

ACKNOWLEDGMENT

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Effect of Preflame Oxidation Reactions on Engine Knock

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EXTENSIVE research by many investigators in recent years has shown that early chemical reactions precede knock in internal combustion engines. These reactions take place in the fuel-air mixture ahead of the normal flame front prior to the occurrence of knock and are generally referred to as precombustion or preflame reactions. Reactions of this type are thought to proceed in a stepwise fashion, during which a large variety of intermediate products are formed, since an instantaneous collision of a fuel molecule with all the oxygen molecules needed for its complete combustion is inconceivable. The exact mechanism of this oxidation process is not well understood because of the inherent difficulties arising from the fact that some of these reactions are very rapid and that many of the products are very unstable. For these reasons, the investigation of precombustion reactions in internal combustion engines has been a difficult experimental problem.

The chemical reactions preceding knock may be divided into two classes. The first type includes those reactions which have been called precombustion reactions and which are characterized by the evolution of relatively large quantities of light and heat with consequent rise in pressure but which do not result in complete combustion. Previous engine studies of these precombustion reactions have been based on pressure-time records of the engine cycle, measurement of temperature of unburned exit gases from nonfired engines, and cool flame detection in motored engines. In the various experimental techniques used to detect the presence of precombustion reactions, it has been shown that the start of the pressure rise due to partial combustion coincides with the detection of radiation (1, 4).

A lesser known work (?) shows that the pressure rise starts at the same time as the rise in temperature of the exit gases from a motored engine. With these facts in mind, it is not unreasonable to assume that these three types of measurement of precombustion reactions refer to three manifestations of the same phenomenon.

The second type of reactions includes those which cannot be detected by any large scale energy release. In this paper they are referred to as small scale or precool-flame reactions. These reactions have been detected by application of absorption spec-

trographic techniques to the processes occurring in the end zone of the engine (12), and extraction of small samples from the engine combustion chamber by means of sampling valves (2).

Research in this field thus far has not indicated the relative importance of these two classes of reactions with regard to effect on engine knock. Although these reactions have been extensively studied outside of the engine and classified into two regimes—namely, τ_1 and τ_2 (5)—no comparable differentiation has been made in engine studies. This paper presents two new investigative techniques for the study of these processes and indicates the effect of these processes on knock.

METHODS FOR PRODUCING PREFLAME OXIDATION REACTIONS

To study the precise relationship between early chemical reactions in the combustion chamber of an engine and the tendency of a fuel to knock, two types of experiments were carried out. The first experiment employed a system of two substantially identical engines, the first of which was motored and not fired, while the second operated in a conventional manner. The engines were connected in such a way that the products leaving the first engine were led directly into the intake manifold of the second engine, in which the knocking tendency of the discharge from the first engine was measured. Thus, it was possible to measure the progress of knock-inducing reactions caused by compression of the fuel-air charge in the first engine.

The second experiment was similar, in that an engine was again employed to measure the effect of precombustion reactions on knock. However, a heated tube, in which temperature of the gases could easily be measured and cool flames detected, was used instead of a motored engine to produce a prereacted charge. For purposes of clarity, the apparatus and results of each experiment are discussed separately.

PRODUCTION OF PREFLAME OXIDATION REACTIONS IN AN ENGINE

The apparatus used in this experiment consisted of two special variable-compression-ratio, valve-in-head, single-cylinder engines of 17.6-cubic-inch displacement arranged as shown in

Figure 1. The fuel and air were inducted into the first engine through a conventional CFR carburetor. The mixture ratio, maintained at 0.077, was determined by volumetric measurements of the fuel and air. This engine had no spark plug and was motored by a dynamometer. The speed of the first engine was adjusted to approximately 780 r.p.m. in order to maintain an absolute pressure of 74.5 cm. of mercury in the manifold between the two engines. The exit gases from this engine (containing the products of the precombustion reactions) were conducted to the intake manifold of the second engine by a pipe about 5 meters long, which was kept at 65° C. in order to minimize condensation. Safety valves were installed in this manifold as a precaution against the generation of excessive pressures. A thermocouple was mounted in the exhaust port of the motored engine. With the first engine operating at 780 r.p.m., the exit gases required 23 seconds to pass from the first engine to the second.

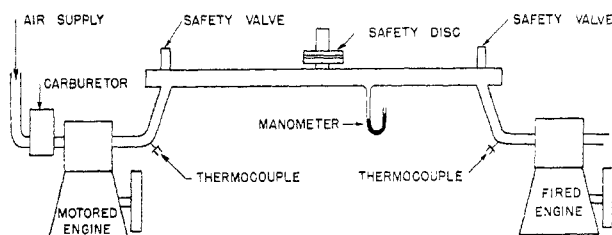


Figure 1. Engine Apparatus Used to Measure Effect of Preflame Oxidation Reactions on Engine Knock

The second engine had no carburetor and was operated at a speed of 900 r.p.m. and maximum power spark advance. Power generated in this engine was absorbed in a constant-speed electric motor. In the sense of power or engine torque, the two engines were entirely separate and distinct.

For each fuel under investigation, the test was carried out in the following manner: The compression ratio of the motored engine was first set at a value of about 8, and the knocking tendency of the exit gases was measured by determining the knock-limited compression ratio of the fired engine. This process was repeated at successively higher compression ratios in the motored engine until the fuel-air mixture autoignited or until the mechanical limit of compression ratio was reached at about 17.

FOUR REGIONS OF REACTION

The general trend of the results obtained in this experiment indicates that, below a limiting compression ratio in the motored engine, the antiknock quality of the exit gases for each particular fuel is constant. As compression ratio is increased progressively above the limiting value, the antiknock quality of the exit gases decreases and then, for some fuels, increases to a value exceeding that for the mixture when the compression ratio of the motored engine is below the limiting value. Thus, four regions of reaction in the motored engine can be distinguished as its compression ratio is increased.

1. The first region is characterized by no change in knocking tendency of the exit gases from the motored engine. In this region the first engine is merely serving as a pump to supply fuel and air to the second engine without altering the chemical nature of the mixture.

2. In the second region, the exit gases from the motored engine decrease in antiknock quality as the compression ratio of this engine is increased. During this stage chemical reactions are occurring in the motored engine which produce knock-inducing products.

3. The third region is distinguished by an increase in antiknock quality of the exit gases as the compression ratio of the motored engine is further increased. This phenomenon is thought to be partly due to the fact that the fuel is undergoing partial oxidation in the first engine, so that the exit gases entering

the second engine have a significantly smaller heat of combustion (9). This was confirmed by a measurement of power developed in the fired engine, which was shown to drop only under these conditions. A second factor is the possible presence of water vapor and possibly other precombustion products which tend to decrease knock in the second engine.

4. The fourth region is characterized by autoignition in the first engine, and consequently no knock ratings can be made in the second engine.

MIXTURES OF ISO-OCTANE AND *n*-HEPTANE. The first experiments were made with a series of mixtures of *n*-heptane and iso-octane (2,2,4-trimethylpentane) ranging from 0 to 100 octane number. The results shown in Figure 2 indicate the first, second, and fourth regions of reactivity in all cases, although the extent to which the second phase occurs for blends with low concentrations of iso-octane is severely limited by the onset of autoignition in the motored engine. At the autoignition limit the values of knock-limited compression ratio indicated for the fired engine were determined by extrapolation of the curve to intersect the autoignition-limited compression ratio of the motored engine.

The mixtures containing high concentrations of iso-octane (above 90 volume % of iso-octane) apparently can tolerate high concentrations of proknock materials such as are seen to lower the compression ratio of the fired engine without causing autoignition in the motored engine. These mixtures exhibit the third region of reactivity, where, as compression ratio of the motored engine is raised, the antiknock quality of the exit gases becomes higher than during the first phase. The limiting compression ratio which marks the beginning of the second phase and the compression ratio at which autoignition occurs in the motored engine are related to the relative concentration of iso-octane and *n*-heptane in the blend.

The fact that the autoignition-limited compression ratio of the motored engine markedly increases for fuels that are capable of producing large scale precombustion reactions gives an indication that these precombustion reactions may be able to suppress knock. This could be done either by the destruction of proknocks or the formation of products with antiknock properties.

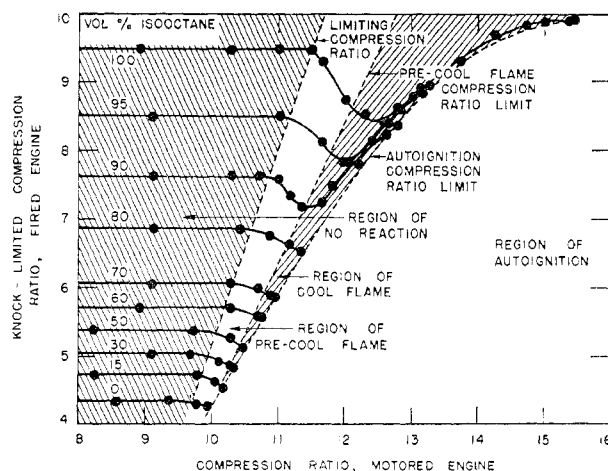


Figure 2. Knocking Tendency of Exit Gases from Motored Engine

Mixtures of iso-octane and *n*-heptane

MIXTURES OF DIISOBUTYLENE AND *n*-HEPTANE. Diisobutylene and two mixtures of diisobutylene and *n*-heptane were also tested. The results of these tests are shown in Figure 3 against a background of the data obtained on the primary reference fuels repeated from the previous figure. Although the work with diisobutylene was conducted up to the mechanical limit of compression ratio in the motored engine, this compression of the

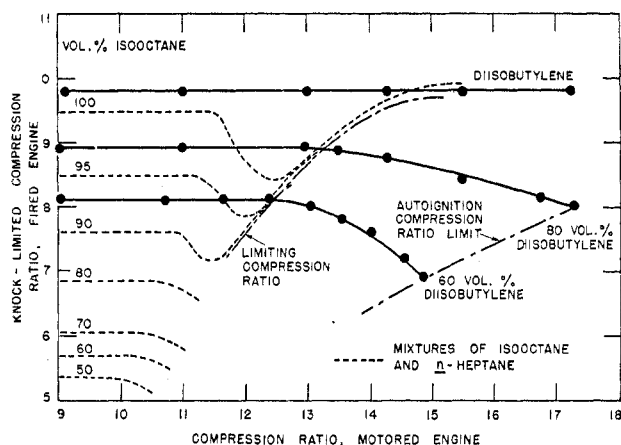


Figure 3. Knocking Tendency of Exit Gases from Motored Engine

Mixtures of diisobutylene and *n*-heptane

fuel-air mixture had no effect on the antiknock quality of the exit gases and was insufficient to cause autoignition.

The mixtures of 80 and 60 volume % diisobutylene in *n*-heptane exhibited the first and second phases of antiknock quality as the compression ratio of the motored engine was increased. When these two mixtures are compared to iso-octane and *n*-heptane mixtures having the same concentration of *n*-heptane, it is seen that diisobutylene seems to have greater ability to suppress the reactivity shown by *n*-heptane than does iso-octane in terms of knocking tendency in the fired engine and autoignition in the motored engine.

Experiments carried out with a number of pure hydrocarbons of various chemical types are shown in Figure 4 against a background of the data for the *n*-heptane-iso-octane mixtures. Again, some fuels (triptene and diisobutylene) show only the first region, some (cyclopentane, methylcyclopentane, cyclohexane, and methylcyclohexane) show the first and second regions, and some (2,2-dimethylbutane) show the full range of effects. It is apparent from Figure 4 that for the cycloparaffins both the limiting compression ratio and the compression ratio for autoignition in the motored engine are higher than for the paraffin fuels.

FUELS CONTAINING TETRAETHYLLEAD. Experiments were also conducted with a mixture of iso-octane and *n*-heptane containing 60 volume % of the former, to which were added various concentrations of tetraethyllead up to 6 ml. per gallon, as shown in Figure 5. These tests indicated, as would be expected, that the antiknock quality of the exit gases increases a great deal with the addition of tetraethyllead. Furthermore, as was the case with the unleaded fuels, the mixtures having higher concentrations of tetraethyllead tended to exhibit reaction in the four regions, while those having lower concentrations of tetraethyllead did not appear in the third region. However, it is important to note that the addition of various quantities of tetraethyllead to the mixture containing 60% iso-octane does not affect the limiting compression ratio in the motored engine. Previous studies have shown that tetraethyllead has no effect on the start of large scale pre-combustion reactions as indicated by pressure-time records (8). In addition, it is now clear that tetraethyllead has no effect on the engine condition required for the start of those small scale, knock-promoting reactions which precede the generation of heat and light. Similar effects were observed with a series of mixtures of iso-octane and *n*-heptane, each containing 6 ml. of tetraethyllead per gallon as shown in Figure 6.

This work shows, as do other studies (9), that tetraethyllead in a fuel retards the onset of autoignition and thereby permits a greater large scale reaction to be obtained prior to autoignition. Thus, for a paraffin, at least part of the knock-suppressing action

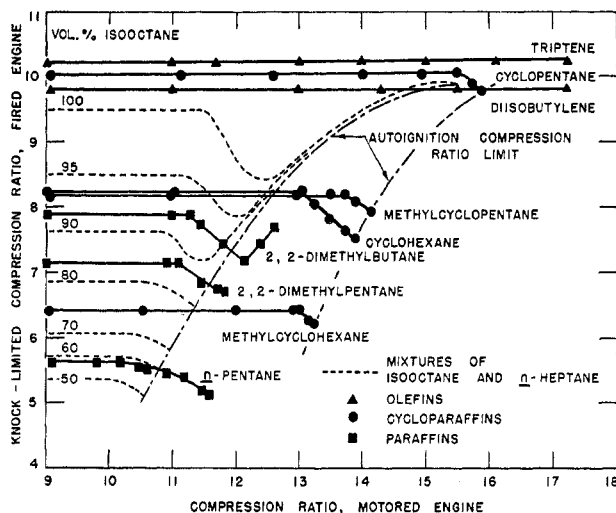


Figure 4. Knocking Tendency of Exit Gases from Motored Engine

Various pure hydrocarbons

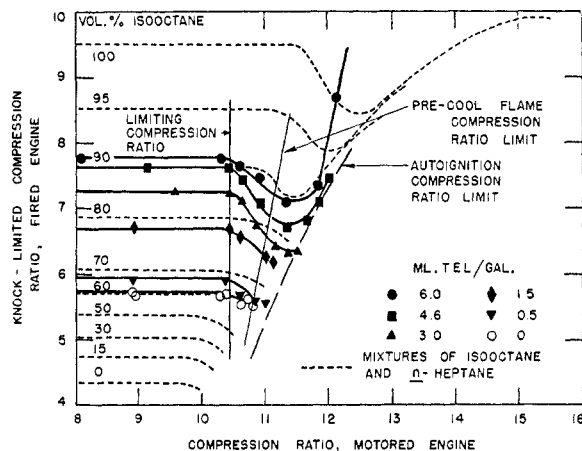


Figure 5. Knocking Tendency of Exit Gases from Motored Engine

Mixture of 60% by volume of iso-octane in *n*-heptane plus various amounts of tetraethyllead

of tetraethyllead might be merely attributed to the greater extent of the large scale precombustion reaction for the leaded than for the unleaded base fuel at the respective knock-limited compression ratios for the two fuels.

To determine the nature of the reactions occurring in the fuel-air mixture in the motored engine, some experiments were carried out in which the temperature of the exit gases from the motored engine was measured at the same time that the antiknock quality of these gases was evaluated in the fired engine. These data, obtained with iso-octane as the fuel, are shown in Figure 7. They show that the point at which the exit temperature increases to a measurable degree is coincident with the point at which the third region develops. This is also shown in Figure 8 for data obtained in the same manner on a mixture of 60 parts of iso-octane and 40 parts of *n*-heptane containing various concentrations of tetraethyllead. Thus, those reactions which occur during the second region, and which have a large effect on knocking tendency, do not result in the evolution of measurable quantities of heat.

ANTI-KNOCK ACTION IN MOTORED ENGINE. That some of the fuels tested, such as *n*-heptane, showed only three regions of reactivity in the motored engine, while others, such as iso-octane,

exhibited all four regions should not be taken as an indication of a fundamental distinction between the fuels. This difference is due instead to the particular engine operating conditions involved in this experiment because in a particular engine, the presence or absence of precombustion reactions depends on the time-temperature-pressure conditions as well as on the fuel type. An example of this would be *n*-heptane, which just below the auto-ignition limit has a temperature of 450° C. and a pressure

similar to knock, may be due to the degeneration of the stable peroxides when a critical concentration is obtained, and such degeneration may be an exothermic process. It has been shown that the addition of tetraethyllead to a paraffinic fuel does not affect the formation of proknock materials, presumably peroxides, but does delay autoignition. This implies that the action of tetraethyllead is to interfere with the autoignition-promoting properties of peroxides.

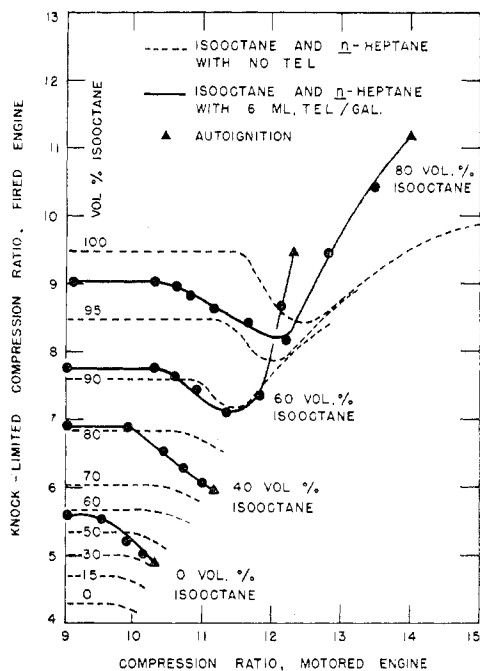


Figure 6. Knocking Tendency of Exit Gases from Motored Engine

Mixtures of iso-octane and *n*-heptane with 6 ml. of tetraethyllead per gallon

of 17.7 atmospheres, and which appeared to go through no precombustion reactions. However, in a motored engine operating just above the autoignition limit, the *n*-heptane-air mixture reached a temperature of 765° C. and a pressure of only 8.85 atmospheres. Under the latter conditions, the mixture of *n*-heptane and air reacted with considerable evolution of heat, thus implying the presence of precombustion reactions. These data are in agreement with those obtained by others in experiments with tubes and bombs as well as with engines, and change in reactivity with change in time-temperature-pressure path may account for the commonly observed changes in antiknock quality of some fuels with changes in engine operating conditions.

When the detailed aspects of the experiment are carefully considered, it is obvious that the proknock materials produced in the motored engine must be relatively stable, since the time lapse between the formation of these reactive products and their induction into the fired engine was about 23 seconds. Thus, it is highly improbable that reaction products such as free radicals caused the knock increase in the second engine. On the other hand, relatively stable compounds such as hydroperoxides, dialkyl peroxides, aldehydes, ketones, esters, and other oxygenated compounds would be carried into the second engine. On the basis of other work (2), it is thought that the proknock effect observed in the fired engine is probably due to peroxides. In addition, the stable proknock materials must be produced in the motored engine by reactions that are essentially thermoneutral, since no rise in temperature of the exit gases from the motored engine was noted during the production of these materials. The onset of autoignition, however, which is presumably chemically

PRODUCTION OF PREFLAME OXIDATION REACTIONS IN A TUBE

In order to produce partial oxidation reactions in a fuel in another way and to measure variations in antiknock quality, an experiment was conducted in which the reactions were produced in a tube. The apparatus used in this experiment (Figure 9) consisted essentially of a heated tube which was used to produce preflame reactions in the fuel-air mixture passing through it. The exit gases from the tube were then inducted into a variable-compression-ratio knock-test engine with a displacement of 17.6 cubic inches, which was used to measure the antiknock quality of the products of these reactions. The similarity between this experiment and the previous one, where the reactive products were produced in an engine instead of a tube, is readily apparent; in fact, the same fired engine was used in both experiments.

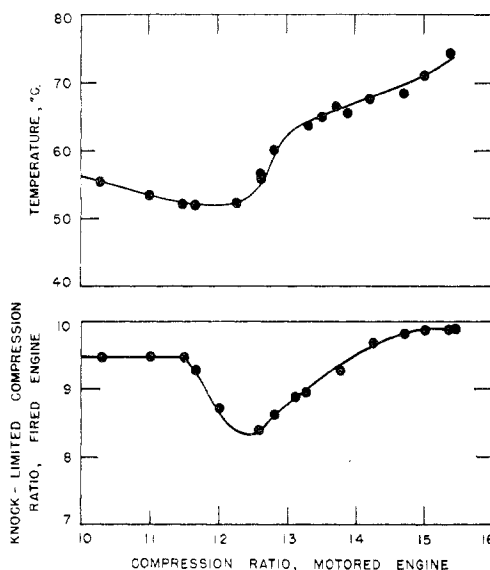


Figure 7. Temperature and Knocking Tendency of Exit Gases from Motored Engine

Iso-octane

The tube was a Corning Pyrex EC glass tube 76.2 cm. long with an inside diameter of 17 mm. It had a transparent metallic coating 66 cm. long on the outside surface, which enabled it to be electrically and uniformly heated in air to temperatures up to 350° C. This temperature is well within the range of the temperatures needed to produce cool flames for most hydrocarbons having antiknock levels below 100 octane number. The test-fuel container consisted of a 100-ml. glass jar submerged in a constant-temperature bath. The desired fuel-air mixture was obtained by allowing a regulated amount of air to pass over the surface of the fuel and thus pick up the fuel vapor. The heated-tube apparatus was placed in a darkened enclosure to permit visual observation of the cool flame. Gas temperatures were measured by means of a thermocouple which entered the tube from the exit end and could be moved along the axis of the tube.

The production of a stabilized cool flame depends to a large extent on the temperature of the tube, the linear flow rate of the

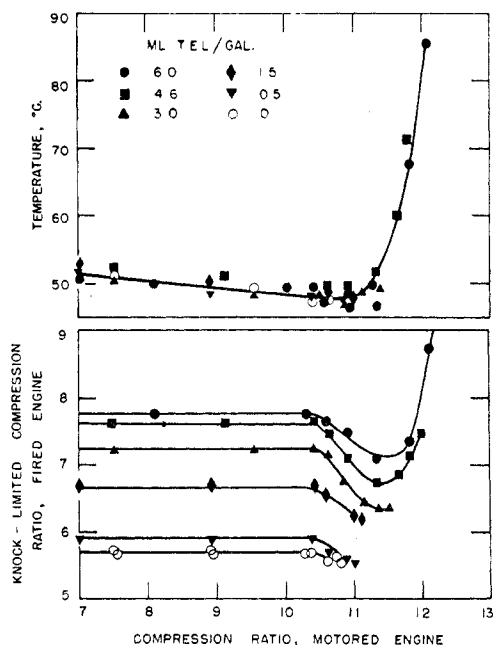


Figure 8. Temperature and Knocking Tendency of Exit Gases from Motored Engine

Mixture of 60% by volume of iso-octane in *n*-heptane plus various amounts of tetraethyllead

gases through the tube, and the particular hydrocarbon being investigated. Linear flow rates of from 7 to 20 cm. per second are necessary for cool flame stabilization—pulsation effects result from a flow rate less than 7 cm. per second and excessively flat and spread-out flames from rates above 20 cm. per second. With *n*-heptane, stationary and reproducible cool flames were observed when the fuel-air ratio was chemically correct, the gas temperature 270° C., and the linear flow rate 11 cm. per second. The exit gases from the tube were drawn into the intake manifold of the test engine which was operating on *n*-heptane at a high compression ratio and with a relatively closed throttle. Only 2.5% of the total *n*-heptane entering the engine passed through the tube. In these tests, the engine was operated at 900 r.p.m., 0.066 fuel-air ratio, and 32° C. inlet air.

As the gas temperatures were increased from 39° to 350° C., the knock-limited compression ratio was reduced by a substantial amount. From Figure 10, in which knock-limited compression ratio is plotted against the temperature of the heated gas, it is evident that no large decrease in antiknock quality is noticeable

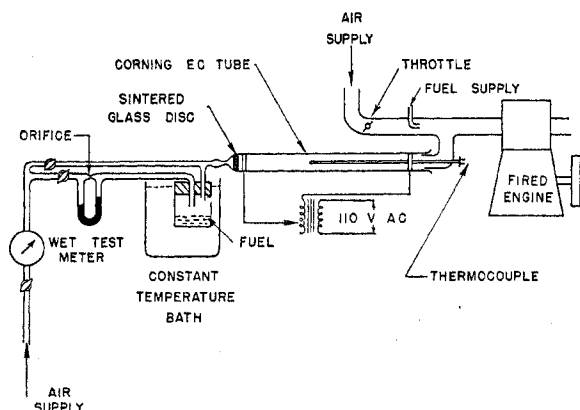


Figure 9. Tube Apparatus Used to Measure Effect of Preflame Oxidation Reactions on Engine Knock

until a temperature of about 210° C. is reached. As the gas temperature is further increased to 270° C., the resistance to knock steadily and sharply decreases. In this temperature range, however, no cool flames were observed, and no evolution of heat could be detected by means of the thermocouple which could be moved along the axis of the tube. Further increases in gas temperature resulted in the appearance of cool flames with very little change in knocking tendency.

From this, it is apparent that some proknock compounds must be produced in the heated tube by reactions that cannot be detected by the appearance of cool flames or by the evolution of heat. As a result, these reactions are thought to be similar to those occurring in the motored engine which resulted in no significant evolution of heat but produced a product of lower antiknock quality.

MECHANISMS OF PROKNOCK PRODUCTION

Thus, from the motored engine and the heated tube experiments, it becomes evident that the proknock materials must be produced by reactions which involve very little, if any, evolution of heat or visible radiation. The proknock materials must be stable enough to exist for at least 20 seconds at a temperature of about 65° C.

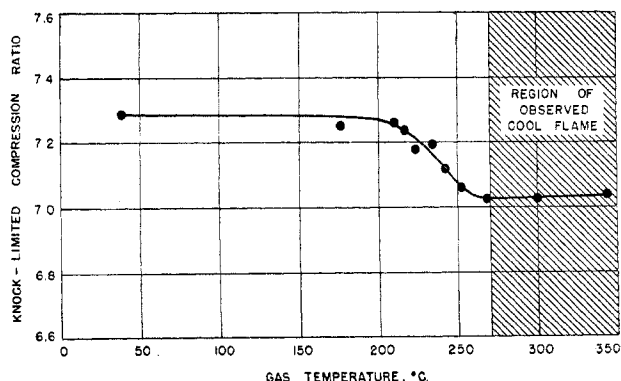
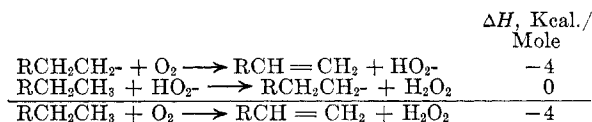


Figure 10. Influence of Precool-Flame Reactions on Knock

On the basis of existing theories regarding the possible mechanisms of the low-temperature oxidation of hydrocarbons and reactions which produce knock in internal combustion engines, it is now possible to speculate as to the chemical nature of the proknock intermediates that may be involved. The fact that these proknock materials must be relatively stable implies that they are compounds which have probably already been prepared and identified, such as hydrogen peroxide, alkyl hydroperoxides, and dialkyl peroxides.

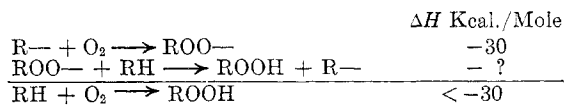
Several facts are known which indicate that the simplest of these compounds, hydrogen peroxide, may be the proknock material produced by the early small scale reactions. This compound can be made by a reaction scheme which is essentially thermoneutral:



A reaction scheme of this kind has recently been postulated by Wilson (11) to explain results obtained in the oxidation of propane and is based on the actual analysis of propylene and hydrogen peroxide formed in the reaction. Furthermore, Shtern and Pollyak (8) have detected the presence of hydrogen peroxide in

the unburned gases removed from an engine with a sampling valve. However, it is questionable whether sufficient hydrogen peroxide could be produced to account for the proknock effect actually measured in the present work. Studies of Egerton and Ubbelohde (3), of Downs, Walsh, and Wheeler (2), and in this laboratory show that hydrogen peroxide is a weak proknock in comparison to dialkyl peroxides and alkyl hydroperoxides.

An alternative mechanism by which a proknock of sufficient activity could be produced would be that suggested by Walsh (10):



The amount of heat evolved in the first reaction, when a peroxy radical is formed, is estimated by Wilson (11) at 30 kcal. per mole and at 24 kcal. per mole for the isopropoxy and the *n*-propoxy radicals, respectively. Walsh (10) suggests that the second reaction is also exothermic, so that the over-all reaction by which peroxides are produced is definitely exothermic. However, when the small scale reactions were produced in the motored engine and in the heated tube, no liberation of heat was detected. The engine experiment alone does not serve to eliminate this reaction mechanism, because the engine technique could detect a minimum of about 5 kcal. of heat evolved per mole of fuel in the engine, whereas this mechanism, with a heat of reaction of -30 kcal. per mole of fuel reacted, would produce only about 0.3 kcal. per mole of fuel in the engine when enough peroxide formation is assumed to account for the proknock effect produced in this experiment [1.5 mole % of peroxide in the fuel causes a drop in compression ratio of 2 units (2)]. However, when proknock materials are produced in a heated tube, the temperature measurements are sufficiently accurate to detect the amount of heat produced by such a reaction mechanism. The formation of sufficient hydroperoxide in the heated tube before the appearance of the cool flame to account for the proknock effect observed (0.1 mole of peroxide per mole of fuel in the tube) would evolve over 3 kcal. per mole of fuel for an over-all temperature rise of about 8° C. Therefore, if the estimation of the heat of formation of the hydroperoxide from the hydrocarbon and oxygen is correct, it is possible to accept the mechanism of Walsh only if the reactions which result in the formation of hydroperoxides are accompanied by other endothermic reactions, thus resulting in no appreciable net evolution of heat.

The third scheme which has been proposed for the oxidation of hydrocarbons is that of Lewis and von Elbe (5). This reaction mechanism supposes the oxidation of an alkyl radical from the peroxy radical with subsequent decomposition to form an aldehyde and an oxyalkyl radical. Clearly, any aldehyde would be too weak a proknock compound to be considered as the material producing the knock-inducing effect encountered in this work. The oxyalkyl radical is then thought to decompose to form formaldehyde and an alkyl radical, which in turn undergoes further decomposition. It appears likely, however, that by the time of this stage of the oxidation, large amounts of heat would

have been liberated. Thus, it is difficult to point with certainty to any particular phase of this reaction scheme which would produce a stable proknock before the liberation of an appreciable amount of heat.

CONCLUSIONS

The existence of two classes of chemical reactions which can precede knock in internal combustion engines is shown by this investigation. It is determined that relatively stable knock-inducing materials may be produced by reactions which have a ΔH smaller than 1 kcal. per mole of hydrocarbon when a chemically correct mixture of *n*-heptane and air is passed through a heated tube at about 225° C. A similar phenomenon can be observed in a motored engine at compression temperatures above 450° C. Below this temperature no detectable knock-inducing products are obtained by the compression of hydrocarbon-air mixtures used in this investigation. Thus, one class of pre-combustion reactions exists which is characterized by the thermo-neutral formation of proknock compounds. No previously proposed reaction scheme for the "low-temperature" oxidation of hydrocarbons appears to account for these results. The second class of reactions, which occur at somewhat higher temperatures and are accompanied by radiation and by the evolution of considerable quantities of heat, does not increase the knocking tendency of a fuel-air mixture. Tetraethyllead does not affect the start of either of these two classes of reactions but does retard the onset of autoignition, presumably by destroying the effectiveness of the proknock materials produced by the first class of reactions.

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