Summary

1. When triacetylinulin is dissolved in chloroform and acted on by nitric acid the greater part of the material is converted into triacetylfructose dinitrate, the esterification being preceded by the opening of the anhydro-linkages.

2. One component of triacetylinulin present to the extent of 20% is resistant to the hydrolytic action and is isolated as triacetyl-anhydrofructose (m. p. 123°; $[\alpha]_D + 1.5°$ in chloroform). The same compound can be obtained in similar yield from other reactions in which triacetylinulin is used as the starting material.

3. Anhydrofructose (m. p. 143–145°; $[\alpha]_D + 30.17°$ in water) has been prepared from the triacetate by the action of dimethylamine. The compound is quantitatively convertible into fructose but is much more stable toward hydrolysts than the known derivatives of γ-fructose.

4. Anhydrofructose has been converted into trimethyl-anhydrofructose, which was isolated in a dimeric form.

5. The main conclusion drawn is that inulin is not related exclusively to a single form of γ-fructose but contains two classes of components in the approximate ratio of 4:1. Of these, one is relatively much more stable toward hydrolysis. The additional complication introduced into the constitutional study of inulin through these results is discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. II. OCTANES WITH BRANCHED CHAINS

BY J. C. POPE, F. J. DYKSTRA AND GRAHAM EDGAR

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I. Introduction

In Part I of this paper[1] data were presented on the vapor phase oxidation of *n*-octane, which indicated that under the conditions in question the oxidation proceeds almost entirely according to certain simple reactions. These reactions are: (1) the formation of octaldehyde; (2) the oxidation of octaldehyde to carbon monoxide, water and aldehydes of successively smaller number of carbon atoms; and (3) a side reaction in which octaldehyde is oxidized to carbon dioxide, water and aldehydes of successively smaller number of carbon atoms.

In Part II data are presented on the vapor phase oxidation of five isomeric octanes, 3-methylheptane, 3-ethylhexane, 2-methyl-3-ethylpentane, 2,5-dimethylhexane and 2,2,4-trimethylpentane. These data were ob-

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[1] Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875 (1929).

tained in the course of a general survey of the oxidation characteristics of hydrocarbons, and are consequently somewhat fragmentary in nature. In three of the five cases only a single experiment was carried out, and the temperature range covered was not always as great as could be wished. Nevertheless, the data, when taken in conjunction with the much more detailed study of *n*-octane, seem to throw much light on the oxidation characteristics of branched-chain hydrocarbons, about which no information has been available heretofore, and it has been thought wise to publish them in their present form, since circumstances have prevented this Laboratory from carrying out the work more exhaustively.

The data are of especial interest in connection with the behavior of these hydrocarbons as fuels in the internal combustion engine, a subject which will be discussed in Part III of this paper.

II. Apparatus and Experimental Methods

(a) **General.**—The apparatus and experimental procedure were identical with those described in Part I. The runs were made with slowly rising temperature, except in the case of 2,5-dimethylhexane, in which several runs under constant temperature conditions were carried out.

(b) **Materials.**—The hydrocarbons were synthesized in this Laboratory by methods analogous to those described for the isomeric heptanes,[2,3] with the exception of 2,2,4-trimethylpentane, which was synthesized by the method described by Edgar.[4] The boiling points indicated a fair state of purity and were as follows: 3-methylheptane, 117.5–120.5°; 3-ethylhexane, 116–119°; 2-methyl-3-ethylpentane, 113–116°; 2,5-dimethylhexane, 108–110°; 2,2,4-trimethylpentane, 99.2–99.4°.

III. Experimental Data

(a) **General.**—The experimental data are expressed graphically in Figs. 1, 2, 3, 4 and 5, in which the oxygen consumed and the carbon oxides formed per mole of octane input are plotted against the temperature. As in the case of *n*-octane, the temperatures are the average values for the few degrees temperature range during sampling. The oxygen–fuel ratios were not always the theoretical values for complete combustion (12.5 moles O_2 to 1 mole octane), but they were usually not far from this value. The actual values are given in the figures.

(b) **Individual Cases.**—Before discussing the data it seems desirable to point out certain facts in connection with the behavior of the individual hydrocarbons. It will be recalled that in the case of *n*-octane, two abrupt changes in the nature of the reaction occurred, each involving luminescence

[2] Edgar, Calingaert and Marker, This Journal, 51, 1483 (1929).

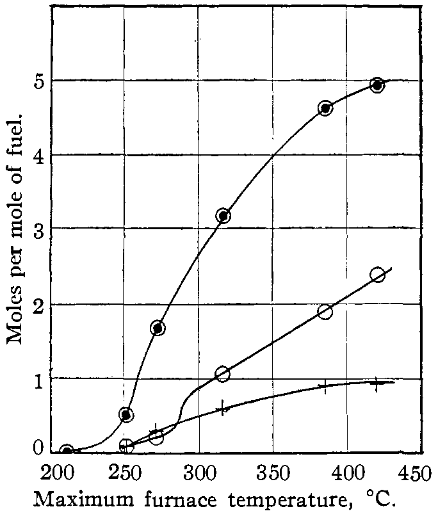
[3] The authors are indebted to Dr. J. W. McKinney and Mr. R. E. Marker for the actual preparations.

[4] Edgar, *Ind. Eng. Chem.*, 19, 145 (1927).

and strong pulsations in the oxygen and nitrogen flowmeters. The first of these was considered to be due to the incidence of a "chain" reaction involving the oxidation of an aldehyde to carbon monoxide, another aldehyde and water; the second, occurring at much higher temperatures, involved complete oxidation of all products to carbon dioxide and water. For the sake of convenience these phenomena will be referred to as "low temperature disturbance" and "high temperature disturbance," respectively.

In the case of 3-methylheptane and 3-ethylhexane low-temperature disturbances, similar to those of *n*-octane, were observed, occurring between temperature ranges of 280–305 and 285–302°, respectively. In the other three cases the low temperature disturbance was not observed.

The high-temperature disturbance was observed in the cases of 3-ethyl-hexane, 2-methyl-3-ethylpentane and 2,2,4-trimethylpentane, occurring at 510, 526 and 560°, respectively. In the other two cases, the temperatures were not carried high enough for such disturbances to occur, but judging from the behavior of many hydrocarbons studied by this Laboratory, this phenomenon would undoubtedly have occurred had the temperatures been carried high enough.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 1.—3-Methylheptane (oxygen/fuel ratio = 9.6/1).

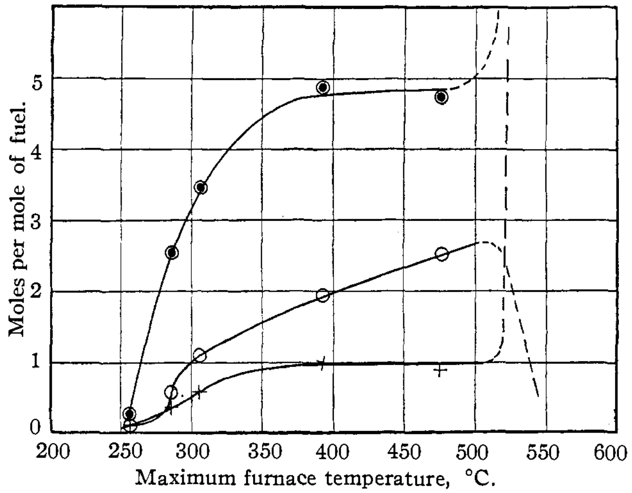
As in the case of *n*-octane, the low temperature disturbance was accompanied by an increase in the rate of formation of carbon monoxide, and the high-temperature disturbance by complete reaction to carbon dioxide and water.

NOTE.—In the case of 2-methyl-3-ethylpentane an experimental point was obtained at 431° in which very much less oxidation had occurred than at somewhat lower temperatures. A negative temperature coefficient of reaction is frequently observed in reactions of the type studied, but in the case in question the drop in the reaction rate is so pronounced as to suggest experimental error, such as might be caused by a temporary clogging of the fuel feed, or leakage of air into the sampling tube. There was no evidence of such occurrence, but it has been thought advisable to regard this experimental point as of doubtful significance when unverified by other determinations, and the curve has been drawn accordingly.

In the case of 2,5-dimethylhexane, the data refer to a series of constant temperature runs, rather than rising temperature runs, as in the other cases. Judging from the authors' experience with *n*-octane these data should, however, be reasonably comparable with the others.

IV. Discussion of Data

(a) General.—It might be expected that differences in resistance to oxidation would exist among these hydrocarbons, but no previous data are available to suggest the course of the reaction in such cases. It has been indicated by Stephens,[5] in the case of aromatic hydrocarbons with aliphatic side chains, that the oxidation of such hydrocarbons begins at a secondary carbon atom, but the nature of the hydrocarbons and the experimental conditions were so different from those involved in the present investigation as to make his conclusions of doubtful applicability.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 2.—3-Ethylhexane (oxygen/fuel ratio = 12.6/1).

Inspection of Figs. 1, 2, 3, 4 and 5 shows that distinct differences actually exist in the behavior of the different hydrocarbons. With the exception of the data for 2,2,4-trimethylpentane, the various curves show a marked similarity in general nature to those for *n*-octane (Part I), the oxygen consumption curves, for example, rising rather abruptly at temperatures below 300° and then showing little further rise over a considerable temperature range. The extent to which oxidation proceeds, however, before the reaction slows down, varies greatly among the different hydrocarbons. 2,2,4-Trimethylpentane shows characteristics differing from the others. The significance of these variations will be discussed below.

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[5] Stephens, This Journal, 50, 2523 (1928).

Although the data are not as complete as could be wished, it seems desirable to subject them to careful scrutiny in order to determine if possible (1) whether the reaction mechanism is similar to that of *n*-octane, and (2) the point of initial attack. These two questions will, therefore, be considered in order.

(b) **Main Course of Reaction.**—In the case of *n*-octane it was found that the total oxygen consumption per mole of octane input (at temperatures below the high-temperature disturbance) was very nearly equal to the total of one mole (to form an aldehyde), plus the number of moles of carbon monoxide (since the oxidation of an aldehyde to 1 mole of carbon monoxide, water and another aldehyde requires one mole of oxygen), plus 1.5 times the number of moles of carbon dioxide (since the oxidation of an aldehyde to carbon dioxide, water and another aldehyde requires 1.5 moles of oxygen), indicating that no other reactions than those suggested were occurring to an appreciable extent. Calculations on a similar basis for the four isomeric octanes, which are oxidized at low temperatures, give the results in Table I.

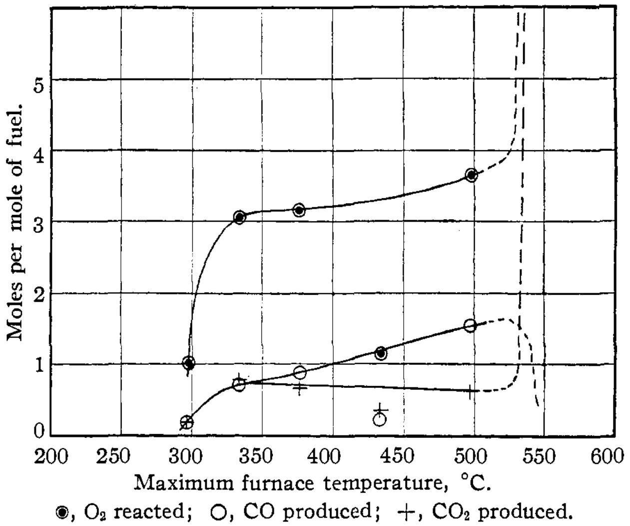


Fig. 3.—2-Methyl-3-ethylpentane (oxygen/fuel ratio = 11.75/1).

The experimental data for oxygen reacted agree reasonably well in most cases with those calculated, suggesting that the mechanism of oxidation is analogous to that of *n*-octane. The oxygen consumed is usually slightly greater than that calculated, indicating that a small amount of oxygen may have reacted to form olefins (small amounts of gas absorbable in fuming sulfuric acid were found experimentally) or some products other than those involved in the theory, but such reactions cannot be a major factor in the

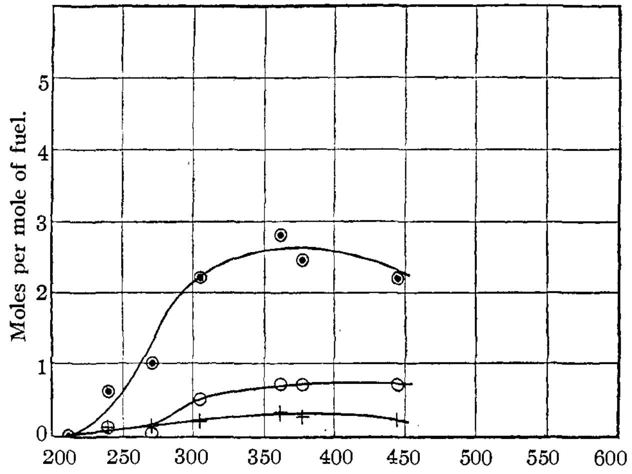
TABLE I

RESULTS OF CALCULATIONS

Moles of CO	Moles of CO_2	Moles of O_2 consumed	(1 + CO + 1.5 CO_2)	Moles of CO	Moles of CO_2	Moles of O_2 consumed	(1 + CO + 1.5 CO_2)
	3-Methylheptane				2-Methyl-3-ethylpentane		
0.2	0.3	1.65	1.65	0.75	0.8	3.05	2.95
1.1	.6	3.2	3.0	.90	.65	3.20	2.90
1.9	.9	4.6	4.25	.20	.3	1.15	1.65
2.4	.95	4.9	4.85	1.55	.60	3.70	3.45
	3-Ethylhexane				2,5-Dimethylhexane		
0.6	0.35	2.55	2.15	0.50	0.2	2.2	1.80
1.1	.6	3.45	3.0	.7	.30	2.80	2.15
1.95	1.0	4.90	4.45	.7	.25	2.45	2.07
2.5	.9	4.75	4.85	.7	.2	2.20	2.00

Data for 2,2,4-trimethylpentane are not included since it does not exhibit the low-temperature oxidation phenomena shown by the others.

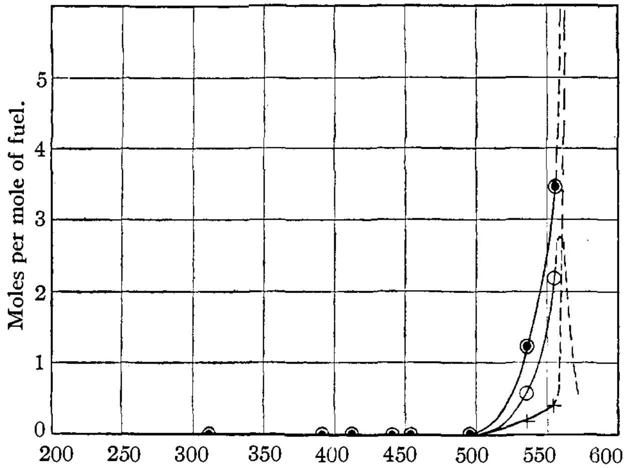
oxidation, since nearly all of the oxygen consumed is accounted for on the hypothesis outlined above. It seems reasonable, therefore, to assume for the four cases cited that, as in the case of *n*-octane, the primary product of oxidation is an aldehyde; that this aldehyde is further oxidized (a) by a "chain" reaction producing aldehyde, carbon monoxide and water and (b) by a reaction producing aldehyde, carbon dioxide and water; and that these reactions proceed until products are formed which resist further oxidation until temperatures are reached which are high enough for general disintegration to occur, accompanied by complete oxidation to carbon dioxide and water.



◉, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 4.—2,5-Dimethyhexane (oxygen/fuel ratio = 9.1/1).

(c) **Point of Initial Attack.**—The data in the preceding paragraph indicate that the point of initial attack is a methyl group, rather than a secondary or tertiary atom. This view is substantiated by several facts: (1) the over-all similarity of the oxidation curves to that of *n*-octane and the similar phenomena observed during the reaction; (2) the hydrocarbons containing secondary or tertiary atoms are more resistant to oxidation than those not containing them, and the more highly condensed the structure, the more resistant the hydrocarbons become; (3) oxidation of secondary carbon atoms would be expected to result in a rapid degradation of the hydrocarbon into molecules of low molecular weight, which would be oxidized with difficulty even in the form of aldehydes (see Part I). The result of such reactions would be a large consumption of oxygen without production of correspondingly large amounts of carbon oxides, which is contrary to the experimental data. It appears, therefore, that secondary and tertiary atoms are points of strength rather than weakness, and that the initial attack is at a methyl group, as in the case of *n*-octane. With *n*-octane, however, only the methyl groups at the ends of the molecule are available for oxidation. In the case of most of the isomeric octanes the initial attack might theoretically be at any one of several points.



●, O_2 reacted; ○, CO produced; +, CO_2 produced.

Fig. 5.—2,2,4-Trimethylpentane (oxygen/fuel ratio = 12.3/1).

Examination of Figs. 1, 2, 3 and 4 gives a clue to the actual point of attack. In the case of 2,5-dimethylhexane, the oxidation does not increase with rising temperature after a total of one atom of carbon has been oxidized away as gas. In the case of 2-methyl-3-ethylpentane the reaction stops similarly when approximately two carbon atoms have been oxidized away. In the case of 3-ethylhexane, the reaction stops when three carbon atoms have been oxidized away. In the case of 3-methylheptane more than three atoms of carbon have been oxidized away at the highest temperature recorded, and the reaction is still increasing with rising temperature. Now the longest unbranched, open-end straight chain of these compounds is one, two, three and four carbon atoms in length, respectively. It seems reasonable, therefore, to interpret the reactions as follows. (1) Oxygen attacks the methyl group at the end of the longest open-end straight chain of the hydrocarbon, forming an aldehyde and water. (2) The aldehyde is oxidized with the formation of an aldehyde of one less carbon atom, water and either carbon monoxide or carbon dioxide. (3) This reaction proceeds until a branch in the hydrocarbon chain occurs, making the oxidation product a ketone instead of an aldehyde. (4) When this stage has been reached the low-temperature oxidation slows down markedly, as it would be expected that a ketone would resist further oxidation more than an aldehyde.

2,2,4-Trimethylpentane has, like 2,5-dimethylhexane, an open-end straight chain of only one carbon atom, and might be expected to behave similarly. Evidently, however, the highly condensed structure renders the hydrocarbon so resistant to oxidation that no reaction occurs at all until such high temperatures are reached that the reaction, once started, goes rapidly to completion, the high-temperature disturbance setting in at once.

(d) **Low-Temperature and High-Temperature Disturbances.**—As pointed out above, evidence was presented in Part I of this series that the low-temperature disturbance involves the oxidation of an aldehyde to carbon monoxide, an aldehyde of a smaller number of carbon atoms and water, the reaction being undoubtedly of the "chain reaction" type. That similar phenomena occur in the case of two out of five of the isomeric octanes is further evidence that at least in these cases a chain reaction occurs, involving the oxidation of an aldehyde. It is significant that in the three cases in which the phenomenon was not observed it is found that for 2,5-dimethylhexane and 2-methyl-3-ethylpentane less than one mole of oxygen has been consumed in this reaction, and hence it would be expected that the results of this reaction would be less apparent than in the other cases; in the case of 2,2,4-trimethylpentane, no low-temperature reaction occurs at all. In the case of 3-ethylhexane, the disturbance was only slight, and it is not surprising that it was not noticeable in the cases involving still less of the reaction in question.

The high-temperature disturbance presumably occurs when the hydrocarbon itself, or its primary oxidation products, are brought, together with oxygen, to a temperature sufficiently high for the reaction to go semi-explosively to completion. Two questions seem worthy of consideration: (a) does the reaction at the point of the high-temperature disturbance pass through the same steps as occur at lower temperatures, and (b) is some entirely new mechanism involved in the oxidation at this point? It is hardly possible to answer either of these questions definitely from the available data, but a probable answer can be given to the first one. If the oxidation proceeds always through the steps involved in the low-temperature oxidation, it would be expected that the temperature at which the high-temperature disturbance sets in would be determined (a) by the extent to which the primary oxidation has proceeded, (b) by the nature of the oxidation products and (c) by the excess oxygen present. The experimental facts seem to be in accord with this hypothesis. Thus *n*-octane, mixed with the theoretical quantity of air for complete combustion, does not react completely until a temperature of 667° has been reached, which may mean that oxygen has been consumed so readily in forming primary oxidation products that the concentration of oxygen is much reduced, and a very high temperature must be reached before the primary products can undergo semi-explosive reaction. On the other hand, in the case of 2,2,4-trimethylpentane, when oxidation begins at 515°, the concentration of oxygen is higher and the evolution of heat of the initial oxidation brings about the semi-explosive reaction at a lower temperature than is the case with *n*-octane. The behavior of other isomeric octanes presumably falls between these two cases, the temperature of the high-temperature disturbance depending partly on the oxygen concentration and partly on the nature of the primary oxidation products.

On the hypothesis that the reaction is the direct oxidation of the hydrocarbon, without passing through the low-temperature stage, it is most surprising that a readily oxidized hydrocarbon such as *n*-octane shows this reaction at a higher temperature than 2,2,4-trimethylpentane. The first hypothesis is therefore favored.

It should be realized, of course, that the actual temperatures at which these reactions occur are undoubtedly influenced by such factors as design of apparatus, oxygen concentration and oxygen–fuel ratio. The actual data given refer only to the particular conditions in question.

The reaction proceeds so rapidly at the point of the high-temperature disturbance that it is impossible to determine whether or not some new mechanism, such as "cracking," or simultaneous attack of the molecule at several points, is involved.

(e) **Temperature of Initial Attack.**—There is little relation between the temperature of initial attack and the other oxidation characteristics. Thus 2,5-dimethylhexane is attacked at a temperature about equal to that for *n*-octane, while 2,2,4-trimethylpentane is not attacked at all until very much higher temperatures have been reached. The other isomers are all attacked at slightly higher temperatures than *n*-octane, a slight trend being observed with increasing condensation of the molecule.

V. Probable Behavior of Other Hydrocarbons

In the first place, it should be emphasized that the conclusions reached in this paper should not be taken as indicating that oxidation of even these particular hydrocarbons must follow the course outlined above under all conditions. Many reactions of oxygen with hydrocarbons are thermodynamically possible, and the reaction under different conditions of oxygen concentration, oxygen–fuel ratio and experimental technique may doubtless follow courses quite different from those observed in this paper. It is particularly probable that the liquid-phase oxidation and the oxidation under static conditions may follow a course distinctly different from those discussed herein. The present data are perhaps of particular interest in connection with the behavior of fuels in the internal combustion engine, in that air and not pure oxygen was employed for the oxidation, and in that the dynamic method employed involves a time of contact more closely related to that of the internal combustion engine than does the static method. It is interesting to speculate on the possible behavior of hydrocarbons other than those studied. It may be reasonably expected that all normal paraffins of intermediate molecular weight will show characteristics similar to *n*-octane. Certain branched-chain hydrocarbons offer interesting possibilities which may be only guessed at. Thus hydrocarbons, similar to 2,5-dimethylhexane but of higher molecular weight, might conceivably be attacked toward the center of the molecule as well as the end. Highly condensed hydrocarbons such as hexamethylethane, in which the oxidation of an aldehyde could not occur in the manner noted above, might well be extremely resistant to oxidation, and hydrocarbons in which a chain is branched at a quaternary carbon atom also involve possible complications of the general scheme. It would be interesting to have data for such cases. The oxidation of olefins also is a question of much interest. A few preliminary data available in this Laboratory indicate that the oxidation of *α*-*n*-octene begins at a higher temperature than the oxidation of *n*-octane, and is otherwise analogous to the case of *n*-octane, which certainly suggests that the oxidation does not begin at the double bond, but at the opposite end of the hydrocarbon, and follows a course similar to that of the saturated hydrocarbons. It is to be hoped that many more data than those contained in this paper will soon be available, in order to determine many of the points which must remain for the present in doubt.

VI. Summary

1. Data have been presented on the vapor phase oxidation of five branched-chain octanes. Distinct differences exist in the behavior of these hydrocarbons toward oxygen.
2. The data have been interpreted as indicating that in general oxygen first attacks the methyl group at the end of the longest free straight chain

and that it proceeds in a manner analogous to that observed for *n*-octane (Part I) until a branch in the chain occurs, the oxidation slowing down markedly at this point.

3. Certain points of interest bearing on the general problem of hydrocarbon oxidation have been briefly discussed.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ETHYL GASOLINE CORPORATION]

THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. III. THE EFFECT OF TETRA-ETHYL LEAD AND THE RELATION OF OXIDATION TO ENGINE DETONATION

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I. Introduction

The marked effect of tetra-ethyl lead and other "anti-detonants" upon certain characteristics of the combustion of hydrocarbons in the internal combustion engine is a phenomenon which has attracted the attention of numerous investigators. In several cases the oxidation of hydrocarbons in the presence of anti-detonants has been studied, and theories have been propounded connecting the phenomena observed with the behavior of fuels in the internal combustion engine.[1] It cannot be said, however, that these theories have given a complete explanation of the effect of anti-detonants on engine detonation, and no data at all have been presented in explanation of the wide differences in engine behavior of isomeric hydrocarbons.[2] Any data bearing upon these subjects seem, therefore, to be worthy of careful scrutiny.

In Parts I and II of this paper data have been presented upon the vapor phase oxidation of six isomeric octanes and simple interpretations have been given of their behavior. In Part III there are presented data upon the oxidation of *n*-octane and of *n*-heptaldehyde in the presence of tetraethyl lead. The relation between the data in Parts I, II and III and the detonation tendencies of paraffin hydrocarbons in the internal combustion engine is discussed.

[1] (a) Callendar, Aeronautical Research Committee (London), Reports and Memoranda No. 1062 (1927); (b) Lewis, *J. Chem. Soc.*, 1555 (1927); (c) Moureu, Dufraisse and Chaux, *Compt. rend.*, **184**, 413 (1927); (d) Weerman, *J. Soc. Petrol. Tech.*, 13, 300 (1927); (e) Egerton and Gates, *ibid.*, 13, 273, 281 (1927); (f) Mardles, *J. Chem. Soc.*, 872 (1928); (g) Rideal and Brunner, *ibid.*, 1162 (1928); (h) Millikan, American Petroleum Institute Bulletin, September, 1928, Project 11; (j) Layng and Youker, *Ind. Eng. Chem.*, 20, 1048 (1928); (k) Maxwell and Wheeler, *ibid.*, 20, 1041 (1928); (l) Berl, Heise and Winnacker, *Z. physik. Chem.*, 139, 453 (1928); (m) Butkov, *C. A.*, **22**, 2050 (1928); **23**, 966 (1929).

[2] Edgar, *Ind. Eng. Chem.*, 19, 145 (1927).