77. *An Examination of the Mechanism by which "Cool" Flames may give rise to "Normal" Flames. Part II. The Inflammable Ranges of Higher Paraffin Hydrocarbons in Air: The Establishment of "Cool" Flame Ranges at Ordinary Temperatures and High Pressures.*

By M. S. HSIEH and D. T. A. TOWNEND.

The relationship between the " spontaneous ignition " and the " inflammability " ranges of ether–air mixtures being established (cf. preceding paper), it could be predicted from the known similarity of the characteristics of spontaneous ignition of ether–air mixtures and those of the paraffin hydrocarbons containing three or more carbon atoms that with the latter similar composition ranges for " normal " and " cool " flame inflammability should be determinable for artificially ignited mixtures at ordinary temperatures. In view of the facts that (*a*) the minimum pressures and (*b*) the time-lags for spontaneously developed cool flames were greater than with ether–air mixtures, and that both (*a*) and (*b*) decreased as the paraffin series was ascended, it could also be predicted that " cool " flame ranges would be located at progressively decreasing initial pressures in the same order.

These ranges have now been located at 100°, as follows : ether, below atmospheric pressure; hexane, above 5 atm.; butane, above 9 atm.; propane, above 12 atm.

THE influence of increasing pressure on the limits of inflammability of mixtures of combustible gases with air or oxygen has not hitherto been studied extensively. Pressures up to 10 atm. were employed by Terres and Plentz (*J. Gasbeleucht.*, 1914, **56**, 990, *et seq.*) and by Payman and Wheeler (J., 1923, **123**, 426) with the simpler combustible gases; later, Berl and Wenger (*Z. angew. Chem.*, 1927, **40**, 245) examined a wide range of both gaseous and liquid hydrocarbons in admixture with air at pressures up to 600 atm., and, in the case of the last-named, temperatures up to 100°, finding generally small changes in the lower limits, but a very marked widening in the upper limits of inflammability. A general feature of Berl and Wenger's observations was that, although the inflammable ranges were usually considerably widened at high pressures, at moderate pressures a narrowing might at first be observed; it is not clear, however, how far this narrowing was due to the conditions of ignition employed in the work. About the same time, Bone, Newitt, and Smith (*Proc. Roy. Soc.*, 1928, *A*, **117**, 553) published the results of determinations of the inflammable ranges of mixtures with air of hydrogen, carbon monoxide, and methane, the explosive media being confined in a spherical enclosure of 3″ diameter, and ignition being effected by means of the electrical fusion of a fine platinum wire. Their results with hydrogen and methane were as follows.

Initial press., atm.	1	5	10	30	50	125
H_2, %	9·9 —	9·9 —68·4	10·0^{+}—68·5	10·0^{+}—71·9	10·0^{+}—73·3	9·9^{-}—74·8^{+}
CH_4, %	5·6 —14·3	5·7 —16·4	6·0^{-}—17·1^{+}	5·9 —24·6^{+}	5·4 —29·0^{+}	5·7 —45·5^{+}

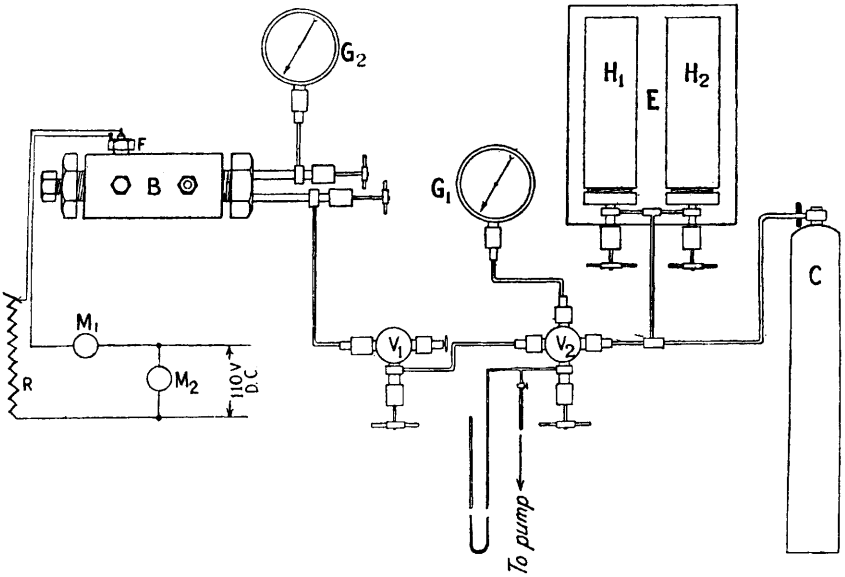
With carbon monoxide the ranges for the dry mixtures were found to become narrower and for the almost saturated mixtures hardly to vary over the same pressure range.

During 1930—1932, one of us (D.T.A.T.) in collaboration with S. Potash and S. Stevens investigated the behaviour of some higher paraffin hydrocarbons, the explosive mixtures being fired in a long cylindrical explosion vessel, of 2″ internal diameter, and found the general effect of pressure to be much the same as with methane–air mixtures. The widening of the upper limit with increase of pressure, however, was not only progressively greater as the series was ascended, but in each case on the attainment of an adequate pressure which decreased in the same order, it became accentuated abruptly. Owing to the high working pressure and also to deposition of tarry material at the upper limits, the use of a window to observe the travelling flames was not considered likely to be of any great advantage, and it was hoped, by means of a Petavel recording manometer, to measure the pressure development in the explosions and to employ this in conjunction with analyses of the products of combustion as criteria of the inflammability limits (cf. Bone, Newitt, and Smith, *loc. cit.*). Unfortunately, the completeness of combustion near the limits was very defective, and the recorded pressure differences were not sharp enough to enable the limits to be decided with precision; the matter was therefore left open for further investigation.

The recognition of the relationship between the "spontaneous ignition" and "inflammability" ranges of ether–air mixtures (cf. preceding paper, Fig. 1, p. 338) at once threw light upon the whole problem; for, in view of the similarity between the cool-flame ranges with both ether and the higher paraffins in spontaneous-ignition experiments,* it became obvious that corresponding cool-flame inflammation ranges ought to exist with the higher paraffins at ordinary temperatures in much the same way as those located by White with ether–air mixtures. Moreover, these cool-flame ranges would probably not be found below atmospheric pressure, and this would account, not only for their never having been previously observed, but also for the difficulty found in the earlier work in determining with precision the higher limits of inflammability with these materials.

Accordingly, a redetermination of the limits of inflammability of representative higher hydrocarbons has been made, and by working in an explosion vessel provided with quartz windows the cool-flame ranges have been located precisely in accord with this prediction.

FIG. 1.



Apparatus for Determining the Inflammable Ranges of Higher Hydrocarbon–Air Mixtures at High Pressures.

EXPERIMENTAL.

The apparatus employed is illustrated diagrammatically in Fig. 1. The vessel, *B*, was provided with an explosion cavity 3·8 cm. in diameter and 15·3 cm. long; at one end it carried a plug fitted with inlet and outlet valves, and at the other a second plug carrying a quartz window for visual observation of the flames. An ignition plug, *F*, and a second quartz window plug were located at each end of the cavity along the horizontal axis of the vessel, ignition being effected by the electrical fusion of a short length of platinum wire (0·005 in. diam.) stretched between two studs 7 mm. apart, and projecting downwards from the ignition plug into the explosion chamber. The vessel was heated by means of externally wound nichrome resistance wire, and the whole body was well lagged with asbestos. The flames were propagated horizontally from the ignition plug towards the end plug carrying the valves. Two high-pressure cylinders, H_1 and H_2, fitted with control valves served as storage cylinders for the mixtures, ½" glass balls introduced into these cylinders facilitating rapid mixing of the constituents. The cylinders were housed in a well-lagged electric heater, *E*, fitted with a thermostatic regulator so

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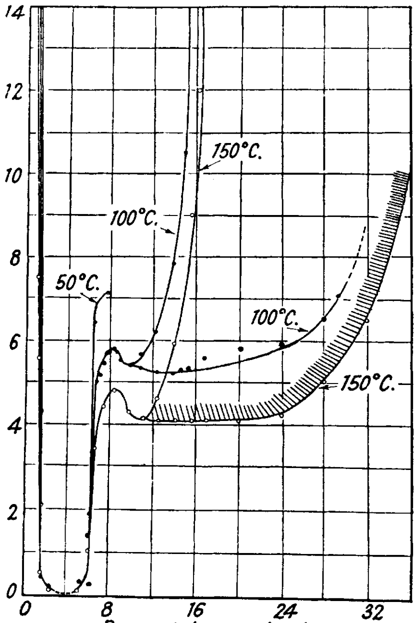
* Cf. previous papers on this subject: J., 1938, 238; *Proc. Roy. Soc.*, 1937, *A*, **158**, 415; *Chem. Reviews*, 1937, **21**, 259.

that combustibles liquid at room temperature could be maintained homogeneously in the vapour phase in admixture with air or oxygen under pressure. All connexions in the filling system were also wound with asbestos-covered nichrome resistance wire and could be heated to any desired temperature up to 200°.

The experimental procedure was essentially that employed for the experiments at reduced pressure (this vol., p. 333), complete propagation of flame occurring when the flame reached the side window fitted at the end remote from the ignition plug. Cool flames were characterised by a slow-moving blue flame accompanied by low-pressure development, and the production of intermediate products strongly aldehydic in character. The minimum ignition pressure for any particular mixture could usually be located within 0·1 atm. at pressures between 5 and 10 atm., and 0·05 atm. between 1 and 5 atm.

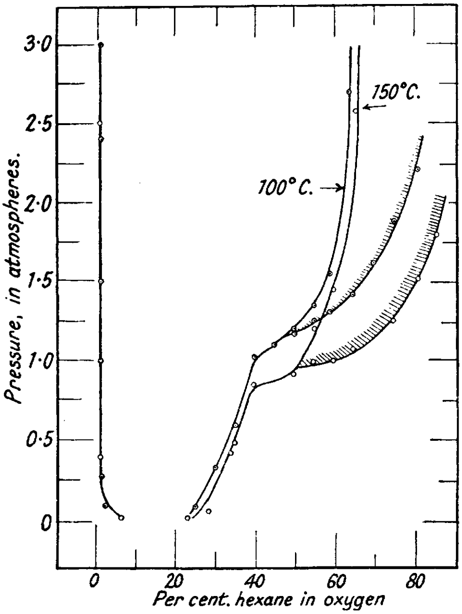
A. *Hexane–Air Mixtures.*—Comparatively few data are available in the literature concerning the limits of inflammability of hexane–air/oxygen mixtures. The principal more recent investigations have been those of Berl and his collaborators; the values given at atmospheric pressure by Berl and Hartmann (*Z. physikal. Chem.*, 1930, **146**, 281) were 1·6% (lower) and 6·4% (upper). With increasing pressure, the lower limit was lowered and the upper limit progressively raised, so that at, *e.g.*, 25 atm., the ranges of inflammability (as read from the published curves) were about 0·6% (lower) and 17% (upper) (cf. Berl and Bausch, *ibid.*, **145**, 451).

FIG. 2.



Influence of Pressure on the Inflammable Ranges of Hexane–Air Mixtures.

FIG. 3.

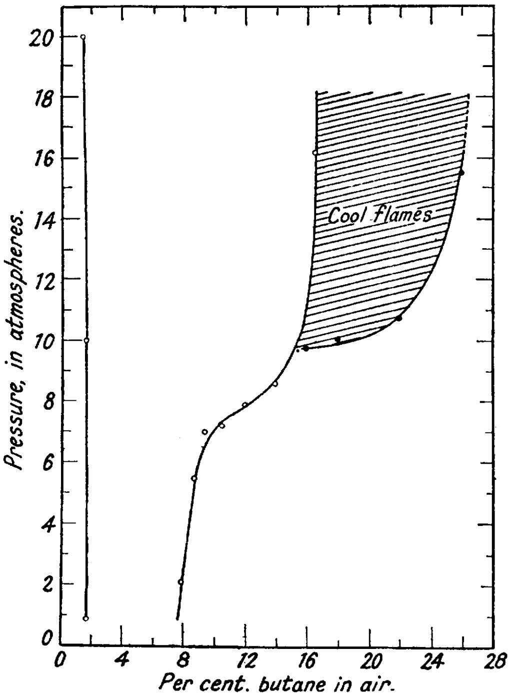


Influence of Pressure on the Inflammable Ranges of Hexane–Oxygen Mixtures.

In Fig. 2, curves are plotted showing the observed variation with pressure of the inflammable ranges for mixtures of hexane contents in air between 1 and 35% and at initial temperatures of 50°, 100°, and 150°. No difficulty was ever experienced in repeating the determinations closely. Below 1 atm. pressure the results agreed closely with those obtained in the 1 m. long glass tube (this vol., p. 334). Reference to the results at 150° shows that at pressures up to 4·1 atm. there was only one range of inflammable mixtures, *viz.*, that for the normal flames. This was at first almost unaffected by increase in initial pressure, the lower limit being lowered by about 0·3% and the higher limit raised by about 1% of hexane at pressures up to 4 atm. At a pressure of 4·1 atm. a cool-flame range was located with mixtures of composition between 11 and 22% of hexane, the normal range at the same pressure extending over mixtures of hexane content between 1·2 and 7·0%. The "normal" and "cool" flame ranges were thus separated by a range of non-inflammable mixtures containing between 7 and 11% of hexane. At pressures higher than 4·8 atm. the two ranges of inflammability became superposed, so that at, *e.g.*, 6·5 atm., mixtures containing between 1 and 14·5% of hexane were capable of propagating " normal " flames, and those between 14·5 and 32% " cool " flames.

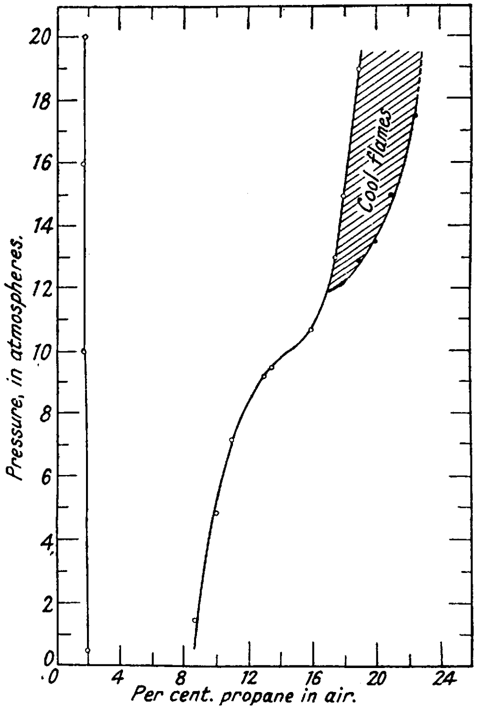
These results therefore confirmed the prediction that separate inflammability ranges, one for " normal " and the other for " cool " flames, should be located, provided high enough experimental pressures are employed. Moreover, the earlier observation of a discontinuity in the upper pressure limits with hexane–air mixtures is now seen to be accounted for by the incidence of the " cool " flame range on the attainment of an adequately high pressure; and in explanation of the difficulty encountered in determining suitable criteria for the upper limits, it should be added that, whereas the flames with mixtures containing up to 6·5% of hexane showed a whitish or yellowish emission, those of mixtures containing 6·5—11% were orange or reddish in colour and were accompanied by a heavy deposition of carbon with the weaker, and tarry material with the rich, mixtures. The cool flames, however, were always blue, and the explosion products had a characteristic aldehydic odour, no carbon being deposited.

FIG. 4.



Influence of Pressure on the Inflammable Ranges of Butane–Air Mixtures at 100°.

FIG. 5.



Influence of Pressure on the Inflammable Ranges of Propane–Air Mixtures at 100°.

In general, the characteristics of the inflammable ranges are much the same as those observed with ether–air mixtures.

B. *Hexane–Oxygen Mixtures.*—In order ultimately to arrive at an interpretation of the probable processes occurring in cool flames, it is necessary to study the behaviour of undiluted combustible–oxygen mixtures. In preliminary experiments some difficulties were encountered in effecting this with ether–oxygen mixtures in glass tubes; these have now been overcome, and our new results will be published separately. Hexane–oxygen mixtures were successfully investigated in the heavy explosion vessel at 100° and 150°, and the results are shown in Fig. 3, the curves indicating the observed variation of the inflammable ranges with increase in initial pressure for mixtures of hexane contents between 1 and 90%. The results correspond closely with those obtained with the air mixtures; for instance with the normal flames the lower limit varied little with increase of initial pressure, and the higher limit was progressively raised until a pressure (1·15 atm. at 100° and 0·90 atm. at 150°) was reached at which a cool-flame range became superposed upon the normal-flame range; thereafter an abrupt widening of the limits occurred.

An interesting observation was that, as with the ether–air mixtures, with both the hexane–air and the hexane–oxygen mixtures the cool-flame ranges apparently centred upon the mixture having a combustible : oxygen ratio 1 : 1. The values of the minimum pressures at 150° for cool-flame propagation with mixtures having this ratio, *viz.*, 4·1 and 0·9 atm., respectively, did not suggest that the nitrogen diluent was in any way preventing chain breaking on the walls of the vessel. We had no evidence, however, as to the respective characters of the flame envelopes in the two series of experiments.

C. *Butane–Air Mixtures.*—The inflammable ranges plotted in Fig. 4 show that, as predicted, butane–air mixtures give rise to a cool-flame range, and that this is located at higher pressures than in the case of hexane–air mixtures. The experiments were extended to pressures up to 20 atm. at 100°. There is now no range of non-ignitable mixtures between the " normal " and " cool " flame ranges; this is no doubt attributable to the fact that the normal-flame range extends across the minimum pressure portion (1 : 1 mixture) of the cool-flame range (cf. also Fig. 3).

D. *Propane–Air Mixtures.*—As far as we are aware, propane is the simplest paraffin hydrocarbon known to give rise to cool flames. It was a matter of interest, therefore, to know what pressure would have to be employed to locate the inflammable range of these flames with this hydrocarbon.

The inflammable ranges at 100° over a pressure range up to 20 atm. are shown in Fig. 5. The cool-flame range was found at 12 atm. pressure and it extended over a comparatively narrow range of mixtures; with the simpler paraffin hydrocarbons requiring a smaller proportion of air for their complete combustion, it is obvious that the normal-flame range will overlap the cool-flame range to a greater extent. There is also again evidence that the cool-flame range centres upon the mixture having the 1 : 1 combustible–oxygen ratio.

The limits determined in the 1930—1932 experiments at 100° were as follows, the agreement being very good :

Press., atm.	6·4	19·3
Lower limit, %	2·0	1·9
Upper limit, %	11·4	23·4

The discovery of the ability of all higher hydrocarbons to propagate cool flames through mixtures in certain composition ranges when artificially ignited in the cold has opened up an important new field of investigation into the mechanism of the processes concerned.

We are greatly indebted to the National Government of the Republic of China for a Scholarship which enabled one of us (M. S. H.) to devote his whole time to the work. We also gladly acknowledge such guidance as could be taken from the unpublished results of Potash and Stevens.

The work recorded herein was carried out at the Imperial College, London.

UNIVERSITY OF LEEDS.

[*Received, December 29th,* 1938.]