The iodo and bromo compounds are probably isomorphous. The chloro and fluoro compounds, being triclinic, may be considered either dimorphous with forms which fall in the iodo–bromo series or distinctly different. In the case of the chloro compound we have many similarities to the bromo especially in the optical properties, so the first supposition is probably correct. With the fluoro compound there is no evidence which shows such a similarity; in fact, what evidence there is seems to support the second supposition, although that cannot be definitely established from the crystallographic data.

Summary

4-Fluoro-, 4-chloro-, 4-bromo-, 4-iodo- and 3-iodophthalic anhydrides have been condensed with phenol to form phenol-halo-phthaleins. From the 4-halophthalic anhydrides, mixtures of isomeric phthaleins were obtained but in the case of 3-iodophthalic anhydride only one phthalein was found.

Data obtained by Dr. Slawson have shown that 4-fluorophthalic anhydride does not fit into the same crystallographic scheme with the three other 4-halophthalic anhydrides.

ANN ARBOR, MICHIGAN

THE MECHANISM OF THE VAPOR PHASE OXIDATION OF ISOMERIC OCTANES. I. NORMAL OCTANE[1]

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

I. Introduction

The oxidation of hydrocarbons represents a subject which has attracted the attention of many investigators, yet it cannot be said that the fundamental mechanism of such reactions has been made perfectly clear. Perhaps this has been partially due, on the one hand, to a natural tendency to generalize from results obtained on the simpler hydrocarbons and, on the other, to failure to differentiate between liquid phase reactions and vapor phase reactions.

The results of the present investigation on octanes may perhaps contribute to the interpretation of the behavior on oxidation of hydrocarbons intermediate in complexity.

No attempt will be made to give an elaborate survey of the literature on the general subject of oxidation, but a few references to vapor phase oxidation of normal paraffins may be cited. Bone[2] and his associates demon-

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[1] Presented in part at the Fall Meeting of the American Chemical Society at Swampscott, Massachusetts, September, 1928.

[2] Bone and co-workers, *J. Chem. Soc.*, **81**, 535 (1902); **83**, 1074 (1903); **85**, 693 (1904); **89**, 660, 1614 (1906).

strated that the simpler normal hydrocarbons oxidize with the intermediate formation of aldehydes. These authors interpreted their results as indicating that an alcohol is first formed which is then rapidly oxidized to an aldehyde, a theory since well known as the hydroxylation theory. Wheeler and Blair[3] investigated the oxidation of hexane and noted the copious formation of aldehydes. A process of oxidation was formulated based on the hydroxylation theory and involving the possibility of several simultaneous points of attack on the hexane molecule.

Recently Callendar[4] has reported "acetaldehyde, formaldehyde, valeraldehyde, etc.," among the products of the vapor phase oxidation of normal hexane.

It is not possible from these data to determine by what process oxygen attacks a long carbon chain in the vapor phase and by what steps the reaction progresses.

In the present study octanes were selected for investigation because their molecular weight is about the average of commercial gasolines, the mechanism of whose oxidation is a problem of great interest. Part I presents data on the oxidation of n-octane and the oxidation of n-heptaldehyde and n-butyraldehyde, which were studied in order to clarify certain observations on the oxidation of n-octane; Part II will discuss the oxidation characteristics of five isomeric octanes. The reactions were studied entirely in the vapor phase, by the dynamic method.

II. Apparatus and Experimental Methods

(a) General.—Mixtures of octane vapor and air were passed through a heated glass tube and samples of the gas were taken for analysis. In certain experiments the liquid products of, oxidation were collected and examined. Certain details of technique seem worthy of full description. The entire apparatus is illustrated in Fig. 1.

(b) Furnace and Thermocouples.—The furnace was a tube of pyrex glass 1″ in internal diameter and about 36″ long with a reaction space of 367 cc. It was wound with resistance wire and heavily lagged with asbestos. The lagging was thicker at the ends so that in the absence of reaction the temperature was approximately constant over the entire furnace length. Temperature was controlled by external resistance. When runs were made with rising temperature, the heating current was altered by hand to keep the temperature rising smoothly. A run over the range of 200–650° usually occupied about two hours.

Two thermocouples were provided, one of which was inserted through either end. They could be moved to investigate the temperature gradient of the furnace but were usually placed in definite positions, one at the entrance end, 2 inches from the reaction mixture inlet (see below), the other at about 10 inches from the exit end.

(c) Method of Obtaining Combustible Mixture.—Where it is necessary to preheat the fuel for vaporization, as is the case with a high-boiling material like n-octane, it becomes essential to avoid exposure to oxygen until the proper experimental temperature

³ Wheeler and Blair, *J. Soc. Chem. Ind.*, **42**, 491T (1923).

⁴ Callendar, Aeronautical Research Committee, London, Reports and Memoranda, No. 1062, "Dopes and Detonation," second report.

is reached.   Hence the principle followed was to preheat and vaporize the fuel in nitrogen only, and to mix it as suddenly as possible with the requisite amount of oxygen when the furnace temperature had been reached.

The vaporization and mixing devices are shown in Fig. 1.   The fuel was led from a 50-cc. buret reservoir to a 5-cc. buret graduated in 0.02 cc., from which it was allowed to flow at intervals into the slightly inclined arm of the feed device.   The liquid head in the latter was thus maintained at any selected point by intermittent additions of small volumes.   The difference in head on the shallow incline, produced by each addition, was so slight and the resistance of the capillary tube so great, that very constant rates of feed were obtained.   Further, the volume fed from the small buret was read every few minutes, thus giving a continuous oversight of the fuel mixture.   From the inclined arm the fuel passed through a long capillary ending in a flat ground surface within the
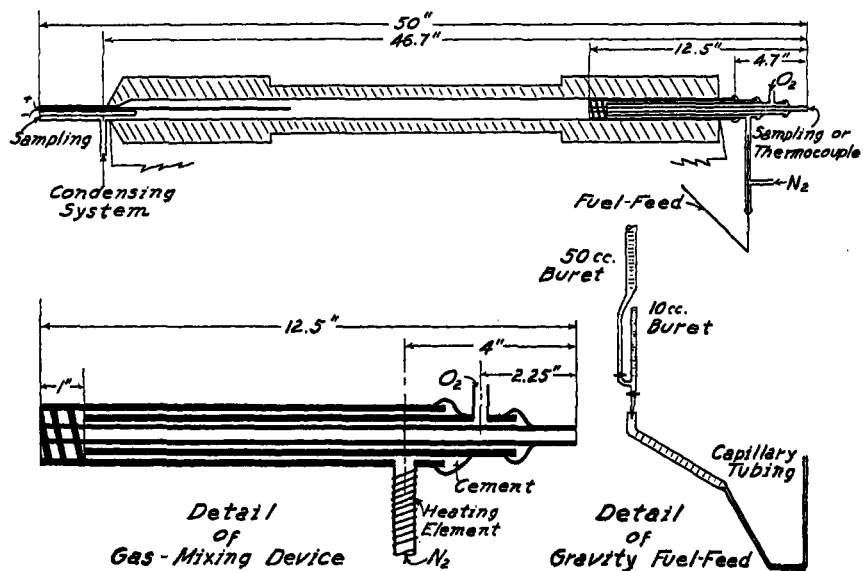

Fig. 1.

preheater tube.   Here nitrogen purified by passage through alkaline pyrogallol and dried over the calcium chloride was passed over the emerging liquid and the resulting mixture was then led to the large annular tube by which it entered the furnace.   Oxygen dried over calcium chloride was led into the furnace by the inner annular tube. (The two annular tubes extended about 6 inches within the furnace heating coil.) Mixing took place in a device consisting of a glass spiral placed concentrically with the annular tubes carrying the two gases.   On meeting the gases were diverted from their straight course and forced together round the spiral, in which process they became intimately mixed.   The efficiency of mixing was proved by tests with oxygen and nitrogen alone, in which the gases were analyzed shortly after leaving the mixing tube.

(d)   Control of Mixture.—The oxygen and nitrogen were passed into the furnace at a rate identical for all experiments and were measured and controlled by flow meters. The final mixture of these gases contained about 20.5% of oxygen.   The oxygen–fuel ratio was governed entirely by the amount of fuel used, and in the experiments described herein with n-octane was between 11 and 13 to 1, the theoretical ratio for octane being 12.5 to 1.   These figures refer to the input of materials.

(e) Period of Contact.—The minimum time necessary for the gases to pass through the furnace was about 25 seconds at 650° and the maximum about 50 seconds at 200°. Since the reaction occurs almost entirely in a narrow zone, the actual time of reaction is less than these figures indicate.

(f) Sampling System.—Gas samples were taken over mercury. They were collected through a T-piece placed in the line beyond the condensing system, except when investigating the course of the reaction at different positions in the furnace. The samples correspond to a narrow range of temperature, when taken on a rising temperature, since the sampling occupied about ninety seconds, corresponding to a rise of furnace temperature of not over 6°. The mean sampling temperature was used as the reaction temperature of such samples.

For collecting the liquid condensate when required, four units were used, one ice-cooled glass coil, one filter cartridge to stop mist and two glass coils, cooled with carbon dioxide snow.

(g) Analytical Methods.—Gas samples were analyzed in an apparatus of the Burrell type. Analysis was made for carbon dioxide, gases absorbed by sulfuric acid, oxygen and carbon monoxide. Occasional analyses were carried through for hydrogen and methane. A blank analysis was made in each experiment of the oxygen–nitrogen mixture without fuel.

Determinations of the following constituents, acid, aldehyde, peroxide and water, were made on certain condensates from the oxidation of normal octane. The condensate was weighed, then washed from the various condensing units with water and a little alcohol, and the total volume of the solution determined. After thorough mixing, samples of known volume were taken for the determinations. Acid was determined by titration with $N/100$ sodium hydroxide, with phenolphthalein as indicator. Following the neutralization, aldehyde was determined on the same sample by the method of Ripper.[5] For the determination of peroxide, an acidified solution of potassium iodide was added to a condensate sample and the flask flushed with nitrogen, blanks (lacking only condensate sample) being treated similarly. The flasks were kept in a dark place. The titrations with $N/10$ thiosulfate were carried out in a stream of nitrogen, the addition of thiosulfate being continued until no further liberation of iodine was observed.

NOTE.—It may be stated that if this determination is carried on in the presence of air, as has usually been done by previous investigators, much higher results for peroxide are obtained, caused probably by interaction of aldehydes and oxygen during the shaking. A sample of pure heptaldehyde in the presence of air will give a test for peroxide, and since aldehyde and air are both present among the reaction products in the present investigation, the actual source of the peroxides found is uncertain.

For the determination of water, a separate collection of condensate was made and the liquid allowed to remain in the condensing train after weighing. The whole train was then connected to a series of gas-drying tubes containing anhydrous copper sulfate and air at room temperature was aspirated through towers of anhydrous copper sulfate and allowed to evaporate the condensate and carry it through the weighed tubes. Passage of air was continued until the weight of copper sulfate remained approximately constant.

(h) Materials Used.—The n-octane used was synthetic material with a boiling range 124.9–125.3° (763 mm., uncorr.).

The aldehydes were Eastman products, further fractionated. The boiling ranges were n-heptaldehyde, 152.1–152.6°; n-butyraldehyde 74.0–74.6° (763 mm., uncorr.).

[5] Ripper, *Monatsh.*, **2**, 1079 (1900).

III.   Description of Results

n-Octane

(a)   **General.**—In studying exothermic reactions of this character, where the actual temperatures of the reacting mixture may be considerably higher than the furnace temperature, and always vary at different positions in the furnace, it is somewhat of a problem to decide what temperatures are to be considered as the temperatures of reaction.   Since the greater part of the reaction occurs in a short zone of the reaction tube, it was considered in this investigation that the actual temperature registered by the thermocouple in this zone was the most satisfactory basis for comparison, and these "maximum furnace temperatures" have been employed throughout in considering the effect of temperature.

Experiments were carried out in two ways: (a) at constant furnace temperature, for the purpose of examining the temperature distribution at different parts of the furnace, of collecting liquid oxidation products and of observing the extent of reaction at different positions in the furnace (for this purpose the heating current and fuel feed were held constant for a long period of time to secure equilibrium conditions before samples were taken); (b) with slowly rising temperature (about 4° per minute), gas samples being taken for analysis from time to time until any given temperature range had been covered.   The mean temperature while the sample was being taken was recorded as the temperature of reaction.

As far as gaseous products were concerned the two methods gave results differing slightly quantitatively, as would be expected because of the somewhat different relationship between the temperature of the wall and that of the charge.   These differences were not sufficient, however, to indicate any appreciable change in the nature of the reaction.

As will be indicated below there are certain temperature ranges in which rather abrupt changes occur in the reaction characteristics, and in these ranges it was impracticable to maintain constant temperature conditions. The phenomena observed in these temperature ranges contributed greatly to the interpretation of the reaction and the runs with rising temperature have, therefore, been selected for the detailed discussion.

(b)   **Runs at Constant Temperature.**—The analyses of the gaseous products of oxidation at constant temperature do not add materially to the knowledge gained from the runs at slowly rising temperature, which will be discussed fully below.   They will, therefore, not be considered further, except to point out that it was clear from the results that the reaction when considerable in extent was largely localized in the first 20% of the tube length.   This was shown by temperature measurements at different positions in the tube, which showed a sharp rise in temperature immediately after mixing when the reaction was proceeding to a considerable extent,

and by analysis of the gaseous products, which showed little change in oxygen consumption between 20% of the tube length and the extreme end. While no corresponding measurements were made in runs with the furnace temperature rising, it seems most probable that the results would be essentially the same. A few runs at constant temperature were carried out for a sufficient length of time to collect a small portion of liquid, condensed as indicated above, from the gaseous products. These liquid oxidation products invariably contained considerable aldehyde and water. At low temperatures some unoxidized octane was recovered. Aldehyde and water were the first oxidation products detectable. Traces of peroxide (probably) were found, and at low temperatures small amounts of acid were present, diminishing as the temperature was raised and disappearing entirely at about 400°. The general nature of the oxidation products at low temperatures is shown by the following analyses at 260° (figures per mole of octane input): unoxidized octane, 0.55; aldehyde, 0.33; acid, 0.25; peroxide (?), 0.07; water, 0.36. On account of the difficulty in analyzing these small amounts of liquid and because of the possible presence of small amounts of other substances which might escape the analytical methods employed, these figures must be considered as very approximate. For these reasons the quantitative aspects of the liquid products will not be considered in the detailed discussion of the mechanism of the reaction.

(c) **Runs with Slowly Rising Temperature.**—The reactions may be divided fairly definitely into three temperature zones: 200–270°, 270–650°, above 650°, the significance of which will be discussed below. For convenience the phenomena covering the whole temperature range are described under the heads (1) oxygen consumption, (2) gaseous oxidation products and (3) luminescence. The analytical results on oxygen consumption and gaseous products are expressed graphically in Fig. 2. All data are expressed on a basis of moles per mole of octane input, and the temperatures are those recorded by the thermocouple in the center of the reaction zone. Data from five separate runs are included.

(1) **Oxygen Consumption.**—Below 200° no oxygen consumption is indicated by analysis. Between 200 and 270° the oxygen content of the gas decreases regularly until the consumption calculated per mole of octane amounts to about two moles. At a temperature of about 270° some alteration in the nature of the reaction is indicated by pulsations of the flow meters. The pulsations at first occur at ten to fifteen seconds apart, but gradually become more frequent and weaker until at 300–320° they are no longer noticeable. During this time there is a slightly increased rate of rise of temperature of the first thermocouple, followed by localization of the heat evolution near the thermocouple, which may then record a temperature more than 100° higher than that given by the other. Throughout this period the oxygen consumption rises steadily, but the curve gradually

becomes less steep (Fig. 2) and above 350° rises very gradually, the oxygen consumption increasing by one 1 mole from 350 to 650°, where it is nearly 6 moles.   Above 650° the nature of the reaction changes again, strong pulsations are noted in the flow meters and the oxygen consumption rises to approximately the theoretical for complete combustion to carbon dioxide and water.

(2)   **Gaseous Oxidation Products.**—The gaseous oxidation products of *n*-octane are carbon monoxide, carbon dioxide and a small amount of some gas absorbed by fuming sulfuric acid, the nature of which was not determined.   Its amount was normally less than half that of the carbon

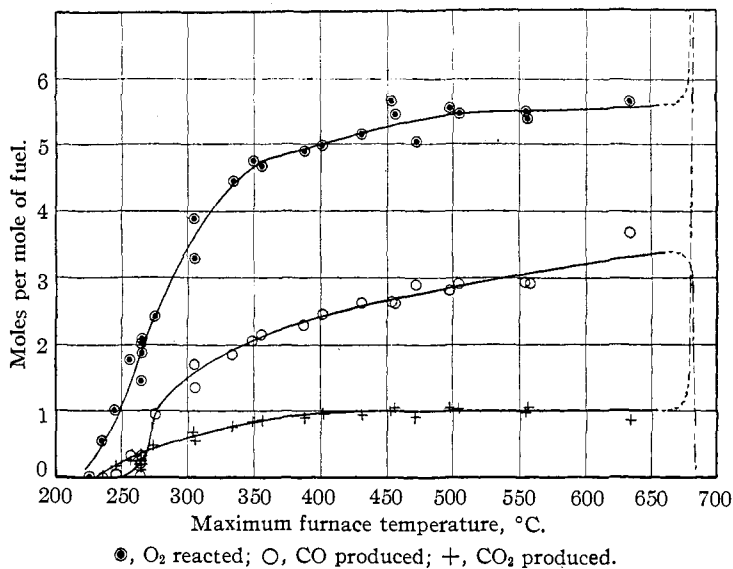●, O_2 reacted; ○, CO produced; +, CO_2 produced.

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

dioxide, and may represent only uncondensed organic residues, such as aldehyde vapors.   Hydrogen and methane could not be detected in any case examined for these gases.

Although there is an appreciable consumption of oxygen between 200 and 270°, the gaseous oxidation products are very small in amount.   Carbon monoxide is practically absent until temperatures just below 270° are reached.   Carbon dioxide rises regularly from zero at 200° to about 0.4 mole at 270°.

The change in reaction character noted above, occurring at about 270°, is marked by the sudden appearance of carbon monoxide in relatively large amount.   This gas is found consistently after the first pressure surge and within a range of a few degrees progressive samples may be obtained containing no measurable carbon monoxide and quantities greater

than one-half mole. By the time the surges cease the gas contains about one mole of carbon monoxide per mole of octane. Thereafter the carbon monoxide increases almost mole for mole with the oxygen consumption and at 650° it is present to the extent of 3.5 moles.

Entrance into the second stage of reaction (at 270°) makes no change in the rate of carbon dioxide production. The amount of this gas rises regularly until it reaches one mole at 400°, after which it remains practically constant. This appears to be the case under all conditions of heating. With the incidence of the third stage (above 650°), the carbon monoxide is reduced to a very low figure and is replaced by carbon dioxide.

(3) **Luminescence.**—The oxidation of octane is luminescent in certain stages. The first temperature zone, 200–270°, does not show luminescence. The entrance into the second zone may be noticed in the dark by the sudden filling of the tube with a feeble white glow which appears to move counter current to the gas. It forms repeatedly, coincident with the pressure surges, dying away completely in the intervals between them. As the temperature rises, the intervals between flashes grow successively shorter, the initial point of the flash apparently moving toward the inlet point. Ultimately the glow becomes stationary on the gas inlet, where it remains up to 650°. The high temperature pulsations, above 650°, are character- ized by a much brighter blue flash which seems to move in the same di- rection as the gas stream. After the passage of the blue flame, the original pale glow of the second stage is still visible at the inlet. When the tem- perature becomes sufficiently high, the blue flame likewise settles at that point. The phenomena may be observed in reverse order on cutting off the heating current.

Heptaldehyde and Butyraldehyde

(a) **General.**—The oxidation of the two aldehydes was studied in a manner similar to that used with *n*-octane. The same oxygen–nitrogen mixture was used and the fuel rate adjusted to give sufficient oxygen for complete combustion. Thus the oxygen–fuel ratio was about 10–1 for heptaldehyde and about 6–1 for butyraldehyde. The time of passage through the furnace was essentially the same as in the case of *n*-octane. The curves showing the oxygen consumption and carbon oxides formation for heptaldehyde and butyraldehyde are presented in Figs. 3 and 4, re- spectively, referring to rising temperature runs.

(b) **Heptaldehyde.**—Heptaldehyde commences to absorb oxygen at about 150°, the oxygen consumption curve rising steeply, but slightly less so than in the case of octane. At about 300° the curve becomes almost flat; it then rises more gently. In contrast to the behavior of *n*-octane, both carbon monoxide and dioxide are produced together from the begin- ning, until at about 235° they are each present to the extent of about 0.5 mole. At this point pulsations in the flow meters occur as with octane,

accompanied by luminescence, and carbon monoxide is at once produced in larger quantities, rising to over 2.0 moles at 275°. (That the carbon monoxide formed is produced by oxidation of n-heptaldehyde and not by
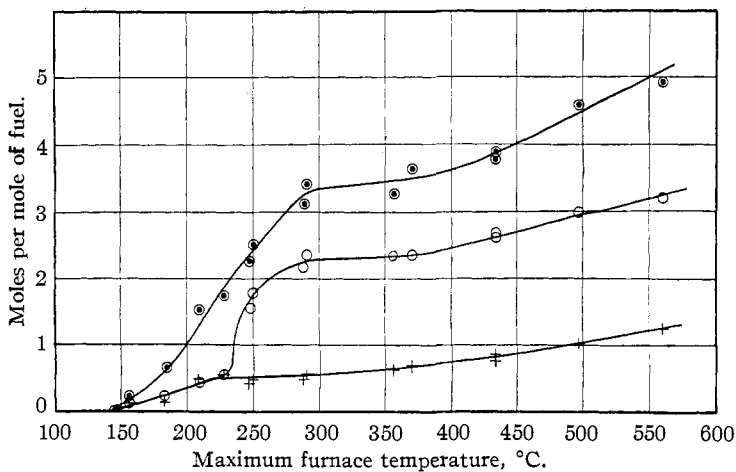
●, O_2 reacted; O, CO produced; +, CO_2 produced.

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

thermal decomposition was proved by experiments with both heptaldehyde and butyraldehyde made in the absence of oxygen, in which carbon monox-
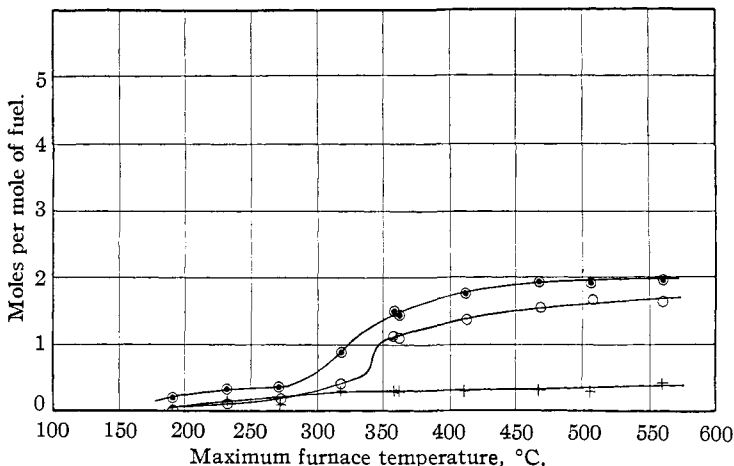
●, O_2 reacted; O, CO produced; +, CO_2 produced.

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

ide was not observed at the temperatures in question.) As in the case of octane, also, the carbon dioxide is unaffected by this critical point and it proceeds to rise at the same rate at least up to 570°.
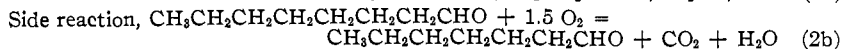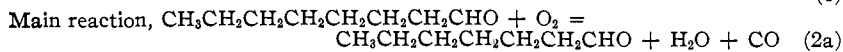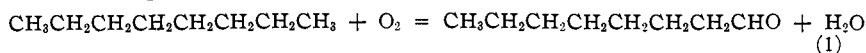
The high temperature pulsations, observed with heptaldehyde under somewhat different conditions, were not encountered in these experiments.

(c) **Butyraldehyde.**—The oxidation of butyraldehyde presents the same general features as that of heptaldehyde. It exhibits, however, a long period (200–335°) over which there is a very slight oxygen absorption, with small amounts of carbon monoxide and dioxide. A sharp rise in carbon monoxide occurs at 335°, corresponding to flow meter pulsations. These pulses, however, are very feeble and the temperature range of their duration is very short. The carbon dioxide remains almost constant after this stage, at about 0.3 mole. The high temperature pulsations were not observed in these experiments, in which the maximum temperature was 560°. No luminescence observations were made.

IV.   Discussion of Results

(a) **General Course of the Reaction.**—So many possibilities exist as to the reactions which may take place in the oxidation of as complex a molecule as that of n-octane, and so involved do the phenomena described above appear that it seemed at first most unlikely that the data could be interpreted by any simple set of reactions. Careful consideration of the data, however, led to the conclusion that the reaction proceeds below 650° practically entirely according to a very simple mechanism, and all phenomena observed may be accounted for on this basis. The nature of the reaction above 650° will be discussed below.

The early appearance of aldehyde and water among the reaction products, the invariable presence of considerable aldehyde under all conditions and the general similarity of the oxidation curves of n-octane and the aldehydes suggest strongly that the primary oxidation product of octane is an aldehyde, and that this aldehyde is further oxidized with the formation of other aldehydes of lower molecular weight. The simple hypothesis was therefore made that the oxidation of n-octane proceeds according to the following steps:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + O_2 = CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + H_2O \quad (1)$$

Main reaction, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + O_2 =$
$$CH_3CH_2CH_2CH_2CH_2CH_2CHO + H_2O + CO \quad (2a)$$

Side reaction, $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CHO + 1.5\,O_2 =$
$$CH_3CH_2CH_2CH_2CH_2CH_2CHO + CO_2 + H_2O \quad (2b)$$

Reaction (2) was assumed to continue in the same way, yielding each time an aldehyde of the next lower number of carbon atoms to that oxidized.

This hypothesis was tested as follows. (1) According to the assumptions above, the oxidation of n-octane differs from that of an aldehyde only by the amount of oxygen necessary to convert octane to octaldehyde. Therefore, under conditions in which no unoxidized octane remains, the number of moles of oxygen consumed by n-octane should be greater by one mole

than that consumed by heptaldehyde or butyraldehyde for corresponding quantities of carbon monoxide and carbon dioxide formed.   The results of calculations based on the curves of Figs. 2, 3 and 4 are given in Fig. 5, in which the sum of the moles of carbon monoxide and 1.5 times the moles of carbon dioxide is plotted against the experimental oxygen consumption. It is clear that the curve for heptaldehyde and butyraldehyde differs from that of *n*-octane by a figure very close to unity.

(2) The total oxygen consumed by *n*-octane at any temperature should, therefore, be the sum of unity (Reaction 1) plus the moles of carbon monoxide produced (Reaction 2a) plus 1.5 times the moles of carbon dioxide produced (Reaction 2b);   while for heptaldehyde and butyraldehyde the

Oxygen consumption, observed, moles.

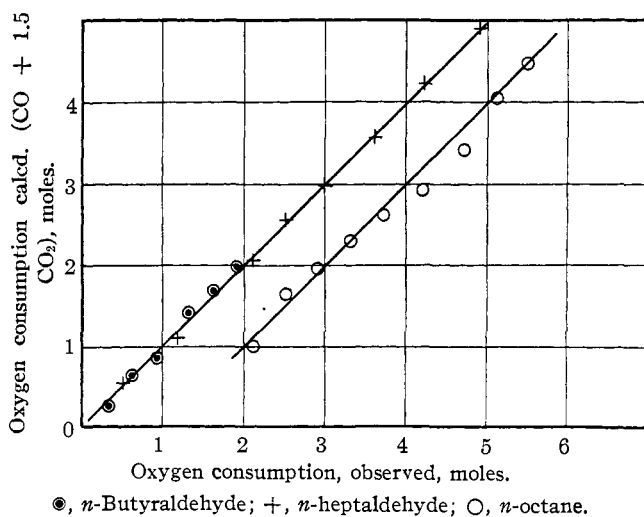⊚, *n*-Butyraldehyde; +, *n*-heptaldehyde; ○, *n*-octane.

Fig. 5.

total oxygen consumed should be the sum of the moles of carbon dioxide produced plus 1.5 times the moles of carbon dioxide produced.   Calculations were made accordingly and the data are compared in Fig. 6 with the experimental data for oxygen consumed.   The agreement is surprisingly good, considering the complexity of the octane and aldehyde molecules and the number of reaction products which are possible.

It was found possible to fit the experimental data for *n*-octane reasonably well by making other hypotheses concerning the initial point of attack, but no other hypothesis than the one cited above gave a simple interpretation of the oxidation of the aldehydes as well.   Any attack of the aldehyde chain other than at the end would involve more oxygen consumption for a given amount of carbon oxides formation than is found experimentally. Such consumption of oxygen, if appreciable, whether by the formation of water and an unsaturated compound, or the formation of a glycol, or ketone

(which would lead to the rupture of the carbon chain at some other position than the end) would make the calculated figures for oxygen consumption diverge from the experimental more widely than is found to be the case. Since practically all of the oxygen consumed is accounted for by the reactions in question, it seems reasonable to suggest that the oxidation of n-octane in the vapor phase proceeds substantially according to the simple hypothesis postulated above.

Lines—calculations.   Points—experimental.   +, n-Heptaldehyde;
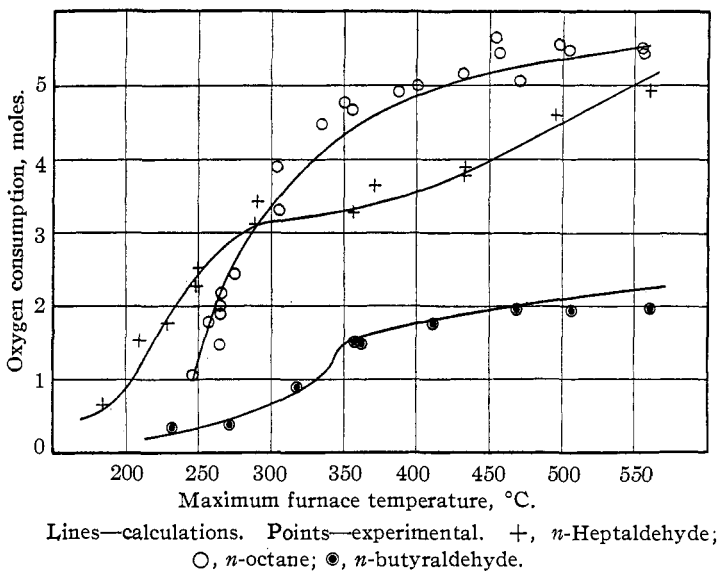O, n-octane; ⊛, n-butyraldehyde.

Fig. 6.

(b)   **Mode of Initial Attack.**—(1) It has been suggested that the initial attack of oxygen upon a hydrocarbon molecule involves the formation of peroxides.   The data cited above offer little evidence for or against such an hypothesis, since such compounds would be expected to be unstable and to exist at any one time in very small amount.   Traces of substances reacting with aqueous potassium iodide were found in the liquid oxidation products examined, their actual concentration varying very little.   It has been pointed out above that their significance is doubtful.   It would appear from this that if those substances represent the peroxides supposedly involved in the initial attack of the hydrocarbon, they are involved in the further oxidation of the aldehydes also, since they appear at temperatures where several moles of oxygen are consumed as well as at low temperatures where the primary oxidation is chiefly concerned.   Certainly there is no evidence here of their accumulation at any stage of the reaction.

(2) As in the case of other investigations of vapor-phase oxidations no experimental evidence was obtained of the formation of alcohols.   This

has been explained, by proponents of the hydroxylation theory, by the supposed ready oxidation of such alcohols to aldehydes. The recent work of Layng and Youker[6] on the oxidation of heptyl alcohol (which confirms the authors' experience with ethyl alcohol) has indicated that alcohols are oxidized in the vapor phase with extreme difficulty in the absence of catalysts. It appears, therefore, much more probable that aldehydes and not alcohols are the primary oxidation products.

(c) **Formation of Carbon Monoxide and Carbon Dioxide.**—There appears to be a distinct difference in the nature of the reactions forming carbon monoxide and carbon dioxide. The latter reaction is unaffected by the rate of heating, and shows no abrupt change at any point. It does not become a large factor in the total reaction until temperatures above 650° are reached. Apparently it is a side reaction presenting no unusual characteristics and has been so considered by the authors.

The reaction involving the formation of carbon monoxide appears to be of an entirely different type. The suddenness with which it appears at about 270°, the sharp decrease in its temperature coefficient at slightly higher temperatures and its accompaniment by pressure surges and luminescent flashes, suggest that it belongs to the class of photochemical "chain" reactions, to which several simpler types of oxidation reactions have been shown to belong. This is supported by certain of the authors' experiments on the oxidation of n-octane in which the reaction tube was filled with glass tubing to increase surface exposure. The formation of carbon monoxide was substantially suppressed under these conditions, while the carbon dioxide formation was little affected. It seems probable that toward the end of Zone 1 activated molecules of some type are beginning to accumulate. That these molecules are those of aldehyde rather than of octane is indicated by (1) the fact that octane oxidizes at these temperatures very readily to aldehyde, and it is therefore present to a very small extent at the exit end of the reaction tube where the luminescent flashes originate; (2) the fact that entirely similar phenomena occur in the oxidation of heptaldehyde and butyraldehyde. The temperature at which they occur with a comparable aldehyde (heptaldehyde) is lower (235° against 270°), but it must be remembered that the concentrations and energy conditions of all reactants are somewhat different in the two cases.

The sudden reaction initiated by these accumulated activated molecules presumably corresponds to the surges and luminescence, the reaction becoming quiescent while fresh accumulation occurs. As the temperature is raised the intervals between the surges become shorter and the reaction is initiated nearer the inlet, finally occurring smoothly at this point.

With heptaldehyde alone the formation of carbon monoxide proceeds slowly at low temperatures without the appearance of surges or lumines-

6 Layng and Youker, *Ind. Eng. Chem.*, **20**, 1048 (1928).

cence, probably because at these temperatures accumulation of active molecules is not occurring at a sufficient rate to initiate the sudden intermittent reactions which occur at somewhat higher temperatures.

(d) **High Temperature Reaction.**—At high temperatures (660–670° for n-octane, and higher than 570° for heptaldehyde and butyraldehyde) the oxidation proceeds practically explosively to carbon dioxide and water. When this reaction begins the temperature in the furnace rises rapidly to a point where it is necessary to discontinue the experiments in order to prevent softening of the glass. No detailed study of this phase of the reaction could therefore be made, and it is not possible to state definitely whether or not the fuels burn directly to carbon dioxide and water, or whether the primary oxidation products are further burned at this stage. The fact that the luminescence associated with the carbon monoxide reaction was still visible between the blue flashes of the second type of explosion would seem to argue for the latter explanation. Further discussion of this point will be given in Part II.

The abrupt changes in reaction character occurring at about 270 and 650° for n-octane have some similarity to certain phenomena involved in the spontaneous ignition of octane–oxygen mixtures, a matter which will be discussed in a later paper.

(e) **Interpretation of the Oxygen Consumption Data.**—In the light of the above interpretation of the experimental facts, it is interesting to examine the oxygen consumption curve (Fig. 2) of n-octane somewhat more closely. The first part of the curve (200–250°) must represent largely formation of water and aldehyde, the latter not oxidizing to any great extent until its concentration becomes appreciable. Its oxidation at these temperatures is largely to carbon dioxide (Reaction 2b) and perhaps partially to acid. As the temperature rises, the oxidation to carbon monoxide predominates, the reaction becoming luminescent and more intense (as evidenced by the sharp rise in temperature immediately after mixing). By the time the temperature has reached 400° the reaction has produced largely aldehydes of the order of butyraldehyde or lower, and these are so much more difficultly oxidized than those of higher molecular weight (compare heptaldehyde and butyraldehyde), particularly in the reduced oxygen concentration, that further reaction occurs very slowly as the temperature is raised until this becomes high enough (above 650°) to carry the oxidation completely to carbon dioxide and water. The oxidation of heptaldehyde slows down similarly when lower aldehydes, sufficiently difficult to oxidize, are formed. It is perhaps significant that the slowing down occurs with heptaldehyde when about three moles of oxygen have reacted, as compared with the similar slowing at five moles of oxygen reacted for n-octane. Presumably the nature of the oxidation products at these respective stages is very similar.

The oxygen consumption curves of heptaldehyde and butyraldehyde are somewhat similar to that of *n*-octane, but the difference in the nature of the early reaction is shown by the fact that in the case of the aldehydes the oxygen consumption corresponds to the carbon oxides formed, while in the case of octane the early stage involves very little of these oxidation products. Altogether it appears that the interpretation of the oxidation phenomena outlined above is in excellent agreement with the experimental facts and affords a simple explanation of most of the phenomena observed.

V.   Summary

1.   The vapor phase oxidation of *n*-octane, *n*-heptaldehyde and *n*-butyraldehyde has been studied in detail.

2.   The results may be simply interpreted on the theory that the initial oxidation product of *n*-octane is octaldehyde, which in turn is further oxidized to aldehydes of successively smaller number of carbon atoms, carbon monoxide and some carbon dioxide being simultaneously formed.

3.   The existence of luminescent "chain" reactions is indicated, apparently corresponding to the oxidation of the aldehydes to lower aldehydes, carbon monoxide and water.

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TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS.   II

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By the combination of spectroscopic and chemical evidence presented in a previous paper[1] it has been shown that the quinonoid modification of 3-methyl-4-hydroxytriphenylcarbinol is not a mixture of the fuchsone and the benzenoid form of the carbinol. Further studies of the absorption spectra of the above-mentioned carbinols, of 3-methoxy-4-hydroxytriphenylcarbinol and of the 5-chloro- and 5-bromo-derivatives of 3-methyl-4-hydroxytriphenylcarbinol have given further evidence of the quinonoid forms of these hydroxytriarylcarbinols.

The quantitative absorption curves of ether solutions of the methanes, benzenoid modifications, quinonoid modifications and the fuchsones of the aforementioned carbinols have been determined and the points in the visible and ultraviolet portions of the spectrum (7600–2350 Å.) at which a maximum and a minimum of energy is absorbed by these solutions have been located. We have found in the curves for some of the quinonoid forms that the absorption band in the violet region and in the ultraviolet region adjacent to the visible is at a position different from that which it has in the corresponding fuchsone (Table I). This is a positive indication in

[1] Anderson and Gomberg, THIS JOURNAL, 50, 203 (1928).