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TECHNICAL NOTE 2958

REACTION PROCESSES LEADING TO SPONTANEOUS IGNITION OF HYDROCARBONS

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SUMMARY

The vapor-phase oxidation of isooctane at 550° C under conditions leading to rapid quenching of the reaction yields hydrogen peroxide, diisobutylene, and isobutylene as the major reaction products. As the reaction time increases, the formation of acetone and formaldehyde becomes of primary importance. Under otherwise similar conditions, n-heptane is attacked at 350° C to yield a mixture of organic peroxides as the major initial product. The next phase of reaction develops with extreme rapidity, leading mainly to the formation of a mixture of aldehydes and ketones (principally formaldehyde). The marked differences between the oxidation behavior of these two hydrocarbons are interpreted on the basis of the temperature required for oxidative attack and of the thermal stability of the alkyl and peroxy radicals obtained. Preliminary results on the oxidation of isobutane and 2,2,5-trimethylhexane afford additional evidence for these generalizations.

INTRODUCTION

A considerable amount of data is available on the formation of peroxides, aldehydes, and other intermediates by the partial oxidation of hydrocarbons. However, there is a lack of quantitative information concerning the variation in the nature and amounts of these key intermediates with hydrocarbon structure and with reaction conditions. Such information is basic to an understanding of spontaneous ignition and other combustion phenomena. Accordingly, the present study has been initiated with the objective of uncovering fundamental data regarding the oxidation intermediates leading to the spontaneous ignition of hydrocarbons. This investigation was conducted at the Applied Science Research Laboratory of the University of Cincinnati under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

DESCRIPTION OF APPARATUS

The apparatus comprises essentially three parts: (1) The hydrocarbon-oxygen mixing tube, (2) the oxidation chamber, and (3) cold traps. These are illustrated in figure 1. Traps 9 in figure 1 were cooled in a dry-ice - chloroform mixture, while in most experiments trap 10 comprised a solution of 2,4-dinitrophenylhydrazone to catch any volatile carbonyl compounds which had failed to condense. The three parts of the apparatus are described below:

(1) Oxygen from a cylinder first was dried by bubbling it through sulfuric acid. It then was passed through a flowmeter and bubbled into the hydrocarbon, which was held at a constant temperature (vapor bath) to secure a constant fuel-oxygen ratio. The mixture of fuel and oxygen entered the oxidation chamber through a glass tube heated slightly higher than the vapor bath to prevent any condensation. This tube contained a plug of glass wool to inhibit the propagation of the reaction from the oxidation chamber back to the fuel reservoir. Despite this precaution, an explosion did occur in the fuel reservoir on two occasions; accordingly, the apparatus should be shielded to minimize this hazard. In the case of isobutane, a second flowmeter was used instead of the hydrocarbon-oxygen bubbler. The oxidations employed a stoichiometric or a near-stoichiometric mixture of oxygen and hydrocarbon.

(2) Reaction has been carried out either in the single 1/16-inch inside-diameter glass tube illustrated in figure 1 or in a bundle of six such tubes employed to obtain larger amounts of product. In the latter case, thermal contact was obtained by substituting a glass tube packed with iron filings and containing the six oxidation tubes for the drilled steel rod (item 6 in fig. 1). The various contact times and temperatures are listed in the several tabulations of experimental results. The temperature distribution throughout the reaction tube was measured at various temperature settings at zero gas flow rate. The characteristic curves obtained are shown in figure 2. Another series of readings was made at 550° C and at several gas flow rates. Since the only appreciable difference in readings occurred within the first inch of the furnace length, the temperature distribution throughout the furnace was considered essentially unchanged within the range of gas flow rates employed.

(3) The third stage consisted of a series of two dry-ice - chloroform traps and a 2,4-dinitrophenylhydrazone solution through which the gas was bubbled after leaving the traps. Substantially all the condensable products collected in the first dry-ice trap. However, in all cases where considerable reaction occurred, an appreciable portion of the carbonyl fraction also was collected in the dinitrophenylhydrazone trap. The exit gas was checked in some runs for carbon monoxide, carbon dioxide,

hydrogen, oxygen, and volatile hydrocarbons by means of a Burrell Industro gas analyzer. However, in view of the large amounts of unreacted oxygen present, this determination was not sufficiently sensitive to give meaningful results.

In a number of the n-heptane runs, persistent "fogs" were obtained which could not be condensed in cold traps or in solvents (ref. 1). A quantity of this fog was collected and allowed to stand overnight in a stoppered flask. An oily film was deposited on the walls of the flask; no attempt to identify this material was made.

TEST PROCEDURE

All of the hydrocarbons used in this study were obtained from the Phillips Petroleum Co. and were of a 99-mole-percent purity.

At the conclusion of a reaction, the walls of the inlet tubes and traps in stage 3 were coated with a solid icelike substance. At room temperature this melted to an isooctane-immiscible liquid exhibiting strong reactions to the peroxide and carbonyl tests. This material contained most of the hydrogen peroxide and formaldehyde, undoubtedly partly as the carbonyl-peroxide addition product $HOOCH_2OH$ (ref. 1). The water present in this phase was not determined. Major components of the hydrocarbon layer were olefins, organic peroxides, and carbonyl compounds. The following procedure for separating the reaction products was employed in most of the isooctane work and for the products obtained from heptane, 2,2,5-trimethylhexane, and isobutane.

Water was added to the reaction mixture to dissolve the icelike phase. This water solution then was transferred to a volumetric flask and the hydrocarbon phase was washed with more water. About six such extractions removed the water-soluble components from the hydrocarbon phase. The washings were collected in the volumetric flask, in which they were then diluted to a standard volume, and aliquot portions were analyzed for hydrogen peroxide, total peroxide, total carbonyl, formaldehyde, and acid content. The hydrocarbon phase was analyzed for total peroxide and total olefin. A sample was then distilled and an aliquot sample taken for olefin determination; where highly volatile olefins were present, they were distilled separately as outlined below.

A slightly different procedure was used in the earlier isooctane work. This was somewhat more time consuming than the above procedure since the icelike and hydrocarbon phases were analyzed separately.

The isooctane solution was poured from the icelike phase which adhered to the walls of the receivers and tubes. The icelike phase then was dissolved in water and diluted to a standard volume. Aliquot portions were taken and individual analyses were made for hydrogen peroxide, total peroxides, formaldehyde, total carbonyl, and acids. Individual portions of the hydrocarbon phase then were analyzed for hydrogen peroxide, total peroxide, formaldehyde, and total carbonyl. In determining olefins, the hydrocarbon mixture was distilled from the dinitrophenylhydrazones in the total-carbonyl determination, and this liquid phase was used for the total-olefin determination. The organic phase from the hydrogen-peroxide determination was distilled and a center cut was collected which was used for the C_8 olefin determination. This was a simple distillation for the purpose of removing products with low or high boiling points which might interfere with the determination of the unsaturation in the C_8 fraction.

ANALYTICAL METHODS

Total Peroxides

Total peroxides were determined iodometrically. A piece of dry ice was added to 10 cubic centimeters of glacial acetic acid in the titration flask to sweep out the air. Excess potassium-iodide solution and an aliquot portion of the product then were added; the flask was stoppered loosely and allowed to stand 1/2 hour in the dark. The liberated iodine was titrated with 0.1-normal thiosulfate.

Hydrogen Peroxide

Hydrogen peroxide was determined colorimetrically by the procedure of Eisenberg (ref. 2) using titanium-sulfate reagent. The transmission at 420 millimicrons was measured with a spectrophotometer, and the hydrogen-peroxide content read from a standard curve prepared with known samples of hydrogen peroxide. The difference between the total-peroxide and hydrogen-peroxide determinations was assumed a measure of the organic peroxides.

Total Carbonyl

Total-carbonyl content was obtained by precipitation of the 2,4-dinitrophenylhydrazones using the reagent solution described by Shriner and Fuson (ref. 3). The precipitate was filtered, washed, and transferred to a weighing bottle after being dissolved in ether. The ether was removed and the product was dried under reduced pressure and weighed.

The chromatographic procedure of Roberts and Green (ref. 4) was investigated as a means of separating the 2,4-dinitrophenylhydrazones. This method involves the development of the chromatogram on a silicic-acid - Super Cel column with a 4-percent solution of ether in petroleum ether. However, difficulty was encountered in attempting to identify the various bands on the column, since several recrystallizations usually were necessary and the amounts of material were small. Accordingly, the chromatographic method as used so far in this work served mainly as an indication of the number of carbonyl compounds present and of their relative amounts. The following analysis is typical of a carbonyl fraction obtained by the oxidation of isooctane:

Fraction	Weight, mg	M.p. (crude), °C
1	3.6	188
2	6.1	168
3	12.8	124-134
4	29.4	156-158

Fraction 4 (most strongly adsorbed) is largely the formaldehyde derivative (melting point, 166° C); fraction 3 is largely the acetone derivative (melting point, 124° C). Fractions 1 and 2 indicate the presence of other carbonyl compounds in smaller amounts. In chromatographing such mixtures, the precipitate of mixed dinitrophenylhydrazones usually contains a small amount of the reagent itself which tends to crystallize with the derivatives. Since the reagent is more strongly adsorbed than any of the derivatives, it is removed most conveniently by chromatographing through a short column, that is, one of sufficient length to adsorb the reagent only.

In most of the work, the aldehyde component of the total carbonyl was determined by precipitation of the methone (5,5-dimethyldihydroresorcinol) derivative (ref. 5). In all cases this aldehyde fraction was found to be largely formaldehyde; this was determined by the melting point and by digestion with acetic acid which permits the separation of the methone derivative of formaldehyde from those of other aldehydes (ref. 5).

Aldehyde

Miscellaneous analytical procedures used on occasion for approximating aldehyde content, or as a qualitative check for acetone, comprised the bisulfite titration (ref. 6) and the acetone-o-nitrobenzaldehyde reaction to yield indigo (ref. 7).

Total Olefins

Total olefins were determined throughout most of this work by the catalytic hydrogenation procedure (ref. 8) rather than the bromate-bromide titration. This was necessary since bromine substitution is an appreciable factor with the more highly branched hydrocarbons. Hydrogenation of the product from isobutane was not attempted, however, because of its extreme volatility; in this case a cold isooctane solution of the hydrocarbon fraction was titrated with a freshly standardized solution of bromine in carbon tetrachloride.

Identification of the olefin fraction was attempted only with the isooctane oxidation products. In this case, isobutylene and diisobutylene were found to be the major olefin constituents. The identity of other olefins which may be present was not established, but it is probable that there are traces in the C_7 range. In addition, with one of the earlier isooctane oxidations, a polymeric material was observed about the exit end of the tube and on the walls of the receiver. The reactor tube in this case extended some 6 inches below the end of the furnace, and apparently this polymeric material resulted from further reaction of the isobutylene and radical fragments before passing into the dry-ice - chloroform - cooled receivers. In subsequent reactions, the reactor tube extended only about 2 inches below the end of the furnace; the formation of this polymeric material has not been observed under these conditions.

Identification of isobutylene and diisobutylene in one of the typical isooctane reaction products (obtained at 550° C and contact time of 0.23 second) was carried out as follows: The temperature of the reaction mixture was allowed to rise from -70° C to room temperature; a small amount of volatile material which was distilled from the mixture was collected in a cold trap. Water was added to dissolve any carbonyl compound and the volatile material was allowed to distill into a cold trap containing bromine. Two samples of pure isobutylene were brominated, one with an aqueous solution of bromine, and the other with pure bromine. Refractive indices were taken on these three samples:

Dibromides	Refractive index n_D^{27}
Isobutylene with -	
Bromine water	1.5158
Pure bromine	1.5157
Sample	1.5154

From these results it is concluded that the olefin fraction contains an appreciable quantity of isobutylene.

The reaction mixture was fractionated and it was observed that the fraction coming over at the boiling point of isooctane contained a definite olefin concentration (by bromine titration). Dry hydrogen bromide (from a bromine-tetralin generator) was passed into the remaining portion of this fraction. The isooctane was removed by a simple vacuum distillation leaving a small amount of a bromo derivative. This derivative was compared with a derivative obtained in a similar fashion from a known diisobutylene-isooctane mixture. The refractive index of the standard was 1.4550 and for the sample 1.4565. The conclusion made on the basis of these data is that one or more C_8 olefins are present in the reaction mixture, and that this C_8 olefin fraction contains the components of diisobutylene.

Acids

Acids were determined by titration with 0.01- or 0.1-normal sodium hydroxide, using phenolphthalein indicator.

PRECISION OF MEASUREMENTS

Contact times were calculated by assuming ideal gas behavior and thus determining the contact time based on the volume of the reaction tube and the rate of flow of the fuel-oxygen mixture.

The precision of the analytical procedures has not been determined accurately. Most of the references cited indicate that the absolute accuracies of the determinations employed are suitable for the present purposes. The major limitation upon the precision of the present work has been in the recovery and separation of the small amounts of products obtained. With this in mind, most results have been given to only two significant figures; where the extent of reaction was small, only one significant figure is reported. This degree of precision is believed ample in view of the major objective of the work, that is, to identify some of the early reaction products and to show the trends in relative amounts of these products with conditions and extent of reaction.

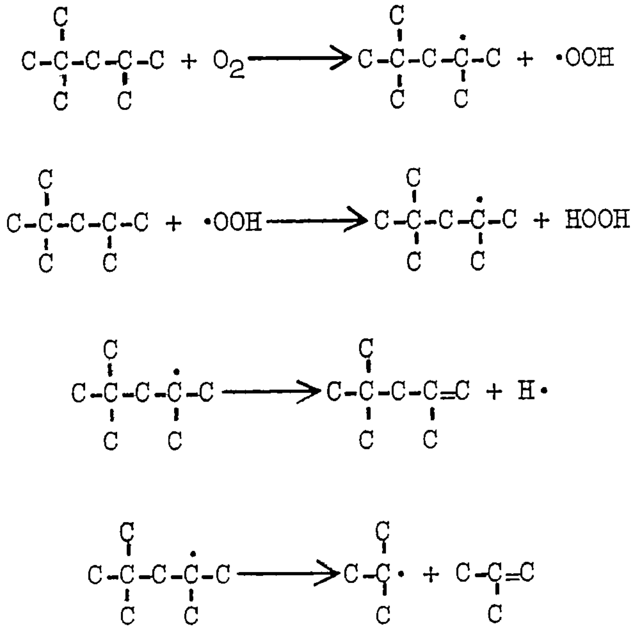
The study of isooctane oxidation was more thorough and the data more extensive than with the other hydrocarbons investigated. In addition, the oxidation of n-heptane was less readily controlled and gave rise to a greater variety of products. Accordingly, the results of the isooctane work undoubtedly are more precise than those of the other hydrocarbons listed. This will be pointed out in greater detail in the next section.

RESULTS AND DISCUSSION

Isooctane

Tables I and II and figure 3 summarize the more significant data obtained on the oxidation of isooctane at several temperatures and contact times and at a single molar ratio of oxygen to hydrocarbon of 12:1. The major reaction products at very short contact times are hydrogen peroxide, isobutylene, and diisobutylene. The small diameter of the reaction tube is probably as important a factor leading to this specificity of reaction as is the short contact time. Thus, the greatly enhanced wall effect under these conditions would be expected to suppress chain-branching reactions effectively and prevent their ascendency over the simpler process leading to hydrogen peroxide and olefins.

These data might suggest that the major initial reactions under these conditions comprise the following:



$$C-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}-C + O_2 \longrightarrow C-\underset{C}{\overset{C}{C}}-C-\underset{C}{\overset{\bullet}{C}}-C + \cdot OOH$$

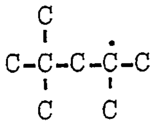
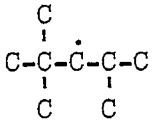
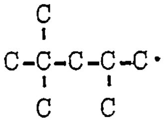
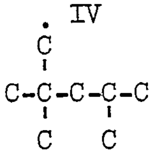
$$C-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}-C + \cdot OOH \longrightarrow C-\underset{C}{\overset{C}{C}}-C-\underset{C}{\overset{\bullet}{C}}-C + HOOH$$

$$C-\underset{C}{\overset{C}{C}}-C-\underset{C}{\overset{\bullet}{C}}-C \longrightarrow C-\underset{C}{\overset{C}{C}}-C-\underset{C}{C}=C + H\cdot$$

$$C-\underset{C}{\overset{C}{C}}-C-\underset{C}{\overset{\bullet}{C}}-C \longrightarrow C-\underset{C}{\overset{C}{C}}\cdot + C-\underset{C}{C}=C$$

This mechanism starts with an attack at the tertiary hydrogen atom of isooctane just as is commonly proposed. There are three reasons why an alternative mechanism is proposed to account for these and subsequent oxidation products: (1) The presence of 17 primary and secondary hydrogens in the molecule, (2) the known shielding effect of nine hydrogen atoms on a position, which is five atoms removed (here, the tertiary hydrogen) (ref. 9), and (3) the failure to isolate any appreciable quantity of hydroperoxide.

From a compilation of the available data on the combustion of paraffins, Boord (ref. 10) has shown that the approximate relative reactivity of primary, secondary, and tertiary C-H bonds is 1:3.6:6.9. The total reactivity of the various C-H bonds in isooctane then could be estimated as follows:

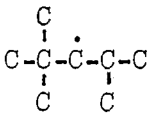
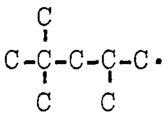
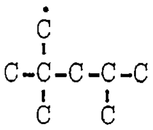
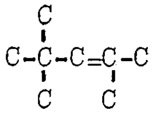
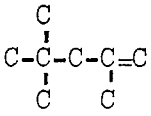
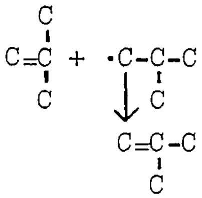
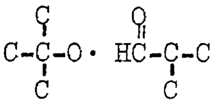
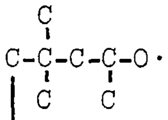
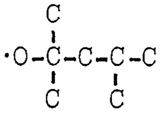
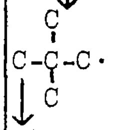
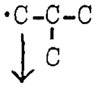
	I 	II 	III 	IV 
Number of C-H bonds	1	2	6	9
Reactivity of C-H bond	7	3.6	1	1
Total reactivity of bonds	7	7	6	9

The above tabulation would predict approximately the same contribution of each of the four radicals listed to the total oxidation products. The general agreement of these relative reactivity ratios throughout the field of free-radical chemistry is too consistent to permit one to formulate a combustion mechanism based solely on attack at the tertiary C-H bond.

The above reasoning would predict that only about 25 percent of the reaction products arise from radical I. However, there is another aspect of the structure of isooctane which should be considered. Newman (ref. 9) points out numerous examples where the umbrella effect of a _t_-butyl group markedly inhibits reaction at the sixth position from the nine hydrogen atoms of the _t_-butyl group. While this "rule of six" was formulated most specifically for addition reactions, it would appear a general phenomenon that the greater the number of atoms in the six position, the greater the steric hindrance. It is therefore proposed that attack at the tertiary C-H bond in isooctane actually accounts for much less than the 25 percent of the reaction which would be predicted on a normal reactivity basis.

It is of interest that a similar explanation for the lack of reactivity of isooctane in liquid-phase oxidation recently has been suggested (ref. 11). This would explain the failure to detect appreciable quantities of organic peroxide which would be expected if reaction occurred at the tertiary C-H bond.

If the above reasoning is true, then attack at the other positions in the isooctane molecule must be able to account for the major products obtained: Isobutylene, diisobutylene, formaldehyde, and acetone. This is believed to be feasible on the basis of the following tabulation.

	II	III	IV
Radical	 $C-\overset{C}{\underset{C}{C}}-\dot{C}-\underset{C}{C}-C$	 $C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-C\cdot$	 $C-\overset{\dot{C}}{\underset{C}{C}}-C-\underset{C}{C}-C$
C_8 olefinic products	 $C-\overset{C}{\underset{C}{C}}-C=\underset{C}{C}-C$	 $C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}=C$	None
C_4 olefinic products (directly from initial radical)	None[1]	None[1]	 $C=\overset{C}{\underset{C}{C}}$ + $\cdot C-\underset{C}{C}-C$ ↓ $C=\underset{C}{C}-C$
Some of possible oxygen-containing products from C_8 radical (through ROO)	 $C-\overset{C}{\underset{C}{C}}-O\cdot$ $\overset{O}{\overset{\|}{HC}}-\underset{C}{C}-C$ ↓	HCHO +  $C-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-O\cdot$ ↓	HCHO +  $\cdot O-\overset{C}{\underset{C}{C}}-C-\underset{C}{C}-C$ ↓
Some of possible oxygen-containing products from subsequent radicals	CH_3COCH_3 + $CH_3\cdot$ ↓ etc.	 $C-\overset{C}{\underset{C}{C}}-C\cdot$ + CH_3CHO ↓ etc.	CH_3COCH_3 +  $\cdot C-\underset{C}{C}-C$ ↓ etc.

[1] May get some isobutylene if odd electron shifts to tertiary position.

Most of the diisobutylene would be expected to arise from radical II, and probably somewhat less from radical III; the major amount of isobutylene would come from radical IV. Less directly, all three radicals can give rise to isobutylene, formaldehyde, and acetone (for possible reaction mechanisms, see ref. 12). In addition, other products are obtained in smaller amounts. Any radical I formed, of course, can be shown to supplement the amounts of major reaction products formed. The above conclusions are admittedly tentative and of necessity based on considerable speculation as well as fact. However, at this stage of the work they appear to fit the data at hand better than any other.

Despite the initial dominance of the reactions leading to hydrogen peroxide and olefins, the formation of carbonyl compounds is not completely suppressed even in the earliest stages of reaction. This indicates that some of the isooctyl (and t-butyl) radicals undergo oxidation as well as cleavage and dehydrogenation. It is significant that formaldehyde has been identified as a major component of the carbonyl products even in the very earliest stages. In the over-all reaction, it also is significant that, while formaldehyde and acetone are the major carbonyl compounds, chromatographic separation of the phenylhydrazones has shown the presence of small amounts of other such products. It is suspected that isobutyraldehyde may be detectible in this mixture; if so, attack at the methylene group must have occurred. Similarly, olefins other than isobutylene and diisobutylene may be present in the hydrocarbon fraction.

As the contact time increases from 0.25 second to 0.68 second (at 550° C), the formation of hydrogen peroxide and olefins no longer dominates the reaction. This abrupt rise in the amounts of carbonyl compounds indicates that a larger number of the simple initial radicals can no longer escape reaction with oxygen molecules and, accordingly, proceed through a series of reactions such as those in the tabulation above. Finally, the formation of considerable quantities of acidic products shows a third series of reactions now coming into prominence, presumably by the oxidation of carbonyl compounds to acids. (Garner and Petty, however, suggest that acids may be formed without carbonyl intermediate (ref. 13).) At these longer contact times, the large amounts of olefins now present in the reaction mixture may be expected to participate in further reactions and thereby contribute to the complexity of the product.

n-Heptane

Results obtained from the oxidation of n-heptane are summarized in table III. The much greater ease of oxidative attack and much greater difficulty of reaction control compared with isooctane are apparent from a comparison of tables I and III. Thus, isooctane in 0.08-second contact time at 550° C gives less reaction than does n-heptane in 0.04-second contact time at 350° C. Also, raising the reaction temperature 50° with n-heptane results in a most marked increase in extent of reaction, the aldehyde fraction, for example, increasing more than a hundredfold. All these results are consistent with the view (ref. 10) that all the secondary C-H bonds in a normal paraffin are attacked with substantially the same ease and that, once initiated, a rapid chain-branching reaction ensues. It is of interest to note also that after these threshold conditions are passed (reaction 2, table III), changes in the extent and type of reaction over the next 100° temperature rise are relatively slight.

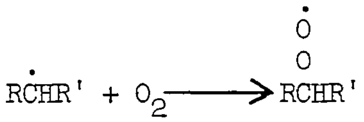
The deep-seated nature of the degradation involved from almost the very outset of n-heptane oxidation (in contrast with that of isooctane) is most apparent from the formation of large amounts of carbonyl compounds. These were much more complex mixtures than those obtained from isooctane and, as evidenced by the blank spaces in table III, were considerably more difficult to isolate quantitatively. Thus, extraction of the hydrocarbon phase with water failed to remove all the carbonyl compounds, suggesting the presence of ketones and aldehydes containing four or more carbon atoms (cf. ref. 13). Under conditions of reaction 5 the ratio of aldehyde to ketone was indicated to be approximately 5:2 by determining total carbonyl as the phenylhydrazones and total aldehyde as the methone derivatives. Treatment of the methone derivatives of the aldehydes with acetic acid (ref. 5) gave a molar ratio of formaldehyde to other aldehydes of approximately 6:1. Chromatographic separation of the dinitrophenylhydrazones of the water-soluble carbonyl compounds gave a molar ratio of formaldehyde to total carbonyl of 5:1. While it is not possible to relate these ratios directly, all evidence points to the formation of formaldehyde as the major carbonyl product.

The dominance of organic peroxides over hydrogen peroxide at 350° C and the marked increase in hydrogen-peroxide formation at higher temperatures are believed significant indications of the reaction mechanisms involved. At 350° C, the reactivity of the oxygen molecule is slight, so that the amount of hydrogen peroxide formed by the initiation reactions (1a) and (1b) is relatively small:

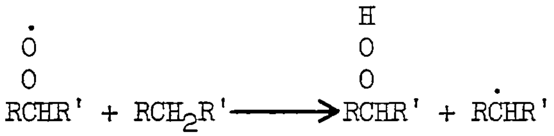
$$RCH\,R'_2 + O_2 \longrightarrow R\dot{C}HR' + \cdot OOH \qquad (1a)$$

$$RCH_2R' + \cdot OOH \longrightarrow R\dot{C}HR' + HOOH \qquad (1b)$$

On the other hand, the stability of the $R\dot{C}HR'$ and $RCH(OO\cdot)R'$ radicals is adequate to permit fairly efficient chain propagation, as in equations (2) and (3):



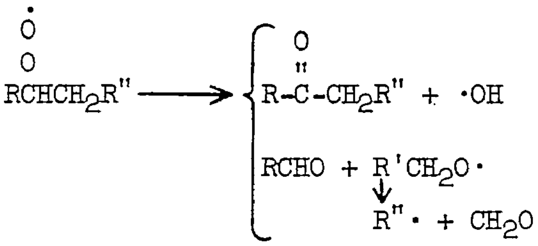
$$R\dot{C}HR' + O_2 \longrightarrow R\overset{\overset{\dot{O}}{\overset{|}{O}}}{C}HR' \tag{2}$$



$$R\overset{\overset{\dot{O}}{\overset{|}{O}}}{C}HR' + RCH_2R' \longrightarrow R\overset{\overset{H}{\overset{|}{O}}}{\overset{|}{O}}\!\!CHR' + R\dot{C}HR' \tag{3}$$

From 400° to 500° C, the reactivity of the oxygen molecule has increased sufficiently (see ref. 14) to permit the formation of hydrogen peroxide in much larger amounts (eqs. (1a) and (1b)). Since at the same time the thermal stability of the $R\dot{C}HR'$ and $RCH(OO\cdot)R'$ radicals will have decreased, reactions (2) and (3) leading to organic peroxide now are of relatively minor importance because of the ascendency of the decomposition reactions (4) and (5):

$$R\dot{C}HCH_2R'' \longrightarrow RCH{=}CHR'' + H\cdot \tag{4}$$



$$R\overset{\overset{\dot{O}}{\overset{|}{O}}}{C}HCH_2R'' \longrightarrow \begin{cases} R{-}\overset{O}{\overset{\|}{C}}{-}CH_2R'' + \cdot OH \\ RCHO + \underset{\displaystyle R''\cdot + CH_2O}{\underset{\downarrow}{R'CH_2O\cdot}} \end{cases} \tag{5}$$

This view of the initial stages of the reaction is not only consistent with the data of table III but also with the more recent concepts of hydrocarbon oxidation (ref. 12). Exploratory reactions on two additional hydrocarbons, isobutane and 2,2,5-trimethylhexane, also lend support to the above generalizations.

2,2,5-Trimethylhexane

The oxidation of 2,2,5-trimethylhexane is of particular interest for comparison with that of isooctane. As expected, this hydrocarbon lies between isooctane and n-heptane in ease of oxidative attack. As shown in table IV, it is less oxidized in 0.04 second at 450° C than is n-heptane at 350° C. The 2,2,5-trimethylhexane resembles n-heptane in that organic peroxide is dominant over hydrogen peroxide in the initial reaction products. On the other hand, it resembles isooctane in that the yield of olefins exceeds the yield of carbonyl compounds through an appreciable period of the initial reaction (compare reaction 3, table I, reaction 2, table IV, and reactions 1 and 2, table III).

Isobutane

Like isooctane, isobutane yields mainly hydrogen peroxide and olefin in the early stages of reaction (table V). This is consistent with the structural similarities of these two hydrocarbons and with the fact that both require high temperatures for appreciable oxidative attack. These similarities are apparent from a comparison of reactions 2 and 3 in table I with reactions 1 and 2 in table V. While the data on isobutane are not so complete as those on isooctane, certain differences also are indicated. One of these is the somewhat greater ease of oxidative attack of isooctane, which is in line with its higher molecular weight and, accordingly, greater number of C-H bonds. Another is the higher ratio of hydrogen peroxide to organic peroxide obtained with isooctane.

Hydrogen-Peroxide Formation

Observations regarding hydrogen-peroxide formation are not only of theoretical interest but also of potential commercial importance. For this reason, the data on hydrogen-peroxide formation from all four hydrocarbons studied are listed in table VI at several temperatures and extents of reaction. While the information is not directly comparable, a sufficient number of points are available to indicate certain trends.

These trends fit in with the general concepts already outlined regarding the effect of reaction temperature on the facility with which the oxygen molecule can attack the hydrocarbon directly and on the stability of the alkyl radicals formed. Thus, hydrogen peroxide is obtained most efficiently (i.e., in highest percentage yield) from isooctane, apparently because it combines difficulty of oxidative attack with poor thermal stability of the alkyl radicals initially formed. Isobutane is slightly more difficult to attack but gives slightly more organic peroxide, apparently because of a somewhat greater stability of the alkyl radicals formed. Accordingly, at optimum conversions (that is, less than 20 percent of the hydrocarbon reacting), the percentage yield of hydrogen peroxide from the four hydrocarbons investigated lies in the order of isooctane>isobutane>2,2,5-trimethylhexane>_n_-heptane.

CONCLUSIONS

Analysis of the products obtained by the vapor-phase oxidation of isooctane, _n_-heptane, 2,2,5-trimethylhexane, and isobutane at temperatures of 350° to 550° C, contact times of 0.04 to 0.68 second, and in a 1/16-inch-diameter reactor has led to the following conclusions regarding the initial reaction processes:

1. If a hydrocarbon is attacked at temperatures where the alkyl and peroxy radicals have adequate thermal stability, the hydroperoxide can be obtained as the major product.

2. If the hydrocarbon is attacked at higher temperatures where the peroxy radical is quite unstable and the alkyl is still fairly stable, carbonyl compounds can be obtained as the major products, with olefins of secondary importance.

3. If the hydrocarbon is attacked at temperatures so high that decomposition of the alkyl radical tends to occur before the peroxy radical can form, olefins and hydrogen peroxide will comprise the major products.

4. The structure of the hydrocarbon influences not only the ease of oxidative attack but also the thermal stability of the alkyl and peroxy radicals formed. Accordingly, the extent to which the initial reaction follows course 1, 2, or 3 will depend upon structural factors as well as temperature.

5. Major products obtained at successive stages in the oxidation of isooctane comprise: (a) Hydrogen peroxide and olefins and (b) formaldehyde and acetone. Acids come into prominence only after relatively large amounts of carbonyl compounds have formed.

6. The failure of isooctane to yield appreciable quantities of organic peroxide, together with other considerations, leads to the proposal that the initial oxidative attack occurs largely at the primary and secondary C-H bonds rather than at the tertiary C-H bond.

7. Major products obtained at successive stages in the oxidation of n-heptane comprise: (a) Organic peroxides and (b) carbonyl compounds (mainly formaldehyde). Stage (b) develops with much greater ease and rapidity than in the case of isooctane.

8. The resistance to oxidative attack is in the following order: Isobutane>isooctane>2,2,5-trimethylhexane>n-heptane.

9. In line with general conclusions 1 to 4, the potential efficiency of hydrogen-peroxide formation from these hydrocarbons is indicated to be in the following order: Isooctane>isobutane>2,2,5-trimethylhexane>n-heptane.

University of Cincinnati,
Cincinnati, Ohio, Sept. 10, 1952.

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TABLE I

ANALYSIS OF ISOOCTANE-OXYGEN REACTION MIXTURES

[Molar ratio:Oxygen:Hydrogen = 12:1]

Reaction mixture number	1	2	3	4	5	6	7	8
Conditions:								
Composition, mole fuel/mole oxygen	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Temperature, °C	550	550	550	550	550	450	450	350
Contact time, sec	0.04	0.08	0.16	0.24	0.68	0.24	0.68	0.24
Analyses:								
Hydrogen peroxide, millimoles/mole isooctane passed through reaction tube	0.51	1.6	5.5	7.4	89.0	0.8	14.7	----
Other peroxides, millimoles/mole isooctane passed through reaction tube	0.05	0.16	0.23	0.28	3.0	[a]0.5	1.4	----
Olefin total, millimoles/mole isooctane passed through reaction tube	0.8	3.5	14	25	150	2	46	Trace
Olefin, C_8, millimoles/mole isooctane passed through reaction tube	0.8	1.8	7	9	64	[a]2	26	Trace
Carbonyl total[b], millimoles/mole isooctane passed through reaction tube	Trace	1.1	3.5	6.3	254	Trace	35	-----
Formaldehyde, millimoles/mole isooctane passed through reaction tube	Trace	0.6	1.3	2.1	97	Trace	12	-----
Acid, millimoles/mole isooctane passed through reaction tube	-----	----	----	0.33	48	-----	6.5	-----

[a] Approximate content.

[b] Assuming an average molecular weight of carbonyl compounds of approximately 44.

TABLE II

RELATIVE VALUES OF ANALYSES IN TABLE I BASED ON VALUE OF HYDROGEN PEROXIDE OF 10

Reaction mixture number	1	2	3	4	5	7
Conditions:						
Temperature, °C .	550	550	550	550	550	450
Contact time, sec	0.04	0.08	0.16	0.24	0.68	0.68
Relative values:						
H_2O_2	10	10	10	10	10	10
Other peroxides .	1.0	1.0	0.42	0.38	0.33	0.96
Total olefin . . .	16	22	26	34	17	32
C_8 olefin	16	11	13	12	7.2	18
Total carbonyl . .	----	7	6.4	8.5	29	24
Formaldehyde . . .	----	3.8	2.4	2.8	11	8.4
Acid	----	----	----	0.45	5.4	4.5

TABLE III

ANALYSIS OF n-HEPTANE-OXYGEN REACTION MIXTURES

Reaction mixture number	1	2	3	4	5
Conditions:					
Composition, mole fuel/mole oxygen	0.09	0.09	0.09	0.09	0.09
Temperature, °C	350	400	450	500	350
Contact time, sec	0.04	0.04	0.04	0.04	0.08
Analyses:					
Hydrogen peroxide, millimoles/mole n-heptane passed through reaction tube	0.3	63	79	86	37
Other peroxides, millimoles/mole n-heptane passed through reaction tube	9.1	11.3	2.1	1.0	10.4
Olefin, millimoles/mole n-heptane passed through reaction tube	2.9	58	78	93	[a]70
Total carbonyl, millimoles/mole n-heptane passed through reaction tube	----	----	----	----	[a]360
Aldehydes[b], millimoles/mole n-heptane passed through reaction tube	2.6	360	360	310	250
Acid, millimoles/mole n-heptane passed through reaction tube	4.0	57	60	40	34

[a] Approximate content.

[b] Obtained with methone reagent and, for simplicity, considering derivative mixture to have molecular weight of formaldehyde derivative (292).

TABLE IV

ANALYSIS OF 2,2,5-TRIMETHYLHEXANE-OXYGEN REACTION MIXTURES

Reaction mixture number	1	2
Conditions:		
Composition, mole fuel/mole oxygen	0.07	0.07
Temperature, °C	450	420
Contact time, sec	0.04	0.08
Analyses:		
Hydrogen peroxide, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	0.03	6.8
Other peroxides, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	2.0	5.7
Olefin, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	0.4	16
Total carbonyl, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	Trace	12
Formaldehyde, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	None	[a]2.1
Acid, millimoles/mole 2,2,5-trimethylhexane passed through reaction tube	None	3.7

NACA

[a] Approximate content.

TABLE V

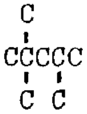
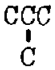
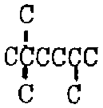
ANALYSIS OF ISOBUTANE-OXYGEN REACTION MIXTURES

Reaction mixture number	1	2
Conditions:		
Composition, mole fuel/mole oxygen	0.15	0.15
Temperature, °C	550	550
Contact time, sec	0.08	0.16
Analyses:		
Hydrogen peroxide, millimoles/mole isobutane passed through reaction tube	1.2	3.6
Other peroxides, millimoles/mole isobutane passed through reaction tube	0.6	0.8
Olefin, millimoles/mole isobutane passed through reaction tube	[a]2.5	[a]5.6
Total carbonyl, millimoles/mole isobutane passed through reaction tube	[a]0.2	[a]0.8
Formaldehyde, millimoles/mole isobutane passed through reaction tube	[a]0.1	[a]0.4
Acid, millimoles/mole isobutane passed through reaction tube	----	----

[a] Approximate content.

TABLE VI

H_2O_2/ROOH RATIO

Structural unit	Temperature, °C	Approximate extent of reaction (as indicated by sum of olefin, carbonyl, and acid), millimoles/mole hydrocarbon									
		0.5	1.0	2.0	5.0	10	20	50	100	200	500
 $C\overset{C}{\underset{C}{C}}C\underset{C}{C}C$	550		10				24				30
	450			1.6					10		
 $C\underset{C}{C}C$	550			2	4						
 $C\overset{C}{\underset{C}{C}}CC\underset{C}{C}C$	450	0.015			1.2						
CCCCCCC	500										86
	350					0.033				3.7	

1 To flowmeter and oxygen tank
2 Hydrocarbon-oxygen bubbler
3 Vapor bath
4 Heating mantle
5 Combustion furnace
6 Steel rod $1\frac{1}{4}$ in. in diam., 12 in. long
7 Reaction tube of 1/16-in.-I.D. Pyrex
8 Traps for reaction products
9 Dewar flasks
10 Trap containing carbonyl reagent
11 Coil for mild heating

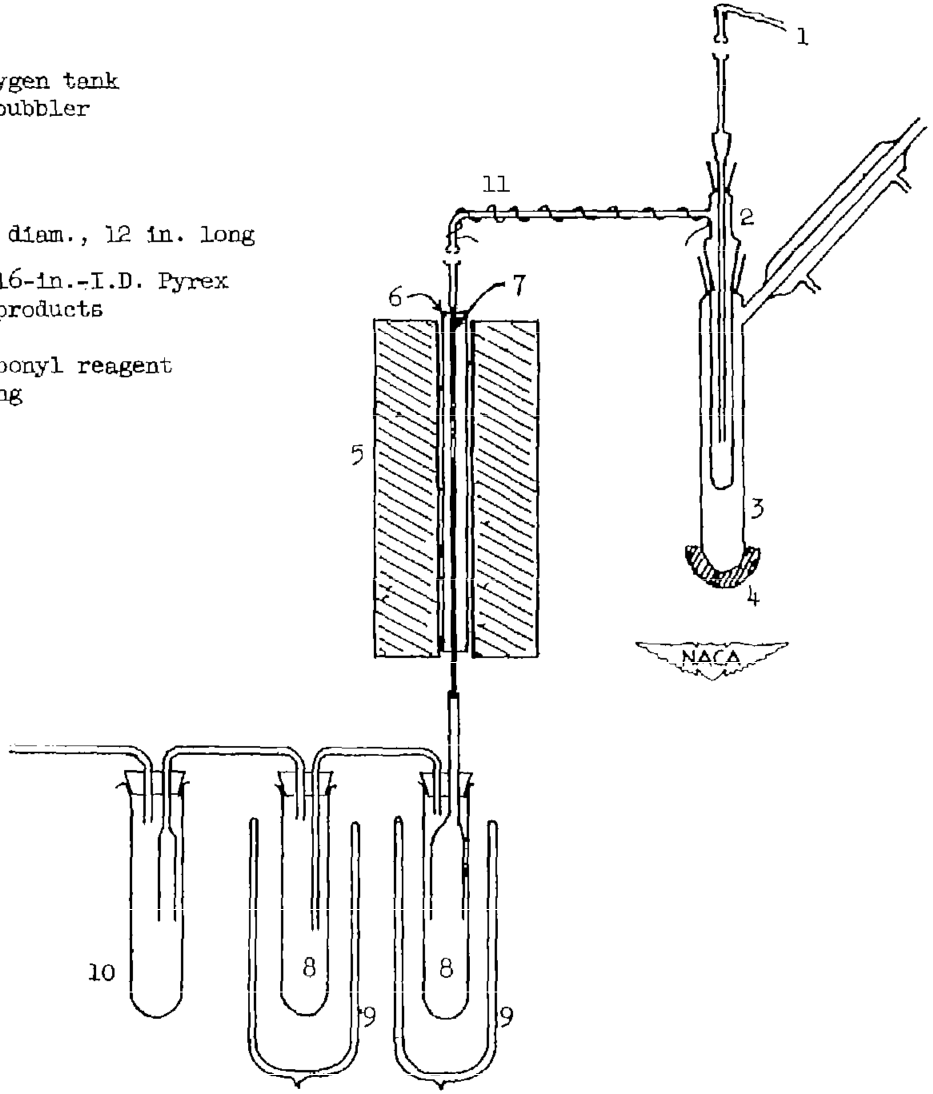


Figure 1.- Apparatus.

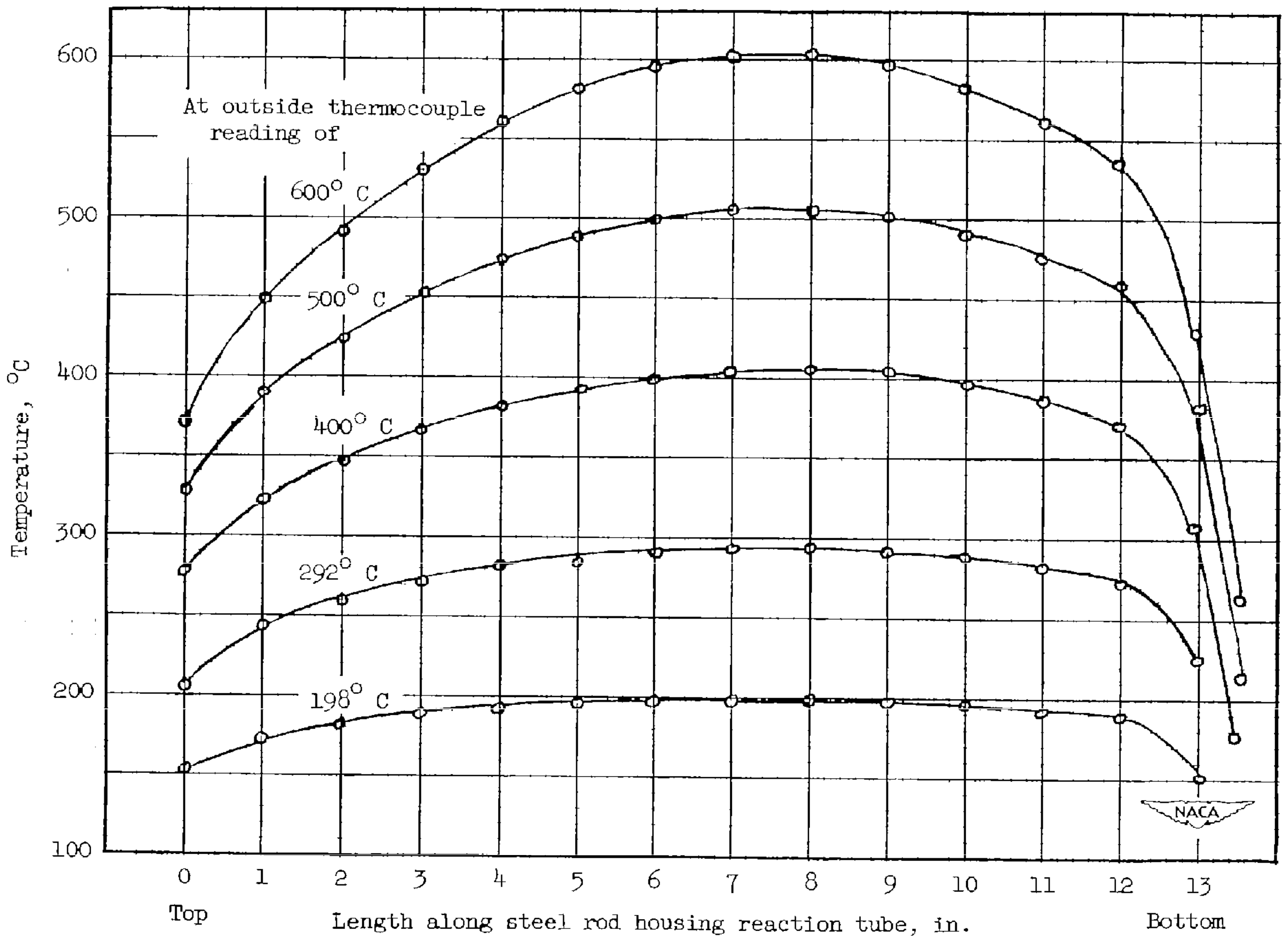


Figure 2.- Temperature distribution in reactor tube.

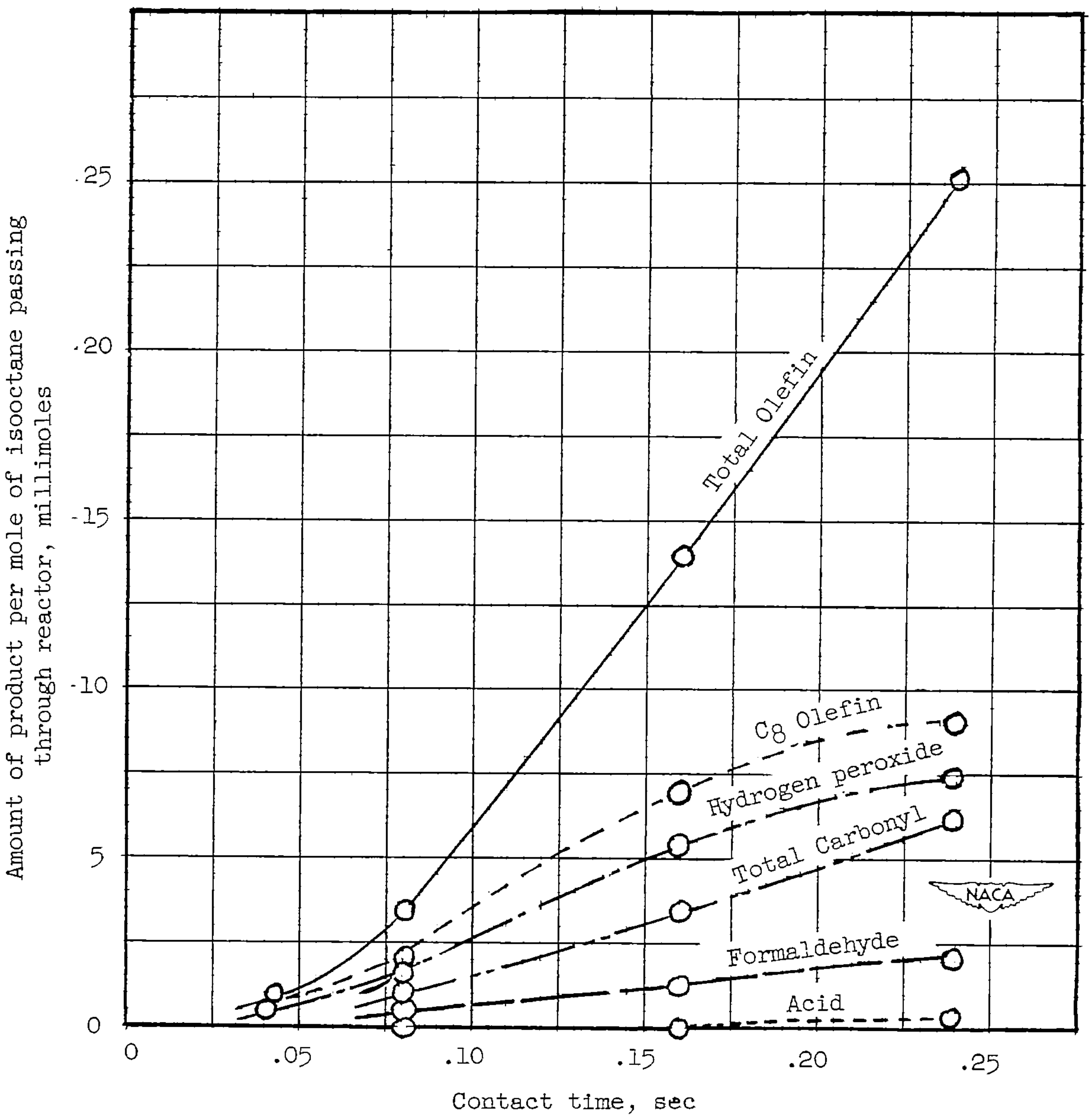


Figure 3.- Product composition of a series of isooctane-oxygen reaction mixtures from runs at 550° C and various contact times.