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Investigations on the reaction kinetics of
the oxidation of n- and i-paraffins.

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The theory that engine knocking is due to the self-ignition of the compressed fuel-air mixture has started numerous laboratory tests on the oxidation reactions that precede the self-ignition of hydrocarbon-air mixtures. These reactions can be conveniently followed if they take place at considerably lower pressures (atmospheric pressure and less) than engine conditions. The simplest test arrangement consists in passing a hydrocarbon-air mixture at normal pressure through a reaction oven, the temperature of which is gradually stepped up. The outgoing gases are then analysed. The oxygen consumption generally gives a measure of the reaction progress and thus of the reaction velocity. Many such tests were made, e.g. in American laboratories (Edgar and co-workers, Pease etc.). Some years ago we published tests (1) covering orientation measurements on the stability of various hydrocarbons in the presence of oxygen. The question of the origin of the strikingly different behaviour of various hydrocarbons prompted attempts to obtain a closer look into the reaction progress, by more thorough tests on various compounds. The tests dealt with in this report had the purpose of achieving if possible a closer look into the oxidation reactions of n- and i-paraffins. Also to explain the exceptional stability to oxygen produced by the ramification of the C-atom chain, whilst other properties topped by the thermal stability of the molecules are only negligibly affected.

Test methods. - A static equipment was used. The tests were carried out in the usual way, by letting a mixture prepared in a stock flask overflow, as result of a sudden pressure equalization, in the previously evacuated reaction cylinder. The latter was made of Jena glass, about 6 cm. bore and 700 cu.cm. capacity, and it was placed in an aluminium block oven-assuring a constant temperature. The temperature was measured by a thermocouple fitted in the centre of the reaction cylinder by means of a cast-in small tube. The reaction was measured by suddenly interrupting it at the desired moment; to this purpose the gases were allowed to overflow from the reaction cylinder into a previously evacuated flask kept at room temperature. The reaction products and the uncombined oxygen were subsequently analysed. The oxygen consumption immediately gave a measure of the reaction progress; also the resulting CO and CO₂ concentrations were determined. The following results will mainly deal with the effect of different test variables, such as temperature, pressure, mixture strength, reaction time and inert gas addition on the oxygen consumption.

Test results. - The temperature effect on the reaction was at first investigated under the described test conditions. Fig. 1 shows the curves for n-heptane and n-hexane. The results coincide with previous results on flowing gases as well as with those of other scientists.

(1) Jost, v. Müffling and Rohrmann, Zs. f. Elektrochem. 42 (1936) 488

Above 200°C considerable oxidation takes place with n-paraffins with boiling points usual in commercial fuels; at first it increases as the temperature rises, until it reaches a maximum at a little over 300°C. The region of negative temperature coefficient then begins, which extends over about 150°C, till a steep rise of the reaction velocity appears again close to 500°C within a small temperature interval; this leads to ignition.

If we compare the results on highly branched paraffins (Fig. 2), i.e. i-octane (2:2:4-trimethylpentane) and hexamethylethane, we see the entirely different behaviour of these fuels. A noticeable reaction appears first near 500°C; with mounting temperature it leads very rapidly to ignition. This rise in the oxidation velocity of i-paraffins near 500°C can be best compared with the last rise in n-paraffins below 500°C; the whole region below that, especially that of negative temperature coefficient, is here completely absent.

Let us further consider the progress of the reaction. Fig. 3 shows the reaction in stoichiometric n-heptane-air mixture as a function of the reaction time at two different temperatures. It is clear that the reaction velocity has at first a maximum value; then it sinks steadily until after a short time the reaction dies down. The resulting products are apparently stable to further oxidation. The rate of oxygen consumption at which the reaction dies down depends on the temperature. At higher temperatures the final state is reached earlier than at lower ones.

Fig. 4 shows the progress of the reaction at two temperatures in the region of the negative temperature coefficients. Within the first minute the reaction at higher temperature exceeds that at low temperature. Then whilst the reaction at 300°C practically dies down, at 400°C it still proceeds slowly, probably implying that here the intermediate products are slowly subjected to further oxidation. The observation of the CO and CO₂ content of the reaction products gives a first indication on the process, although the products characterising the intermediate reactions are not determined by the gas analysis. Fig. 5 shows however that at 300°C oxygen as well as CO and CO₂ tend to constant concentration, whilst at 400°C the CO concentration falls off again after reaching a maximum, nearly in the same measure as the CO₂ concentration simultaneously goes up. To a certain extent the continuation of the reaction at higher temperatures is nothing but a slow, possibly heterogeneous CO oxidation.

If we consider now the reaction in an i-paraffin, viz. i-octane, the picture is entirely different (Fig. 6). At first the reaction velocity rises, reaches a maximum and then sinks gradually. The curve of the reaction velocity as a function of the reaction time is called degenerate explosion by Semenov, i.e. the reaction does not become an explosion, only because the concentrations of the reactants are already too weak. The turning point of the curve in Fig. 6, i.e. the maximum of the reaction velocity, is reached after 90 sec., with a 30 to 40% O₂ consumption. A slight pressure increase results in the attained explosion limit, (see Fig. 7,) which proves the exceptionally strong pressure effect on the reaction.

In this respect too n-paraffins show an entirely different picture (Fig. 8). At the lowest temperatures no noticeable pressure effect is apparent; it becomes more distinct however as the temperature mounts, though here too it is still considerably weaker than with i-octane, and the curve has an entirely different shape. With rising pressure the reaction tends to a constant final value with a shape that is different from that of an i-paraffin. Between 250° and 300°C the reaction presents a region of discontinuity. For instance we see in the 292°C curve that explosion occurs spontaneously with a small pressure increase beyond a critical limit. This development can

be particularly well observed in mixtures containing hydrocarbons in excess of the stoichiometric level. In these mixtures the critical point moves towards lower pressures and temperatures. Fig. 9 shows the corresponding curve for a double-stoichiometric n-heptane-air mixture at 250°C. The discontinuity appears at about 400 mm. pressure. This process is very similar to the thermal behaviour of certain peroxides, which according to Harris, Egerton etc. decompose with an explosion above a certain critical pressure, and dissociate slowly below it. A dissociation process must occur here too, as proved first of all by the 20% pressure rise and secondly by the gas analysis, which gave a nearly equal content of CO and H₂ (about 17%); the latter can only be the result of dissociation, the lack of oxygen preventing its further oxidation. The simplest compound, the decomposition of which would give equal quantities of CO and H₂, is HCHO, which often appears in oxidation processes. To what extent the position of the point of discontinuity depends on accidental conditions is proved by a special point in Fig. 9, obtained when the test was repeated at a pressure far above 400 mm. This point connects exactly with the values obtained at lower pressures, as shown by the broken line. Presumably similar displacements are due to small variations in the surface condition of the vessel wall, which has a strong influence indeed on the whole process.

Fig. 10 shows the oxidation process in richer mixtures as a function of temperature. In double and triple stoichiometric mixtures the discontinuity appears in the shape of a sudden steep ascent at about 250°C; the richer the mixture, the lower the temperature at which the first peak appears. At the pressures in question, the discontinuity does not appear in the theoretical mixture. It should also be noted that the oxygen consumption as a % of the theoretical quantity, i.e. in molecules per molecule of hydrocarbon, varies but little for the various mixtures. As regards the further shape of the curves, it must be borne in mind that in richer mixtures the available O₂ quantity is only a fraction of the theoretical value; in the triple stoichiometric mixture with 33% O₂ consumption the reaction must die down owing to lack of oxygen.

Fig. 11 and 12 show the reaction as a function of time and pressure: the O₂ consumption appears to be directly proportional to the available hydrocarbon quantity and independent of the O₂ concentrations. In both cases the results are compared with the corresponding curve for the theoretical mixture, showing practically no difference.

It was therefore surprising that the oxygen consumption should go up in a mixture in which 1/4 of the air nitrogen had been replaced by oxygen, so that the initial O₂ concentration was 40% (fig. 13 and 14). This effect is clear only at the lowest temperatures, at which a reaction can just be observed under these test conditions. As the graphs show, this process largely disappears at higher temperatures. At very low temperatures the reaction is presumably characterised by heterogeneous processes; it can therefore be inferred that this effect is probably due to absorption processes which are repressed at higher temperatures.

As already shown above, the effect of pressure on reaction velocity is extremely different in n- and i-paraffins. In the preceding tests the pressure was varied by admitting into the reaction cylinder varying quantities of a previously prepared hydrocarbon-air mixture. Also the concentrations of the reactants were always varied in equal proportion. Now it is known that in chain reactions, as is always the case here, important conclusions can be drawn on the chain mechanism from the results obtained by keeping constant the concentrations of the reactants, and varying only the pressure by adding inert gases. As a result of the changed diffusion ratios, the

recombination process of the chain carriers also varies. Fig. 15 shows the reaction in i-octane and n-hexane-oxygen mixtures of theoretical composition as a function of the nitrogen addition; the conditions are such that the same reaction takes place without inert gas. The different behaviour of n- and i-paraffin is quite clearly marked. With i-octane a pressure increase of not quite double produces the explosion, whilst practically no change is apparent in n-hexane. According to the theory of chain reactions we could expect a curve like the one we obtain for the i-octane-oxygen mixture, provided that: 1. the primary reaction occurs in the gaseous state, 2. that chain branching takes place in the gas phase and 3. that the chain breaks on the cylinder wall with a probability not much less than 1, which practically assures that the active particles reaching the wall are really neutralized there. In chain reactions the reaction velocity becomes independent of external gas pressure either when there is a very slight probability of the chains getting broken on reaching the wall, or when both the induction and the breaking of the reaction chains take place on the wall. The N_2 has no effect in the n-hexane oxidation; that this is not due to the low probability of the chain carriers getting de-activated as they reach the wall, will be proved below. In tests recently published by Maess (1), the oxidation of n-heptane was induced artificially by the addition of azomethane which was then photochemically decomposed by ultra-violet rays; the resulting radicals induced an oxidation of heptane at temperatures, at which no spontaneous oxidation would occur. There is no doubt therefore that in these circumstances the radicals are produced and the reaction chains are induced in the gaseous phase. It is interesting that in these circumstances a N_2 addition intensified considerably the reaction, as shown in Maess' table.

Numerical table

Test No.	mm. Heptane	mm. Azomethane	mm. Oxygen	mm. Nitrogen	mm. oxygen absorption
79	40.0	38.2	90.4	64.4	11.4
74	39.8	38.0	92.2	104.0	19.5
80	39.0	39.2	91.8	349.4	28.9
75	40.0	38.4	101.6	387.2	31.4
76	39.0	59.2	92.6	512.8	47.4

Table: Influence of nitrogen on n-heptane oxidation (175°C)
photochemically induced by means of azomethane.

If we plot the values as a function of the N_2 addition (Fig. 16), correcting the latter value to the same azomethane pressure used in the other tests, we see that the reaction velocity grows as a near-linear function of the pressure, as expected. This applies when chain induction occurs with very great probability in the gas volume with chain breaking on the wall, and when no chain branching takes

(1)

R. Maess, Öl u. Kohle 15 (1939), 249 u. 321.

place, which is indeed the case with the special test conditions, viz. very low temperature.

From these results we can draw the conclusion that the addition of gas has no effect in the case of n-hexane only because chain induction and breaking occurs on the wall, whilst with i-octane the reaction begins in the gaseous phase.

The oxidation has often been explained with the thermal decomposition of the hydrocarbons. This might be the case in i-octane, especially as the oxidation becomes noticeable in a temperature region, in which also a measurable thermal dissociation sets in. The assumption that in our test conditions the oxidation of certain types of hydrocarbons is induced by a thermal dissociation, is confirmed by tests on ketones (unpublished tests by Maess). Low boiling point or strongly branched ketones are equally stable in the presence of oxygen as strongly branched paraffins. Their decomposition can be easily detected with our test arrangement through the resulting CO. It was found for instance that in methylthylketone, to which once air was added and another time nitrogen, the oxidation became noticeable only in a temperature region within which, in the presence of N₂, CO resulted from thermal decomposition. The fact that with i-paraffin oxidation is induced in the gaseous phase confirms the assumption that thermal dissociation is the first stage.

This parallel between thermal dissociation and oxidation start cannot be detected in n-paraffins under our test conditions. Thermal dissociation is still quite negligible at about 200°C, when the oxidation becomes noticeable. As the above tests have shown, the first stage of the oxidation reaction does not occur in the gaseous phase but on the cylinder wall; the assumption of a heterogeneous catalysis can indeed be made. The question still remains open why the strongly branched paraffins cannot react similarly. So far only hypotheses can be advanced, that this catalytic reaction requires the presence of at least two adjacent secondary C atoms in the molecule.

As to the application of these results to engine conditions, it must be borne in mind that considerably higher pressures and very short reaction times are involved; diffusion processes from and to the cylinder wall can certainly play only a secondary part. Moreover in our tests whenever possible we have produced an equal temperature in the whole reaction volume; strong temperature differences prevail in the engine, and particularly in the decisive stage the cylinder wall is much cooler than the gases, which affects its catalytic efficiency. One of the indications that in altered conditions the process develops differently is in the fact that the temperatures at which self-ignition occurs in conditions similar to the engine with n-heptane and i-octane differ by only 100°C; whereas in our tests a temperature difference of about 300°C was found between the start of a noticeable oxidation in the two fuels.

Summary

When subjected to slow oxidation at pressures below one atmosphere, straight chain paraffins mixed in correct proportion with air at over 200°C present an initial oxidation; this remains nearly constant for a considerable temperature range or even abates slightly. In these conditions it is only at about 500°C that the oxidation velocity increases again as the temperature rises, then to turn rapidly into ignition. Tests on the effect of inert gas additions on the reaction velocity show that at low temperatures the oxidation is induced by the formation of active centres in a catalytic reaction on the cylinder wall; also that it is not directly connected with the

thermal stability of the molecules.

In contrast to the above, the oxidation of strongly branched paraffins is noticeable only beyond a temperature at which the thermal dissociation of the compounds also appears. Tests on the action of inert gases show that the reaction begins in the homogeneous gaseous phase, thus probably connecting directly thermal dissociation and oxidation.

These tests were carried out in 1936 in the Institut für Physikalische Chemie der Technischen Hochschule Hannover, as part of research work entrusted to W. Jost by DVL, Berlin-Adlershof.

Fig. 1 - Graph.

Fig. 2 - Graph

Fig. 3 - Graph

Fig. 4 - Graph

Fig. 5 - Graph

Fig. 6 - Graph

Fig. 7 - Graph

Fig. 8 - Graph

Fig. 9 - Graph

Fig. 10 - Graph

Fig. 11 - Graph

Fig. 12 - Graph

Fig. 13 - Graph

Fig. 14 - Graph

Fig. 15 - Graph

Fig. 16 - Graph