IGNITION REGIONS OF HYDROCARBONS

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Received July 26, 1937

INTRODUCTION

Until comparatively recently any experimental evidence that the influences of such factors as varying temperature, pressure, or dilution on chemical reactions were other than in accord with simple laws would have been received by chemists with reserve, yet today many such apparent anomalies are recognized and their frequent occurrence in elementary combustion processes has contributed much evidence largely drawn upon in the development of the theory of chain reactions.

It is not surprising, therefore, that investigations into the combustion of complex hydrocarbons, designed in the first place to throw light on the problem of "knock" in internal-combustion engines, have shown when extended over wide enough temperature and pressure ranges that the mechanisms involved are far from simple; for such combustions are known to give rise to a variety of intermediate oxidation products, the concentrations of which at any stage of the reaction depend upon temperature, pressure, mixture composition, and environmental influences (cf. Newitt and collaborators (19, 17, 21, 18, 20)).

Systematic work on the influence of reaction temperature on the slow combustion of the higher paraffins, etc., in admixture with air was first published in 1929 by Pope, Dykstra, and Edgar (27, 2, 8) who, working in a flow system, established that, although initial oxidation commenced at 150–200°C., becoming active between 250°C. and 270°C. in which range the products were luminescent and then mildly explosive (cool flames) between 270°C. and 300°C., at higher temperatures the combustion was less rapid until about 500°C. had been reached. Parallel observations were also made by Pease (24, 26, 25), and a temperature range in which a negative temperature coefficient of reaction velocity occurred became recognized. Edgar also produced strong evidence that with straight-chain paraffins the methyl group at the end of the chain was first attacked with the formation of the corresponding aldehyde and water, the aldehyde being subsequently oxidized to a lower aldehyde, etc.; with side-chain isomers the same process occurred until the side chain was reached, when a ketone was formed, and since ketones oxidize more slowly than aldehydes the reaction was slowed down, the luminescent combustion being less intense.

About the same time the cool-flame phenomena were examined by Emeleus (10), who showed the emission from several combustibles to exhibit spectra which differed from that of their normal flames but had a series of bands in common, recently identified as due to energized formaldehyde (cf. Ubbelohde (36) and Konratjew (14)). Prettre (28) also studied the character of the cool flames observed with many combustibles in a flow system. They were not observed with methane and ethane; rich mixtures of propane, pentane, hexane, heptane, and octane gave rise to them in a temperature range usually between 230°C. and 300°C., above which normal inflammation did not occur until about 600°C. had been reached. Aldehydes and ether readily exhibited cool flames, but amylene and amyl alcohol were the simplest olefin and alcohol, respectively, to give rise to them.

In 1933 Townend and Mandlekar (35), while studying the influence of pressure on the slow combustion of butane-air mixtures in a static system, observed that although at low pressures spontaneous ignition did not occur below 500°C., on the attainment of a critical pressure which varied somewhat with mixture composition it occurred abruptly in a temperature range below about 370°C., which was later recognized as that in which only cool flames are normally observable. The matter was therefore systematically investigated and extended to cover a wide range of combustibles.

The determination of ignition points over wide ranges of pressure and temperature, with which this paper is concerned, has been very fruitful in throwing light on the whole problem, for they provide information of the precise circumstances in which a maximum reaction velocity may be obtained under variable experimental conditions. It is now proposed briefly to review the field which has been covered so far and to indicate the general direction in which the results are leading, more detailed discussions of the possible chemical mechanisms involved being embodied in other papers contributed to this symposium.

IGNITION REGIONS OF THE PARAFFINS

In figure 1 curves have been drawn showing the influence of pressure on the ignition points of corresponding rich mixtures with air of methane, ethane, propane, butane, and hexane (curves 1, 2, 3, 4, and 5). The curve for the methane-air mixture fell rapidly from above 700°C. to about 500°C. as the pressure was raised to 5 atm.; thereafter it fell progressively to about 460°C. with increase of pressure to 30 atm. Similar curves have been obtained with other mixture compositions, that exhibiting the lowest ignition points having a methane content between 30 to 40 per cent ($CH_4:O_2$ ratio = 2:1). The intermediate products normally found in the slow combustion of methane are methyl alcohol and formaldehyde; the characteristics of the ignition point curves of both these materials are much the same as found with methane, but the order of ease of ignition is formaldehyde > methyl alcohol > methane, and small additions of formaldehyde strongly promote the combustion of the other two combustibles (12, 5).

With the ethane–air mixture (No. 2) at pressures up to 15 atm. the curve was as found with methane, ignition now occurring at somewhat lower temperatures. At this pressure (and at about 430°C.) a sharp inflection occurred, the ignition points following an imposed lower system, settling down to temperatures about 325–340°C. at 25 to 30 atm. Another interesting feature of the experiments was the very long preignition time-lags recorded, for, whereas with methane these had increased progressively from 3 to 40 sec. with fall in ignition temperature to about 460°C., with ethane the increase was from 20 sec. at 550°C. to a few minutes at 435°C., the point of inflection; thereafter the lengthening was very marked and at 325–340°C. the lags had reached two *hours* or more.

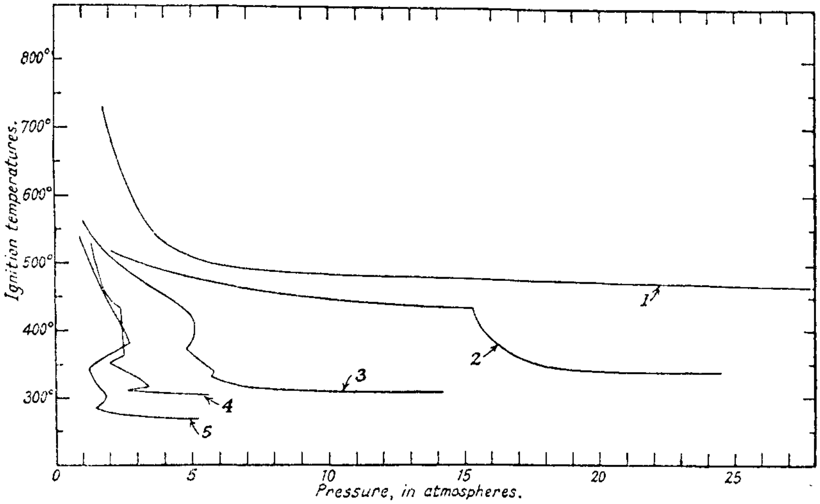

FIG. 1. Curves 1, 2, 3, 4, and 5 are for 13 per cent of methane, 10 per cent of ethane, 5 per cent of propane, 3.8 per cent of butane, and 2.7 per cent of hexane, respectively, in air.

With two carbon atoms in the molecule the number of intermediate compounds known in the intermediate products is greater than with methane, and it was thought not unlikely that at lower temperatures the longer life of some comparatively unstable material might well be responsible for the superposed lower ignition system; in particular acetaldehyde, which is known strongly to promote the combustion of ethane at 316°C. (7), might well function in this way. This was soon borne out by a comparative study of the ignition point curves of ethane (with and without addition of acetaldehyde), ethyl alcohol, and acetaldehyde (figure 2, curves 1, 4, 2, and 3).

A comparison of curves 1 and 4 leaves little doubt that the superposed lower system found with ethane was in some way attributable to the formation of acetaldehyde during slow combustion, for the addition of 1 per cent of it to the mixture not only markedly promoted ignition in the lower system but reduced the time-lags from more than two hours to a few seconds. Moreover, this effect was limited entirely to the lower system, for above 435°C. the aldehyde had no influence whatever; if anything, it tended to retard the ignitions. This result also throws an interesting light on the apparent disagreement between the observation of Bone and Hill (7), who found that the presence of 1 per cent of acetaldehyde caused the ignition of an ethane–oxygen mixture at 316°C. and 710 mm. pressure under conditions when normally the reaction proceeded quite slowly, and the more recent observation of Steacie and Plewes (32), who found that with a $C_2H_6 + 2.3\ O_2$ mixture at 452°C., acetaldehyde, while virtually eliminating the "inhibition" period, had little or no effect upon the subsequent oxidation of the ethane.

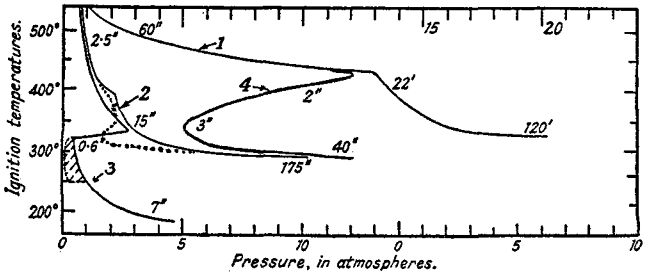

FIG. 2. Curves 1, 2, and 3 are for corresponding mixtures with air of ethane, ethyl alcohol, and acetaldehyde; curve 4 is as 1, but with addition of 1 per cent of acetaldehyde to the mixture.

The curve for the ethyl alcohol–air mixture (No. 2) also exhibited a superposed lower system, ignition occurring at much lower pressures over the whole temperature range than with the corresponding ethane–air mixture (No. 1); moreover the presence of 1 per cent of acetaldehyde in the mixture (dotted curve) exhibited a like effect to that found with the ethane–air mixture. Finally, determinations of the ignition points of acetaldehyde–air mixtures (No. 3) left little doubt that the formation of acetaldehyde was responsible for the characteristic curves of ethane and ethyl alcohol, for at temperatures above about 330°C. a strong negative temperature coefficient of reaction velocity was apparent, a "throw back" in the ignition point curve being observed. It should also be mentioned that cool flames were observed for the first time with acetaldehyde–air media, and that they occurred within the temperature and pressure limits defined approximately by the dotted boundary curve enclosing the shaded area. When true ignition occurred in this temperature range at an adequately high pressure (defined by curve 3), it always followed at a definite short time interval following the formation of a cool flame. The simplest interpretation of these results would seem that at the upper temperature limit of the lower system the life of intermediately formed acetaldehyde is inadequate to promote the combustion as a whole; it may equally well be, however, that this applies to some product to which the aldehyde gives rise or, alternatively, that some other process sets in which renders the aldehyde innocuous; pending further chemical evidence, however, judgment should be suspended.

Reverting again to figure 1, curves 3, 4, and 5, pertaining to propane–, pentane–, and hexane–air mixtures, it will be observed that with all paraffins containing three or more carbon atoms an abrupt fall in the ignition points occurred, an important observation being the occurrence of two pressure minima of ignition, one at about 280–330°C. and the other at about 340–370°C., both being lowered progressively as the hydrocarbon series was ascended. These observations have recently been extended by Mr. M. Maccormac in these laboratories to cover heptane, octane, and decane, with results which are in conformity with the behavior of the lower members of the series.

It is also important to note that as the series was ascended not only did the minimum pressures for ignition in the lower range decrease, but the preignition time-lags were also materially reduced; for instance, with propane lags of the order of 3 to 5 sec. were reduced to less than 1 sec. with hexane.

With members containing three or more carbon atoms there were also fairly well defined pressure and temperature limits within which cool flames were propagated, those for three propane–air mixtures containing 2.6, 5.0, and 7.5 per cent of the combustible being illustrated by the diagonally shaded areas associated with the ignition point curves, Nos. 1, 2, and 3 in figure 3. When cool flames were propagated a slow-moving, pale bluish flame was observable through the windows provided in the explosion vessel; this was accompanied by the development of a small pressure pulse and a considerable formation of intermediate compounds strongly aldehydic in character. The phenomenon was quite different from normal flames which are usually fast travelling, giving rise to a whitish emission and high pressure development, the products containing only traces of intermediate compounds. As will be shown later the cool flames occurred after a definite time-lag which was usually of the order of 20 to 30 sec. at the lower temperature boundary; as at any selected pressure the temperature was raised, these lags were appreciably shortened and the cool flames became more intense up to about 360°C. Above this temperature the lags became very short and the intensity of the flames rapidly diminished, until above the upper temperature limit they were no longer observable. At a stated temperature the cool flames also increased in intensity as the pressure was raised from the lower pressure limit; and when a pressure adequate for true ignition was attained a two-stage process occurred, the full ignition following rapidly after the formation of a cool flame. Such behavior may be regarded as characteristic of all the higher paraffins.

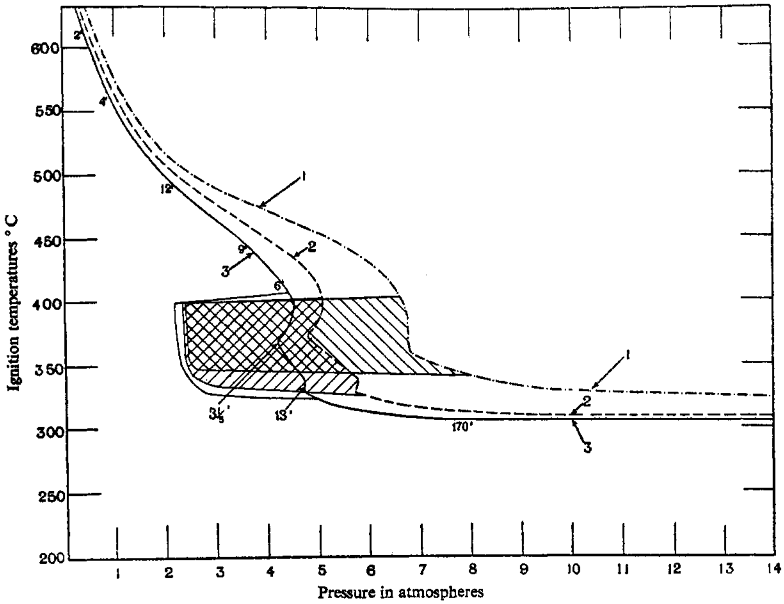

FIG. 3. Propane–air mixtures. Percentage mixtures for the curves: curve 1 = 2.6; curve 2 = 5.0; curve 3 = 7.5

It should perhaps be stated here that the method employed in the determinations so reviewed was that which originated with Mallard and Le Chatelier, the mixture under investigation being admitted rapidly into an evacuated vessel maintained at the experimental temperature; the vessel employed had a cylindrical cavity 17 cm. x 3.75 cm., capacity = 170 cc., and was provided with a mild-steel liner. If liners of other materials were employed, ease of ignition seemed to depend on their catalytic inactivity; moreover, alteration in the dimensions of the cavity, while influencing the precise location of the curves according to circumstances, was without effect on the general character of the phenomena. Owing to the extreme violence of the ignitions usually found when undiluted combustible–oxygen mixtures were employed (particularly with those containing excess of oxygen) and also because a main interest has been in correlating ease of spontaneous ignition under pressure with the known "knocking" propensities in engine practice of the fuels concerned, the investigations so far completed have been mainly restricted to mixtures made with air. Recently, however, Newitt and Thornes (22) have made a close examination both of the ignition characteristics of an equimolecular propane–oxygen mixture in silica vessels and also of the intermediate products at all stages of the combustion, which has thrown further light on the subject; of particular interest has been their observation that in certain circumstances it is possible for as many as five cool flames to succeed one another. Elsewhere, Neumann and his collaborators (1) and Prettre (29) have studied the behavior in the cool-flame regions of mixtures of butane and pentane with oxygen, their observations agreeing in all essentials with those already described but being more directed towards their kinetic interpretation.

THE RELATIONSHIP BETWEEN SPONTANEOUS IGNITION AND KNOCK

It is now generally recognized that the behavior of any fuel in an engine is largely influenced by the chemical reactivity of the unburnt medium ahead of the flame (cf. 9, 37, 38, and 30), this being controlled by the degree of compression, the working temperature, and speed of running. In such circumstances where the available time interval is short any *appreciable* chemical reaction must *ipso facto* be intense, and conditions will proximate closely to those of the ignition point; indeed, since the work of Tizard and Pye (33) it has been well appreciated that there is in general a close relationship between both ignition points and temperature coefficients of reaction velocity of fuel–air media and their knocking propensities in an engine. There have been, however, certain practical difficulties to an unqualified acceptance of this relationship; also, although it was early recognized that a limit was set to engine design by critical compression ratios depending on the fuel employed, the part played by pressure other than by raising the working temperature remained obscure, there being no reason to suppose that its influence on ignition points was abnormally great and other than quite progressive.

When it was discovered with the higher paraffins that (*1*) the lower ignition region approximated to the ordinary compression temperatures attained in an engine, (*2*) ignition occurred abruptly in this region with a minimum time-lag on the attainment of a critical pressure, while at higher temperatures the mixtures were non-ignitible, (*3*) mixtures rich in combustible ignited at a lower critical pressure than those containing excess of air, (*4*) not only did ignition occur at progressively lower pressures as the series was ascended but the time-lags were also materially reduced, and (*5*) the presence of an antiknock raised the pressure necessary for ignition, it became clear that it was to the pressure requisite for ignition in the lower range that the standard knock ratings of fuels were probably related.

In considering the ignition point determinations in the light of their probable application to internal-combustion engines, however, the question of time-lag was of predominating importance, because in such conditions the maximum lag permissible would not exceed a few thousandths of a second. It is not possible with the method of working in the investigations described herein to determine with precision lags of much less than 0.5 sec. Propane–air mixtures, however, while exhibiting the behavior characteristic of the higher paraffins generally, have much longer time-lags than found with the higher members, so that it was possible to indicate the general influence of pressure on them.

In figure 4, curve 1 shows the ignition points of a 7.5 per cent propane–air mixture plotted against pressure in the ordinary way; the lags printed against the curve were those at these minimum ignition pressures and as previously pointed out they were variable, being usually shortest in the cool-flame temperature range. The figures in the cool-flame area are the lags observed at 360°C. and 370°C. prior to the appearance of a cool flame; they decreased with increase of pressure and corresponded with the lags observed for true ignition when the requisite pressure had been attained.[1] The temperature of minimum lag on curve 1 was found at about 370°C.; at higher and lower temperatures on the curve this lag increased, but by increasing the pressure above the minimum the lags were shortened. Curve 2 is the curve so plotted for ignition with a lag of 3.2 sec. Similarly, curves 3, 4, and 5 were plotted for lags of 2, 1, and 0.6 sec., respectively.

Marked pressure minima persist in the iso-lag curves at higher pressures, an interesting feature being that the temperatures at which the minima are located do not remain fixed but show an immediate sharp rise from 370°C. to 415°C., thereafter apparently remaining constant; this tempera-

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[1] Cf. inset, figure 4. When true ignition occurred the lags showed a slight increase due to the two-stage process already referred to. The dotted curve shows the lags for the same mixture, but with an addition of 0.05 per cent of lead tetraethyl.

ture corresponds with the upper limit for cool flames. Also when the time-lags become short by increasing initial pressure the ignitions are extremely violent and akin to detonation, a matter which is being further investigated by Dr. G. P. Kane in these laboratories.

With higher hydrocarbons (cf. hexane (34)) an iso-lag curve of the type shown by No. 5, figure 4, would relate to extremely short lags, immeasurable without special methods; and when it is recalled that the compression temperature of the working fluid in an engine varies with the compression ratio employed somewhat as follows: 4:1, 385°C.; 5:1, 410°C.; 6:1, 430°C. (although in engine practice other factors such as dilution with explosion products, the formation of reaction centers during the compression stroke, and the part played by the advancing flame call for consideration), there would seem little doubt at all as to the general significance of the curves. Incidentally also it is clear why slow running is conducive to knock for, although this has been attributed in some quarters to better volumetric efficiency, it is more likely due to the increased available lag period.

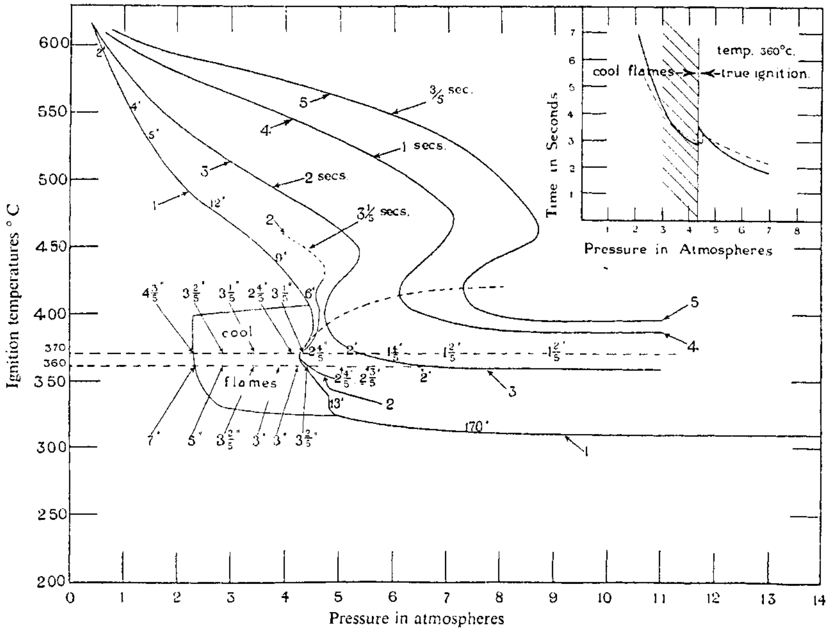

FIG. 4. Influence of pressure on time-lags. 7.5 per cent propane–air mixture

While so far we have confined this discussion to the straight-chain paraffins, it remains to state that no exception has yet been found to the relationship between knocking propensity of any fuel and the pressure requisite at the compression temperature for its spontaneous ignition within a short time-lag. Thus the knock ratings of ethane, ethyl alcohol, and acetaldehyde (14.0, 7.5, badly knocking) would be inferred at a glance from the curves in figure 2. To illustrate the behavior of side-chain paraffins, in figure 5A the ignition point curves of corresponding mixtures with air of butane, isobutane, and isoöctane (2,2,4-trimethylpentane) have been drawn (curves 1, 2, and 3). Figure 5B contrasts the behavior of mixtures of hexane and cyclohexane (curves 1 and 2). Materials such as methane and benzene (11), which do not knock, exhibit ignition point curves which apparently show no lower system at all (curves 1 and 2 in figure 6). The behavior of the simpler olefins will now be described.

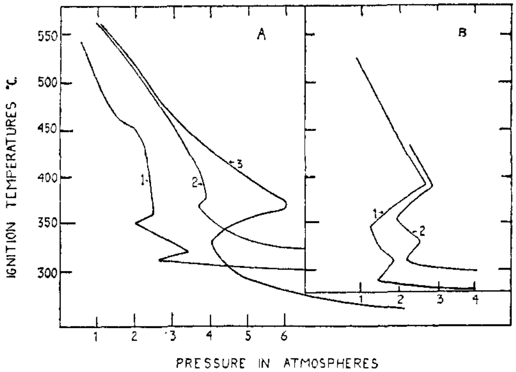

FIG. 5. (A) Theoretical mixtures with air of butane (curve 1), isobutane (curve 2) and isoöctane (curve 3). (B) Theoretical mixtures with air of hexane (curve 1) and cyclohexane (curve 2).

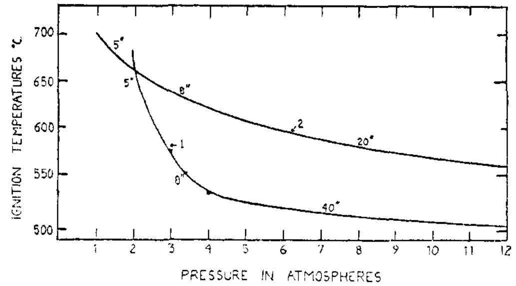

FIG. 6. Theoretical mixtures with air of methane (curve 1) and benzene (curve 2). Small figures along the curves denote time-lags.

IGNITION REGIONS OF THE SIMPLER OLEFINS

Recently Kane and Townend (13) published an account of an extension of the investigations into the influence of pressure on the spontaneous ignition of hydrocarbon–air media to the simpler α-olefins,—ethylene, propylene, butylene, and amylene. In figure 7, curves 1, 2, and 3 show the influence of pressure on the ignition points of theoretical mixtures with air of ethylene, propylene, and butylene.

With the ethylene mixture (No. 1) the ignition points fell progressively with increase of pressure, a smooth curve of the type previously observed with methane–air mixtures being obtained. There was never any indication of the formation of cool flames, even though the curves for rich mixtures fell to about 300°C. at sufficiently high pressures, nor was any irregularity in the time-lags observed; these increased from 4 to 5 sec. at 550°C. to about 30 sec. at 370°C. and 240 sec. at 310°C., varying slightly with mixture composition.

The fact that the ignition point curves for ethylene–air mixtures are quite smooth and that no superposed lower system as found with ethane–air mixtures was observed is a matter of interest, because, as has already been pointed out, strong evidence was adduced that with ethane this was attributable to an adequate formation of acetaldehyde, which is a principal product in its slow oxidation. If this be correct it seems possible that the known formation of acetaldehyde in the slow combustion of ethylene (6, 15, 17) arises not as a direct immediate oxidation product but as the outcome of a slower secondary process less likely to influence ignition. This would be in agreement with the view that acetaldehyde arises by an isomeric change from a primary product (cf. Bone (4)) and also with Norrish's atom chain mechanism as applied to ethylene (23). Formaldehyde, on the other hand, which is known to promote the main combustion (6) was always a product of the preflame combustion and the curve is consistent with its playing such a rôle, as in fact it does with methane (cf. p. 261).

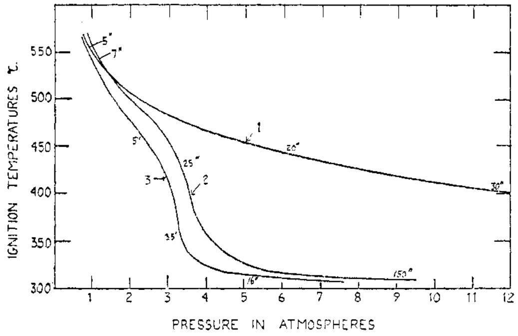

FIG. 7. Theoretical mixtures with air of ethylene (curve 1), propylene (curve 2), and butylene (curve 3). Small figures along the curves denote time-lags.

Pressure had a far more marked influence on the ignition points of the propylene–air mixture (No. 2). The ignition points fell progressively at the lower pressures to about 440°C.; further increase of pressure, however, caused an abrupt fall over a temperature range where cool flames were also observable, but below about 330°C. increase of pressure had little further influence. Although the ignition points fell rapidly no irregularities in the time-lags were observed; in this respect and in the fact that the curves showed no pressure minima propylene differs from propane. A study of the respective behaviors of propane and propylene may better be made by comparing figure 8, which shows both the ignition point curves and the cool-flame areas for three propylene–air mixtures containing 3.0, 4.5, and 6.0 per cent of the combustible, with figure 3. The main difference, however, lay in the weakness both of the pressure pulses and of the luminosity associated with the cool flames of propylene, a fact which made impossible precise determinations of the pressure and temperature limits for them. Moreover, although for corresponding mixtures those with propylene were ignitible at slightly lower pressures than those of propane, not only were the time-lags longer with the former but their rate of decrease with increase of pressure was not as great; curves 4 and 5, in figure 8, relate to ignitions of the 4.5 per cent mixture No. 2 with a constant lag of 3 and 2 sec., respectively, and may be compared with the curves for a 7.5 per cent propane–air mixture (figure 4).

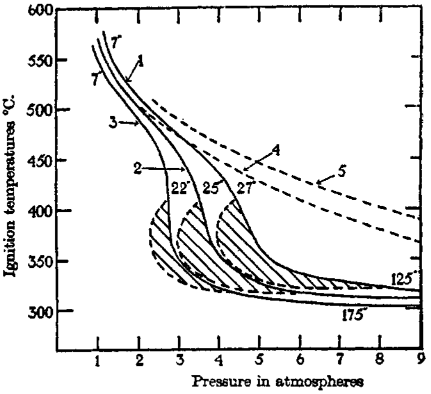

FIG. 8

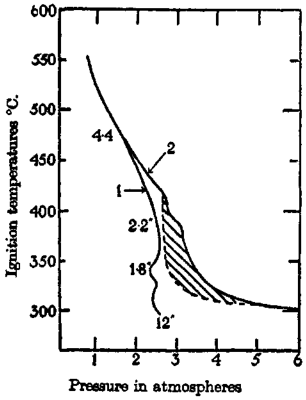

FIG. 9

FIG. 8. Propylene–air mixtures. Percentage mixtures for the curves: curve 1 = 3.0; curve 2 = 4.5; curve 3 = 6. Curves 4 and 5, for the 4.5 per cent mixture, relate to ignition with constant lags of 3 and 2 sec. Shaded areas indicate cool-flame regions.

FIG. 9. Amylene–air mixtures. Curve 1 = 2 per cent of α-amylene; curve 2 = 2 per cent of isomeric amylenes.

The ignition point curve for the α-butylene–air mixture (No. 3, figure 7) resembled closely that obtained with the propylene–air mixture, the minimum ignition points, however, occurring at lower pressures. Although there was still no indication of pressure minima of ignition in the lower temperature range characteristic of the higher paraffins, the lags, which were much shorter than those observed with either ethylene or propylene, showed an irregularity in this range as found with the paraffins; thus they were reduced from about 5 sec. at 450°C. to a minimum value of 3.5 sec. at 370°C., thereafter increasing to 16 sec. at still lower temperatures. The cool flames were also more pronounced in regard to both the accompanying pressure pulses and luminosity.

Amylene as supplied commercially (b. p. 36–40°C.) consists of side-chain isomers. A small quantity of α-amylene (b. p. 30.3°C.) was specially synthesized, but only sufficient was available to complete the ignition point curve of a mixture containing 2 per cent of it (theoretical mixture,—2.7 per cent); this is shown in figure 9, No. 1. Other curves were determined with a sample of purchased material containing more stable isomers; No. 2 relates to a 2 per cent mixture of this material.

The ignition points of the α-amylene mixture (No. 1) gave for the first time definite evidence of the pressure minima in the cool-flame temperature range, invariably found with the higher paraffins; the higher minima occurred at 340°C. and the lower at 312°C. The time-lags were also irregular as with the paraffins, a minimum value of 1.8 sec. being observed at 340–350°C. Cool flames were observable between 310°C. and 410°C., the pressure pulses being marked between 310°C. and 360°C. Moreover, as would be anticipated, the mixture of the side-chain isomers No. 2 was not nearly as easily ignitible as that of the α-olefin.

COMPARISON OF THE RESPECTIVE BEHAVIORS OF PARAFFINS AND OLEFINS

From the results obtained with the four simpler olefins it may be stated that the influence of pressure on their spontaneous ignition in admixture with air is not unlike that found with the paraffins. Thus, ethylene behaves like methane, and although propylene and butylene did not reveal strong negative temperature coefficients of reaction as found with the corresponding paraffins, the ignition point curves exhibited a sharp fall over narrow critical pressure ranges to a lower system where cool flames were normally observed; and finally a 2 per cent α-amylene–air mixture showed all the characteristics typical of higher paraffin–air mixtures.

Also the minimum pressures requisite for ignition in the lower temperature range with corresponding mixtures, considered in the light of the observed time-lags, indicate that the knock ratings of both olefins and paraffins should fall as the series is ascended. This is in accord with the "critical compression ratios" of Boyd, as table 1 shows. The results of the investigation as a whole are, in fact, in conformity with the general conclusions of Boyd (16), that (*1*) in an homologous series, whether paraffinic or olefinic, the tendency to knock increases with increasing length of the saturated carbon chain, and (*2*) in an isomeric series, knock decreases progressively with the centralization of the double bond.

Reverting to the chemical processes operative in the combustion of either paraffins or olefins containing more than three carbon atoms, at least three conditions call for consideration: namely, (*i*) that giving rise to cool flames in the temperature range usually between about 280–410°C.; (*ii*) that ultimately resulting in true ignition in the products from cool flames, there being usually two distinct zones of activity, (a) 300–330°C. and (b) 340–370°C., respectively; and (*iii*) that occurring above the upper limit for cool flames, i.e., above about 410°C. It would seem that with most fuels conditions conducive to (*i*) are mainly responsible for knock,[2] and that the phenomenon itself involves essentially the processes occurring in (*ii*) which are intense at sufficiently high pressures.

TABLE 1

Comparison between critical compression ratios and minimum ignition pressures

HYDROCARBON	CRITICAL COMPRESSION RATIO (BOYD)	MINIMUM IGNITION PRESSURE AT 350°C.	TIME-LAG
		atm.	*sec.*
Olefins:			
Ethylene	8.5		
Propylene	8.4	5.0	30
α-Butylene		3.35	3.5
α-Amylene	5.8	2.4	1.8
Paraffins:			
Ethane	14		
Propane	12	6.8	3
Butane	6.4	3.4	2
Pentane	3.8	2.2	1.4
Hexane	3.3	1.9	1
Isobutane	8.9	4.4	3

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[2] This holds without doubt for fuels of "critical compression ratios" < 6 to 8. At higher compression ratios the compression temperature would doubtless approach 500°C., which is probably in the upper ignition range even with very short time-lags. It is significant that propylene (C. C. R. = 8.4) is the only olefin to exhibit a knock rating lower than that of the corresponding paraffin (C. C. R. = 12), and reference to figures 4 and 8 shows that whereas in the lower range the iso-lag curves for propane occur at much lower pressures than with propylene, in the higher range the reverse is true.

There is little doubt that the processes giving rise to cool flames are of a chain character and probably associated with the presence of higher aldehydes and other active intermediate bodies. That aldehydes are important intermediate products may be seen from figure 10, which shows the ignition points of a 7.5 per cent propane–air mixture, No. 1, which contains defect of air with which 1 and 2 per cent of propionaldehyde, Nos. 2 and 3, and 1 and 2 per cent of acetaldehyde, Nos. 4 and 5, had been admixed. The influence of acetaldehyde on the cool-flame area has also been illustrated. There is little difference in the behavior of the two aldehydes in facilitating ignition; both induce ignition in the lower temperature range at much lower pressures and temperatures than are observed with the simple mixture, and both have much less influence on the ignition points at higher temperatures and comparatively none above 550°C. A similar effect was also found on addition of 1 per cent of acetaldehyde to a 4.5 per cent propylene–air mixture.

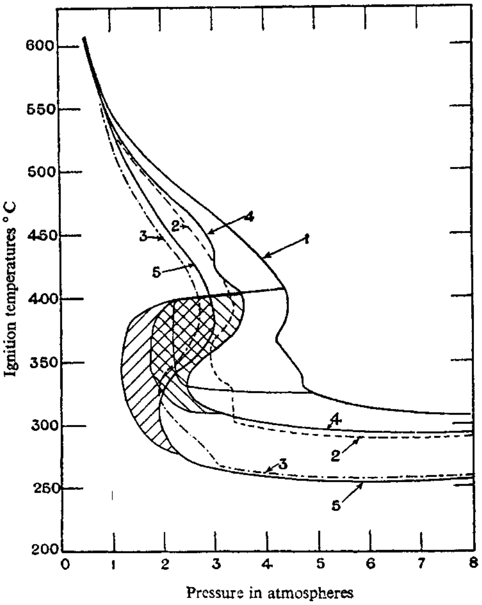

FIG. 10. Curve 1 = 7.5 per cent propane–air mixture; curves 2 and 3 = the same with addition of 1 and 2 per cent of propionaldehyde; curves 4 and 5 = the same with addition of 1 and 2 per cent of acetaldehyde.

While the behavior of the α-olefins under pressure is not unlike that of corresponding paraffins, the main difference lies in the reduced luminosity of the cool flames and the feeble pressure pulses observed with them, indicating that the processes operative in the low-temperature system are less intense than with the paraffins; moreover the preflame time-lags were not only greater but decreased less rapidly with pressure. There would seem no reason to postulate any difference in the intermediate products (or chain initiators) responsible for promoting reaction with both homologs, and these probably result from the formation of higher aldehydes. This view would be in agreement with the well-known researches of Beatty and Edgar (2). Kane and Townend (13) regarded the degenerate branching view of Semenoff (31) as attractive in explaining their results, for the less vigorous behavior of the olefins may be attributable either to a slower building up of active centers depending upon aldehyde concentration by virtue of difference in the chemical stages involved, or to the intervention of stronger inhibiting processes. The former explanation is readily interpretable by comparing the respective stages involved in building up higher aldehydes from propane and propylene (cf. 3, 23). With regard to the kinetics of the chain mechanisms involved, Aivazov and Neumann (1) have developed an empirical equation agreeing closely with experiment for the relation between the preignition time-lags for cool flames, which are regarded as ignitions giving rise to stable intermediate products, and the experimental temperature, pressure, vessel diameter, and minimum cool-flame pressure. Their expression is based on Semenoff's theory of spontaneous ignition as arising by a process of interacting chains in accordance with the expression

$$\frac{dn}{dt} = n_0r - (g - f)n + f^1n^2$$

where n_0 = the number of active centers formed, r = the length of the primary chain, g = the chain-breaking factor, f = the chain-branching factor, and f^1n^2 takes account of chain interaction, f^1 being small. No suggestions are made, however, as to either the character of the interacting centers or the products likely to be produced from them. Prettre (29) has also related the time-lags observed with pentane–oxygen mixtures with a simple chain mechanism.

No complete explanation has so far been forthcoming to account for the upper temperature limit for cool flames. Recent experiments on ether–air mixtures in these laboratories leave little doubt that the mechanisms operative are the same whether the flames are ignited artificially in cold media by means of a hot wire or whether they are developed spontaneously in a sufficiently heated vessel. It would appear that for some reason there is an upper temperature barrier to the flames which is never exceeded. This may possibly be due to thermal instability or elimination by other means of a chain initiator or material giving rise to a chain initiator; or it may also well be that an intermediate product (e. g., acetaldehyde) breaks down by a chain process. From a thermal point of view the temperature restriction may perhaps be likened to the limitation imposed in high-temperature flames by the dissociation of carbon dioxide and water; an important clue would seem to be the presence in the flames of energized formaldehyde.

THE INFLUENCE OF NITROGEN DIOXIDE

Interesting light on the problem has recently been thrown by studying the influence of small amounts of nitrogen dioxide on the ignition points (13). In figure 11A the influence of successive additions of 0.1 and 1 per cent of nitrogen dioxide to a 7.5 per cent propane–air mixture (curve No. 1) may be seen from the corresponding ignition point curves (Nos. 2 and 3).

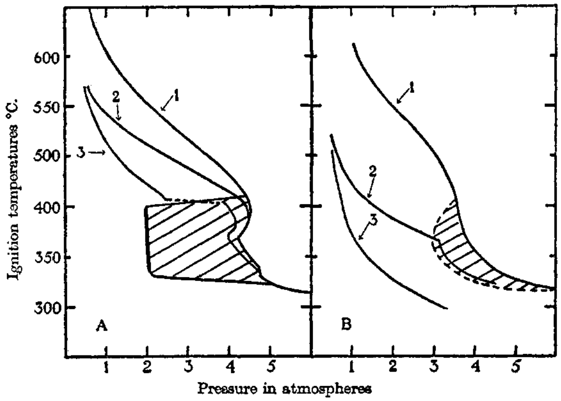

FIG. 11. (A) Curve 1 = 7.5 per cent propane–air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide. (B) Curve 1 = 4.5 per cent propylene–air mixture; curves 2 and 3 are the same but with 0.1 and 1.0 per cent additions of nitrogen dioxide.

By far the greatest influence of the promoter was not only to reduce the time-lags, but to effect ignition at much lower pressures in the temperature range above the upper limit for cool flames. There now appeared, in fact, an abrupt transition from the sensitized ignition typical of the upper system to ignition arising as a sequence of cool flame formation, as indicated by the dotted line (curve No. 3). Thus in the low-temperature range the presence of nitrogen dioxide had by comparison no great influence in extending the cool-flame limits, and the ignition limits while being slightly reduced at temperatures between about 330°C. and 400°C. were, if anything, raised at lower temperatures.

There was thus important and independent evidence of different chemical mechanisms in the two ignition ranges, and the results suggest the possibility of mutual destruction of active centers in the lower system. The comparative ineffectiveness of nitrogen dioxide in promoting combustion in the cool-flame range is of great interest, because it is in keeping with the observation of Egerton and collaborators (9, 37) that it was without influence in inducing knock with butane, heptane, and petrol, although with hydrogen it did so.

In figure 11B a corresponding set of curves has been drawn showing the respective influence of addition of 0.1 and 1 per cent of nitrogen dioxide (curves 2 and 3) to a 4.5 per cent propylene–air mixture (curve 1). Apart from reduction in the time-lags the presence of nitrogen dioxide was still without influence on the limits within which cool flames were observed. With regard to true ignition, however, the presence of 0.1 per cent of nitrogen dioxide not only very greatly reduced the limiting pressures in the upper system but promoted ignition resulting in the lower system in the cool-flame products (curve 2); and 1 per cent of it so sensitized the combustion that a smooth curve (No. 3) was obtained, ignition occurring over the whole range without any apparent prior cool-flame reaction whatever. This marked difference in the relative influence of nitrogen dioxide in the lower system with propane and with propylene seems in agreement with the views already expressed concerning the two combustions, for the rate of chain development with propylene, which is by comparison with propane a slow process, would be the more enhanced by the addition of active centers to the system.

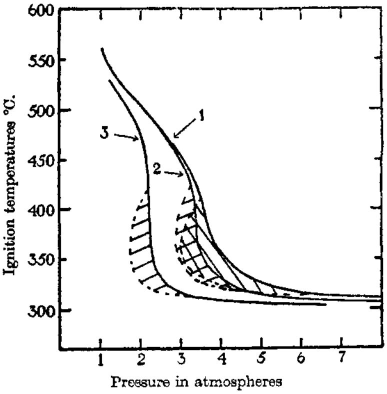

FIG. 12. Curve 1 = 4.5 per cent propylene–air mixture; curves 2 and 3 are the same but with 0.1 and 0.5 per cent additions of diethyl ether. Shaded areas indicate cool-flame regions.

THE INFLUENCE OF ETHER

It is well known that ether vapor when added to a fuel–air mixture acts as a strong proknock. Newitt's recent discovery (20) of the formation of mixed ethers in the slow combustion of olefins has revealed another class of intermediate compounds, the influence of which calls for investigation. In figure 12, curves 2 and 3 show the influence of additions of 0.1 and 0.5 per cent of ether to a 4.5 per cent propylene–air mixture (No. 1). Ether plays a rôle rather like, but much more powerful than, that of acetaldehyde, for 0.1 per cent of it (No. 2), while facilitating combustion in the lower range below 425°C., was without influence at higher temperatures; an addition of 0.5 per cent of it (No. 3), however, powerfully promoted the combustion, this being marked even up to 500°C. So far as the matter has been tested a similar effect has been found with propane–air mixtures.

The interpretation of the respective influences of higher aldehydes, ether, and nitrogen dioxide on the combustion as described is now forming the subject of further investigation.

SUMMARY

Researches into the combustion of complex hydrocarbons, designed to throw light on the problem of knock in internal-combustion engines, have revealed generally that the mechanisms involved are far from simple. Much new light has recently been thrown on the subject by systematic investigation of the influence of pressure on the spontaneous ignition points of these materials.

Inflammable mixtures with air of the paraffins containing three or more carbon atoms, while not spontaneously ignitible at low pressures below about 500°C., give rise abruptly to ignition at higher pressures in a temperature range between about 310°C. and 370°C., where normally only "cool flames" are initiated; and although neither methane–air nor ethane–air mixtures appear to develop cool flames, the latter are ultimately ignitible in a lower temperature system less complex than that characteristic of the higher members. There is general agreement between ease of ignition in the lower temperature range and the knock ratings of the materials concerned. This holds good for side-chain paraffins, olefins, naphthenes, and aromatic fuels.

All olefins higher than ethylene behave in a similar manner; they differ from the paraffins in that the cool flames are less intense and the preflame time-lags are not only greater but decrease less rapidly with increase of pressure.

The influence of higher aldehydes, nitrogen dioxide, and diethyl ether as promoters of ignition is also discussed.

REFERENCES

(1) AIVAZOV AND NEUMANN: Acta Physicochim. U. R. S. S. **4**, 575 (1936); Z. physik. Chem. **B33**, 349 (1936); Acta Physicochim. U. R. S. S. **6**, 57, 279 (1937).
(2) BEATTY AND EDGAR: J. Am. Chem. Soc. **56**, 102, 107, 112 (1934).

(3) Bone: Bakerian Lecture. Proc. Roy. Soc. (London) **A137,** 243 (1932).
(4) Bone: J. Chem. Soc. **1933,** 1599.
(5) Bone and Gardner: Proc. Roy. Soc. (London) **A154,** 297 (1936).
(6) Bone, Haffner, and Rance: Proc. Roy. Soc. (London) **A143,** 16 (1933).
(7) Bone and Hill: Proc. Roy. Soc. (London) **A129,** 434 (1930).
(8) Dykstra and Edgar: Ind. Eng. Chem. **26,** 509 (1934).
(9) Egerton, Smith, Ll., and Ubbelohde: Phil. Trans. Roy. Soc. (London) **A234,** 433 (1935).
(10) Emeleus: J. Chem. Soc. **1929,** 1733.
(11) Fisher and Townend: Unpublished results.
(12) Kane, Chamberlain, and Townend: J. Chem. Soc. **1937,** 436.
(13) Kane and Townend: Proc. Roy. Soc. (London) **A160,** 174 (1937).
(14) Konratjew: Acta Physicochim. U. R. S. S. **4,** 556 (1934).
(15) Lehner: J. Am. Chem. Soc. **54,** 1830 (1932).
(16) Lovell, Campbell, and Boyd: Ind. Eng. Chem. **23,** 26, 555 (1931); **25,** 1107 (1933); **26,** 475, 1105 (1934).
(17) Newitt and Bloch: Proc. Roy. Soc. (London) **A140,** 427 (1933).
(18) Newitt and Burgoyne: Proc. Roy. Soc. (London) **A153,** 448 (1936).
(19) Newitt and Haffner: Proc. Roy. Soc. (London) **A134,** 591 (1932).
(20) Newitt and Semerano: Proc. Roy. Soc. (London) **A157,** 348 (1936).
(21) Newitt and Szego: Proc. Roy. Soc. (London) **A147,** 555 (1934).
(22) Newitt and Thornes: J. Chem. Soc. **1937,** 1656.
(23) Norrish: Proc. Roy. Soc. (London) **A150,** 36 (1935).
(24) Pease: J. Am. Chem. Soc. **51,** 1839 (1929).
(25) Pease: J. Am. Chem. Soc. **57,** 2296 (1935).
(26) Pease and Munro: J. Am. Chem. Soc. **56,** 2034 (1934).
(27) Pope, Dykstra and Edgar: J. Am. Chem. Soc. **51,** 1875, 2203, 2213 (1929).
(28) Prettre: Bull. soc. chim. **51,** 1132 (1932).
(29) Prettre: Compt. rend. **203,** 1152 (1936); Ann. combustibles liquides **11,** 669 (1936).
(30) Rassweiler and Withrow: Ind. Eng. Chem. **24,** 528 (1932).
(31) Semenoff: Chemical Kinetics and Chain Reactions, p. 73. Oxford University Press, London (1936).
(32) Steacie and Plewes: Proc. Roy. Soc. (London) **A146,** 583 (1934).
(33) Tizard and Pye: Proc. N. E. Coast Eng. **31,** 387 (1921); Phil. Mag. **44,** 78 (1922); **1,** 1094 (1926).
(34) Townend, Cohen, and Mandlekar: Proc. Roy. Soc. (London) **A146,** 113 (1934).
(35) Townend and Mandlekar: Proc. Roy. Soc. (London) **A141,** 484 (1933).
(36) Ubbelohde: Proc. Roy. Soc. (London) **A152,** 354 (1935).
(37) Ubbelohde, Drinkwater, and Egerton: Proc. Roy. Soc. (London) **A153,** 103 (1935).
(38) Withrow and Rassweiler: Ind. Eng. Chem. **23,** 769 (1931).