shows that the amount of water added to the hydrogen was without effect on the quantity of water resulting from reaction.

There are several factors which may have affected the amount of water collected. The presence of nitrous oxide and the increase in total pressure due to it may have increased the quantity of water condensing in the trap. The experiments with liquid air indicate that the presence of nitrous oxide had no such effect. As stated above, the measurements were not accurate enough to show whether the amount of water collected varied with the nitrous oxide pressure and hence total pressure. Changes in the pressure may have changed the rate of decomposition of water in the discharge and hence the amount of water leaving. The increase in the water collected upon adding nitrous oxide can be attributed in part to the sum of all the above disturbing factors without altering the general conclusions presented below.

TABLE I

THE FORMATION OF WATER IN THE REACTION OF HYDROGEN ATOMS WITH NITROUS OXIDE AT 25°

P_{H_2}, mm.	P_H, mm.	P_{N_2O}, mm.	Total flow rate cc./min. (25°, 760 mm.)	Milliamperes in discharge	H_2O collected in 30 min.
0.220	0.040	0.178	60.1	230	12.2
.220	.040	0	53.6	230	11.7
.202	.061	0	50.6	230	19.0
.202	.061	.323	63.2	230	23.1
.202	.061	0	49.6	230	18.7
.202	.061	.164	55.7	230	19.4
.097	.029	0	28.8	215	14.8[a]
.097	.029	.010	28.3	215	17.9[a]

[a] Water collected by cooling with liquid air.

The reaction expressed by the equation $H + N_2O \longrightarrow N_2 + OH$ must possess considerable activation energy even though it is exothermic and obeys the spin rule. The hydroxyl formed should yield water as a final product. If the data of Table I are used and the upper limit for the increase in water collected upon adding nitrous oxide is assumed to be 4 mg. in thirty minutes, then the approximate lower limit for the activation energy is 10 kg. cal. Since the reaction shown above is a slow one, then the relatively fast mercury-photosensitized reaction of hydrogen and nitrous oxide[3] must be attributed to some other primary reaction than the one given above. Manning and Noyes[4] have shown that nitrous oxide possesses an abnormally large cross-sectional area for quenching excited mercury. It thus seems most probable that in a system of hydrogen and nitrous oxide the excited mercury transfers most of its energy, which is given up in collision, to the nitrous oxide.

(3) Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

(4) Manning and Noyes, THIS JOURNAL, **54**, 3907 (1932).

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONN.

RECEIVED AUGUST 29, 1933

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

The Vapor-phase Oxidation of Hydrocarbons. I. The Amount and Rate of Oxidation of *n*-Heptane as a Function of Temperature[1]

BY HAROLD A. BEATTY AND GRAHAM EDGAR

Introduction

This series of three papers presents briefly certain data which appear to be of general interest, selected from studies on hydrocarbon oxidation carried on during the past two years in this Laboratory. No attempt has been made to give the material theoretical analysis or to correlate it with the results of other investigators, since the authors feel that the subject as a whole is so complex and the available data are so limited that such procedure is of little utility at the present time.

The present paper reports the effect of temperature on the extent and rate of oxidation of pure *n*-heptane in air, under the same experimental conditions as were used in previous work on the octanes.[2] Our knowledge of the effect of temperature on reactions of this type is decidedly meager. In general, it seems to have been taken for granted that both the amount and rate of oxidation increase with temperature.[3] Different hydrocarbons are spoken of as having a low or high "temperature coefficient of reaction," the criteria for these statements being simply the temperature of initial attack or of initial rapid reaction, or the

---

(1) Presented in part at the Spring meeting of the American Chemical Society at Washington, D. C., April, 1933.

(2) Pope, Dykstra and Edgar, THIS JOURNAL, **51**, 1875, 2203 (1929).

(3) Mondain-Monval and Quanquin, *Ann. chim.*, [10] **15**, 309 (1931); Prettre, *Bull. soc. chim.*, **51**, 1132 (1932).

slope of the initial rise in the oxygen-consumption *vs.* temperature curve.[4]

Actually, these hydrocarbon oxidations are complex chain reactions for which such simple or general characterizations are usually invalid. The temperature coefficient, for example, not only tends to be irregular but may even become less than one or "negative." Indication of this appears in unpublished data of Pope, Dykstra and Edgar, but no reference to this anomaly has been made in the literature except by Pease,[5] who reported that the propane–oxygen reaction is inhibited by dilution with oxygen and other gases and the "suppression . . . is greater at higher temperatures so that the reaction under these conditions has a negative temperature coefficient." The present paper describes a well-defined example of this type of temperature coefficient. It shows also that the reaction as a whole may be divided into several distinct steps or stages, in a manner dependent on the temperature.

Experimental Method

The conventional flow method was used, employing the apparatus and technique previously illustrated and described.[2] The electrically heated Pyrex tube furnace was 2.41 cm. in diameter and 106 cm. in length, of which the first 41 cm. contained a preheater, leaving a reaction chamber 65 cm. long with a volume of 296.5 cc. The furnace was cleaned when necessary (*e. g.*, after using fuel containing tetraethyllead) with nitric acid, acetone and water.

Pure *n*-heptane (from Jeffrey pine oil) was vaporized in a current of nitrogen, and the nitrogen–fuel and oxygen streams, after being separately preheated, were quickly and completely mixed by turbulence at the inlet to the reaction chamber. The oxygen–nitrogen ratio was the same as in the air, and the oxygen–fuel molal ratio was approximately 11 to 1, the theoretical for complete combustion. This gives a concentration of fuel vapor of only 1.9%, which has certain distinct advantages, *e. g.*: (1) the volume change in the gas as a result of reaction is very small, permitting more accurate calculation of the contact times; (2) small variations in oxygen and fuel concentrations have no effect on the results, if these are expressed in relation to the fuel input; (3) the heat evolution of the reaction can be conveniently measured, but is not so excessive as to destroy the significance of temperature determinations; (4) the analysis of the products is in certain respects facilitated.

The flow rate was maintained constant at about 254 ml. (N. T. P.) per minute of gas mixture, giving contact times of from forty seconds at 200° to twenty-three seconds at 550°. Shorter contact times were obtained, without changing the flow rate, simply by withdrawing gas samples through a 2-mm. sampling tube inserted along the furnace axis, its tip being placed 5 or 25 cm. from the inlet.

Temperatures were measured along the furnace axis with movable thermocouples. In each experiment the furnace was allowed to come to constant temperature, *i. e.*, thermal equilibrium, before making any analyses.

The amount of reaction was determined by measurement of (1) the oxygen consumed per mole of fuel input and (2) the percentage of fuel input which was oxidized. The former quantity, with the aid of a precision Orsat apparatus, was determined with an accuracy of about 0.05 mole. To measure the amount of unoxidized heptane, the exit gas was scrubbed with concentrated sulfuric acid, then passed through an empty 100-ml. trap followed by a 250-ml. trap packed with glass wool, both at −78°, the packed trap being necessary to condense the persistent mist or fog present in the gas. At the end of a run the condensate was purified by distillation in a slow current of air through another sulfuric acid scrubber, then was recondensed and weighed. This product had the properties of pure *n*-heptane; the refractive index never differed by more than 0.0001 from that of the original fuel. The maximum error in the figure for percentage of fuel oxidized should be less than 1.0.

The reaction products form a complex mixture of which a satisfactory analysis has not yet been completed. Although such an analysis will undoubtedly add much to our knowledge of the reaction mechanism, nevertheless for the purpose of this paper it is sufficient to state only that there is no marked qualitative change in the nature of the products, as the temperature is raised.

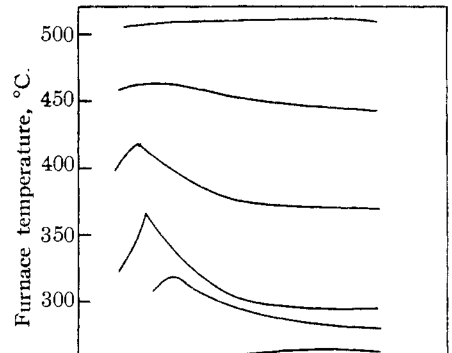

Fig. 1.—Temperature gradients along the furnace axis.

Description of Results

Temperature Gradients.—A general idea of the effect of temperature on the reaction velocity is given by a survey of different temperature gradients along the furnace axis shown in Fig. 1, each representing a separate experiment at thermal equilibrium. The curves could be extended to 60 cm. (5 cm. from the exit) with a further decline of not more than 5 or 10°. In the

---

[4] Wilken-Jordan, *J. Chem. Met. Mining Soc. So. Africa*, **32**, 248, 283, 332 (1932); Mardles, *Trans. Faraday Soc.* **27**, 681 (1931).

[5] Pease, THIS JOURNAL, **51**, 1839 (1929).

absence of reaction, the furnace temperature was uniform from the preheater to the 60-cm. point.

The curves show that at 265° the gas mixture is nearly uniform in temperature. At this point, a slight increase in the heat put into the furnace initiates a relatively rapid or extensive reaction, indicated by a marked evolution of heat near the inlet, the maximum temperature in the gas now being 75° above that of the thermally uniform zone. However, above 380° this effect diminishes, suggesting a decrease in the amount or rate of reaction. Finally at some indefinite point over 500° (not shown in the figure), inflammation occurs near the inlet, with a corresponding sharp rise in temperature.

As Pease[5] points out, the significance of temperature measurements in these rapid exothermic reactions is decidedly vague. In view of the steep gradients which may exist, we prefer to select the maximum temperatures in the gas as being characteristic for the reaction. We feel that these maxima are more truly representative of the actual energy conditions of the mixture, in the zone where most of the reaction occurs, than are any other values such as wall temperatures. Accordingly, all temperature quotations given in the tables and figures are these maximum values.

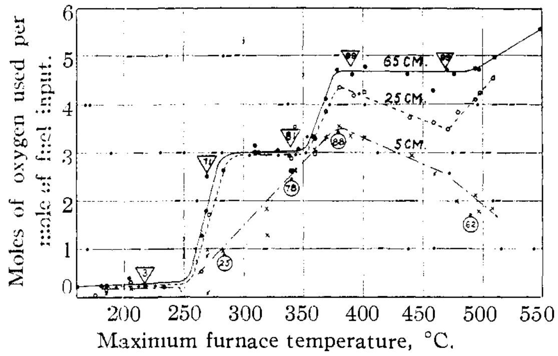

Fig. 2.—Oxygen used: ×, at 5-cm. point; ○, at 25-cm. point; ●, at 65-cm. point. Percentage of fuel input oxidized: ▽, at 65-cm.; ȯ, at 5 cm.

Oxygen and Fuel Consumption.—The experimental determinations of oxygen consumption, at points 5, 25 and 65 cm. from the inlet, are plotted in Fig. 2. A few points are evidently in error by more than 0.1 mole, due either to an irregularity in the behavior of the reaction, or to the fact that, in eight cases, the precision apparatus was not used for the analysis.

The results are given in terms of fuel input, which was known in every case. To express these data in terms of fuel oxidized, it is necessary to know the percentage of heptane input which reacted. The results of such determinations (each requiring a special experiment) are given in Table I, and the figures for the percentage of fuel oxidized are also shown in Fig. 2, enclosed by triangles and circles.

TABLE I

HEPTANE OXIDIZED, PER CENT. OF INPUT

Point of sampling, cm. from inlet	Mean[a] temp., °C.	Heptane, grams Input	Heptane, grams Recov.	% heptane input oxidized	O_2 used per mole of fuel oxidized[b]
65	217	3.282	3.189	2.8	9.0[c]
65	270	3.413	1.008	70.5	3.0[d]
65	340	3.432	0.652	81.0	3.70
65	390	4.0	trace	99+	4.70
65	470	7.0	*ca.* 0.05	99+	4.70
5	283	5.246	3.957	24.6	4.0[c]
5	343	3.378	0.728	78.4	3.31
5	380	3.764	0.440	88.3	3.96
5	490	5.890	2.231	62.1	2.94

[a] In runs made above 300°, the maximum temperature fluctuated within a 5 or 10° range due to the slight variations in the heating current over a period of several hours. [b] These are calculated values obtained by dividing the values per mole of fuel input (taken from the curves of Fig. 2) by the percentage of fuel oxidized. [c] This value may be in error by as much as 25%, as will be apparent from an examination of Fig. 2. [d] The slope of the oxygen-consumption curve is too great at this point for accurate calculation of this value: it should lie between 2.8 and 3.6.

As stated, the gas samples were taken at three different distances from the inlet; at 5 and 25 cm. (by means of the sampling tube), and at 65 cm., the furnace exit. Obviously, the true contact times corresponding to these distances vary with the temperature and, to a very slight extent (neglected in the calculations), with the amount of reaction. Nevertheless, the distance may be taken as proportional to the contact time through the range of temperature used without significant error, due to the fact that most of the reaction occurs within 5 cm. and, below 380°, is essentially complete within 25 cm. from the inlet. This can be shown by plotting the available data for oxygen and fuel consumption against the time of reaction. We can then estimate with a fair degree of accuracy the slopes of the various isotherms in the neighborhood of the plotted points, and thus calculate the oxygen and fuel consumption for a fixed contact time. These data are compared in Table II with the results experimentally obtained at a fixed contact distance. The volume of the sampling tube has been included in computing the size of the reaction zone.

TABLE II

EFFECT OF SUBSTITUTING REACTION ZONE LENGTH FOR CONTACT TIME

Moles of oxygen used

	Temperature, °C.	250	300	340	380	470	500
O_2 used	In 2.8 seconds contact time	0.25	1.40	2.45	3.52	2.62	2.15
	At 5 cm. from the inlet	0.25	1.50	2.50	3.50	2.50	1.90
	In 10 seconds contact time				4.30	3.48	4.37
	At 25 cm. from the inlet				4.35	3.50	4.30

Per cent. of heptane oxidized

	Temperature, °C.	283	343	380	490
% Oxidized	In 2.8 seconds contact time	22	78	89	65
	At 5 cm. from the inlet	24.6	78.4	88.3	62.1

General Description and Discussion of the Reaction.—In the furnace used in this work, a slow oxidation begins at a very low temperature, around 150°, and mist appears in the exit gas at 175°. There is no evidence of any induction period, and the low rate of reaction and large oxygen consumption per mole of heptane oxidized at 217° (see Table I) suggest the presence of a heterogeneous reaction resulting in nearly complete combustion of each fuel molecule that is attacked.

At about 250° the main reaction begins, and increases rapidly in rate and amount so that at 270°, 70.5% of the heptane is oxidized, of which about 24% disappears in the first 5 cm. The oxidation is now definitely of the "homogeneous," chain-mechanism type and is accompanied by visible chemiluminescence (see paper No. III of this series). At about 270° it reaches a critical condition, typical of these chain reactions, which results in a so-called ignition—a sort of mild explosion causing a pulsation of the flowmeters and visible, flame-like movements in the luminescent gas within the furnace, but without any particular increase in oxygen consumption. These ignitions, at first eight or ten seconds apart, occur more rapidly as the temperature is raised until at about 305° they become continuous.

It is during this stage that the marked local evolution of heat becomes apparent, with the result that the maximum temperature in the gas rises abruptly to 350°; the reaction velocity increases rapidly, as shown by the 5-cm. curve, but the amount of oxidation remains constant at 3.00 moles. In view of the fact that the reaction in this range seems to be practically complete at 25 cm., it is surprising to find only 81% of the heptane oxidized at 340°. This may be an erratic result, since the position and value of the maximum temperature in this run fluctuated in an irregular manner, and the latter for a time dropped to 302°, as a result of the extreme sensitivity of the reaction at this stage. However, it seems equally probable that all the reaction took place in the hot zone near the inlet, so that any fuel passing through this zone remained unattacked (the temperature from 20 to 65 cm. being, probably, less than 275°).

It is important to note that the two analyses for unoxidized heptane at 5 cm. near the beginning and end of this temperature range (*i. e.*, at 283 and 343°) each give an oxygen consumption per mole of fuel oxidized of 3 or more moles, and the analysis at 490° likewise gives a value of 3 within experimental error. This strongly suggests that it would be difficult or impossible (with the present set-up) to isolate primary reaction products corresponding to less than 3 moles of oxygen used. Accordingly, we shall call this 3-mole oxidation the *primary reaction;* its velocity is measured by the rate at which the heptane disappears.

Continuing up the temperature scale, we find from 350 to 380° a sharp increase in the total amount of oxidation, from 3.00 to 4.70 moles of oxygen. This increase may be considered as a *subsequent reaction.* The rate of the primary reaction rises from 78.4 to 88.3% complete in 5 cm., while at the furnace exit only a trace of unoxidized fuel is recovered. The latter was found to be dissolved in the electrically charged mist present in the exit gas, suggesting that it is carried through the furnace in a condition in which it is protected from oxidation.

From 380 to 490° no change whatever in the total amount of oxidation (at 65 cm.) takes place, although the oxygen used is only 42.7% of the theoretical for complete combustion. (Oxidation of all the carbon monoxide present to carbon dioxide would raise this figure only to 56.3%.) This extraordinary passivity implies an unexpectedly high stability of the reaction products with respect to oxygen. Identification of these products, a matter of obvious interest, has not yet been completed. We may, however, point out at this time that the amount of carbon oxides formed is quite similar to that found for n-octane.[2] Carbon dioxide appears first, and increases steadily to the amount of 0.75 mole per mole of fuel input at 380°, which amount then remains constant up to the inflammation point. On the other hand, the amount of carbon monoxide formed increases, with the oxygen consumption, in a step-wise manner, and reaches 2.15 moles at 380°; it then rises slowly but steadily with further increase in temperature, attaining a value of 3.0 moles at 470°.

Finally, at some indefinite temperature from 500 to 525° inflammation occurs, probably initiated by a breakdown of the reaction products such as is indicated by the increase in oxygen consumption. Complete combustion to carbon dioxide and water follows, the temperature in the gas rises rapidly and the ignition, at first intermittent, becomes continuous (see paper No. III of this series).

Although the amount of reaction from 380 to 490° remains constant, the rate undergoes a remarkable change, as shown by the 5- and 25-cm. curves. From 380 to 470° the temperature coefficient of velocity is markedly negative; the percentage of reaction completed in 25 cm. falls from 93 to 75 (in ten seconds, from 92 to 74.5%); the distance or time required for the uptake of 3.5 moles of oxygen increases from 5 to 25 cm. or from 2.70 to 10.1 seconds, corresponding to a 10° coefficient of 0.86. If, in this calculation, the volume of the sampling tube be neglected—and it seems improbable that much reaction occurs in such a narrow (2-mm.) tube—the contact times become 2.25 and 9.9 seconds, giving a coefficient of 0.85.

Moreover, the two analyses for unoxidized heptane at 5 cm. at 380 and 490° show clearly that both the primary 3-mole and the subsequent 1.7-mole reactions are affected by the negative coefficient. The primary reaction, as shown, decreases from 88.3 to 62.1%. The corresponding oxygen consumptions per mole of heptane oxidized are 3.96 and 2.94 moles, whence, after deducting from these figures the primary 3 moles, there remains for the subsequent reaction about 1 and 0 mole, respectively. It is therefore apparent that the negative temperature effect derives from some condition or process common to the reaction as a whole, and is not concerned only with the initial attack on the fuel molecule. Nevertheless, there must be some well-defined difference or distinction between the primary and secondary reactions, inasmuch as the latter, at about 470°, appears to increase in rate, as indicated by the 25-cm. curve, while the primary reaction continues to decline.

Summary

The effect of temperature on the amount and rate of autoxidation of a theoretically equivalent mixture (2%) of *n*-heptane vapor in air has been studied by the flow method at atmospheric pressure in a clean Pyrex tube.

As the maximum temperature in the gas is increased, the oxidation proceeds in a series of well-defined stages, as follows:

1. 150–250°—There is a very small amount of reaction, possibly heterogeneous.
2. 250–350°—With rapidly increasing velocity, a primary reaction, using 3.00 moles of oxygen per mole of fuel input, takes place and is terminated within the furnace.
3. 350–470°—A subsequent reaction raises the oxygen used to 4.70 moles (42.7% of the theoretical), which remains constant. The velocity of both the primary and subsequent reactions *decreases* rapidly with increasing temperature, the 10° temperature coefficient being about 0.85 from 380 to 470°.
4. 470–510°—The velocity of the primary reaction continues to decrease, but the subsequent reaction now becomes accelerated, and above 490° the final amount of oxygen used is increased.
5. About 510°—Inflammation occurs.

DETROIT, MICH. RECEIVED JULY 6, 1933