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

The Vapor-phase Oxidation of Hydrocarbons. II. The Relative Oxidizability of *n*-Heptane, 1-Heptene, 3-Heptene and *n*-Heptane-2,2,4-Trimethylpentane Mixtures

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Introduction

The amount and rate of oxidation of pure *n*-heptane in air as a function of temperature have been described in the first paper of this series.[1] The present paper compares the oxidation of heptane with that of (1) two corresponding olefins, 1-heptene and 3-heptene, and (2) a structurally dissimilar paraffin, 2,2,4-trimethylpentane (hereafter called by its familiar name, isooctane), alone and in mixtures with heptane.

The behavior of the olefins is of interest since it has generally been considered that the attack of oxygen occurs at the double bond,[2] and that these compounds are more readily oxidized than the corresponding paraffins.[3] In the present investigation it is shown definitely that, at least under the particular experimental conditions employed, this is not the case. As found for heptane, the effect of temperature on the oxidation of the olefins is complex, and cannot be expressed by a simple statement such as that of Mardles,[4] who reports that "the temperature coefficient of gaseous reaction" is lower for three pentenes than for normal and isopentane.

The oxidation of mixtures of *n*-heptane with the relatively inert isooctane furnishes a clear example of gas-phase inhibition and induced oxidation. This type of reaction has received almost no investigation, although Mardles[5] found that the oxidation of hexane, pentane and pentene is retarded by benzene, which is converted to phenol, at temperatures where the benzene alone is inert to oxygen.

Experimental Method

Using the apparatus and technique previously described,[1,6] a mixture of 2% of fuel vapor in air was oxidized by the flow method in a Pyrex tube furnace, and the oxygen consumption determined by analysis of the exit gas.

The results for heptane and the heptenes are not directly comparable with those reported for heptane in the previous paper,[1] for two reasons. The furnace, designated No. 1, used in the present case (and also, formerly, for the octanes[6]) was considerably less active than that one, No. 2, used in the previous work on heptane; furthermore, the present data were obtained in part, not at thermal equilibrium, but with the temperature rising about 2° per minute, a method which permits the investigation of a wide range of temperature in a single experiment, but gives results quantitatively not in agreement with those from runs at thermal equilibrium. In particular, the rising temperature runs tend to give smooth oxygen consumption *vs.* temperature curves, the stepwise nature of the reaction being obscured. However, the rising temperature data show very good reproducibility, and appear to give a satisfactory basis for comparison of relative oxidizability. The foregoing remarks apply also to the experiments on isooctane, except that for this fuel both furnaces were used.

Determinations of the percentage of hydrocarbon which reacted were not made for the heptenes and for pure isooctane, but for the heptane-isooctane mixtures it was essential to measure as accurately as possible, not only the amount of unoxidized fuel, but also the concentrations of heptane and isooctane in this fuel. Blank tests showed that the unoxidized fuel was recovered quantitatively by the method of purification and condensation previously described.[1] The material so recovered was assumed, on the basis of its chemical and physical properties and mode of production, to contain only *n*-heptane and isooctane. No satisfactory chemical method could be found for the analysis of this hydrocarbon mixture; for example, fuming nitric acid (d. 1.4) acts vigorously on isooctane and has no apparent reaction with *n*-heptane at room temperature, but in a 50-50 mixture of the two hydrocarbons, the heptane is destroyed almost as fast as the isooctane. Of the possible physical analytical methods, the temperature of miscibility with aniline was found to be the most satisfactory. A standardized test was adopted, which consisted of determining the temperature at which the mixture of 1.6 volumes of a hydrocarbon mixture with 1 volume of aniline separates into two layers. Tests made on known heptane-isooctane mixtures indicated that there is a linear relationship between these temperatures and the molar composition of the hydrocarbon mixture. The temperatures of miscibility of the pure hydrocarbons with aniline under these conditions differed by 10.25° and, since the temperatures were determined to the nearest 0.05°, the compositions of the reaction product mixtures were determined to 0.5%, with a probable accuracy of twice that variation, or 1.0 in the percentage figure. This is equivalent to about 0.1 in the molar ratio of isooctane to heptane oxidized.

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(1) Beatty and Edgar, THIS JOURNAL, **56** 102 (1934).

(2) Lenher, *ibid.*, **52**, 3737, 3752 (1930).

(3) Lewis, *J. Chem. Soc.*, 1555 (1927); 759 (1929); Pidgeon and Egerton, *ibid.*, 676 (1932).

(4) Mardles, *Trans. Faraday Soc.*, **37**, 700 (1931).

(5) Gill, Mardles and Tett, *ibid.*, **24**, 574 (1928); Mardles, *ibid.*, **27**, 681 (1931) See also, Brunner, *Helv. Chim. Acta*, **13**, 197 (1930).

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

The *n*-heptane and isooctane used were the very pure commercial products obtained, respectively, from Jeffrey pine oil and by hydrogenation of diisobutylene. Two blends were prepared, containing 50 and 75 ± 0.2% by volume (47.0 and 72.7 mole per cent.) of isooctane. The 1-heptene, b. p. 93.5–93.8° and the 3-heptene, b. p. 96.0–96.2°, were synthesized by Mr. Donal T. Flood of this Laboratory, and purified by repeated fractional distillation.

Experimental Results

Heptane, 1-Heptene and 3-Heptene.—The relative amount of oxidation of these three hydrocarbons as a function of temperature is shown in Fig. 1. All of these data were obtained in furnace No. 1 with slowly rising temperature, using the full length of the furnace tube. The temperature distribution in the furnace at two different stages, under conditions of thermal equilibrium, is shown in Fig. 2, and the amount of oxidation at different points within the furnace, likewise at thermal equilibrium, is shown in Fig. 3.

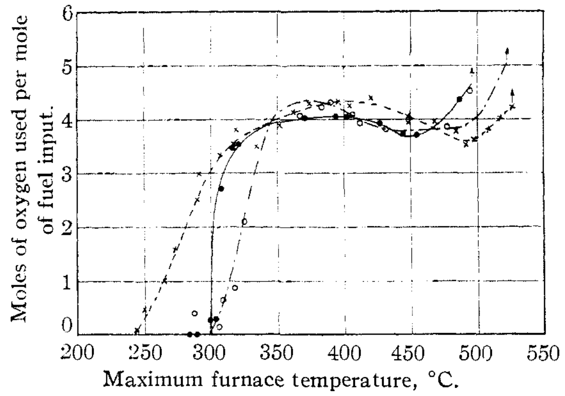

Fig. 1.—×, *n*-heptane; ●, 1-heptene; ○, 3-heptene; ↑, inflammation point.

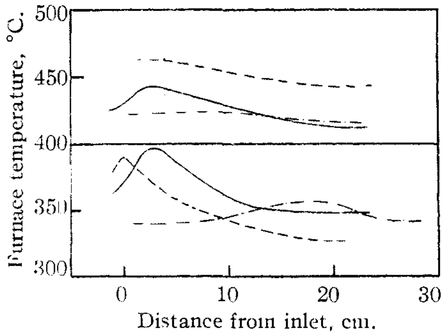

Fig. 2.—Temperature gradients along the furnace axis: ———, 1-heptene; —·—, 3-heptene; — — —, *n*-heptane.

It is clear from Fig. 1 that the oxidation for heptane (in Furnace No. 1) begins at 244°, while the heptenes do not react until 300° has been reached. This suggests that, under these conditions at least, the oxidation of the olefins does not begin at the double bond, a conclusion previously reached for 1-octene.[6] In all three cases the oxygen consumption proceeds rapidly to a maximum value which is only about 40% of the theoretical for complete combustion. About 400° a slight decline in the oxygen consumption is evident, due, as will appear later, to the negative temperature coefficient of reaction velocity.

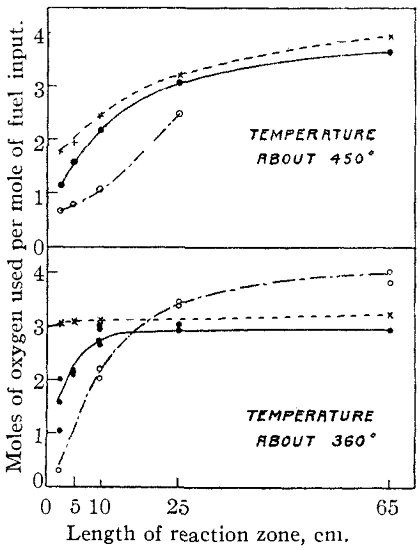

Fig. 3.—Oxygen consumption *vs.* contact time: ●, 1-heptene; ○, 3-heptene; ×, *n*-heptane.

Although the course of the oxidation appears from Fig. 1 to be similar for each of the hydrocarbons in question, the respective *rates* of reaction are distinctly different. Indication of this is given by the temperature gradients plotted in Fig. 2, which show that the heptane reacts closer to the furnace inlet than 1-heptene, and that in turn closer than 3-heptene. Comparison of the curves at low and high temperatures indicates definitely a negative temperature coefficient for all three hydrocarbons.

A more precise determination of the relative rates of reaction is given by measurements of the amount of oxidation at different contact times, obtained by analyzing samples collected through a sampling tube inserted along the furnace axis. These data are given in Fig. 3 and show at both low and high temperatures a decided increase in reaction velocity in going from 3-heptene to 1-heptene and thence to *n*-heptane.

Isooctane Alone.—The previous publication on isooctane by Pope, Dykstra and Edgar[6] gave only the results of two rising-temperature runs. Their unpublished data for seven constant-temperature runs in furnace No. 1 are shown in Fig. 4, together with our results from similar runs made in the more active furnace No. 2. The agreement between these two sets of experiments makes it evident that in this case the reaction is not much influenced by the specific activity of the furnace walls.

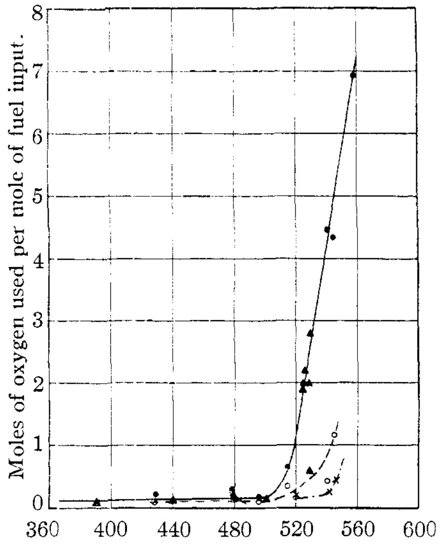

Fig. 4.—Oxygen used: ×, at 5-cm. point; ⊙, at 25-cm. point; ●, at 65-cm. point; ▲, results of Pope, Dykstra and Edgar.

Chemical tests for the initial appearance of aldehydes, carbon dioxide and water showed that a trace of oxidation below 500°, indicated by the gas analysis, does occur and begins at about 250°. No determination of the unoxidized fuel was made, but it appears that the reaction, in this region, is similar to that found for *n*-heptane at about 200°, where only a small part of the fuel reacts but is oxidized almost completely. It seems, therefore, very probable that this trace of oxidation is the result of a heterogeneous reaction.

At 500° the main reaction begins, and increases rapidly in amount until, at about 550°, inflammation occurs. At 545° the final oxygen consumption (at 65 cm. from the inlet) is well over 4 moles, but the reaction velocity, as shown by the samples taken at 5 and 25 cm. from the inlet, is very low; there is evidently a sort of induction period, which was not found in the case of *n*-heptane.

Heptane-Isooctane Mixtures: Amount and Rate of Oxygen Consumption.—For the blend containing 50 volume per cent. of heptane, a comparison of Curve A of Fig. 5, obtained in furnace No. 1 at slowly rising temperatures, with the corresponding curve for heptane alone (Fig. 1) shows that the reaction of the mixture begins about 10 or 15° higher, and attains a maximum oxygen consumption per mole of total fuel input of 68% of that of heptane alone; the negative temperature coefficient appears as before. The reaction velocity at 374° appears from Fig. 6 to be somewhat less than that of pure heptane (Fig. 3), in agreement with which it was observed that the maximum temperature rise in the gas was only 44 or 20° per mole of oxygen used, whereas the corresponding figure for heptane alone is 24° per mole.

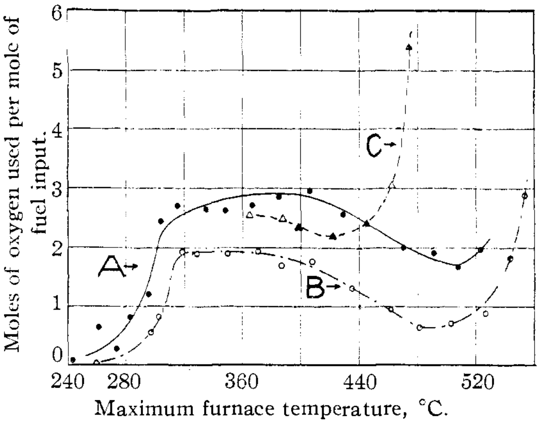

Fig. 5.—●, 50-50 heptane-isooctane blend; ○, 25-75 blend; each in the old furnace. ▲, 25-75 blend, new furnace; △, same, at thermal equilibrium.

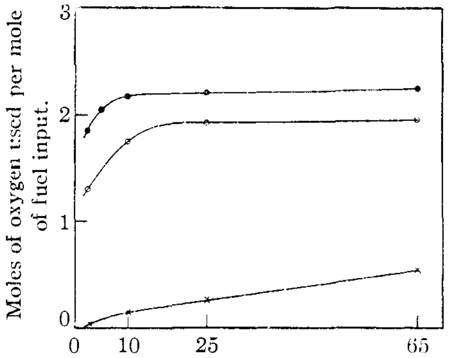

Fig. 6.—Oxygen consumption *vs.* contact time: ●, 50-50 heptane-isooctane blend at 374°; ○, 25-75 blend at 367°; ×, at 504°.

For the mixture containing 25% of heptane, Curve B of Fig. 5 resembles the corresponding Curve A. The reaction begins at some 20° higher temperature; the maximum oxygen consumption is again much greater than could be accounted for by the oxidation of only the heptane; the negative temperature coefficient appears as before. In this case the two constant-temperature runs at 365 and 504° show good agreement with the rising-temperature values, probably due to the lower evolution of heat within the furnace. These two runs are plotted in detail in Fig. 6, and indicate a reaction velocity at *ca.* 370° slightly less than that of the 50% mixture; the maximum temperature rise in the gas was 31 or 16° per mole of oxygen used. The very low velocity at 504° is apparent from the figure.

At this point in the investigation, furnace No. 1 was damaged beyond repair, and No. 2 was constructed. Its greater activity is displayed by Curve C of Fig. 5, which shows an oxygen consumption of 0.6 mole more than that of Curve B. This increase appears extraordinary, inasmuch as the reaction at 365° in furnace No. 1 was terminated long before the gas reached the furnace exit, as shown in Fig. 6.

The inflammation temperatures for the two mixtures were not accurately determined, but were, in furnace No. 1, in the neighborhood of 550°, somewhat higher than for *n*-heptane. In furnace No. 2, however, the unusually low value of 480° was found for the 25% mixture; although only one determination was made, it was probably valid, as indicated by the upward slope of Curve C of Fig. 5 at about 420°. The significance of these values is uncertain, since we know little or nothing as to the relation between the temperature of inflammation and the nature of the slow oxidation process.

Heptane–Isooctane Mixtures: Fuel Consumption and Induced Oxidation.—Having determined the oxygen used per mole of total fuel input, there remained the problem of finding the amount of each fuel which reacted, in order to arrive at (1) the true oxygen consumption, that is, per mole of fuel oxidized, and (2) the amount of induced oxidation. These determinations were all made at thermal equilibrium.

For the 50% mixture, a crude analysis at 375° gave a recovery of unoxidized fuel of 12% by weight of the input, from which it is clear that most of the isooctane was oxidized. The oxygen used per mole of fuel oxidized is then about 2.6 moles. In like manner, at 490° some 9% of the hydrocarbon mixture was recovered; the oxygen used was 2.83 moles or 3.1 moles per mole of fuel oxidized.

For the 25% mixture, accurate determinations and analyses of the unoxidized fuel were made at 383° at 5 and 65 cm. from the inlet, and at 462° at 65 cm., all in furnace No. 2. Gas analyses were made on the 65-cm. samples only; the oxygen used at 5 cm. was estimated to be 80% of the corresponding 65-cm. value, this being the ratio found in furnace No. 1 at 367° (Fig. 6). The results are given in Table I and Fig. 7.

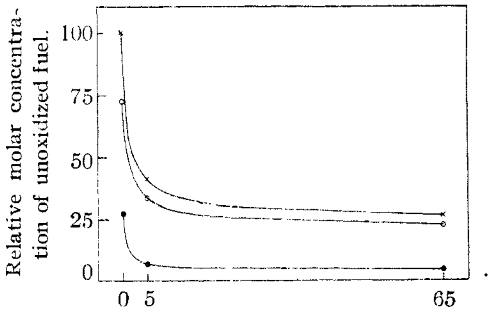

Fig. 7.—●, Heptane; ○, isooctane; ×, total fuel.

The oxygen consumption per mole of fuel oxidized is seen to be fairly high, and constant. Since we cannot tell the proportion in which this is divided between the two hydrocarbons, it is impossible to make any statement as to how the amount used by the heptane compares with the 4.70 moles previously found for the uninhibited reaction. If we assume, as a probable maximum, this value of 4.70 moles for the heptane in this case, there still remains about 2.8 moles of oxygen for each mole of isooctane which reacted.

The amount of induced oxidation is striking, and appears to be very nearly proportional to the concentration of isooctane present relative to that of heptane present. That is, the ratio of isooctane to heptane oxidized increases as the gas mixture passes down the furnace and the ratio of isooctane to heptane remaining unoxidized becomes greater. At 383°, the value of the latter ratio at any point in the furnace may be estimated with good accuracy from a large-scale plot of the similar, "smooth" curves of Fig. 7. We may then obtain graphically, for a given length of the reaction zone, the mean value of this ratio (isooctane/heptane unoxidized) calculated with respect to the rate of disappearance of heptane. From 0 to 5 cm. and from 5 to 65 cm. these mean values are, respec-

TABLE I

AMOUNT OF EACH OXIDIZED IN A MIXTURE OF 25% OF *n*-HEPTANE IN ISOOCTANE

Maximum furnace temperature, °C.		383	383	383	462
Reaction zone limits, cm. from the inlet		0–5	5–65	0–65	0–65
Mole % of input oxidized	Heptane	73.2	13.0	86.2	95.9
	Isooctane	53.7	16.0	69.7	84.3
	Total fuel	59.0 (88.3)[a]	15.2 (11)[a]	74.2 (99+)[a]	87.5 (99+)[a]
Moles isooctane/heptane oxidized		1.95	3.28	2.15	2.33
Oxygen used, moles per mole of total fuel oxidized		3.41 (3.96)[a]		3.39 (4.70)[a]	3.45 (4.70)[a]

[a] For comparison, the corresponding data for *n*-heptane alone from Paper I of this series[1] are given in parentheses.

tively, about 3.44 and 5.21, or in the proportion of 1 to 1.51. The corresponding values of the ratio of isooctane to heptane oxidized are seen from Table I to be 1.95 and 3.28, respectively, or in the proportion of 1 to 1.68.

At the same time that the gas is passing down the furnace and the relative concentration of isooctane is increasing, the reaction velocity, as indicated by the rate of disappearance of the heptane, undergoes a striking decrease (see Fig. 7). This decrease, which is much greater than that found for *n*-heptane alone,[1] cannot be accounted for by the decline in the partial pressure of heptane; rather, it appears that as soon as the relative concentration of isooctane becomes higher than 4 or 5 to 1, its inhibitory effect becomes marked.

Heptane–Isooctane Mixtures: Anti-Knock Value.—It is generally recognized that the tendency of a hydrocarbon mixture to cause detonation in an internal combustion engine is, at least in part, a function of its autoxidation characteristics. It seems, therefore, of interest to compare the above described behavior of heptane–isooctane mixtures with the corresponding anti-knock values of such mixtures. Campbell, Lovell and Boyd[7] have shown that the absolute anti-knock value, determined as the compression ratio for incipient knock, of heptane–isooctane blends increases slowly and linearly from 2.75 at 0% to 4.0 at 70% of isooctane; with further increase in the percentage of isooctane, the anti-knock value accelerates upward to 6.90 at 100%. It is evident that the effect of isooctane on the anti-knock value is parallel to its inhibitory influence in the slow oxidation, the relative increase in each effect becoming marked at high concentrations of isooctane.

Summary

Using a Pyrex furnace and the flow method, a comparative study has been made of the oxidation, at different temperatures, of theoretically equivalent (2%) mixtures with air of *n*-heptane, 1-heptene, 3-heptene, isooctane (2,2,4-trimethylpentane), and isooctane mixed with one or three volumes of *n*-heptane.

The temperature of initial oxidation of the two olefins is the same for each, and is 56° higher than that of *n*-heptane. The general course of the reaction and the maximum oxygen consumption (about 40% of the theoretical) are alike for these three hydrocarbons, but the relative reaction velocities are distinctly different, increasing in the order: 3-heptene–1-heptene–*n*-heptane. It appears that, under the conditions used, the oxidation of the olefins does not begin at the double bond.

Isooctane, itself very inert toward oxygen, when mixed with *n*-heptane exercises a slight inhibitory effect on the oxidation of the latter fuel and undergoes induced oxidation. There is evidence that this effect is much more pronounced at higher relative concentrations of isooctane, resulting in a very low rate of reaction and in an induced oxidation of over three moles of isooctane per mole of heptane oxidized, a behavior parallel to the anti-knock characteristics of such mixtures.

From about 400 to 500° a marked negative temperature coefficient of reaction velocity is observed for each fuel, with the exception of pure isooctane which undergoes only a trace of oxidation in this range.

DETROIT, MICH.

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(7) Campbell, Lovell and Boyd, *S. A. E. Journal*, **26**, 163 (1930).