Dodecane boils higher than the peroxide but below most fuels.)

The procedure adopted is the following. A weighed 4-mL sample of oxidized fuel was put into a 25-mL flask with a short neck and a glass joint 23 mm in diameter to hold a Viton O-ring. The other part of the joint was attached with a clamp to 30 cm of 10-mm Pyrex tubing, bent at a 135° angle 12 cm above the joint. The bend led to a 25 mL distilling flask, used as receiver. The fuel was then distilled at ~ 1 torr with a very small flame until the pot was nearly dry. The 12 cm of vertical tubing provided some reflux and returned "bumped" liquid. The clamp was then removed (for space considerations) and the pot and vertical part of the distilling setup were immersed in a glass bath 6 cm in diameter and 20 cm high. This bath was nearly full of a mixture of ~80% ethylene glycol and 20% water. It was heated to smooth and gentle boiling with a gas flame. The temperature was maintained at 130° by occasional replacement of the evaporated water. The distilling set-up was left at this temperature for five minutes to provide a reproducible point for completing the gum determination. The set-up was then removed from the bath, clamped, cooled, and eventually opened to air The side arm was rinsed with reagent acetone to separate this hold-up from the rest of the fuel. The hold-up in the formerly vertical tube and the residue in the pot were then transferred with several portions of reagent acetone (total ~ 2mL) to 50 mg aluminum pans from which the solvent was evaporated on a warm hot plate. These pans were then heated for 20 h at 200°C in a slow stream of nitrogen.

Although the absolute values of our gum determinations are of dubious significance, the gum contents are assumed to provide valid comparisons. By use of data for oxidation, Experiment K89A with Fuel 14 during 28 days at 100°C, some educated guesses can be made about the extent of gum formation. Fuel 14, normalized to 100 g, absorbed 1.65 mmoles, 52.8 mg of oxygen and gave about 90 mg of dimers and higher oligomers and then 32.4 mg of "gum" after heating for 20 hours at 200°C. This "gum" contains 0.03% of the original carbon in the fuel and about 8% oxygen, 2.67 mg, 5.1% of the oxygen absorbed. This experiment also yielded a black film on the Pyrex flask. The film was thoroughly rinsed with hexane and then extracted with an acetone/ethanol/benzene mixture. After evaporation of this solution and drying at 1 torr, the deposit weighed 32.24 mg; it was not heated. That 5% of all the oxygen absorbed appeared in the film gum and probably another 5% in the deposit, even after significant losses at 200°, was surprising. This situation is discussed further in Section 3.3.

Our evaporation technique in gum determination has been tested by using the oxidized Fuel 14A from Experiment L4A. Four pairs of evaporations were performed with 2-3.5 g samples of fuel: (1) evaporation to a 6-mm circle of liquid, (2) evaporation to dryness (no flow), (3) evaporation to dryness and then for 10 minutes longer, and (4) by vacuum distillation. In the last procedure, the fuel was concentrated almost to dryness at 1 torr. A cold finger containing dry isce was then inserted and the distillation was continued to dryness, all parts of the distilling flask being heated to about 100°C. This procedure is expected to remove all monomeric products. The residue was then transferred to the usual aluminum dish with reagent acetone. Although the first weights of the four dishes before heating varied considerably, the final weights of the residues after 20 hours of heating all fell between 118.6 and 124.7 mg/100 g fuel and averaged 121.2. Thus, for large residues (4 mg on the dishes), the differences among these evaporation procedures are insignificant and reproducibility is excellent.

3. RESULTS AND DISCUSSION

3.1. Oxidation and Gum Formation

Our data on rates of oxidation (R_o) and gum formation (R_g) are summarized in Table I. Most of the headings need no explanation. The abbreviations for the pure hydrocarbons used correspond, respectively, to n-dodecane, tetralin, 2-ethylnaphthalene, 2-methylnaphthalene, phenylcyclohexane, and 1-phenylhexane. When several oxidation periods are indicated for one run number, fresh air was usually supplied for each. Rates for intervals illustrate the reproducibility of our results and how the rates change with time. Runs in which >78% of the oxygen was consumed in any period are omitted because of possible effects on rates. The highest consumptions of oxygen in runs in Table I are: for H55, Fuel B, 78%; L18, EtN, 75%; F87, DOD, 70%; and J37A, DOD, 66%.

Only our first and last TET runs are included. Even with efforts to exclude oxygen and storage at low temperatures, the TET in the last run without t-Bu_2O_2 reacted faster than the first with peroxide, and initially contained titratable peroxide. Aldrich EtN, fractionally distilled in vacuum in a good column at NASA, oxidized faster than Aldrich material distilled with a poor column. MeN oxidized much slower than EtN.

The oxidations of DOD and Fuels B and C are autocatalytic; oxidations of the alkylnaphthalenes and all the other fuels are self-retarding. With other pure hydrocarbons, trends are not clear. No precipitate was obtained from any pure hydrocarbon but most of the fuels gave adherent precipitates (as well as soluble gum) as uniform films on the parts of the flasks in contact with liquid.

In oxidations of Fuel 14, there were no other solids at reaction temperature, but a faint cloudiness appeared on cooling the reaction mixtures. We interpret this cloudiness to decreasing solubility of the deposit in fuel and we count it as soluble gum. We think that the continuous gentle shaking of our reactor causes all the deposits to grow on the surface films. The ratio of insoluble/soluble gum with t-Bu_2O_2 in Experiment K89A, ~ 1, is the largest that we have seen at SRI.

As indicated in Section 2.1, Fuel 14 was fractionated into lower (14A) and high boiling (14B) fractions. The higher-boiling 14B absorbed oxygen 2-3 times as fast as 14A and gave gum deposits about 6 times as fast. The result is that 14B requires only 41% as much oxygen to produce a milligram of gum.

Table I gives some yields of hydroperoxides on the oxygen absorbed. The best yields are associated with the fastest oxidations. It is also clear that initially EtN hydroperoxide does not survive as well as TET hydroperoxide, but may therefore be a better initiator. DOD hydroperoxide is the least stable, especially during the induction period, but may be the fastest initiator of the group.

3.2. Comparison of Results at 100 and 130°C

Rates of oxidation, gum formation, and their ratios in oxidations at 100 and 130° are compared in Table II. Values at 130°C are taken from our previous paper (Mayo and Lan, 1986) and are listed in order of decreasing magnitude in the R_o and R_g columns and in order of increasing magnitude in the R_g/R_o column. Values at 100° come from runs marked with asterisks in Table I and are listed immediately to the right of the 130° values without respect to the 100° rank. With 0.03-0.04 M t-Bu_2O_2 at 100°C, differences among hydrocarbons and fuels are much smaller than at 130° without initiator. The rankings for R_o for and above Fuel C are similar at the two temperatures; the rates at 130° are 1-6 times those at 100°C. However, MeN and Fuels A, 10 and 13 oxidize faster at 100° than at 130°C. Thus, these fuels have less ability to initiate and maintain their own oxidations and have shorter kinetic chain lengths than the other and faster oxidizing fuels; they are self-retarding in oxidations.

Use of t-Bu_2O_2 at 100° also narrows the range of R_g. Again, the faster oxidizers give gum faster at 130 than at 100°; the reverse applies to the slow oxidizers.

The R_g/R_o ratios tell us the relative amounts of gum formed for the oxygen abosrbed. If the mixture of mechanisms for gum formation is the same at 100 and 130°, then the ratios of R_g/R_o for the two temperatures should be the same. The last column of Table II shows that 5 of the 12 ratios are less than 2, 7 less than three, even with large differences in R_o and R_g alone. The experimental error in measuring very low rates of gum formation may contribute to the larger discrepancies.

This section shows that a controlled rate of initiation is important to understand gum formation and that it will be important at lower temperatures where reactions are much slower.

3.3. Effects of Concentration of t-Bu_2O_2

Table III summarizes effects of changes in t-Bu_2O_2 concentrations from three-fold to 76-fold for each of several fuels on R_o, R_g, and their ratios. The smaller effects of t-Bu_2O_2 tend to be associated with the hydrocarbons and fuels that oxidize fastest at 100° without t-Bu_2O_2. However, the R_g/R_o ratios for a single fuel are little affected by the changes in R_o and R_g, showing that the mechanism of gum formation is intimately related to the mechanism of oxidation. The last two columns give the apparent orders (n) of R_o and R_g on the concentration of t-Bu_2O_2, calculated from the relation:

$$\text{Ratio of } R_o \text{ (or } R_g\text{) values} = \text{ratio of } [\text{t-}Bu_2O_2]^n.$$

In conventional long chain oxidations, $\underline{n} = 0.5$ but as the kinetic chain length approaches zero, $\underline{n}$ approaches 1. $\underline{n} = 1$ is also characteristic of inhibited or self-retarding oxidations. The fastest (longest chain) oxidizers, DOD and EtN, have n values of about 0.5 or less. The low values reflect fairly fast oxidations with no $t\text{-}Bu_2O_2$ and neglect of autocatalysis or self-retardation. The other, slower oxidizing fuels have n values closer to 1, corresponding to short chains and/or self retardation.

Table IV presents the same basic data in another manner. The first two columns of data give the mmoles of oxygen absorbed and $t\text{-}Bu_2O_2$ decomposed in the whole reaction mixtures. Details for each experiment are given in Table I. The $t\text{-}Bu_2O_2$ decomposed is calculated from the equation (Raley et al., 1948):

$$\log \frac{\text{initial } t\text{-}Bu_2O_2}{\text{final } t\text{-}Bu_2O_2} = 0.002143\ t \text{ (in hours)}$$

The units for $t\text{-}Bu_2O_2$ are unimportant as long as they are the same. The kinetic chain length (number of molecules of oxygen absorbed in chain propagation for each $t\text{-}BuO\cdot$ radical produced) is equal to $(\Delta O_2 - 1)/\Delta t\text{-}Bu_2O_2$, where the 1 is the net oxygen absorbed in chain termination of two alkylperoxy radicals. The kinetic chain lengths range up to 130 with the pure hydrocarbons (except MeN) and are substantially higher with low $t\text{-}Bu_2O_2$ concentrations and long times than with high peroxide concentrations. The oxygen absorbed at long reaction times probably includes contributions from autocatalysis, which is neglected in the calculation. The fastest oxidizing Fuels B and C also give significant chain lengths, but the other fuels give little chain propagation and therefore little hydroperoxide.

The last two columns of figures in Table IV give the mg of gum formed in the listed experiments and the mg of gum per mmole of $t\text{-}Bu_2O_2$ decomposed. For most single fuels, this ratio changes only moderately with the amount of $t\text{-}Bu_2O_2$ decomposed. As with chain lengths, the highest yields of gum tends to be at the lowest concentrations of $t\text{-}Bu_2O_2$ (Table I) and the longest reaction times where autocatalysis would contribute most. Autocatalysis may account for the deviations in gum yields with DOD and EtN. The yields of gum are in the range 0.01 to 3.0 mole/mole t-Bu_2O_2 decomposed.

We conclude that gum formation is associated mostly with the chain termination reaction and that variations in the yields of gum with different fuels correspond to difference efficiencies in the coupling reaction. On this basis, EtN is the most efficient gum former, followed by 14B, 14A, PCH, 1-PH, TET, 13, 10, B, C, and A. MeN and DOD are the least efficient gum formers. This order agrees poorly with those for R_g and R_g/R_o in Table II, which have different bases.

3.4. Mechanisms of Gum Formation

We now present three mechanisms of gum formation from fuels. The first involves the coupling of two peroxy radicals. Section 3.3 presents strong evidence that it is associated with chain termination in oxidation, as described in the previous paper (Mayo and Lan, 1986).

The second mechanism is the coupling of fuel molecules and their oxidation products in the absence of oxygen. We have two new examples. In one experiment, 10.3 g of oxidation product L18 containing 5.80 mg gum and 0.853 mmole of hydroperoxide was heated for 24 h at 135-150° in an evaluated tube. The usual gum determination then gave 258 mg of yellow oil and white crystals after distillation at 1 torr, and 84.1 mg of "gum" after 20 h heating at 200°, an increase of 78.3 mg, 13.5 times the gum formed in the oxidation step. If the additional material is all dimer ($C_{24}H_{22}$), 0.252 mmole was produced by 0.853 mmole of hydroperoxide, a yield of 30% after (and 95% before) the 20-h heating at 200°.

In another experiment, 9.86 g, 63.1 mmole, of EtN and 1.486 g, 9.84 mmole, of 97.6% t-Bu_2O_2 was heated in a sealed evacuated tube at 150°. An aliquot was then concentrated at 1 torr, finally for 5 min at 130°. The residue corresponded to 2.084 g, 6.71 mmole, of mostly crystalline, white dimer, a yield of 68.2% on the peroxide used.

Thus the coupling of hydrocarbons by peroxides in the absence of oxygen produces dimers (and presumably some oligomers) in good yield without incorporation of oxygen (except possibly from the peroxide). Oxygen prevents this direct coupling and gives gums containing several percent of oxygen. The yield of coupling products in oxidation varies greatly (Section 3.3) and the products contain oxygen. The oxygen pressure at which one coupling reaction replaces the other is unknown.

The extraordinarily high yields of gum for the t-Bu_2O_2 decomposed from the best NASA EtN in Experiments J44B and L18 suggests that another mechanism of gum formation is involved. This mechanism has not yet been investigated, but it might involve some reaction like the condensation of naphthaldehyde and naphthol; both are possible secondary products from the oxidation of EtN.

4. SUMMARY AND CONCLUSIONS

This paper extends our previous work (Mayo and Lan, 1986) on oxidation and gum formation in pure hydrocarbons, jet turbine, and diesel fuels at 130°C without added initiator to 100° with added t-Bu_2O_2. Three of the six fuels and MeN oxidize faster at 100° than at 130°. These fuels have short kinetic chain lengths in oxidation and do not produce much hydroperoxide. Thus, comparison of individual rates of oxidation and gum formation for various fuels at unknown rates of initiation is of dubious significance. However, for any single substrate, the amount of gum produced for the oxygen absorbed (R_g/R_o) tends to be similar at 100° and 130°, even with large changes in rates of oxidation and gum formation and t-Bu_2O_2 concentration. Thus, one mechanism of gum formation is intimately associated with oxidation.

The effects of t-Bu_2O_2 concentration on rates of oxygen absorption and gum formation show that gum formation is associated with chain termination by two peroxy radicals, but that the efficiency of this coupling to dimer and gum varies greatly with the substrate. In general, the pure hydrocarbons have long kinetic chains and give good yields of hydroperoxides. Most of the fuels have short kinetic chain lengths and produce little hydroperoxide but much gum for the oxygen absorbed.

Another mechanism of gum formation is the coupling of substrates by peroxides in the absence of oxygen. This is an efficient mechanism for coupling and the products contain little or no oxygen if they are made from hydrocarbons. This mechanism is replaced by the oxidation termination mechanism when gaseous oxygen is present. The oxygen pressure at the transition is not yet known.

The last paragraph of the previous section proposes that products of oxidation of EtN condense to give high yields of gum by a third mechanism. This is consistent with a report of Kiiko (1982) that a resin is the principal oxidation product of 1-methylnaphthalene and that much more naphthaldehyde than naphthoic acid is formed.

Gum formation by aldol condensations and esterifcation of oxidation products (Mayo, 1975) and by aldehyde-hydroperoxide interactions leading to polyesters (Sauer et al., 1958) have been proposed, but so far we have seen no need for these mechanisms.

ACKNOWLEDGEMENT

Our research on diesel fuels was supported by the U.S. Army Research Office under Contract DAAG 29-84-K-0161. Our research on jet turbine fuels was supported by NASA-Lewis Research Center under Contract NAS3-22510.

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Table I

OXIDATIONS AT 100°C

Expt. Number	Fuel^a	t-Bu$_2$O$_2$, M	Reaction Time, h^b	R_o^c	R_g^d	R_g/R_o	Peroxide^e
F86	DOD	0.010	102.5	1.50^i	0.027	0.018	
F87	DOD	0.10	54.5	2.80^c	0.063	0.022	
J37A	DOD^{f*}	0.038	16	2.73			
			next 24	3.46^i			
			Total 40	3.15	0.29	0.092	
J37B	DOD +	0.051	16	1.02^i			
	3 mole %		next 24	1.36^i			
	anthracene		Total 40	1.08	0.30	0.28	
K92A	DOD	0	52	0.28	0.066	0.111	
			next 49	0.92^i			
			Total 101	0.59	0.066	0.111	
K92C	DOD	0.041	23	2.6	0.26	0.10	
L15A	DOD	0.010	28	1.69	0.28	0.17	77
L15B	DOD	0.100	10	3.2			
			next 12	3.6^i			
			Total 22	3.4	0.42	0.12	77
H96	TET*	0.039	5.0	29.3^c	1.02	0.035	5.6
L27B	TET	0	1.00	32.8	6.23	0.190	144^f
J5 }	EtN	{ 0.066	9	9.7^d	3.6	0.37	31.8
J6 }	Aldrich	{ 0.57	7	28.8^d	15.5	0.54	11.0
L18	EtN	0.106	next 1.00	18			
	NASA		next 1.00	21			
			next 1.00	20			
			next 1.10	28			
			next 1.07	18			
			Total 5.17	21	11	0.51	75
J44B	EtN, NASA	0.034	1.03	36	19	0.53	95.7
J23A	MeN	0.039	3	0.33			
			next 7	0.23			
			next 12	0.25			
			next 26	0.19^d			
			Total 48	0.22	0.87	4.0	

Table I

OXIDATIONS AT 100°C (Continued)

Expt. Number	Fuel[a]	t-Bu_2O_2, M	Reaction Time, h[b]	R_o^c	R_g^d	R_g/R_o	Peroxide[e]
J23B	MeN	0.039	3	0.84			
	Chromat.		next 7	0.61			
			next 12	0.28			
			next 26	0.27[d]			
			Total 48	0.36	1.42	4.0	
L14	MeN,	0.012	16.6	0.42			
	recrystal-		next 72	0.14[d]			
	ized		Total 88.6	0.19	0.47	2.5	22
G37	PCH*	0.030	7	8.9			
			next 8	9.0			
			next 6	5.6			
			Total 21	7.6	0.90	0.12	
L21A	1-PH*	0.037	7	5.0	1.91	0.39	
H63	Fuel A	0	255	0.0059[d]	0.0054	0.91	
H64	Fuel A	0.0045	277(136)	0.054[d]	0.051	0.95	
H57	Fuel A*	0.036	140	0.30[d]	0.28	0.95	~0
H77	Fuel A	0.34	19	5.18[d]	3.02	0.58	3
H33	Fuel B*	0.042	40.5	3.60[i]	0.542	0.151	13
H54	Fuel C*	0.037	52(31)	3.20[i]	0.42	0.130	2.4
F81	Fuel 10	0	209	0.013[d]	0.016	1.19	
F84	Fuel 10*	0.010	113(113)	0.094[d]	0.141	1.49	
F79	Fuel 10*	0.10	60(48)	0.915[c]	1.354	1.48	

Table I

OXIDATIONS AT 100°C (Concluded)

Expt. Number	Fuel[a]	t-Bu_2O_2 M	Reaction Time, h[b]	R_o^c	R_g^d	R_g/R_o	Peroxide[e]
F82	Fuel 13	0	209(120)	0.070[d]	0.105	1.49	
F83	Fuel 13	0.010	113(113)	0.11[d]	0.15	1.34	
F78	Fuel 13	0.10	60(48)	0.50	1.64	3.25	
G54	Fuel 13 Chrom.	0	1510	0.0069[d]	0.0097	1.41	
G59	Fuel 13*	0.029	144(144)	0.44[d]	0.42	0.95	~0
K89A	Fuel 14	0	28 days (28d)	0.025[d]	0.048		
					0.48p	3.8	~0
K89B	Fuel 14	0.037	20 days (7d)	0.22[d]	0.62		
L4C	Fuel 14A*	0.010	10 days (72)	0.105[d]	0.31		
					0.141p	4.3	
L4D	Fuel 14A*	0.101	140(72)	0.763[d]	2.51		
					0.89p	4.5	<30
L22A	Fuel 14B*	0.010	72	0.204			8
			next 68	0.067[d]			
			Total 140	0.14	1.18	8.6	<30
L22B	Fuel 14B	0.16	72	0.69	4.9	7.0	8

[a] Vacuum distilled except as noted.

[b] The number in parentheses is the time when deposit formation was first noted.

[c] i, c, d indicate increasing, constant or decreasing rates with time.

R_o in μmoles O_2/g fuel • h.

[d] R_g in mg gum/100 g fuel • h. Numbers are for formation of soluble gum except when marked p for precipitate; R_g/R_o includes both.

[e] Yield of hydroperoxide on oxygen absorbed.

[f] This DOD was washed with cone. H_2SO_4, dried, distilled, and used in this and subsequent runs.

Table II

COMPARISON OF RATES OF OXIDATION AND GUM FORMATION AT 100° AND 130°C[a]

Fuel	R_o 130°	R_o 100°	$\frac{R_o\ 130}{R_o\ 100}$	Fuel	R_g 130°	R_g 100°	$\frac{R_g\ 130}{R_g\ 100}$	Fuel	R_g/R_o 130°	R_g/R_o 100°	$\frac{R_g/R_o\ 130}{R_g/R_o\ 100}$
TET	69	29	2.4	EtN	42	19	2.2	DOD	0.018	0.092	0.20
EtN	64	36	1.8	B	13	0.54	24	1-PH	0.027	0.39	0.07
1-PH	28	5.0	5.6	TET	6.9	1.02	6.8	TET	0.10	0.036	2.8
PCH	27	7.6	3.6	PCH	5.7	0.90	6.3	PCH	0.21	0.12	1.8
B	22	3.6	6.1	C	5.0	0.42	12	14	0.38	4.3	0.9
DOD	15	3.2	4.8	13	0.85	0.42	2.0	B	0.59	0.15	3.9
C	3.8	3.2	1.2	1-PH	0.75	1.9	0.39	EtN	0.66	0.53	1.3
14	0.77	0.22	3.5	14	0.30	0.97	0.31	C	1.33	0.13	10
13	0.20	0.44	0.45	DOD	0.27	0.29	0.93	A	1.45	0.95	1.5
MeN	0.098	0.22	0.45	MeN	0.16	0.87	5.4	10	1.47	1.5	0.98
10	0.096	0.29	0.33	10	0.14	0.44	0.32	MeN	1.65	1.4	2.4
A	0.038	0.30	0.13	A	0.055	0.28	0.20	13	4.2	0.95	4.4
Spread[b]	1816	164	47		764	83	68		233	120	63

[a] Rates of 130° were measured without added initiator; rates at 100° were measured with 0.03-0.04 M $t\text{-}Bu_2O_2$. 100° data are from experiments marked with * in Table 2.

[b] Ratios of highest to lowest value in column.

Table III

EFFECT OF $[t\text{-}Bu_2O_2]_o$ on R_o and R_g at 100°C

Fuel	Experiment Numbers[a]	Ratios at Higher/Lower $[t\text{-}Bu_2O_2]$				Apparent Order on $t\text{-}Bu_2O_2$	
		$t\text{-}Bu_2O_2$	R_o	R_g	R_g/R_o	R_o	R_g
DOD	F86, 87	10	1.87	2.3	1.22	0.27	0.36
	L15A, B	10	2.02	1.47	0.73	0.29	0.17
EtN	J5, 6	8.63	4.31	1.46	1.46	0.68	0.18
	J44, L18	3.21	1.71	1.73	1.04	0.25	0.25
Fuel A	H64, 77	75.6	96	59	0.61	1.05	0.94
Fuel 10	F79, 84	10	9.73	9.6	0.99	0.98	0.98
Fuel 13	F78, 83	10	4.39	10.8	2.42	0.64	1.03
Fuel 14A	L4C, D	10.1	7.27	7.54	1.05	0.86	0.87
Fuel 14B	L22A, B	10.0	5.05	4.2	0.81	0.70	0.62

[a] Details in Table 2.

Table IV

RELATIONS OF t-Bu_2O_2 DECOMPOSED TO KINETIC CHAIN LENGTHS AND GUM YIELDS

Substrate	Expt. Number	ΔO_2, Millimoles	Δt-Bu_2O_2[a]	Kinetic Chain Length[b]	Gum, mg	Mg Gum / Δt-Bu_2O_2
DOD	F86	1.334	0.046	14	0.24	5.3
	F87	1.241	0.254	2	0.72	2.83
	J37A	0.942	0.066	6.7	0.8	13.3
	L15A	0.351	0.013	13	0.59	46
	L15B	0.561	0.103	2.2	0.68	6.6
	J37B[c]	0.330	0.092	1.3	0.9	9.6
TET	H96	1.427	0.0092	77	0.50	54
EtN	J5	0.278	0.0088	15	1.03	117
	J6	0.650	0.065	4.5	3.5	54
	J44B	0.363	0.0017	106	1.92	1130
	L18	2.209	0.0053	130	11.3	2120
MeN	L14	0.170	0.0421	1.5	0.476	11.3
PCH	G37	1.476	0.028	26	1.76	63
1-PH	L21A	0.296	0.011	13	0.664	60
A	H64	0.121	0.0325	1.3	1.15	35
	H57	0.335	0.1755	0.46	3.18	18.1
	H77	0.796	0.296	0.85	4.64	15.7
B	H55	1.174	0.0732	7.5	1.77	24
C	H54	1.389	0.081	8.0	1.80	22
10	F84	0.1165	0.0540	0.6	1.74	32
	F79	0.0899	0.281	~0	7.8	28
13	F83	0.146	0.055	0.82	1.95	35
	G59	0.400	0.213	0.54	7.7	36
	F78	0.0513	0.237	~0	7.9	42
14	K89B	0.902	0.333	0.80	2.5	75
14A	L4C	0.212	0.069	1.0	6.7	97
	L4D	0.919	0.505	0.4	41	81
14B	L22A	0.298	0.050	3.1	14.5	293
	L22B	0.439	0.30	0.24	31	104

[a] Mmoles t-Bu_2O_2 decomposed during oxidation.

[b] Kinetic chain length = $(\Delta O_2/2\ \Delta t\text{-}Bu_2O_2) - 1/2$.

[c] Contained ~3 mole% anthracene.

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