76. *An Examination of the Mechanism by which "Cool" Flames may give rise to "Normal" Flames. Part I. The Inflammable Ranges of Ether–Air Mixtures in Closed Vessels.*

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Much interest has been aroused in recent years by the discovery that the spontaneous ignition of higher hydrocarbons and their derivatives can be effected under suitable conditions of pressure, temperature, and mixture composition in either of two ways, *viz.*, with or without the prior formation of a cool flame; in the former case a two-stage process is involved.

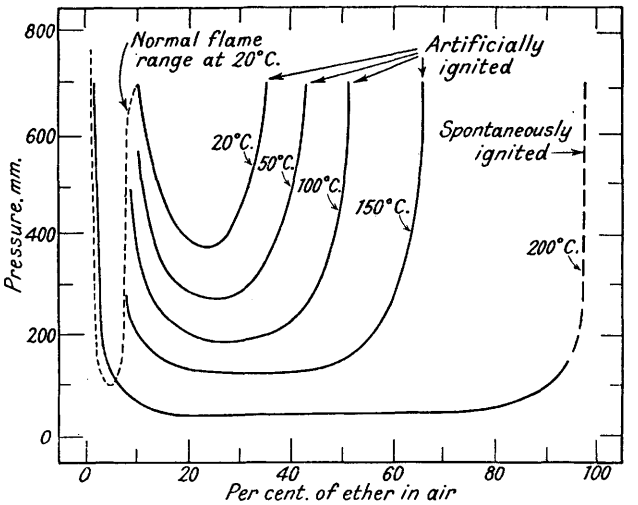
Recently, Townend and Chamberlain (*Proc. Roy. Soc.*, 1937, *A*, **158**, 415) extended to higher pressures White's observation (J., 1927, 498) that at atmospheric pressure and room temperature there are two separate composition ranges of inflammability, one for normal flames and the other for cool flames, finding that at a critical pressure the cool flames may give rise to normal flames by a process involving essentially the initiation of a second flame in the cool-flame products.

In the present paper evidence is produced that the two-stage process is the same whether the cool flames are induced in the media either (a) *spontaneously* at high temperatures and suitably low pressures or (b) *artificially* by means of a heated wire at room temperature and at high enough pressures.

The discovery that the two-stage process is observable in cold media at sufficiently high pressures has opened up a new line of attack for investigating the processes involved.

It was early recognised by Townend and Mandlekar (*Proc. Roy. Soc.*, 1933, *A*, **143**, 168) and later by Neumann and Aivazov (*Nature*, 1935, **135**, 655) that in spontaneous-ignition experiments with certain higher hydrocarbons ignitions are brought about in the temperature range 300—400° by a two-stage process, ignition occurring after the passage of a cool flame and after a definite short time interval. This phenomenon seems to be a general one with all higher hydrocarbons and ethers, although in the case of the former there is frequently a temperature range below the lower cool-flame temperature limit where the separate formation of a cool flame before ignition is never detected. Recently also, Kane (*Proc. Roy. Soc.*, 1938, *A*, **167**) and independently Belov and Neumann (*Compt. rend. Acad. Sci. U.S.S.R.*, 1938, **18**, 333) have shown that if the experimental pressure is sufficiently high, the higher paraffins also ignite in the cool-flame range by a one-stage process; in such circumstances the ignitions are very violent and akin to detonation, thus

Fig. 1.



Cool-flame ranges of ether–air mixtures: (a) *artificially ignited at* 20°, 50°, 100°, *and* 150°; (b) *spontaneously ignited at* 200°.

correlating "knock" as encountered in engine practice with the probable spontaneous ignition of the unburnt charge ahead of the flame.

In following up White's earlier experiments with ether–air mixtures with a view to study the extent to which the "normal" inflammability range might expand into the "cool" inflammability range at pressures above atmospheric, Townend and Chamberlain (*loc. cit.*) observed that at suitably high working pressures there was a range of mixtures of high ether content capable of propagating a cool flame for a considerable distance down a closed tube, but that a second flame, considered to be a normal ignition, would suddenly develop some distance behind the cool-flame front, catch it up, and replace it. Hence, it was difficult to define a criterion for the true limit of inflammability for normal flames as distinct from cool flames, for there was a range of mixtures with the poorer of which this "transition" effect would occur almost immediately following ignition, and with the richer of which it would occur just as the cool flame reached the end of the 1 m. tube.

It was also recognised at once that the mechanism of this "transition" phenomenon in cold ether–air media, ignited artificially by means of a hot wire, would probably be closely related to that observed in spontaneous-ignition experiments. If this proved correct, then a profitable line of attack on the whole problem would be available, for it should now be possible to examine one at a time the separate stages involved in the complete two-stage ignition process. Without such separate examination of these stages, any study of the kinetics of the processes concerned would no doubt be misleading. Accordingly, we

have investigated in greater detail this transition phenomenon, with results which have been very informative.

A Comparison of the Influence of Pressure on the Composition Ranges of Ether–Air Mixtures for Cool Flames when Artificially Ignited in Cold Tubes and when Spontaneously Ignited at 200°.—In order to establish that spontaneous ignition arising from prior cool-flame formation was essentially the same process whether the cool flames were initiated artificially in cold media by means of a hot wire or spontaneously in heated vessels, the cool-flame ranges were first determined in the usual way with hot-wire ignition at initial temperatures of 20°, 50°, 100°, and 150°, in a tube 4·5 cm. in diameter and 120 cm. long, closed at both ends, the criterion of inflammability being complete propagation throughout it. Subsequently, the corresponding range with the mixtures spontaneously ignited at 200° was determined in a silica-lined cylindrical vessel (3·8 cm. × 15·3 cm.), cool-flame formation being observed both visually and by means of the pulse imparted to the manometer connected to the apparatus. The resulting family of curves is shown in Fig. 1, the dotted line indicating the normal flame range with spark ignition at 20° (cf. preceding paper, Fig. 1, p. 334).

There appears to be little doubt that the mechanism of the processes involved is essentially the same with both artificial and spontaneous ignition; in the latter case, ignition probably first arises in a small volume element of the mixture in much the same manner as suggested by Foord and Norrish (*Proc. Roy. Soc.*, 1935, *A*, **152**, 196) in their interpretation of the behaviour of sensitised hydrogen–oxygen mixtures. It is conceivable, of course, that in perfectly homogeneous conditions of temperature and environment, spontaneous ignition could be a uniform process throughout the mass; actually it is doubtful whether this is ever achieved in practice, the pressure limit becoming virtually that for propagation of flame along the cylindrical enclosure. In studying the kinetics of spontaneous ignition in fairly narrow tubes the demarcation between a "fast reaction" and an "ignition" may be conditioned by the limiting conditions for flame propagation in the vessel concerned, a matter which may not always have received adequate attention.

An interesting feature of the curves is that, although at low temperatures the mixtures at the minimum ignition pressures had combustible : oxygen ratios between 1 : 1 and 2 : 1, yet at the higher temperatures ignition occurred almost as easily with mixtures of much higher combustible content, so that in the spontaneous ignition series of experiments at 200° there was no great difference between the minimum pressure for a mixture containing 70% of combustible and that for the 17—30% (2 : 1—1 : 1) range of mixtures.* Further, at 300 mm. pressure it was possible to observe definite cool-flame pulses (although the flames could no longer easily be detected by the eye) with mixtures containing as much as 97—98% of ether. An extension of these observations may help to throw light on the correct interpretation of cool flames generally, for it would seem possible that some product of combustion may act as a promoter of another independent reaction in the main bulk of the material, such as, *e.g.*, an exothermic decomposition.

A Comparison of the Influence of Pressure on the Initiation of "Normal" Flames from "Cool" Flames in Ether–Air Mixtures when (a) *Spontaneously Ignited and* (b) *Artificially Ignited in Cold Media.*—It being now reasonably clear that the cool flames through ether–air media at temperatures below the spontaneous ignition temperatures involve essentially the same chemical processes as when they arise spontaneously, it remained to demonstrate that the setting-up of normal flames in the cool-flame products when adequate initial pressures are employed arises by the same process in both instances.

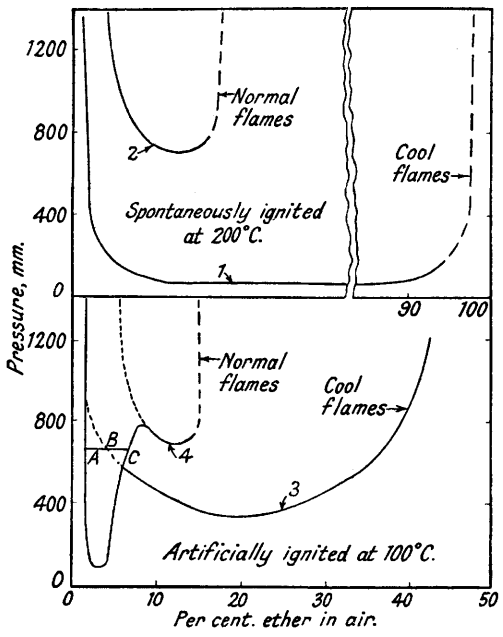
Curves 1 and 2, Fig. 2, show the influence of pressure at 200° on (*a*) the limits for spontaneous formation of the cool flames (the same curve as that for 200°, Fig. 1) and (*b*) the limits for spontaneous ignition of normal flames arising after the prior formation of cool flames. It is clear that, in conformity with all previously published results of spontaneous-ignition experiments in the cool-flame temperature range (cf. Townend and Chamberlain, *loc. cit.*, p. 418, Fig. 1), the minimum critical pressures for such normal

* Prettre (*Ann. Off. Nat. Comb. Liq.*, 1936, **11**, 669) has recently published results with pentane–oxygen mixtures showing the 1 : 1 mixture to exhibit the lowest minimum pressure for spontaneous ignition and correspondingly the shortest time-lag.

ignitions are much higher than for cool flames alone (*i.e.*, about 680 mm. compared with 50 mm.), and that, although the mixture most easily giving rise to normal ignition has a combustible : oxygen ratio of somewhat below 1 : 1, the range for " normal " inflammability does not extend beyond mixtures of composition between 5 and 18% of ether in air over a pressure range extending from 680 mm. to 1400 mm. In experiments in the " cool " flame range of spontaneous ignition the general observation is that the initiation of " normal " flames at a critical pressure is a sudden development of pressure which is considerably greater than that attributable to " cool " flames; along the high-limit boundary, where oxygen is greatly in deficit, however, this criterion could only be established with difficulty and the curve has therefore been dotted.

The corresponding curves, 3 and 4 in Fig. 2, show the influence of pressure on the limits of inflammability for both normal and cool flames in a 2·5-cm. tube at an initial temperature of 100°, and determined by either spark or hot-wire ignition according to the nature of the initial flame concerned. On the attainment of the limiting pressure for normal flames in the cool-flame range, ignition occurred after the cool flame had passed some distance along the tube; the normal flame seemed to be initiated in the cool flame products some distance behind the cool-flame front, as though a time interval were necessary for the accumulation of an adequate concentration of active centres in these products, and, once initiated, the normal flame travelled forward and replaced the cool-flame front.

FIG. 2.



It seems clear that the superposition of the normal inflammable range on the cool-flame inflammable range arises by much the same process for artificial as for spontaneous ignition; and the rather complicated curves of Townend and Chamberlain, showing the influence of pressure on the complete ranges of inflammability of ether–air mixtures when extended to pressures above atmospheric, seem to be simply interpretable by the superposition of the two independent systems, as may be seen from the complete dotted ranges illustrated in Fig. 2. A matter of interest is whether it should be possible to propagate cool flames at pressure above the dotted cool-flame boundary in the normal-flame range. As far as this matter has been tested, it can be stated that usually normal flames are difficult to restrain in this range whatever source of ignition is employed; recently, however, with other media such as certain acetaldehyde–air mixtures, it has been found possible to initiate cool flames well into the range of mixtures which with spark ignition give normal flames. We are also extending this work so as to determine the nature of speeds of the flames initiated across the range *ABC*, for it might reasonably be anticipated that the flame-speed–composition curve in this region would be composite, as indeed was actually observed by Gusev and Neumann (*Compt. rend. Acad. Sci. U.S.S.R.*, 1935, **2**, 377), using pentane–air mixtures; for the relevant conditions for reaction ahead of the flame might be expected to be much more favourable along *BC* than along *AB* owing to the temperature conditions for spontaneous reaction being lowered by some 200°.

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