

28. *An Examination of the Mechanism by which "Cool" Flames give Rise to "Normal" Flames. Part IV. The Chemical Character of the "Blue" Flame Initiated in the "Cool" Flame Products of Ether-Oxygen Mixtures.*

By M. MACCORMAC and D. T. A. TOWNEND.

As an outcome of the work described in previous papers, it has been possible to develop a new method involving a cooled reaction tube incorporated in a flow system for studying the chemical characteristics of the two-stage inflammation of higher hydrocarbons and their derivatives. The main advantage of the method is that, not only is the whole of the reaction zone visible, but subsidiary surface reactions and slow combustion are reduced to a minimum.

The method has conveniently been applied in the first place to an examination of the differences between the "cool" and the "blue" flames of ether; and it is shown that although the "cool" flame produces aldehydes and peroxides, these are decomposed again in the "blue" flame, together with much of the rest of the ether. The "blue" flame is therefore recognised as essentially a zone of luminous decomposition in which heat is evolved, oxidation playing a secondary rôle. In the presence of sufficient oxygen, however, the reactions which start as a spontaneous decomposition of certain of the "cool" flame products lead to normal ignition.

IN investigations into the chemical mechanism of the reactions leading to spontaneous ignition generally, and particularly to the two-stage ignition induced by the prior formation of "cool" flames, one of the chief difficulties is that of securing accurate samples of the reacting medium at any particular stage after the reaction has become autogenous. Usually for such investigations either flow or static systems are employed in which the reaction zone is enclosed in an electrically heated furnace. A disadvantage of electrically heated flow systems, however, is that unless the rate of flow and the length of the heated zone are accurately adjusted, an unknown amount of secondary reaction is likely to occur after the main reaction which is the subject of enquiry has been completed. Moreover, in the desire to avoid pockets of stagnant gas and to maintain a high rate of flow, there is a tendency to employ tubes which are too narrow; this may have the effect of enhancing surface action and inhibiting chain propagation so that results are difficult to interpret. The use of static systems, on the other hand, is necessarily restricted to the study of such media and experimental conditions as allow pre-ignition time-lags adequate to permit the securing of samples prior to ignition. There are two methods available for taking these samples; in one, the silica reaction vessel is plunged into a freezing mixture in order to arrest reaction, and in the other, the sample is taken by adiabatic expansion of a portion of the reacting medium into the cold vessel.

The discovery (Parts I and II; J., 1939, 337, 341) that all materials which give rise to cool flames in a heated reaction vessel will do so even in the cold, provided sufficiently high pressures are employed, suggested an alternative method for investigating the processes leading to the two-stage ignition by using a cold reaction tube. The advantage of such a method over those previously employed is that no heat is supplied to the medium other than that developed spontaneously. The reaction products on this account begin to cool as soon as the main reaction is completed, thus minimising secondary reactions; moreover, as the walls of the reaction vessel are actually cooler than the combustion zone, surface reactions are almost inhibited. Further, close observation can be made of the character of the flames, and if desired, samples of the products may be removed from any desired point of the flame zone.

As it was most convenient to apply this new method of investigation first to a combustible material which would give both "cool" flames and the two-stage inflammation resulting therefrom at or below atmospheric pressure, the fuel considered initially was ethyl ether. The experiments described in Part III (preceding paper) furnished data requisite for the design of suitable apparatus, and an exploratory investigation has been made in the first place of the chemical process giving rise to the "blue" flame in the "cool" flame products.

The "cool" flame of ether was first observed by Davy in 1816, and its oxidation product, "ether-acid" (Aether Lampen-säure) was subsequently investigated by Faraday, Dana, Doebereiner, Marchand, Böttger, Liebig, Martens, Stas, and Schönbein, the last stating that it contained an ozonide. In 1880 Legler attempted to isolate the oxygen-rich compound suspected by Schönbein and obtained a compound having the formula $C_2H_6O_4$. This is now known to be bishydroxymethyl peroxide, $(CH_2OH)_2O_2$, which can be synthesised by the interaction of hydrogen peroxide with two molecules of formaldehyde.

Legler's method of preparing his "ether-acid" bore some resemblance to that employed in the present investigation, in that an artificially heated reaction vessel was not used, but the "cool" flame was stabilised by allowing the reacting medium to stream over a piece of heated platinum, the products from this flame being collected and qualitatively analysed.

Emeléus (J., 1929, 1733) and others have quantitatively examined the products other than peroxides of the cool flame of ether, using heated reaction tubes incorporated in flow systems; and in 1921 Payman* determined the thermal conditions under which the "cool" flame turns into a normal flame; the experimental conditions, however, did not allow the mechanism by which the transition phenomenon occurs to be observed.

Since the purpose of the present investigation was to determine the differences between the "cool" flame and the "blue" flame to which it gives rise, a preliminary series of experiments was undertaken to examine the nature of the permanent gases produced by the flames. In later experiments a cone apparatus for maintaining stationary flames was set up, and this enabled an adequate sample of the liquid products from 1-2 cu. ft. of the explosive mixture to be collected for analysis.

Unfortunately, the complete analysis of the combustion products of ether is very difficult; our preliminary experiments showed, however, that acetaldehyde and the products to which it gives rise played an important rôle in its combustion. On this account we have investigated the combustion of acetaldehyde under like experimental conditions, and we now record the new experimental method as well as the general conclusions of our exploratory work, leaving to a later communication the description of the similar and as yet incomplete work with acetaldehyde. Moreover, we are of the opinion that an interpretation of the "cool" flame processes is likely to be found more easily with acetaldehyde than with ether or other more complex materials.

RESULTS.

An Examination of the Gaseous Products of the "Cool" and the "Blue" Flames.—From Fig. 4 of Part III it was clear that a 50 : 50 ether-oxygen mixture would be satisfactory for preliminary examination, as it produced at adequate pressures a properly coalesced blue flame without a yellowish tail, which otherwise might indicate some thermal decomposition supplementary to the main reaction. An apparatus was therefore set up in which the flames were propagated at almost constant pressure along a glass tube 2.5 cm. in diameter connected through a mercury trap to an expansion chamber; while allowing the products of the "blue" flame to be released immediately in order to prevent pressure increase in the system, the trap prevented the return of unburnt gases to the tube on cooling.

The gas samples were taken from the end of the tube furthest from the igniting wire, condensable gases being removed by cooling in solid carbon dioxide. After standing for at least 24 hours over solid zinc chloride to remove aldehyde, the samples were analysed in a Bone and Newitt apparatus. The results of the analyses are shown in Table I. Their most noticeable feature is that, on the initiation of the "blue" flame, only the relative amounts of hydrogen and of methane underwent any appreciable change, although the absolute amount of all gases produced was considerably increased. The relative amount of carbon dioxide produced actually decreased, thus giving strong support to the view that the "blue" flame is definitely not a "normal" type of flame. It may also be noted that the quantity of acetylene, and to a minor extent that of other unsaturated hydrocarbons (mainly ethylene), underwent unaccountable variations; the sum of these gases, however, varied in a uniform manner. It may well be that the acetylene, ethylene, and

* Private communication.

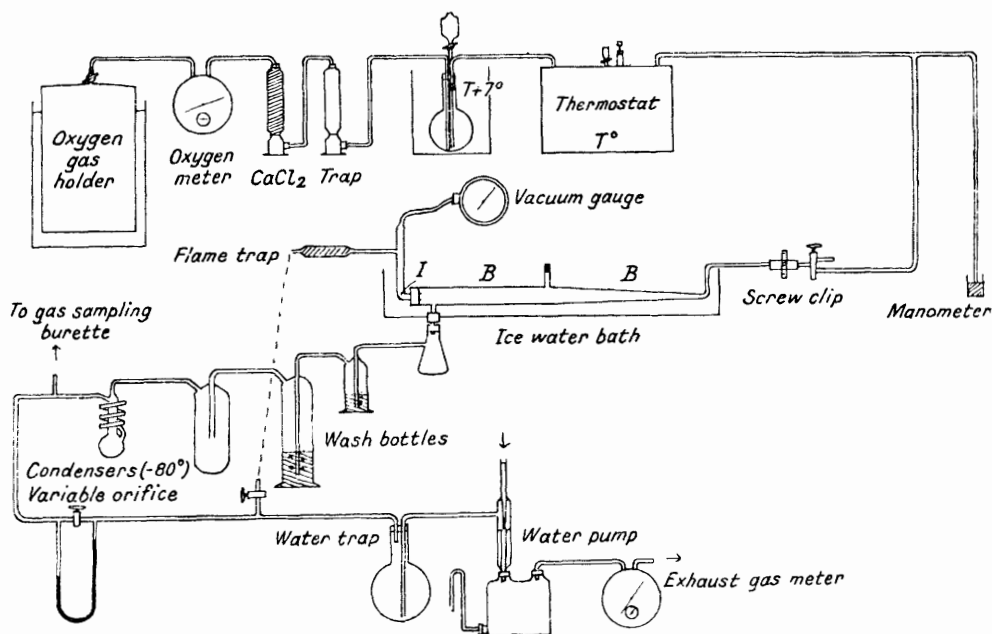
TABLE I.

Permanent gaseous products (% by vol.) of flames travelling under conditions of constant pressure in the 50 : 50 ether-oxygen mixture in a 2.5-cm. tube at 20°.

Type of flame.	Pressure, mm.											
	120.	145.	205.	265.	290.	299.	305.	330.	335.	410.	530.	650.
	Cool flames.						Blue flame initiation behind the cool flames.			Coalesced blue flames.		
CO ₂	5.56	4.51	5.19	5.8	5.10	5.17	4.10	6.35	3.70	2.57	2.84	4.29
C ₂ H ₂	0.61	5.76	1.67	3.48	1.75	2.58	1.5	1.75	1.14	*	2.25	1.67
O ₂	64.5	56.4	32.9	24.2	17.3	24.2	7.17	3.8	3.27	1.0	—	—
C ₂ H ₄	1.9	2.66	6.03	11.3	14.08	12.81	14.55	14.03	15.5	(15.82)	13.7	13.5
CO	23.4	25.5	42.4	40.7	45.6	39.3	43.85	41.1	42.3	43.8	41.9	42.5
CH ₄	2.93	6.1	10.9	13.7	17.0	16.2	22.10	20.7	22.2	23.2	21.65	24.7
H ₂	2.34	1.02	2.65	1.82	1.65	0.49	7.73	12.8	13.45	14.15	18.2	14.2
C ₂ H ₄ +C ₂ H ₂	2.51	8.42	7.7	14.78	15.83	15.39	15.05	15.83	16.64	15.82	15.95	15.17

* Not determined.

hydrogen are produced by the breakdown of the same material, which may give rise either to ethylene or to acetylene and hydrogen.



Apparatus employed for examining the products from "cool" and two-stage flames.

Throughout the cool-flame pressure range the amount of oxygen consumed increased with pressure, at first very rapidly, and thereafter more slowly. The initial rapid increase probably corresponded with the increase in flame speed as the pressure was raised above the lower limit; this in turn, no doubt, depended on the fact that at the lowest pressures the flames did not fill the tube. In general, the flame speed is related to the amount of oxygen burnt in the flame front.

It was at first thought to be significant that the oxygen content in the products decreases to zero with the formation of the coalesced "blue" flame; it will be shown in a subsequent paper, dealing with acetaldehyde, however, that such a flame may not necessarily use up all the available oxygen.

Experiments with Stationary Flames.—To obtain satisfactory amounts of liquid products for analysis, the apparatus illustrated in the figure was used. The burner, B, consisted of a Pyrex-glass tube 24 in. long; this was $\frac{1}{8}$ " in diameter for half its length, then tapered

as a uniform cone to $\frac{1}{8}$ ". Side arms were fitted on opposite sides of the tube at each end of the portion of uniform bore. Preliminary experiments had shown that the igniting wire must not be allowed in the main gas stream (cf. Legler's experiments), as intense surface combustion was liable to take place on it; for this reason it was placed in a $\frac{1}{2}$ " Pyrex tube connected to the end of the burner at *I*; this proved quite satisfactory, as this tube was used only as a by-pass when no products were being collected; normally, therefore, the wire was out of the gas stream. The burner was immersed in iced water.

An early difficulty to be overcome was that of determining the volume of gaseous products leaving the apparatus. It had originally been intended to use a balance of nitrogen entering and leaving the system for this purpose; it was found, however, that if even 5% of nitrogen were present in the oxygen supplied to the ether saturator, the flame in the cone became unstable. In the circumstances, the water pumps which were employed for the evacuation of the gaseous products discharged into gas separators and the gas then passed through a meter. This method of estimating the volume of gaseous products was checked by suitable control experiments using the closed-tube method, the condensable products being frozen out in solid carbon dioxide and the pressure measured.

The procedure when carrying out a run with the stationary flame was to collect the liquid products while about $\frac{1}{2}$ cu. ft. of oxygen was put through; at the same time a sample was taken of the gaseous products. During a run, every effort was made to adjust the rate of flow so as to keep the flame as far from the apex of the cone as possible. In the case of the "blue" flames, however, this could not be achieved, as the pumps used were unable to evacuate fast enough, with the result that the "blue" flame always ran into the narrower part of the burner, where it took on the structure of an uncoalesced flame. It seems probable that the products of a coalesced flame would contain only traces of unburnt ether, aldehydes, and peroxides, instead of the considerable quantities shown in Table III. At the end of the run, the washing and condensing vessels were emptied into a graduated flask, and the solution made up to 1000 c.c. The methods of analysis are given later.

The samples of the gaseous products obtained from the cone usually had much the same composition as those taken in the moving-flame experiments, showing that the main reactions were the same in the two cases in spite of the fact that the cone apparatus was naturally at a higher temperature than the explosion tube. The amount of hydrogen from the "cool" flames, however, was usually somewhat higher than in the tube experiments (varying from 2 to 6%) while the carbon dioxide was also higher (5.5—8%); the latter might be expected from analogy with experiments in heated reaction tubes, since it is generally considered that the carbon dioxide is produced by thermal decomposition of an intermediate product. The analyses of typical samples of the gaseous products from the cone apparatus are given in Table II. Attention may be directed to the unusual

TABLE II.

Gaseous products of stationary cool flames (% by vol.).

	Press., mm.				
	185.	210.	225.	245.	295.
CO ₂	6.6	6.35	8.1	6.1	5.7
C ₂ H ₂	3.9	11.3	3.45	3.1	3.6
O ₂	32.1	32.4	23.0	27.4	20.0
C ₂ H ₄	7.05	0.94	10.2	11.0	13.4
CO	38.8	37.4	39.0	38.4	38.8
CH ₄	9.5	8.65	11.2	8.5	13.1
H ₂	2.1	3.1	7.0	5.5	5.65
C ₂ H ₄ +C ₂ H ₂	11.0	12.3	13.65	14.1	17.0

nature of the sample obtained from the flame at 210 mm. pressure; it was never possible at any other pressure to obtain samples containing such a high concentration of acetylene and low concentration of ethylene.

Table III gives the principal products obtained from the stationary flames when burning at three representative pressures. It will be seen that the amount of acids produced was always quite small; and the quantity of permanent gases was greatly increased

with the appearance of the "blue" flame. The peroxides all reacted with ice-cold potassium permanganate rapidly, so that they were presumably for the most part derivatives of hydrogen peroxide, especially the bishydroxymethyl peroxide prepared by Legler, and the corresponding bishydroxyethyl peroxide derived from acetaldehyde. No attempt was made to estimate the alcohol present; there is also some doubt as to the exact composition of the mixed aldehydes. The chief difference between the "cool" and the "blue" flames was that, whereas the former produced large amounts of aldehyde and peroxides, these compounds seemed to be largely destroyed again in the "blue" flame, so that the "blue" flame is presumably for the most part a series of exothermic decompositions, possibly brought about by the interaction of peroxides with one another or with aldehyde; oxidation reactions probably play only a secondary part. A more precise statement than this cannot yet be made. It was also obvious that acetaldehyde (which in all cases constituted over 62% of the aldehydes present) was playing a predominant part in both the "cool" and the "blue" flames; further examination of the ether has therefore been deferred until the case of acetaldehyde itself has been examined in detail under similar experimental conditions.

TABLE III.

Products (g.-mols.) obtained from 1 g.-mol. each of ether and oxygen.

Type of flame. Pressure, mm.	(Note: The "blue" flame appeared at 300 mm. pressure.)			Type of flame. Pressure, mm.	Cool "Cool" and flames. "blue" flame.		
	Cool flames. 200.	"Cool" and "blue" flame. 290.	"blue" flame. 650.		Cool flames. 200.	"Cool" and "blue" flame. 290.	"blue" flame. 650.
Total peroxides	0.076	0.077	0.019	Unsatd. hydro- carbons	0.10	0.14	0.46
Total aldehydes	0.5	0.548	0.131	O ₂	0.28	0.216	0.0
CH ₃ CHO	0.31	0.335	0.09	CO ₂	0.044	0.05	0.123
H·CHO	0.185	0.21	0.04	Acids (mostly acetic)	0.038	0.0145	0.008
CO	0.32	0.387	1.31	* Unchanged Et ₂ O	0.62	0.73	0.16
CH ₄	0.08	0.153	0.75	* H ₂ O	0.62	0.73	1.1
H ₂	0.016	0.20	0.432				

* Calculated on the assumption that all unaccounted for carbon is ether, and the rest of the hydrogen and oxygen is water. No allowance has thus been made for any alcohols which may be present.

The Flame Temperatures of the "Cool" and the "Blue" Flames.—An attempt has been made to measure the flame temperatures of both types of flame by means of a thermocouple inserted into a piece of Pyrex quill tubing and running the length of the conical burner. The thermocouple was enamelled for electrical insulation, and could be pushed backwards and forwards in the quill tubing so as to locate the hottest zone of the flames. The measurements showed the temperatures of the cool flames to be a maximum on the flame front, falling off uniformly towards the tail of the flame; as anticipated, the transition flame had two maxima, one at the front of the "cool" and the other at the front of the "blue" zone.

The absolute measurement of temperature cannot be regarded as entirely satisfactory, because of unknown catalytic effects induced by the thermocouple sheath; moreover, the enamel insulation on the thermocouple did not withstand the flame temperature very well. Bearing the foregoing remarks in mind, however, the following values may be taken as representing the observed temperature ranges quite closely.

The "cool" flame, 320—395° }
The "blue" flame, 460—510° } depending on the pressure.

These values would probably be higher when the "blue" flame had actually coalesced with the "cool" flame.

DISCUSSION.

It appears that the "blue" flame cannot be initiated thermally, for it always appears in the tail of the "cool" flame where the products of combustion are already beginning to cool; it is more likely, therefore, to result from the spontaneous decomposition of certain materials which have reached a critical concentration. This view is contrary to that expressed in certain quarters that the two-stage ignition is a thermal phenomenon.

Early in the present investigation it appeared likely that the "blue" flame might be initiated by the exothermic breakdown of peroxides produced in the "cool" flame; at present, however, we have insufficient evidence to support this view. Neumann and Toutakin (*Compt. rend.*, 1937, 205, 278) found that diethyl peroxide breaks down explosively when its partial pressure at any given temperature reaches a critical value (*e.g.*, about 1.5 mm. at 320°); they also found that there is a partial pressure of 1.5 mm. of peroxide at the end of the induction period (115 secs.) in a pentane-oxygen mixture at 320°. Moreover, if this amount of diethyl peroxide is added to a fresh mixture, the induction period disappears. This suggests that the spontaneous decomposition of the peroxide initiates the "cool" flame with pentane. Harris and Egerton (*Proc. Roy. Soc.*, 1938, A, 168, 1) agreed qualitatively with Neumann and Toutakin's finding concerning the spontaneous decomposition of diethyl peroxide; they were unable, however, to initiate the "cool" flame in butane-oxygen mixtures by this means. No previous investigation has extended to the second stage in the ignition process.

Analysis of Products.—All gas analyses were carried out in a Bone and Newitt apparatus, the usual methods being used. The contents from both condensers and wash-bottles were combined and made up to 1000 c.c., the analyses being carried out on the solution obtained.

The condensable and the soluble liquid products were estimated as follows.

Acids. The amount of acid produced was so small that no attempt was made to differentiate between acetic and formic acid except in so far as the titration with sodium hydroxide gave different results depending on whether phenolphthalein or methyl-orange was used. The difference between these titrations indicated that the amount of acetic acid was about seven times that of the formic acid.

Total aldehydes. The solution for analysis was neutralised to phenolphthalein by sodium hydroxide. A known excess of the alkali was then added, together with an excess of hydrogen peroxide (10-vol.), and the mixtures steamed in a pressure bottle for 10 minutes. When cold, the excess alkali was estimated by back titration with 0.1N-sulphuric acid. The results were checked by determining the amount of hydrochloric acid set free when a known volume of the solution for analysis was made to react with hydroxylamine hydrochloride. The formaldehyde was estimated by boiling the acid solution (after oxidation with hydrogen peroxide and removal of alcohol) with excess of mercuric chloride: the results obtained, however, were not very satisfactory.

Total peroxides. Three independent methods were used for this determination: (a) Titration with ice-cold potassium permanganate solution in presence of sulphuric acid; (b) colorimetric titration with titanous chloride; (c) liberation of iodine from potassium iodate in presence of ammonium molybdate in acid solution. All these methods gave the same result within 2½%. No attempt was made to estimate alcohol.

We thank the Gas Light and Coke Company for their Fellowship during the tenure of which by one of us (M. M.) the work recorded herein was carried out at the Imperial College, London.