47. *The Spontaneous Ignition under Pressure of Typical Knocking and Non-knocking Fuels: Heptane, Octane;* iso*Octane, Di*iso*propyl Ether, Acetone, Benzene.*

By M. Maccormac and D. T. A. Townend.

Summary.

Previous investigations, which had established a close relationship between ease of spontaneous ignition under pressure and the known knocking propensities in engine practice of the simpler paraffins and olefins, have been extended, and the present paper includes observations with some of the newer 'high-duty' (non-knocking) fuels, notably *iso*octane, di*iso*propyl ether, and acetone.

Much higher pressures are requisite for the spontaneous ignition of side-chain paraffins than for the straight-chain isomers, the temperature ranges in which cool flames are observed and the character of the low-temperature ignition systems induced thereby being much the same in both cases.

The cool-flame zones and the lower-ignition systems of the ethers appear to be composite, and much higher pressures are requisite for the ignition of mixtures of air with di*iso*propyl ether than for those with diethyl ether.

Acetone has been shown to give rise to cool flames and a simple low-temperature system if the observations are extended to sufficiently high pressures; and benzene behaves rather like methane, there being no indication at all of a low-temperature system.

A scheme is suggested whereby the relative knock-rating of a fuel may be assessed from the characteristics of its spontaneous ignition under pressure.

The processes giving rise to the low-temperature ignition systems induced by cool flames are briefly discussed.

In a recent communication (Kane, Chamberlain, and Townend, J., 1937, 436) earlier observations on the spontaneous ignition under pressure of the paraffin hydrocarbons up to hexane were summarised, and the probable influence of intermediately formed aldehydes in promoting combustion was studied by comparing the ignition-point curves of corresponding paraffins, alcohols, and aldehydes containing up to three carbon atoms; the relationship between the pressures requisite for spontaneous ignition within a suitable short time lag and the critical compression ratios for the occurrence of 'knock' in engine practice was also indicated. In parallel observations on the olefins up to amylene (Kane and Townend, *Proc. Roy. Soc.*, 1937, *A*, **160**, 174), it has also been shown that their behaviour is not unlike that of the corresponding paraffins, the ignition-point curves exhibiting a sharp fall over narrow critical pressure ranges to a lower system, where at atmospheric pressure only cool flames are normally observed; and amylene revealed all the characteristics typical of the higher paraffins. The main difference between the two series, however, lay in the weak luminosity and feebleness of the pressure pulses associated with the cool flames of the olefins, indicating that the processes operative in the low-temperature system are less intense than with the paraffins; moreover, the pre-flame time lags were not only greater but decreased less rapidly with increase in initial pressure. It seemed likely that combustion was promoted in both instances by the formation of the same reactive species, which probably result from the formation of higher aldehydes; and the less vigorous behaviour of the olefins may be attributable either to a slower building up of active centres depending upon aldehyde concentration by virtue of difference in the chemical stages involved, or to the intervention of stronger inhibiting processes. New evidence as to the chemical processes leading to the formation of cool flames and ultimate ignition has recently been forthcoming from the work of Newitt and Thornes (J., 1937, **1656**) on propane–oxygen mixtures, a matter of interest being their observation that cool flames seem to depend on the prior formation of a critical concentration of higher aldehydes.

The relationship between ease of ignition under pressure and the knocking propensities of the paraffins up to hexane and the olefins up to amylene seeming conclusive, it became a matter of importance, both from the point of view of their practical application as well as the development of the theory of the combustions concerned, to extend these observations to include *inter alia* some of the newer high-duty fuels, notably side-chain hydrocarbons, ketones, and di*iso*propyl ether. In this paper a brief account and discussion are given of the behaviours of (1) *iso*octane (ββδ-trimethylpentane) in comparison with *n*-heptane and *n*-octane, (2) di*iso*propyl ether, (3) acetone, and (4) benzene. The apparatus and procedure employed were essentially as described by Kane, Chamberlain, and Townend (*loc. cit.*).

Results.

1. n-*Heptane*, n-*Octane and* iso*Octane*.—In Fig. 1 curves have been drawn showing the influence of pressure on the ignition points of corresponding weak mixtures with air (0·65 × theoretical concentration of combustible) of *n*-heptane and *n*- and *iso*-octane. The materials employed were all synthetic products supplied by the Eastman Kodak Company having b. p.'s 98—98·5°, 124—126°, and 98—99°, respectively.

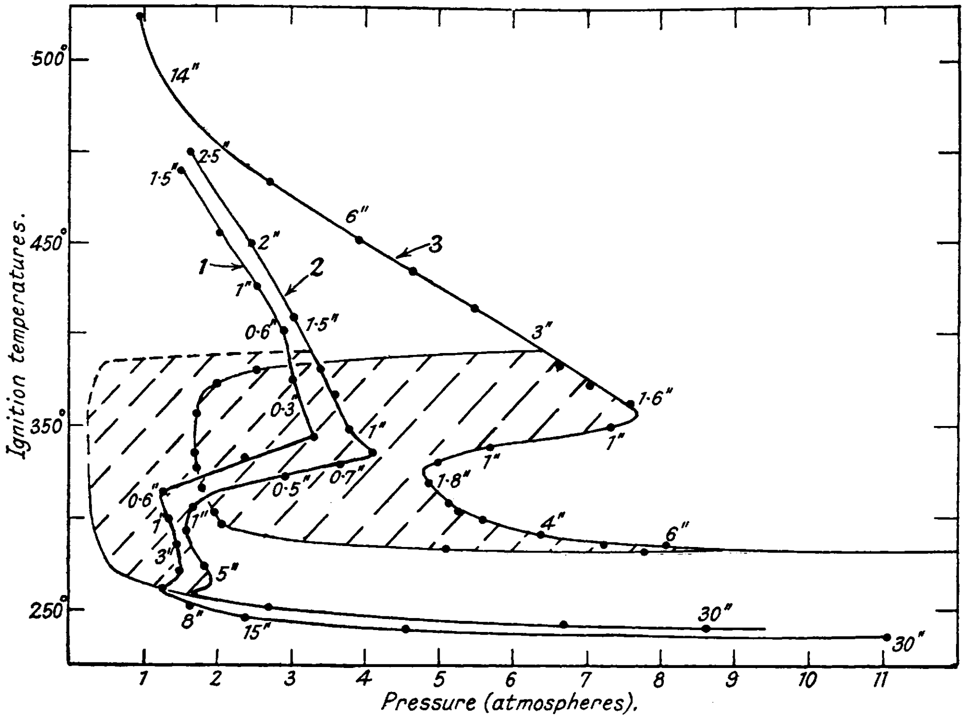
The curves for the two normal paraffins (Nos. 1 and 2) are characteristic of those previously determined for propane, butane, pentane, and hexane, there being two pressure minima of ignition in the low-temperature system; moreover, the minimium ignition pressures and temperatures were found to decrease progressively but more slowly as the series was ascended. This is in accord with the observation of Lovell, Campbell, and Boyd (*Ind. Eng. Chem.*, 1934, **26**, 1105) that the tendency to knock of the normal paraffins increases rapidly up to pentane but more slowly thereafter. Moreover, with heptane and octane the time lags (as indicated along the curves) became very short and were not measurable with accuracy; *e.g.*, that for the octane–air mixture was of the order of 0·3 sec. at 350°. In other experiments attempts to determine the ignition-point curve of a corresponding *n*-decane–air mixture had for this reason to be abandoned, for the time lags in the low-temperature range were now less than the interval required for filling the mixture into the explosion vessel.

The temperature and pressure limits within which cool flames were observable are defined in the usual way for the heptane–air mixture by the diagonally shaded area; also, owing to the very short time lags, it was possible to determine the upper-temperature boundary only approximately. An interesting feature of the experiments on the paraffin series as a whole was the progressive increase in intensity of the cool flames as the series was ascended, this being marked up to the heptane–air mixtures.

*iso*Octane, the well-known standard for knock-rating, is now produced commercially for blending purposes from *iso*butylene *via* di*iso*butylene (Banks, *J. Inst. Pet. Tech.*, 1937, **23**, 63). Curve No. 3, Fig. 1, relates to a mixture of this material with air corresponding with those of the two normal paraffins (Nos. 1 and 2). As anticipated, the pressures requisite for ignition were much greater than for the *n*-octane–air mixture (No. 1) throughout the whole temperature range, and only one pressure minimum of ignition in the low-temperature system could be located (cf. the behaviour of *n*-butane and *iso*butane; Townend Cohen, and Mandlekar, *Proc. Roy. Soc.*, 1934, *A*, **146**, 126); also at corresponding temperatures the time lags were longer for the side-chain isomer. Although, in general, the character of the ignitions as well as of the cool flames was much the same with both isomers, yet mixtures with *iso*octane were by far the more sensitive to surface conditions, particularly in the temperature range below 300°.

The influence of pressure on the spontaneous ignition of all the normal paraffins up to octane, as well as of *iso*butane and *iso*octane, having now been studied, there seems little doubt as to the general relationship between the pressures requisite for spontaneous ignition under conditions of appropriate time-lag and temperature and the knock ratings of the fuels concerned, as may be seen from the following figures relating to (*a*) the minimum pressures for ignition in the lower system, (*b*) the corresponding time lags, and (*c*) the knock ratings (critical compression ratios) of the paraffins concerned :

Fig. 1.



Corresponding mixtures with air of (1) n-*octane*; (2) n-*heptane*; (3) iso*octane*.
[*Figures along curves denote time lags* (*seconds*).]

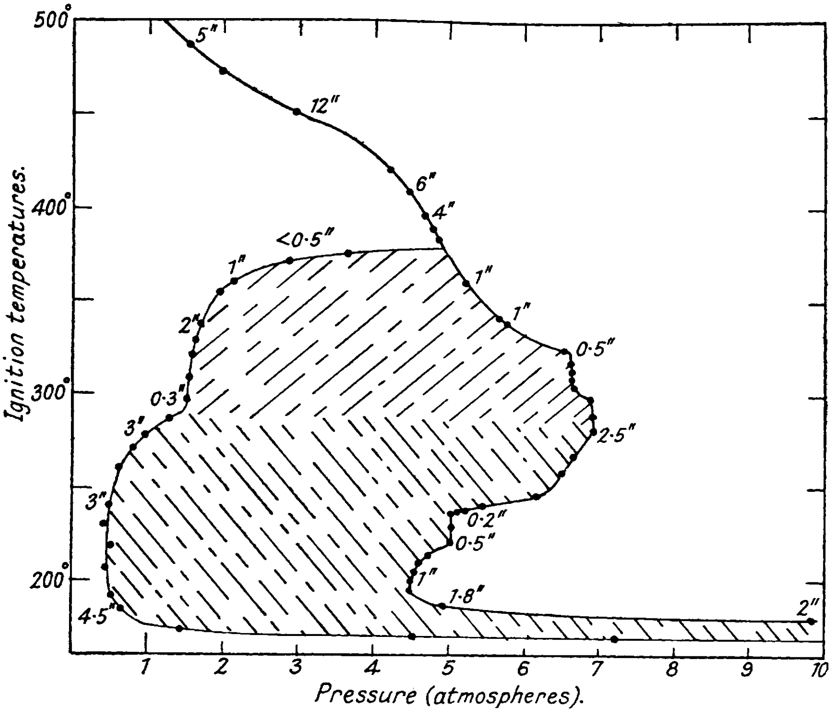
Paraffin.	*A.* Minimum pressure (atm.).	*B.* Time lag (sec.).	*C.* Critical compression ratio (Boyd).	Ratio *A*/*C*.
Methane	—	—	(non-knocking)	—
Ethane	—	—	14·0	—
Propane	6·8	3	12·0	0·57
Butane	3·2	2	6·4	0·50
Pentane	2·2	1·4	3·8	0·57
Hexane	1·9	1	3·3	0·58
Heptane	1·58	0·7	2·8	0·57
Octane	1·3	0·3	<2·8	>0·47
*iso*Butane	4·8	3	8·9	0·54
*iso*Octane	4·85	1·7	7·6	0·64

Similar correspondence has also been observed with the olefins (Kane and Townend, *loc. cit.*).

Although the actual numerical consistency of the relationship between the minimum ignition pressures and the critical compression ratios is striking, we would not overstress its importance because (*a*) under engine conditions the minimum pressures would relate to ignition within a time lag not exceeding a few thousandths of a second and it is doubtful whether the rate of decrease of lag with increase of pressure would conform to the same order with each hydrocarbon, and (*b*) in the case of fuels with critical compression ratios $>$ 6—8 : 1 it seems likely that the compression temperatures would approach 500°, which probably corresponds with the upper ignition range even for very short time lags (cf. Townend and Chamberlain, *Proc. Roy. Soc.*, 1936, *A*, **154**, 108), a matter which is discussed below.

2. *Diiso*propyl *Ether*.—The use of this ether as an anti-knock fuel for blending purposes has only recently been described (Buc and Aldwin, *J. Soc. Auto. Eng.*, Sept. 1936), and in view of its commercial production from propylene, its potentialities as a fuel are considered to be greater than those of *iso*octane (Banks, *loc. cit.*). We are indebted to Messrs. Trinidad Leaseholds Ltd. for a supply of a good sample of the material, which, after treatment with sodium, was fractionally distilled, the fraction of b. p. 67·4—67·7°/747 mm. being employed for our determinations.

Fig. 2.

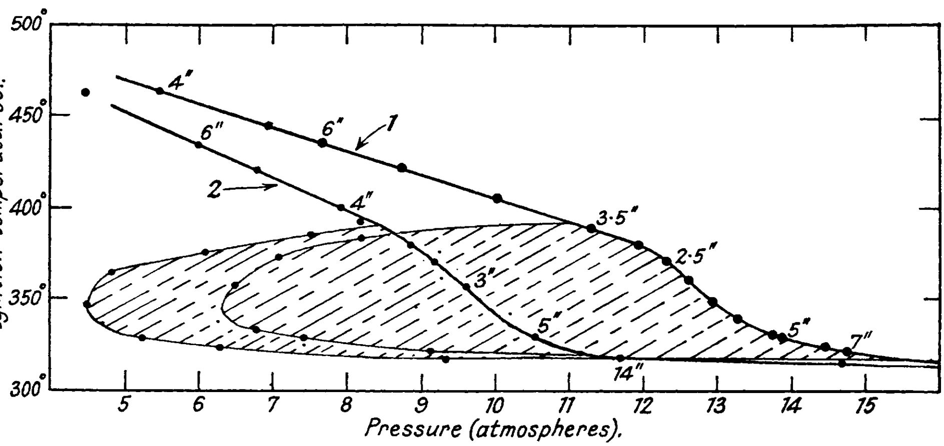


2·5% *Diiso*propyl *ether–air mixture.*
[*Figures along curves denote time lags* (*seconds*).]

Fig. 2 shows the ignition-point curve of a 2·5 % mixture (theoretical mixture = 2·28 %) of this combustible. In general, it resembles that obtained with diethyl ether (Townend and Chamberlain, *Proc. Roy. Soc.*, 1937, *A*, **158**, 415), for the principal lower ignition system was located at much lower temperatures (180—250°) than that usually observed with the paraffin hydrocarbons (240—350°). An interesting feature of the results as a whole, however, was that the cool-flame zone which extended downwards from *ca.* 390° appeared to be composite. Thus a lower cool-flame system giving rise to the principal lower-ignition system extended from *ca.* 170° to 290—300°, the time lags shortening with rise of temperature; at higher temperatures, *viz.*, 300—390°, *i.e.*, in the range where the cool flames of higher paraffins and olefins are found, the lower cool-flame system was replaced by a second system, the time lags increasing abruptly at first and the ignition-point curve in this range being of the type previously observed with the simpler olefins (Kane and Townend, *loc. cit.*). Moreover at pressures above *ca.* 3 atm., experience showed the cool flames to differ somewhat in character, being blue and milder in intensity in the upper system and purple and of greater intensity in the lower system. Further evidence of the dual character of the lower system with the ether is afforded by the occurrence of minimum time lags for ignition at both *ca.* 240° and 320°; the ignitions below *ca.* 240° following cool flames were also much more violent than those at higher temperatures. It may be recalled that two quite separate cool-flame areas were similarly located in the case of diethyl ether–air mixtures (*idem, ibid.*), although the flames in the upper of these were both green and strong in intensity and more akin to weak ignitions. It appears, therefore, that in the combustion of ethers there is one low-temperature system located at *ca.* 200°, which probably arises as a consequence of a primary oxidation, and another at *ca.* 350°, due to the secondary oxidation of an intermediate product also common to the combustion of higher hydrocarbons (possibly acetaldehyde).

It is also clear from the high pressures requisite to effect ignition over the whole temperature range that di*iso*propyl ether, in contrast to diethyl ether, would be expected to be a non-knocking fuel.

FIG. 3.



Acetone–air mixtures: 1 = 5%; 2 = 7·6%.
[*Figures along curves denote time lags* (*seconds*).]

3. *Acetone.*—Although acetone and other ketones have been frequently reported as being employed as efficient anti-knock fuels, *e.g.*, in the Schneider trophy race (Ricardo, Melchett Lecture to the Institute of Fuel, 1935), yet there do not appear to be any data in the literature regarding their precise knock-ratings. In order to test our general views on the subject, however, we decided to ascertain the characteristics of the ignition under pressure of acetone–air mixtures.

Curves 1 and 2, Fig. 3, show the influence of pressure on the ignition points of two acetone–air mixtures containing 5% (theoretical mixture) and 7·6% of acetone, respectively. The mixtures developed cool flames when high enough pressures were employed, and the ignition-point curves showed a steeper but not marked fall with increase of pressure in the cool-flame temperature range. A feature of the experiments was the high pressures necessary to effect ignition below 400°, and in this respect acetone resembles ethane, although cool flames were not detected with the latter. The cool flames observed with acetone–air mixtures were always very weak; and the pressure pulses associated with them were of an intensity which, when expressed as a percentage of the initial pressure in any particular case, would be related to that developed with other materials discussed in this paper somewhat as follows:

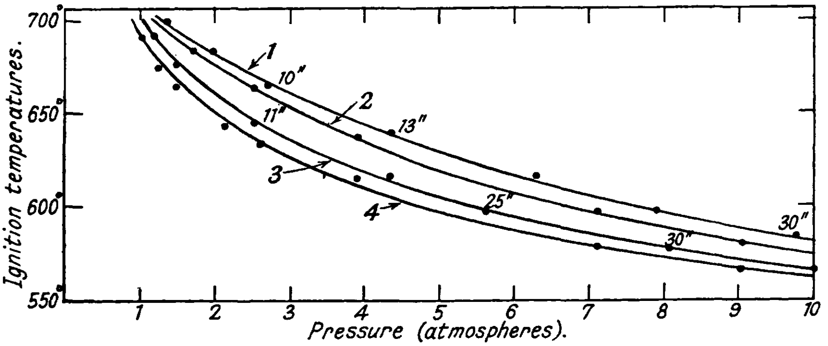
Acetone.	*iso*Propyl ether.	*iso*Octane.	*n*-Heptane.	*n*-Octane.
1	Lower 3·5 Upper 2·5	4·5	9	10

With acetone, however, the cool flames gave rise to a luminescence, lasting up to 10 seconds; this was succeeded by a faint glow which was accompanied by a slow pressure rise, indicating that the cool-flame reaction was prolonged in the circumstances; the normal ignitions were also weak except at temperatures below 330°.

From the high pressures necessary to effect ignition, acetone would obviously be adjudged a non-knocking fuel.

4. *Benzene–Air Mixtures* (With W. A. P. FISHER).—In the early stages of these investigations some determinations were made of the ignition temperatures of benzene–air mixtures under pressure, this material being the oldest and most commonly employed non-knocking blending fuel. In Fig. 4 ignition-point curves of four mixtures containing 1·36, 2·45, 3·2, and 5% of the combustible (theoretical mixture = 2·7%), curves 1, 2, 3, and 4 respectively, have been drawn. It will be observed that there was never any indication at all of a lower-ignition system, the ignition points falling gradually from about 700° to 560—580° with increase in initial pressure from 1 to about 10 atm.; the time lags were also considerable, increasing from *ca.* 6 to 30 secs. over the same range. The determinations were easily reproducible, and lent strong support to our conviction as to the relationship between the knocking propensities of fuels and their ease of spontaneous ignition under appropriate temperature and pressure conditions.

FIG. 4.

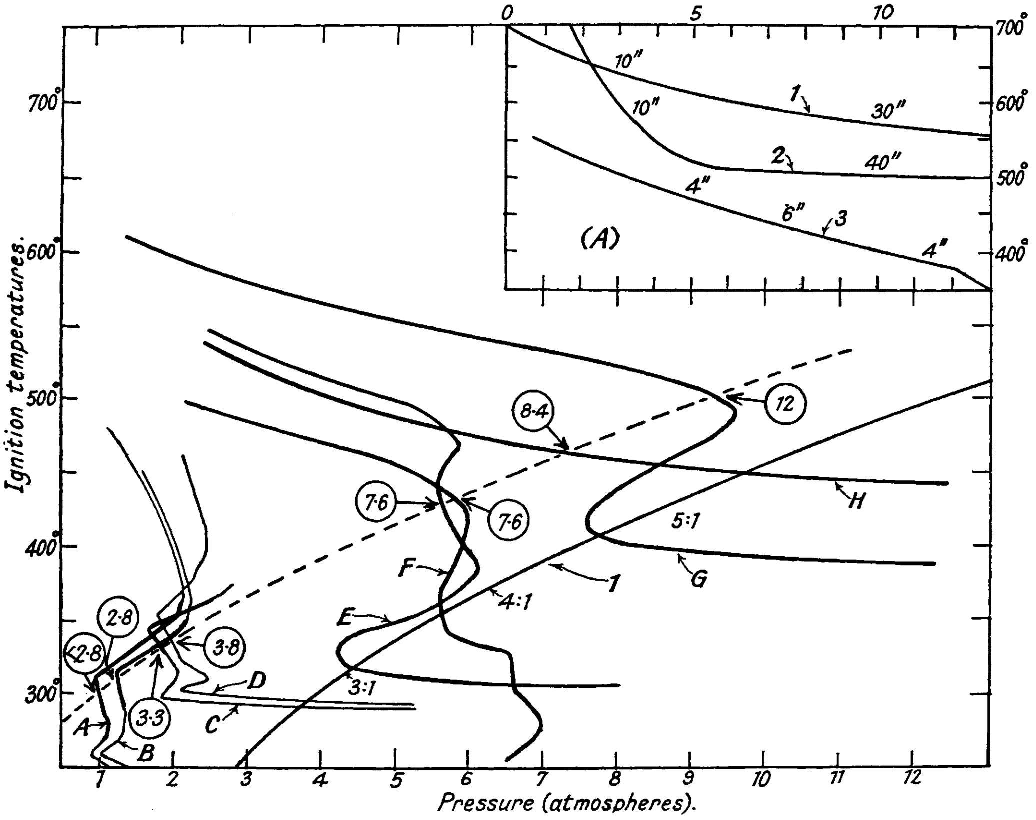


Benzene–air mixtures : 1 = 1·36%; 2 = 2·45%; 3 = 3·2%; 4 = 5%.
[*Figures along curves denote time lags* (*seconds*).]

The General Relationship between Spontaneous Ignition under Pressure and Knock Ratings.—So far in these investigations, we have usually compared (as on p. 240) the pressures requisite for spontaneous ignition in the lower system with the critical compression ratios requisite for the incidence of knock in engine practice of the fuels concerned and, having also in mind the observed time lags, we have found this relationship to hold good in a remarkable manner. In order to study the respective behaviours of chemically dissimilar fuels, however, an attempt at a more precise method of comparison is necessary, involving in particular (*a*) ignition-point curves pertaining to ignition within comparable short time lags, and (*b*) a knowledge of the approximate compression temperatures attained by the explosive media at the end of the compression stroke in the cylinder head. Unfortunately, it is impossible with our present method of working to measure very short lags even approaching those comparable with conditions in an engine, so for the present purpose we have plotted in Fig. 5, as far as our results have allowed, curves relating to approximately theoretical mixtures with air of eight representative fuels, indicating where possible the pressures requisite for ignition in a time lag of 1 sec.; with the higher paraffins, where complete curves are not always available, we have marked with a heavy line the portions pertaining to lags of 1 sec. or less. The curves for benzene, methane, and acetone (Inset A), which are non-knocking fuels, are our normal curves relating to the minimum ignition pressures, the lags being of the order of 4 secs. upwards; the pressures would have to be increased appreciably for ignition to occur within 1 sec.

In order to form an opinion of the approximate pressures and temperatures attained on compression by the various explosive media, we have plotted on the same diagram a typical adiabatic curve (No. 1) for compression ratios up to 6 : 1, calculated according to the relations $T_2 = T_1 \times r^{\gamma-1}$ and $P_2 = P_1 \times r^{\gamma}$. For simplicity, the value of γ has been taken as 1·35, which is generally applicable, and that of T_1 as 130°, corresponding approximately with the temperature of the medium before compression at a compression ratio of 4·5.*

Fig. 5.



One-second lag ignition-point curves: theoretical mixtures with air.
A = *Octane,* B = *heptane,* C = *hexane,* D = *pentane,* E = isooctane, F = *di*iso*propyl ether,*
G = *propane,* H = *propylene.*
Values in circles denote known knock ratings.
Inset (A). *Ignition-point curves:* 1 = *Benzene,* 2 = *methane,* 3 = *acetone.*

It being now generally recognised that knock in an engine is conditioned by the chemical reactivity of the unburnt medium ahead of the flame (cf. Egerton *et al., Phil. Trans.*, 1935, *A*, **234**, 433), according to our view, owing to the extreme shortness of the available time interval, any appreciable reaction will be intense, and conditions will proximate to those of the ignition point. Knock will therefore first be expected with any particular fuel when the compression is so increased that the pressure and temperature adiabatically attained approximate to those requisite for spontaneous ignition within an appropriate short time lag. If this be the case, the points of intersection of curve I with ignition-point curves pertaining to a lag of (say) 0·005 sec. would indicate approximately the conditions requisite for the incidence of knock. Such ignition-point curves, if determinable, would obviously lie in the direction of higher pressures and to the right of the curves plotted in Fig. 5.† In order to illustrate our interpretation, however, we have

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* For more precise data concerning compression temperatures, see Pye, "The Internal Combustion Engine," Oxford University Press, Vol. 1, p. 116; Callendar *et al.*, Rep. and Mem., No. 1062, Aeronautical Research Committee, 1926.

† It should be noted that for shorter time lags the actual shift in the direction of higher pressures of the curves shown in Fig. 5 would be much greater for those located at higher than at lower pressures.

shifted curve 1 quite arbitrarily to the left in the direction of lower pressures (dotted curve) so as to intersect the 1-second lag ignition-point curves. It will readily be observed that as so placed the known critical compression ratios, indicated at the points of intersection, all fall into the same order as the pressures requisite for ignition within the same short time lag at an appropriate compression temperature. Such a method should, we think, provide a general means of assessing in the laboratory the relative knock rating of any fuel under preliminary test.

Taking into account all the factors concerned, we regard the treatment just described as the best viewpoint in considering the results as a whole, and although in engine practice other factors, such as dilution with explosion products, the formation of reaction centres before the end of the compression stroke, and the part played by the advancing flame, all call for consideration, there seems little doubt as to their general significance.

A matter of interest also relates to the question whether the formation of a cool flame in the unburnt medium is always a necessary prelude to knock in an engine; and in view of the fact that cool flames have never been observed in our experiments above 410—420° and that this temperature is almost certainly exceeded when compression ratios greater than 6—8 : 1 are employed, we doubt whether such occurrence is essential to the phenomenon, but more probably a critical reaction velocity irrespective of the precise intervening mechanisms which lead to it. This is supported by the fact that, although the iso-lag curves show propane to be more reactive than propylene in the cool-flame temperature range, yet at higher temperatures they cross; and it is significant that the knock rating of propylene is less than that of propane.

Discussion.

Although the principal purpose of these investigations has been to substantiate the general relationship between ignition pressures and the knocking propensities of the fuels concerned, yet a main interest still centres upon the correct interpretation of the lower-ignition system and in particular the mechanism of formation of the cool flames which give rise to it. In addition to extending the results already obtained with the lower members of the paraffin series, with both straight and side chains, the experiments described in this paper have (*a*) established the occurrence of two cool-flame regions with ethers, mixtures with di*iso*propyl ether requiring much higher pressures for their ultimate ignition than those with diethyl ether, and (*b*) shown for the first time that, if the behaviour of acetone may be taken as typical, ketones also give rise both to cool flames and to a simple lower-ignition system provided the experiments be extended to sufficiently high pressures.

As far as the paraffins are concerned, the similarity in behaviour of all members containing more than three carbon atoms, in regard to both the location of the cool-flame temperature ranges and the dual pressure minima associated with spontaneous ignition arising therefrom, suggests that the same materials are ultimately concerned in all cases. That higher olefins behave in a manner much the same as that of the higher paraffins also suggests that the substances concerned are intermediate oxidation products common to both combustions and therefore likely to be aldehydes. Also, the fact that acetaldehyde is the simplest aldehyde to show a marked pressure minimum corresponding with that exhibited by all higher hydrocarbons (Kane, Chamberlain, and Townend, *loc. cit.*) indicates the intermediate formation of this material as likely to be a principal factor concerned in the process.

If it be conceded from the work of Edgar and his collaborators (*J. Amer. Chem. Soc.*, 1929, **51**, 1875, 2203) that the oxidation of a higher paraffin involves the formation of the corresponding aldehyde and water at an early stage, then it would appear, as indeed these authors have shown, that the succeeding reactions lead rapidly to the same type of products in all cases; moreover, although little is known concerning the thermal decomposition of higher aldehydes, it would seem not unreasonable, by analogy with the work of Norrish and collaborators on the photolysis of such aldehydes (J., 1935, 1504, etc.); that their thermal decomposition might in part give rise to acetaldehyde and a higher olefin.

No adequate explanation has yet been forthcoming either of the mechanism of, or of the upper temperature limit for, cool flames. Recent experiments carried out by Dr. H. S.

Hsieh in these laboratories on diethyl ether–air mixtures, however, indicate 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, therefore, that there is an upper temperature barrier to the flames which is not exceeded, probably owing to the thermal instability of a chain initiator or material giving rise to a chain initiator, the substances concerned being either stabilised products or possibly free radicals. In this connection, in view of the facts that (i) aldehydes, ethers, and ketones all give rise to cool-flame regions of ignition, (ii) the view is now widely held that the thermal decompositions of these materials proceed by chain processes involving free radicals (cf. Rice and Rice, " The Aliphatic Free Radicals," Johns Hopkins Press, **1934**), and (iii) that the presence of oxygen may provide reaction centres accelerating the decompositions (cf. Letort, *Compt. rend.*, 1933, **197**, 1042), it seems not unlikely that their thermal stability may be a factor influencing the low-temperature phenomena. Moreover, the probable interplay of per-acids and peroxides is also as yet not entirely understood.

Among recent theories of the processes involved, von Elbe and Lewis (*J. Amer. Chem. Soc.*, 1937, **59**, 976) have suggested, with regard to the combustion of higher paraffins, the formation of alkyl peroxide radicals of short life as giving rise to multiple branching in the low-temperature range by condensation with an aldehyde, and further oxidation of the product to yield hydroxyl radicals. With higher aldehydes a similar process is presumably involved, the radical concerned being of the type R·CO(OO); and in both cases cool flames are regarded as arising by stepwise degraded oxidation of R·CO radicals (produced from aldehydes) to $CH_3{\cdot}CO$, which is further oxidised to energised formaldehyde, the spectrum of which is characteristic of the emission from cool flames. Although such an explanation shows a possible cause of the low-temperature systems with aliphatic hydrocarbons and higher aldehydes, yet it seems doubtful whether it can be adapted to meet the case of (say) acetone and possibly the ethers.

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