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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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.

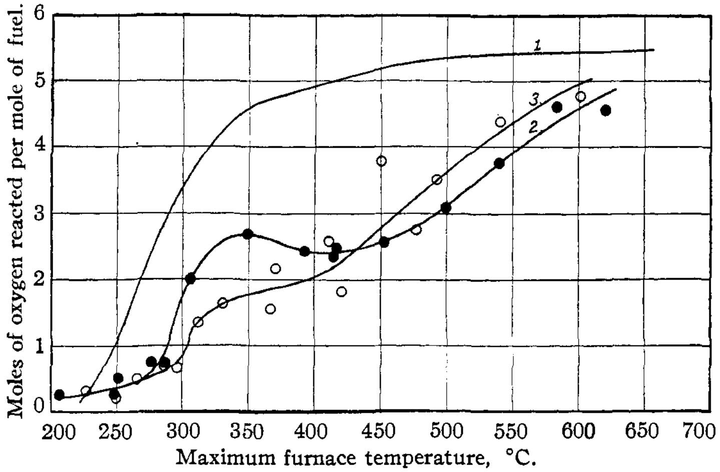
In Parts I and II of this paper data have been presented upon the vapor phase oxidation of six isomeric octanes and simple interpretations have been given of their behavior. In Part III there are presented data upon the oxidation of *n*-octane and of *n*-heptaldehyde in the presence of tetraethyl lead. 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).

II. Experimental Procedure

The oxidation of *n*-octane and of *n*-heptaldehyde in the presence of tetra-ethyl lead was studied in an apparatus and by a procedure identical with that employed with *n*-octane alone (Part I). Tetra-ethyl lead was added to the fuel and vaporized with it. Runs were carried out with slowly rising temperature and with the temperature stationary. In all cases the gaseous oxidation products were determined and in the latter case some analyses were made of the liquid oxidation products. The details of the methods of analysis, etc., were described in Part I.



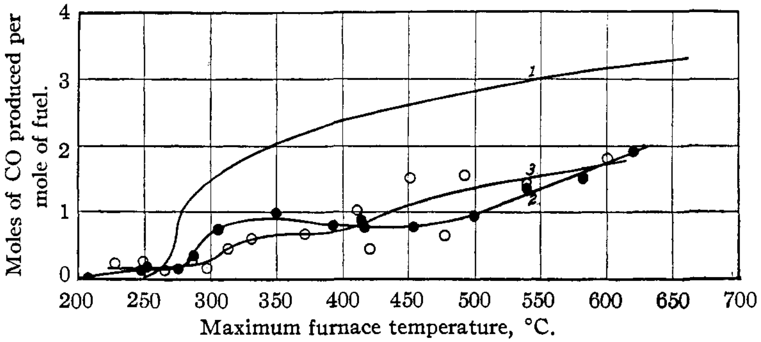
1, *n*-Octane; 2, -●-, *n*-octane plus 0.3% vol. lead tetra-ethyl; 3, -○-, *n*-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 1.—Normal octane (theoretical air/fuel ratio).

III. Experimental Data

Characteristic experimental data from rising temperature runs are expressed graphically in Figs. 1, 2 and 3 for *n*-octane and in Figs. 4 and 5 for *n*-heptaldehyde. For the sake of comparison, the corresponding data from Part I for *n*-octane alone and for *n*-heptaldehyde alone are included. The data on *n*-octane with tetra-ethyl lead were obtained in four individual experiments; for *n*-heptaldehyde the results of three experiments are included.

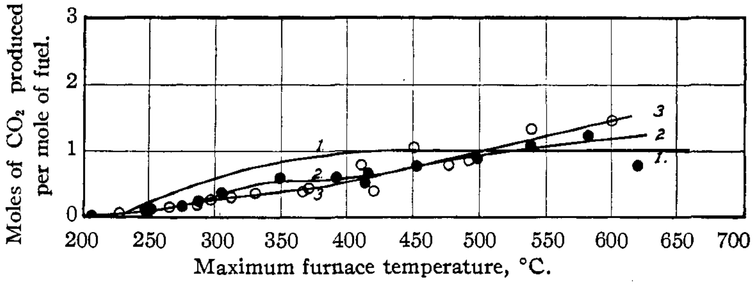
The oxygen consumption and carbon oxides produced are expressed in moles per mole of octane input and the temperatures are the maximum furnace temperature at the average time of sampling. In addition to the data in the figures it may be noted that as usual small amounts of gas absorbable in fuming sulfuric acid were found, in amounts not differing appreciably from those found in the experiments of Parts I and II. The liquid oxidation products contained aldehyde and water in considerable amounts and acid in very small amounts. The data did not differ materially from those found with *n*-octane in the absence of tetra-ethyl lead. The phenomena accompanying the oxidation were similar in most respects to those observed in Part I. Certain differences will be described below.



1, *n*-Octane; 2, -●-, *n*-octane plus 0.3% vol. of lead tetra-ethyl; 3, -○-, *n*-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 2.—Normal octane (theoretical air/fuel ratio).

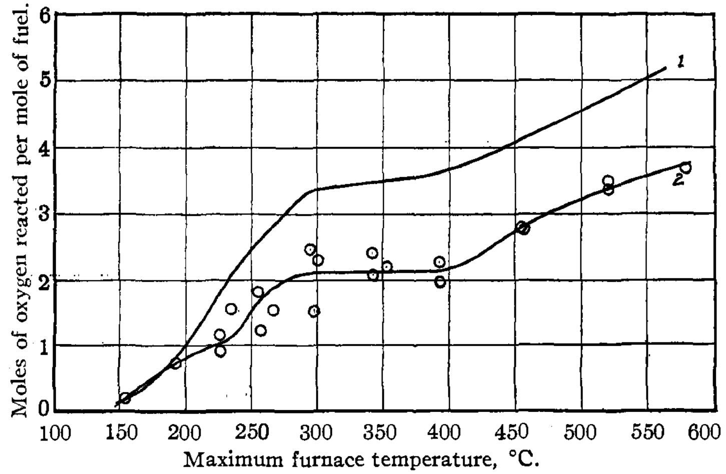
It may be noted that the experimental data in the presence of rather large amounts of tetra-ethyl lead were much more erratic than those observed with the hydrocarbons alone. This is not altogether unexpected, since under the conditions of the experiments tetra-ethyl lead undergoes oxidation, in amount varying with the temperature. The extent of such oxidation, the point at which it occurs in the furnace and the distribution of the products through the furnace undoubtedly vary with the temperature and perhaps between runs, and may account for the somewhat erratic results. The varying effect of tetra-ethyl lead at different temperatures, discussed below, may also be at least partially due to the decomposition phenomena. For the purpose of this paper no distinction is made between tetra-ethyl lead itself and its various decomposition products, as the data



1, *n*-Octane; 2, —●—, *n*-octane plus 0.3 % vol. of lead tetra-ethyl; 3, —○—, *n*-octane plus 1.07% vol. of lead tetra-ethyl.

Fig. 3.—Normal octane (theoretical air/fuel ratio).

herein presented do not permit an analysis close enough to determine such distinctions, if they exist.

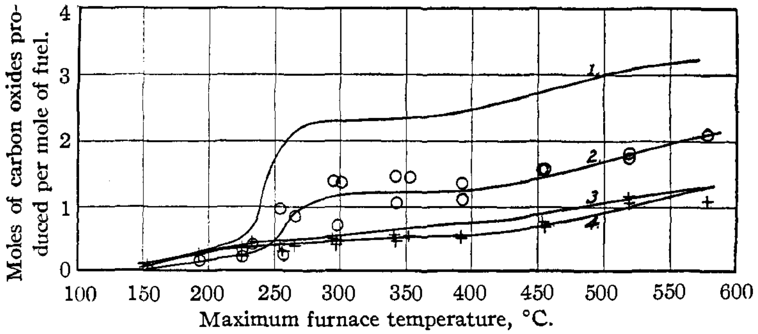


1, *n*-Heptaldehyde; 2, -O-, *n*-heptaldehyde plus 1% vol. of lead tetra-ethyl.

Fig. 4.—Normal heptaldehyde (theoretical air/fuel ratio).

IV. Discussion of Data

Comparison with the Data in the Absence of Tetra-ethyl Lead.—In Fig. 1 a comparison is made of the oxygen consumption of *n*-octane at different temperatures with and without tetra-ethyl lead. In Fig. 2 a similar comparison is made of the carbon monoxide produced and in Fig. 3 of the carbon dioxide produced. In Fig. 4 the oxygen consumption data for heptaldehyde with and without tetra-ethyl lead are compared, and in



n-Heptaldehyde: 1, CO produced; 3, CO_2 produced.
n-Heptaldehyde plus 1% vol. lead tetra-ethyl: 2, -O-, CO produced; 4, - + -, CO_2 produced.

Fig. 5.—Normal heptaldehyde (theoretical air/fuel ratio).

Fig. 5 the carbon oxides formed are compared. An analysis of these data follows.

(1) *n*-**Heptaldehyde.**—Data were presented in Part I indicating that aldehydes are intermediate oxidation products of *n*-octane, and that the carbon oxides formed are the oxidation products of such aldehydes, rather than of *n*-octane directly. In attempting to determine the exact effect of tetra-ethyl lead it seems therefore desirable to consider first the oxidation of *n*-heptaldehyde in the presence of tetra-ethyl lead, since in this case only two of the three reactions involved in the oxidation of *n*-octane are concerned. It is clear from the data in Figs. 4 and 5 that practically the entire effect of tetra-ethyl lead on the oxidation of *n*-heptaldehyde is upon the reaction producing carbon monoxide. The carbon dioxide formed with tetra-ethyl lead differs from that formed in its absence by little more than the experimental error. The carbon monoxide is, however, greatly reduced in the presence of tetra-ethyl lead, and the data for oxygen consumption differ from those without tetra-ethyl lead by an amount corresponding almost exactly to the reduction in carbon monoxide, since one mole of oxygen is consumed in the production of one mole of carbon monoxide. It would be expected that the reaction involving carbon monoxide would be the one most apt to be affected by tetra-ethyl lead, since it is a "chain" reaction (Part I), and such reactions are usually capable of marked retardation by negative catalysts. Presumably the reaction is normally propagated through the medium of a reaction chain in which "activated molecules" in reacting activate other molecules. Tetra-ethyl lead probably retards the reaction by accepting the surplus energy of such molecules and thus breaking the reaction chain.

The temperature at which the "low temperature disturbance" begins with its accompanying luminescence and pulsations, is distinctly raised by tetra-ethyl lead, (235 to 270°), as would be expected from the fact that the reaction producing this disturbance is suppressed. The range over which the disturbance is noticeable is, however, not measurably affected. It may be noted that at very low temperatures tetra-ethyl lead has very little if any effect upon the oxidation of heptaldehyde, a phenomenon perhaps associated with the fact that tetra-ethyl lead is not decomposed appreciably under the conditions of the experiment in this temperature range. The effect also is diminished at quite high temperatures, which may again be associated with the decomposition phenomena.

(2) *n*-**Octane.**—*n*-Octane, according to the view expressed earlier by the authors, differs in its essential oxidation mechanism from *n*-heptaldehyde only by the initial reaction in which aldehyde is produced from the hydrocarbon. The data in Figs. 1, 2 and 3 are fully in accord with this view. Thus the most striking effect of tetra-ethyl lead is in the suppression of the reaction in which carbon monoxide is formed, a suppression which would be expected from the data on *n*-heptaldehyde. There is evidence, however, of another effect of tetra-ethyl lead. Thus while oxidation begins at about the same temperature in the presence of tetra-ethyl lead as in its absence, the oxygen consumption rises with increasing temperature somewhat more slowly than can be accounted for by the suppression of the carbon monoxide alone, particularly at low and intermediate temperatures. This suggests that the primary oxidation of *n*-octane to aldehyde is somewhat retarded and that complete oxidation of the hydrocarbon does not occur in the presence of tetra-ethyl lead until a higher temperature has been reached than is necessary with *n*-octane alone. The data on carbon dioxide production support this view, since they are slightly lower, at low temperatures, in the presence of tetra-ethyl lead than in its absence, as would be expected if the formation of aldehyde (from which the carbon dioxide is produced) is somewhat retarded. The apparent partial reduction in the primary oxidation of *n*-octane suggests the possibility that this reaction may also be of the chain reaction type, but no further evidence is available.

The effect of tetra-ethyl lead on the low temperature disturbance with *n*-octane is similar to its effect upon the corresponding disturbance in the case of *n*-heptaldehyde, in that the temperature at which the disturbance begins is raised (270 to 300°), but with *n*-octane the disturbance is much less vigorous in the presence of tetra-ethyl lead than in its absence, the luminescent flashes are more frequent and the temperature range over which the disturbance lasts is increased. This seems in accord with the hypothesis that the primary oxidation of *n*-octane is partially suppressed and the aldehyde oxidation (to carbon monoxide) strongly suppressed. Other facts worth recording in connection with the oxidation are: (1) that, as with *n*-heptaldehyde, the effect of tetra-ethyl lead seems to decrease at high temperatures; (2) that the data were not extended to the temperature of the "high temperature disturbance," so that it cannot be determined whether or not this point is affected by tetra-ethyl lead; and (3) that increasing the concentration of tetra-ethyl lead from 0.31 vol. per cent. to 1.00 vol. per cent. does not produce a corresponding effect on the oxidation phenomena.

V. Relation of Oxidation Phenomena to Engine Detonation

The facts that tetra-ethyl lead effectively suppresses detonation in the internal combustion engine, and that its chief effect upon the oxidation of a hydrocarbon having a high tendency to detonate (*n*-octane) is the suppression of certain oxidation reactions, suggest a close relationship between the two phenomena. It is interesting in this connection to examine the behavior in the engine of the isomeric octanes whose oxidation characteristics were discussed in Part II. Insufficient amounts of these hydrocarbons were available to enable their tendencies to detonate to be measured on the pure materials; accordingly, they were dissolved in gasoline in the proportion of 10% by volume, and their effect on the tendency of the gasoline to detonate was measured in an engine, employing a technique previously described.[3] The hydrocarbons arranged themselves in the following order, the one having the greatest tendency to detonate being given first: (1) *n*-octane, (2) 3-methylheptane, (3) 3-ethylhexane, (4) 2-methyl-3-ethylpentane, (5) 2,5-dimethylhexane and (6) 2,2,4-trimethylpentane. Now it has been previously shown (Part II) that the first five of these hydrocarbons have their longest open-end straight chains of eight, four, three, two and one carbon atoms, respectively, and that the length of these chains determines the extent to which the low temperature oxidation can proceed. The sixth hydrocarbon (2,2,4-trimethylpentane) was found to be entirely unoxidized at low temperatures.

We have here, therefore, a striking correlation between engine detonation and oxidation characteristics. This may be recapitulated as follows. (1) A "chain reaction" involving the oxidation of an aldehyde to carbon monoxide, water and another aldehyde has been found to be one of the chief oxidation reactions of the five isomeric hydrocarbons which undergo appreciable oxidation at low temperatures. (2) The extent to which this reaction is capable of proceeding without interruption is determined by the length of the longest open-end straight chain of carbon atoms in the mole-

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[3] Edgar, *J. Soc. Automotive Eng.*, 22, 41 (1928).

cule, and the oxidation actually slows down when it has proceeded to a point corresponding to the length of such a chain (unless a secondary disturbance sets in before such point is reached). (3) Tetra-ethyl lead sharply retards this reaction (in the one case studied), and apparently reduces somewhat the primary oxidation of the hydrocarbon. (4) The tendency of these hydrocarbons to detonate follows the same order as that of the extent to which this reaction occurs at low temperatures, and the hydrocarbon showing no low temperature oxidation has less tendency to detonate than any of the others. (5) Tetra-ethyl lead reduces the tendency of a fuel to detonate.

Apparently, therefore, both the temperature of initial oxidation and the extent to which such oxidation proceeds are factors involved in the detonation phenomena. If the relationships found for the six octanes are general, it seems reasonable to predict that as far as the paraffin hydrocarbons are concerned: (a) for normal hydrocarbons the tendency to detonate will increase with increasing molecular weight (this is known to be in accord with experiment); (b) branched-chain hydrocarbons which undergo oxidation at low temperatures will have a tendency to detonate increasing with the length of the longest open-end carbon chain; (c) hydrocarbons resistant to low temperature oxidation will have little tendency to detonate (*e. g.*, 2,2,4-trimethylpentane). These will probably have highly condensed structures. It must be admitted that the data on which these conclusions are based are not as complete as could be wished, but they appear to give quite clear indications of the phenomena to be expected with different paraffin hydrocarbons.

VI. Mechanism of Detonation

It is much more difficult to suggest a satisfactory mechanism of engine detonation. So many factors involved in the combustion of fuels in an engine are widely different from those in the laboratory experiments that too close an analogy can hardly be expected. We know little concerning the chemical changes involved in the combustion of fuel in an engine except that Lovell, Coleman and Boyd[4] have shown that the combustion is more rapid when an engine is detonating than during normal operation. In an engine the air–fuel mixture is first compressed to about five atmospheres in a hot cylinder. It is then ignited with a spark and the mixture burns either with or without the development of detonation. It is probable that temperatures of 400–500° are reached during the compression stroke before the spark is fired. It is quite conceivable that when readily oxidized hydrocarbons are used as fuel appreciable oxidation may occur during the compression stroke, and that the rate of burn of the mixture after the charge is fired (and the tendency to detonate) may depend upon the extent of such

[4] Lovell, Coleman and Boyd, *Ind. Eng. Chem.*, 19, 373 (1927).

preliminary oxidation. It is also possible that the rate of burn of a charge fired by a spark may depend upon factors similar to those which govern the low temperature oxidation. The problem is extremely complicated and the authors do not feel that the data presented in this paper give by any means the complete account of engine detonation. Nevertheless, they represent an interesting correlation of laboratory data with engine operation, and are presented with the hope that they may contribute to clearing up at least certain phases of this important problem.

VII. Summary

1. Experimental data have been presented on the vapor phase oxidation of *n*-octane and *n*-heptaldehyde in the presence of tetra-ethyl lead.

2. The effect of tetra-ethyl lead seems to be chiefly that of slowing down the oxidation of aldehydes to carbon monoxide, water and other aldehydes.

3. The data, combined with those of Parts I and II, are discussed in comparison with the behavior of the hydrocarbons as fuel in the internal combustion engine, and certain correlations are pointed out.

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THE ACTION OF PHENYL ISOCYANATE ON URETHANS, UREAS AND THIOUREAS

BY HANS LAKRA[1] AND F. B. DAINS

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Phenyl isocyanate, which was first obtained by A. W. Hofmann,[2] is characterized by its ability to form addition products with the $N{=}C$ double bonding. Thus with alcohols urethans, $C_6H_5NHCOOR$, are formed while with ammonia and with primary and secondary amines, substituted ureas result. The presence of aryl groups in the secondary amines often tends to slow up or even in some cases to prevent the expected addition, $RR'NH + C_6H_5NCO = C_6H_5NHCONRR'$.

Since the nature of the hydrocarbon (aryl) group has been found to affect the course of the reaction, it seemed worth while to study the reactivity of phenyl isocyanate toward the group $RNH(NH_2)$ when it was linked with a CO or CS complex, in order to determine their influence upon the expected additions.

In the present investigation the compounds chosen were urethans, ureas and thioureas where the primary reaction might be expected to yield (a)

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[1] From a dissertation presented by Hans Lakra to the Faculty of the Graduate School of the University of Kansas, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hofmann, *Ann.*, **74**, 9 (1850); *Ber.*, **3**, 655 (1870).