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Diffusion-Limited, Liquid-Phase Oxidation of n-Dodecane at 200°C

B. D. Boss and R. N. Hazlett

Fuels Branch
Chemistry Division

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NAVAL RESEARCH LABORATORY
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ABSTRACT

Oxidation of *n*-dodecane at 200°C by air at 1 atm was carried out for 5 hr in a borosilicate glass reaction chamber equipped with a gas bubbler. The rate of reaction was limited by the rate of oxygen diffusion from the gas phase due to the rapid consumption of oxygen absorbed into the liquid phase. The reaction products were analyzed in aliquots taken periodically from the reaction chamber. Chemical analyses, gas-liquid partition chromatography (GLC), tandem GLC-mass spectroscopy, and infrared and ultraviolet absorption were used to identify products accounting for 98% of the oxygen reacted. The isomer distribution of the dodecanols and dodecanones formed, as well as the distribution of carboxylic acids, was determined. Three classes of intramolecular reaction products–cyclic ethers, cycle hydrocarbons, and lactones–were detected. Many volatile products were detected. A filterable precipitate obtained after 10 hr of oxidation was studied using infrared attenuated total reflectance techniques. A reaction mechanism has been proposed based on current knowledge of other systems, the products identified, and the stoichiometry of the reaction.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

NRL Problem C01-05
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DIFFUSION-LIMITED, LIQUID-PHASE OXIDATION OF *n*-DODECANE AT 200°C

INTRODUCTION

An understanding of the liquid-phase oxidation of hydrocarbons by molecular oxygen is important in several fields of technology. This includes problems related to the synthesis of oxygenated compounds and to the application of hydrocarbon materials for industrial and military uses. Such oxidation is used to synthesize fatty acids, ketones, alcohols, and other useful molecules. However, these same reactions can be detrimental when they occur in a transformer oil or jet aircraft fuel. A current problem is the high temperatures to which jet fuel is subjected during supersonic flight. Part of the heat developed by the ram effect of the high-speed flight is dissipated by transfer from the hot metal aircraft surfaces to the fuel. The fuel is also used as a heat sink to cool electronic and other gear. In these processes, the fuel is subjected to sufficient stress so that it can form solid, filterable materials (gums, lacquers, and sediments) and volatile materials, which could affect aircraft operation and safety.

Many investigations have dealt with hydrocarbon oxidation, because it is of both practical and theoretical interest. One approach has been to study the fine details of the early stages of the reaction to characterize both the stable and unstable intermediates, *i.e.*, the microscopic mechanism (1-10). The more general, macroscopic features of the mechanism have received some attention for a few hydrocarbons (4, 10-14). Often the materials studied are such complex mixtures that it is difficult to draw conclusions about the reaction mechanisms (4, 11, 15, 16). In some studies, important variables, such as the dissolved oxygen concentration and the catalytic effect of the solid surface, have been ignored. In mixtures, the solvent effect is not completely understood at this time (3, 6, 17).

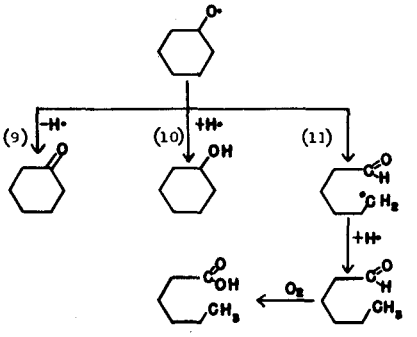
The work reported here is the initial phase of a study aimed at investigating aspects of the oxidation of simple mixtures of hydrocarbons. *n*-Dodecane was selected as the major component of the mixtures because (a) it is an important jet fuel component, (b) its boiling point (216.3°C) permits liquid-phase experiments at high temperatures in an open system, (c) it is relatively stable to oxidation, and (d) it is available in high purity at reasonable cost.

To establish suitable baselines for such studies, the oxidation of *n*-dodecane by itself has been carried out in the liquid phase at 200°C in a borosilicate glass chamber at 1 atm of air. The reaction has been studied over a period of 5 hr, and 98% of the absorbed oxygen has been accounted for in the products identified using gas-liquid partition chromatography (GLC); GLC-mass spectroscopy, infrared spectroscopy (IR); ultraviolet spectroscopy (UV), and chemical analyses. This thorough analysis allows us to suggest a macroscopic reaction mechanism based on the products identified, the stoichiometry of the reaction, and current knowledge of reaction mechanisms tested for similar systems.

The current theory of the initial stages of oxidation is as follows (1,2,10,18-21):

initiation	$2RH + O_2 \longrightarrow 2R\cdot + H_2O_2$	(1)
	$RH + O_2 \longrightarrow R\cdot + HO_2^{\cdot}$	(2)
propagation	$R\cdot + O_2 + M \longrightarrow RO_2^{\cdot} + M$	(3)
	$RO_2^{\cdot} + RH \longrightarrow ROOH + R\cdot$	(4)
branching	$2ROOH \longrightarrow RO_2^{\cdot} + H_2O + RO\cdot$	(5)
termination	$RO_2^{\cdot} + R'CHO\dot{O}R'' \longrightarrow ROH + R'COR'' + O_2$	(6)
	$RO_2^{\cdot} + R\cdot \longrightarrow ROOR$	(7)
	$R\cdot + R\cdot \longrightarrow R\text{-}R$	(8)

At low temperatures where hydroperoxide, ROOH, is relatively stable, we expect the predominant products to be ROOH and equal quantities of alcohols and ketones from reaction 6. At higher temperatures we must add reactions of RO· similar to those delineated for cyclohexane as follows (2):



In this case alcohols and ketones are the predominant products for periods up to several hours at temperatures below 180°C (2).

The work presented here at 200°C lies in the diffusion-limited region of the reaction. Reaction initiation (reactions 1, 2 and 5) was sufficiently rapid that not enough air could be supplied to simultaneously maintain an equilibrium oxygen concentration and maintain the *n*-dodecane as a bulk liquid (*i.e.*, avoid the frothy state). Thus, the reaction was limited by the rate of oxygen diffusion from the gas phase.

The data and mechanism schemes presented here will serve as a foundation for studies of the effect of oxygen concentration, temperature, surface catalysis (22), and solute concentration. Work at lower temperatures will be both in the kinetic and diffusion-limited regions of the reaction.

EXPERIMENTAL PROCEDURE

Reagents

n-Dodecane was obtained from Phillips Petroleum Co. as 99.7+% "pure" grade. The material was passed through Drierite, activated alumina, and silica gel to remove traces of polar impurities. The only major impurity identified by GLC was *n*-hendecane (0.15%).

Apparatus

A diagram of the reaction vessel is presented in Fig. 1. The O-ring seal glands assured a tight fit. The chamber can be conveniently replaced with cylinders of various materials. The borosilicate glass chambers were prepared from different lots of glass stock and exposed to chromic acid cleaning solution for 1 week, followed by soaking and rinsing first in ammonia and then in distilled water. Collection tubes of Drierite, Ascarite, and borosilicate glass wool (cooled in dry ice-acetone) were connected to the chamber exhaust. The exhaust passed finally through a gas sampling valve in a Fisher Scientific Co. Gas Partitioner used to analyze the oxygen concentration. The reaction temperature was maintained by a heated, fluidized alumina bed.

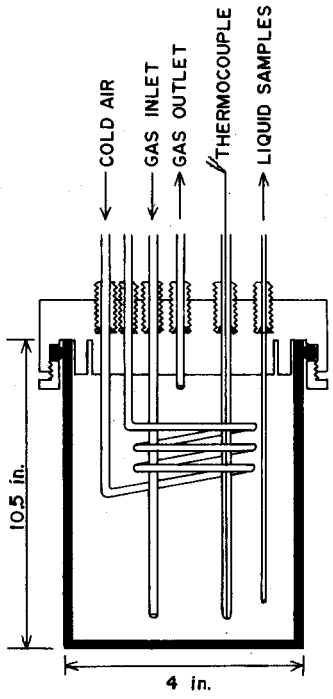


Fig. 1 - Cylindrical reaction chamber with polytetrafluoroethylene cap, cooling coil and silicone rubber O-ring seals

Reaction Conditions

The reaction chamber was maintained at 200.5°C with oscillations of ±0.8°C. The pressure was maintained at 10 mm above the generally prevailing 750 torr atmospheric pressure. Dry air, with the carbon dioxide removed, was bubbled through the liquid at 260 cm^3/min. Diffusion-limited kinetics were expected (23).

The original 325 ml charge of *n*-dodecane was sampled in seven 25 ml aliquots. Three runs were performed using air, and one run was made with nitrogen containing 160 ± 20 ppm of oxygen. In each case an analysis was made of all accessible products in the chamber and in the collection tubes.

A further experiment was performed at 200°C using *n*-dodecane with the airflow rate varied between 260 and 4500 cm^3/min. In Fig. 2 the rate of accumulation of 4-, 5-, and 6-dodecanone is plotted as a function of flow rate. To maintain the reaction in the kinetic region, at least 4000 cm^3/min of air must be bubbled through the liquid using the apparatus shown in Fig. 1.

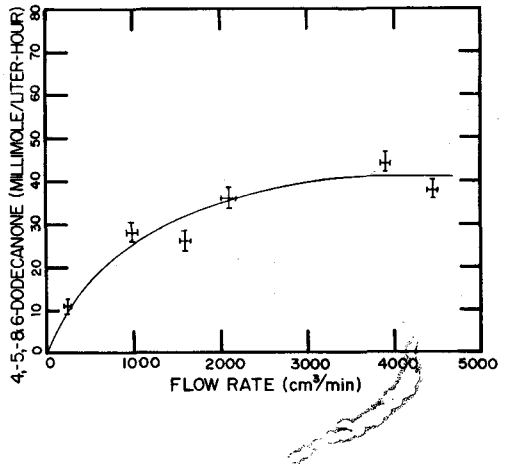


Fig. 2 - Effect of air input flow rate on rate of formation of the combined ketones 4-, 5-, and 6-dodecanone at 200° C. Measurements were made on randomly selected flow rates.

Chemical Tests

Hydroperoxide was determined by a minor variation of the colorimetric iodine method of Heaton and Uri (24) (see also Mair and Graupner (25)). Carbonyl was determined by the very sensitive colorimetric method of Lappin and Clark (26). Acids and esters were determined according to ASTM test methods D974-58T and D94-56T, respectively.

GLC Analyses

Each liquid sample was analyzed by GLC immediately after sampling (Fig. 3). In addition, chromatographs were obtained on the liquid after reaction with benzoylchloride (Fig. 4) and after reaction with hexamethyldisilazane (27) (Fig. 5). These derivative chromatographs were necessary to separate the dodecanol isomers from the dodecanone isomers by analyzing displacements of the alcohol peaks. This analysis is performed in three steps, and to discuss these we refer to the chromatographs as product chromatograph PC (Fig. 3), benzoyl chromatograph BC (Fig. 4), and silyl chromatograph SC (Fig. 5). The total amount of 4-, 5-, and 6-dodecanone is determined from PC. The percentage of each dodecanone is determined from BC, and these two pieces of data are used to dissect SC for the dodecanol isomer concentrations. Figure 6 is a chromatograph of the 5-hr reaction product mixture after reaction with a silylating reagent. This chromatograph differs from SC because the column coating is diethyleneglycolsuccinate. A good separation is obtained showing both the dodecanols and dodecanones. This column was not used routinely since the silylating reagent reacts with the liquid phase.

The distribution of the carboxylic acids formed was determined by extraction of the reaction residue with 1N KOH, neutralization with HCl, and formation of the methyl esters with a methanol-BF_3 reagent mixture (28). Chromatographs of this reaction mixture gave the distribution of the C_6 through C_{12} carboxylic acids. These acids were almost completely retained in the reaction chamber at 200°C. Comparable treatment of a known acid mixture was used to verify the analysis.

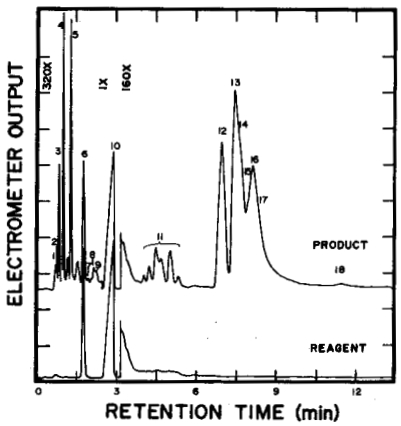


Fig. 3 - Gas chromatographs of the starting material, *n*-dodecane, and of the reaction products after 5 hr. The chromatographs were obtained by using a DC-550 silicone-oil support-coated open-tubular column (100 ft by 0.02 in. I. D.) with a helium carrier gas supplied at 35 psi (4 ml/min). The following temperatures were used: column, 126° C; injector, 200° C; flame ionization detector, 270° C. The products were identified as (1) *n*-hexane, (2) *n*-heptane, (3) *n*-octane, (4) *n*-nonane, (5) *n*-decane, (6) *n*-undecane, (7) decanone, (8) decanal, (9) C_{12} single ring alicyclics, (10) *n*-dodecane, (11) cyclic C_{12} ethers, (12) 6-, 5-, and 4-dodecanone, (13) 6- and 5-dedecanol, (14) 3-dodecanone, (15) 4-dodecanol, (16) 2-dodecanone, (17) 3-dodecanol, and (18) 2-dodecanol.

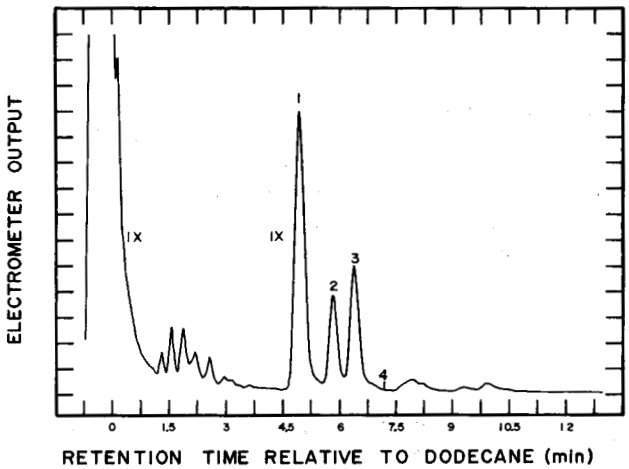
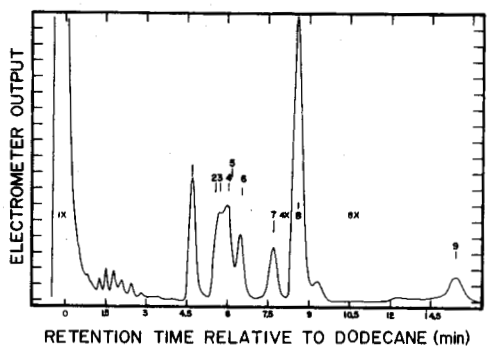


Fig. 4 - Gas chromatograph of the 5-hr reaction products after reaction with benzoyl chloride. Fig. 3 gives the chromatograph conditions. The products were identified as (1) 6-, 5-, and 4-dodecanone, (2) 3-dodecanone, (3) 2-dodecanone, and (4) dodecanal.

Fig. 5 - Gas chromatograph of the 5-hr reaction products after reaction with a silylating reagent. The conditions in Fig. 3 apply. The products were identified as (1) 6-, 5-, and 4-dodecanone, (2) 3-dodecanone, (3) 6- and 5-dodecanol, (4) 2-dodecanone, (5) a minor unidentified product, (6) 4-dodecanol, (7) 3-dodecanol, (8) 2-dodecanol, and (9) 1-dodecanol.



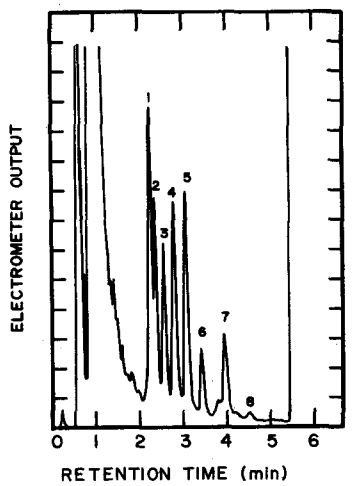


Fig. 6 - Gas chromatograph of the 5-hr reaction products after reaction with a silylating reagent. The conditions in Fig. 3 apply except a diethyleneglycolsuccinate support coating was used. The products were identified as (1) 6- and 5-dodecanol, (2) 4-dodecanol, (3) 3-dodecanol, (4) 2-dodecanol, (5) 6-, 5-, and 4-dodecanone, (6) 3-dodecanone, (7) 2-dodecanone, and (8) dodecanal.

Mass Spectra

The mass spectra were obtained with a CH-4 Atlas mass spectrometer (with a double-ion source) fed by an F & M 810 gas chromatograph (29). The interface was a stainless-steel capillary tube heated to 250°C. The 200:1 exit split on the gas chromatograph effluent which was attained in this manner was effective for qualitative analysis purposes. Neither a polytetrafluoroethylene nor a sintered-glass molecular separator (29) afforded adequate separation of the sample from the helium carrier.

Absorption Spectra

Spectra of the product mixture in the IR (Fig. 7), UV, and visible regions were obtained. A solid material which precipitated after 10 hr of oxidation was examined using IR attenuated total reflectance (ATR) techniques on a Perkin-Elmer 457 dual-grating spectrophotometer.

RESULTS

The blank reaction using nitrogen with 160 ± 20 ppm oxygen contained 0.37 millimole/liter of hydroperoxide as the only product detected after 5 hr. Using air, numerous compounds were detected as listed in Table 1 for a 5-hr experiment. The reaction consumed 9.4% of the starting material, *n*-dodecane, and at least 80% of the products have the same carbon backbone. The listed products account for the consumption of 0.364 mole/liter of oxygen. The oxygen uptake, as determined from the difference between the input and exhaust levels, was 0.370 mole/liter. Thus, 98% of the oxygen is accounted for.

The chromatographs of the starting-material and reaction-product mixture are reproduced in Fig. 3. Intramolecular reaction products–cyclic C_{12} ethers, cyclic C_{12} hydrocarbons, and C_{12} lactones–have been identified using the combined information from mass spectra, GLC, and/or IR.

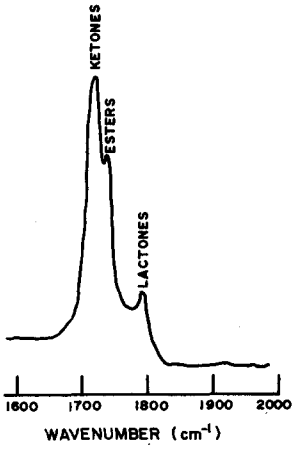


Fig. 7 - IR spectrum of the reaction product mixture at the end of 5 hr under the conditions specified in the text

Concentrations of the major products determined by GLC and chemical analysis are plotted in Figs. 8 and 9. Observe that there is no appreciable induction or autocatalytic period. The net carbonyl concentration is the difference between the total carbonyl and the dodecanone concentration. Note that the net carbonyl concentration builds up at first and levels off rapidly. The peaks in the gas chromatographs which can be assigned to lower-molecular-weight aldehydes exhibit similar behavior.

It would be interesting to calculate the amount of water expected by accounting for all the hydrogen atoms in the product mixture. However, this would require a very accurate knowledge of all the volatile hydrocarbon products that escaped from the chamber. Thus, no such analysis was attempted.

Besides carbon dioxide and water, insoluble products (gums) can form after considerable oxidation. No filterable material was detected after 5 hr, but after 10 hr a considerable amount was formed. This material was easily dissolved in acetone, coated on an ATR plate, and dried for IR analysis. Significant absorptions at 3460 cm^{-1}, 1790 cm^{-1}, 1180 cm^{-1}, 1050 cm^{-1}, and 1730 cm^{-1} indicate that this gum contains appreciable concentrations of hydroxyl, acid, ester, and carbonyl groups. This information indicates that the gum contains highly polar molecules, some of which are capable of forming hydrogen bonds.

In the 5-hr experiment where no gums were formed, a GLC backflush experiment was performed to collect, in a single peak, compounds eluting at a time greater than needed for the dodecanols. If we make the approximation that this peak contains only the acids and esters, then we can calculate the ester molecular weight, since the distribution of acids, the acid content, and the ester content are known from other measurements. Estimation by this method indicates an average ester size of 12 carbons.

Further details of the reaction can be ascertained using GLC. The distributions of dodecanols, dodecanones, and carboxylic acids were examined. The distribution of C_5 to C_{12} straight-chain monobasic acids relative to C_7 [≡10.] is as follows:

C_5	5.	C_9	7.5
C_6	9.	C_{10}	4.5
C_7	10.	C_{11}	0.9
C_8	9.	C_{12}	0.4

Table 1
Identification of Products

Products	Concentration* (millimole/liter)	Method(s) of Identification
C_1 through C_{11} paraffins	(108.0)†	GLC, mass spectra, and chemical tests
n-Nonane	10.2	GLC and mass spectra
n-Decane	11.4	GLC and mass spectra
n-Undecane	Trace	GLC and mass spectra
Pentanal through decanal	(25.)‡	GLC, IR, mass spectra, and chemical tests
Pentanone through decanone	Trace§	GLC, mass spectra, and chemical tests
Pentanol through nonanol	Trace§	GLC and mass spectra
Cyclic dodecanes	10.	GLC and mass spectra
Cyclic C_{12} ethers	23.	GLC and mass spectra
C_{12} lactones	6.	IR and chemical tests
Dodecanols	183.	GLC, IR, mass spectra, and chemical tests
Dodecanones	100.5	GLC, IR, UV, mass spectra, and chemical tests
Total carbonyl	125.	Chemical tests
C_1 through C_{12} carboxylic acids	32.5§	GLC and chemical tests
Esters	23.0	Chemical tests
Hydroperoxides	8.6	Chemical tests
Carbon dioxide	3.0	Absorption on Ascarite
Water	256.♦	Chemical tests

* Products were formed by the end of 5 hr under the conditions specified in the text.
† Calculated from liquid phase and vapor trap materials by assuming loss of materials with low boiling point.
‡ Based on the net carbonyl by assuming only trace amounts of C_5 through C_{10} ketones.
§ Volatility or low concentration obscured complete identification and analysis of the series from C_1 through C_{12}.
♦ Corrected for the capture of volatile polar products other than water.

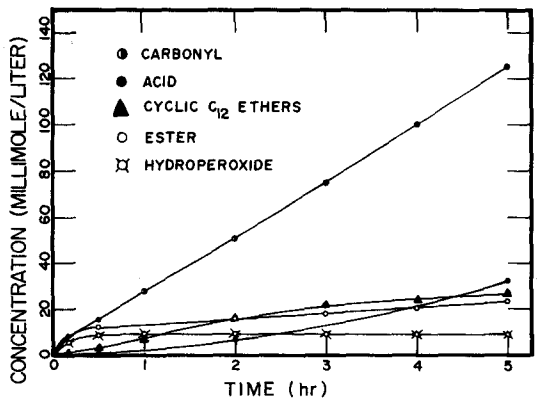


Fig. 8 - Concentration of selected reaction products as a function of time under the conditions specified in the text

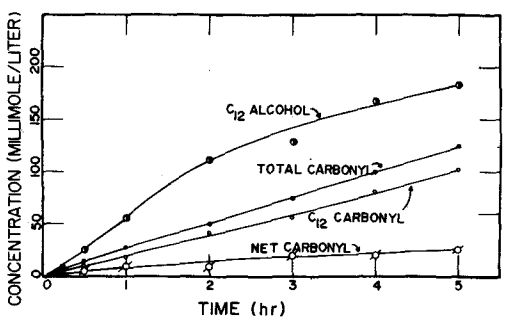


Fig. 9 - Concentration of selected reaction products as a function of time under the conditions specified in the text

Kudo *et al.* (13) have determined the isomer distributions for oxidation of *n*-decane under somewhat different conditions. Their observations are comparable to ours except that for them, decanoic acid was relatively less plentiful than we observed for dodecanoic acid.

The point of oxidative attack along the carbon chain is indicated by the data in Table 2 since the alcohols and ketones are relatively stable products. We conclude that the C-2 position is favored, if the reasonable assumption is made that each of the three isomers determined in the combined C-4, C-5, and C-6 peak constitutes one-third of the total peak. This conclusion disagrees with experiments performed in the kinetic region by other workers, (8, 16, 21), but is in agreement with the excellent work of Dawkins (30).

DISCUSSION

The data should be considered in the light of the restrictions associated with a bubbler reaction chamber operating under diffusion-limited kinetics: loss of volatile products, possible vapor-phase reactions, surface catalysis, and oxygen concentration gradient. In addition, taking samples of finite size (25 ml) changes the surface/volume ratio from 0.64 cm^{-1} at the start to 0.85 cm^{-1} at the end.

The limited mechanism scheme presented earlier in this report provides an adequate, but simplified framework for the major course of the reaction. We note the early appearance of hydro-peroxides and the accumulation of considerable quantities of dodecanols and dodecanones (reactions 9 and 10). Similar isomer distributions for the dodecanols and dodecanones indicate a common precursor (*i.e.*, hydroperoxide).

Table 2
Isomers of Dodecanol and Dodecanone

Time*	Position of the Functional Group	Percentage of Isomer Present	
		Dodedanones	Dodecanols
30 min	C-1	1.1 ± 0.5	–
	C-2	24.5 ± 0.7	25.3 ± 0.7
	C-3	19.0 ± 0.7	18.2 ± 0.7
	C-4, 5, 6	55.4 ± 0.5	55.5 ± 0.5
5 hr	C-1	1.1 ± 0.5	1.0 ± 0.5
	C-2	25.5 ± 0.7	25.4 ± 0.7
	C-3	18.4 ± 0.7	18.5 ± 0.7
	C-4, 5, 6	55.0 ± 0.5	55.1 ± 0.5

*Under the conditions specified in the text.

A slight leveling off of the dodecanol concentration corresponds to further reaction to form the ketone (1, 10). The series of short-chain *n*-alkanes (C_6 to C_{10} in the liquid phase and C_4 to C_8 from the vapor trap) and the series of aldehydes (C_5 to C_{10} seen by the GLC and measured as the net carbonyl concentration) are reaction products predicted by the mechanism scheme for an alkoxy radical undergoing chain scission (reaction 11). For the formation of smaller alkanes and aldehydes from an alkane the reaction would be as follows:

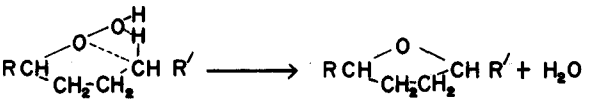
$$\mathrm{RCHOOHR'} \xrightarrow{-\mathrm{HO}\cdot} \mathrm{RC\dot{H}OR'} \longrightarrow \mathrm{RCHO} + \mathrm{R'}\cdot \qquad (12)$$

This reaction has been observed in hydroperoxide decomposition (31). The quantity of C_1 to C_{11} *n*-alkanes cannot be accounted for by chain scission during acid formation from the ketone and/or alcohol (11). We estimate that the net carbonyl concentration plus the carboxylic acids can account for the *n*-alkanes (allowing for loss of volatile components) in support of the above mechanism. Further evidence that acids are formed by a later reaction (*i.e.*, from aldehdyes) is the absence of an induction period for the formation of hydrocarbons but a considerable time-lag for acid formation.

Two other features of the reaction are to be discussed: the formation of esters and the formation of intramolecular compounds. Intramolecular reaction products–cyclic hydrocarbons, cyclic ethers, and lactones–may be the result of vapor-phase reactions. A cyclic C_{12} hydrocarbon may form by the cyclization of a dodecyl free radical with loss of a hydrogen atom:

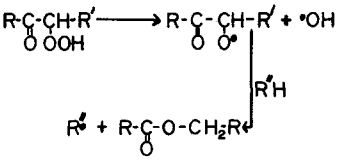
$$\mathrm{R\dot{C}HCH_2CH_2CH_2CH_2R'} \xrightarrow{-\mathrm{H}\cdot} \mathrm{R\underbrace{CHCH_2CH_2CH_2C}HR'} \qquad (13)$$

Loss of water from dodecylhydroperoxide through a 5- or 6-membered transition state may account for cyclic ethers: Both of these products appear early in the reaction. The method of formation of lactones is not clear at this time.



(14)

Esters are an early product of the reaction and cannot be the product of esterification between acid and alcohol molecules since acids are formed after a considerable time-lag. A rearrangement reaction would fit the evidence and be consistent with the interpretation offered for the backflush experiment (*i.e.*, a C_{12} ester). Rearrangement from an α-hydroperoxyketone has been suggested (32): Further evidence based on a parallel reaction is the formation of hydroxyketones; similarly, we suggest the formation of vicinal diketones. Oxidation of paraffins is characterized by a yellowing of the liquid caused by an absorption at 310 mμ, which is characteristic of conjugated unsaturation. Since no carbon-carbon unsaturation was seen in the IR spectrum, a vicinal diketone is postulated. To further account for very early α-hydroperoxyketone formation and yellowing of the reaction product mixture, we propose that a dihydroperoxide is formed almost simultaneously with the hydroperoxide, multifunctional compounds, and esters being derived therefrom.



(15)

An alternative theory has been proposed by Dawkins (30).

A further unexplained observation is the structure found in the backflush peak in Fig. 10. Identification of the different components of the peak could conceivably be useful in our analysis scheme. There has been no success in interpreting the peaks.

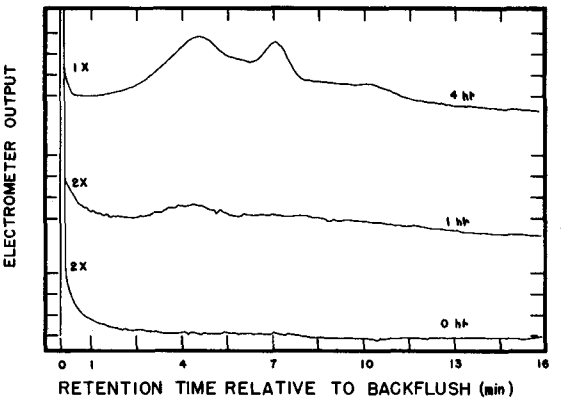


Fig. 10 - Gas chromatographs of peaks obtained in the GLC backflush experiment

The analysis scheme discussed in this report combines and contrasts data from several techniques to aid in elucidating the macroscopic mechanism of n-dodecane oxidation. Temperature, oxygen concentration, and surface catalysis effects need to be considered in the future. In the light of these experiments, studies of the oxidation of simple mixtures of hydrocarbons appears to be a fruitful prospect.

The material studied here, *n*-dodecane, was chosen for its relatively high stability. We conclude, however, that if sufficient oxygen is available and if mixing is reasonably efficient, considerable oxidation will occur. However, oxidation of up to 9% of the *n*-dodecane can proceed without gum formation under these conditions. More problems can be expected where higher temperatures, stronger catalytic effects, or more reactive hydrocarbons, sulfur, or nitrogen compounds are involved. From a practical standpoint such problems are at two extremes: (a) gums form which can hinder heat exchange and filtering equipment associated with the hydrocarbon, and (b) volatile gases are produced which may be a combustion hazard.

In the appendix we discuss the effect of oxygen partial pressure on the extent of oxidation of *n*-dodecane in the diffusion-limited region.

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Appendix

THE EFFECT OF OXYGEN PARTIAL PRESSURE ON THE EXTENT OF OXIDATION OF *n*-DODECANE IN THE DIFFUSION-LIMITED REGION

The oxidation of *n*-dodecane discussed in this report was studied at a flow rate of 260 cm^3/min of air. At this slow rate, several experiments were performed to test the effect of the oxygen partial pressure, p_{O_2}, on the rate of oxidation. We report the results in Fig. 11.

In the diffusion-limited region of the reaction where the rate of oxidation is limited by the dissolution of the oxygen from the gas/liquid interface to the bulk liquid (10), we may hypothesize that the rate of oxidation is linearly proportional to p_{O_2}. To justify this hypothesis we first consider the kinetic equation based on the mechanism in reactions 1 through 8, where the reaction velocity W is given as

$$W = K_4 \; [RH] \, [RO_2 \cdot] \tag{A1}$$

based on reaction 4. The symbol K_4 is the reaction rate constant. We may write the kinetic equation for this mechanism by assuming the usual steady-state approximation, assuming that the chain length is long, and using W_1 for the rate of initiation:

$$W = K_4 \; [RH] \; W_1^{1/2} \, K_6^{-1/2} \; 2^{-1/2} \left[1 + \frac{K_7 \; K_4 \, [RH]}{K_6 \; K_3 \, [O_2]} + K_8 \left(\frac{K_4 \, [RH]}{K_3 \, [O_2]} \right)^2 \right]^{-1/2} \tag{A2}$$

This reduces for the case of low $[O_2]$ so that $W = K_3 K_8^{-1/2} \; 2^{-1/2} \; W_1^{1/2} \; K_6^{-1/2} \; [O_2]$. In our case the reaction is limited by the oxygen concentration gradient between the liquid near the gas-liquid surface S, where $[O_2] = [O_2]_s$, and the bulk liquid, where $[O_2] = [O_2]_{liq}$. Thus, for the gas phase

$$-d[O_2]/dt = LS \left([O_2]_s - [O_2]_{liq} \right) = LS \left(\gamma p_{O_2} - [O_2]_{liq} \right) \tag{A3}$$

where γ is the Henry's law constant and L is a proportionality constant dependent on oxygen diffusion in the liquid and the stirring rate. Under steady-state reaction conditions, $\gamma p_{O_2} - [O_2]_{liq}$ has a positive value, C, other than zero for the diffusion region and approaches zero for the kinetic region where L and S become very large. In either case LSC is equal to the rate of oxygen reaction, which is also assumed to be given by W. If $[O_2]_{liq}$ is small, we may write

$$LSC = K_3 K_8^{-1/2} K_6^{-1/2} \; 2^{-1/2} \; W_1^{1/2} \, [O_2]_{liq} \equiv \delta \, [O_2]_{liq} \tag{A4}$$

We solve this for $[O_2]_{liq}$ and obtain

$$[O_2]_{liq} = \frac{LS\gamma \, p_{O_2}}{\delta + LS} \tag{A5}$$

This implies that if $[O_2]_{liq}$ is small in either the kinetic region ($LS \gg \delta$) or the diffusion region ($\delta \gg LS$), then $[O_2]_{liq} \approx p_{O_2}$ and $W \approx p_{O_2}$. Clearly a test of this relation to p_{O_2} does not distinguish between the two regions.

In Fig. A1 the concentration of oxygen in the gas escaping the chamber is plotted vs the rate of reaction W. Clearly there is curvature to the plotted data. We attribute this curvature only slightly to the decreasing value of C and mostly to the large contribution of the chain branching reaction 5 which effects the assumption of long chains by increasing the steady-state free-radical concentration changing W_1. The data show C is large for the low flow rates used here.

A thorough analysis of the products indicated no significant changes in the product distribution. Changing p_{O_2} has about the same effect as changing the time of reaction.

We conclude that the rate of reaction can be reduced by lowering p_{O_2} of air in contact with *n*-dodecane at 200°C, but the reaction rate is slowed only slightly greater than linearly.

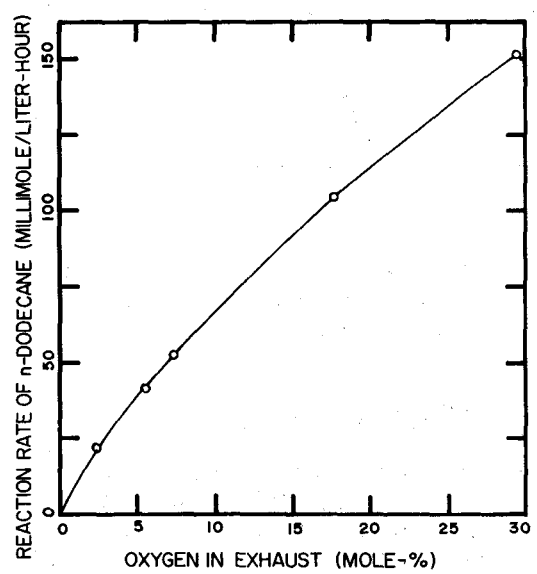

Fig. A1 - Reaction velocity W for *n*-dodecane plotted as a function of the partial pressure of p_{O_2} leaving the reaction chamber p_{O_2} for experiments lasting 2 hr at 200° C under diffusion-limited conditions specified in the text

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13. ABSTRACT

Oxidation of n-dodecane at 200° C by air at 1 atm was carried out for 5 hr in a borosilicate glass reaction chamber equipped with a gas bubbler. The rate of reaction was limited by the rate of oxygen diffusion from the gas phase due to the rapid consumption of oxygen absorbed into the liquid phase. The reaction products were analyzed in aliquots taken periodically from the reaction chamber. Chemical analyses, gas-liquid partition chromatography (GLC), tandem GLC-mass spectroscopy, and infrared and ultraviolet absorption were used to identify products accounting for 98% of the oxygen reacted. The isomer distribution of the dodecanols and dodecanones formed, as well as the distribution of carboxylic acids, was determined. Three classes of intramolecular reaction products—cyclic ethers, cyclic hydrocarbons, and lactones—were detected. Many volatile products were detected. A filterable precipitate obtained after 10 hr of oxidation was studied using infrared attenuated total reflectance techniques. A reaction mechanism has been proposed based on current knowledge of other systems, the products identified, and the stoichiometry of the reaction.

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