75. *The Inflammation of Mixtures of Air with Diethyl Ether and with Various Hydrocarbons at Reduced Pressures: Green Flames.*

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In a recent investigation into the inflammable ranges of diethyl ether–air mixtures, Townend and Chamberlain (*Proc. Roy. Soc.*, 1937, *A*, **158**, 415) observed a remarkable variation with pressure of the character of the visible emission from the normal flames; in particular, with certain mixtures at reduced pressures intense "green" flames were found.

In this paper it is shown that these green flames are observable to a greater or less extent with all the simpler paraffin hydrocarbons, and that they are attributable to the C_2 (Swan) bands which dominate the visible emission at the reduced pressures and in the composition ranges indicated.

In following up White's investigation (J., 1927, 498) into the dual inflammable ranges of ether–air mixtures, Townend and Chamberlain (*loc. cit.*) formed the opinion that, although the normal flames were probably propagated thermally in general accordance with the classical Le Chatelier view, yet the cool flames seemed to require an interpretation based more on a chain mechanism; for their velocities and composition limits of inflammability appeared to depend, not upon the available heat in the mixtures, but upon an initial slow reaction between ether and oxygen, the most reactive mixtures being in the molecular proportion between 1 : 1 and 2 : 1 (*i.e.*, 18% and 29% of ether in air). Further, these velocities were abnormally low, and although within the error of experiment they were approximately constant and independent of mixture composition, initial temperature, and pressure, yet they were markedly affected by tube diameter; such factors as convection and the area of the flame envelope being neglected for the present, the limiting pressures (p) for cool flame propagation were found to be related to tube diameter (d) in accordance with Semenoff's relation pd^n = const., n being approximately equal to unity.

Before proceeding with a more thorough investigation of the cool flames and of the mechanism by which they give rise to normal flames when the pressure is sufficiently high, it was necessary to determine more precisely than had been previously possible both the location of the composition limits of inflammability for normal flames and also the character of the green flames.

For the purpose of the observations recorded herein the inflammable ranges were determined in a glass tube 4·5 cm. in diameter and 120 cm. long, closed at both ends and mounted horizontally. The tube was housed in a large darkened chamber with apertures on the top and on one side for visual observation of the flames. Experiments at various initial temperatures were carried out by heating the tube electrically with asbestos-covered nichrome wire, and propagation throughout the length of the tube was adopted as the criterion of limiting inflammability; and although this may be criticised on the grounds that in such circumstances the flame may be extinguished before reaching the end of the tube owing to compression of some of the medium ahead of it as well as to contraction of the burnt products behind it, any error due to such cause is usually not great (cf. White, J., 1922, **121**, 1244), and our main interest was actually concerned with the character of the flames in this region. This apart, however, when the effect of wide initial pressure variation on the limits of inflammability is being studied, the method is evidently that most convenient, and consistent results may be obtained with it.

A high-tension spark from an induction coil, passed between two platinum-covered electrodes separated by a gap of 1 cm., served to initiate the normal flames with which this paper is mainly concerned, the primary current being supplied from accumulators at a potential of 14 volts. Tests made with larger coils and with variations in (*a*) the resistance of the primary circuit, (*b*) the voltage of the primary current, and (*c*) the capacity of the secondary circuit, upon the minimum pressures for ignition of characteristic mixtures showed the spark so employed to exceed the minimum intensity requisite to record the true limits of inflammability. As a further check on the method of sparking, separate tests were carried out with a Fraser break arc in a circuit supplied from the mains at 110 volts; no appreciable difference was ever observed in the limiting compositions; if anything, the coil sparks gave slightly wider values.

In the new experiments the explosive mixtures were made up and stored in bulk, and not separately prepared *in situ* for each experiment as in the previous work; the ether was a specially prepared dry sample uncontaminated with aldehydes or peroxides and stored in an atmosphere of nitrogen.

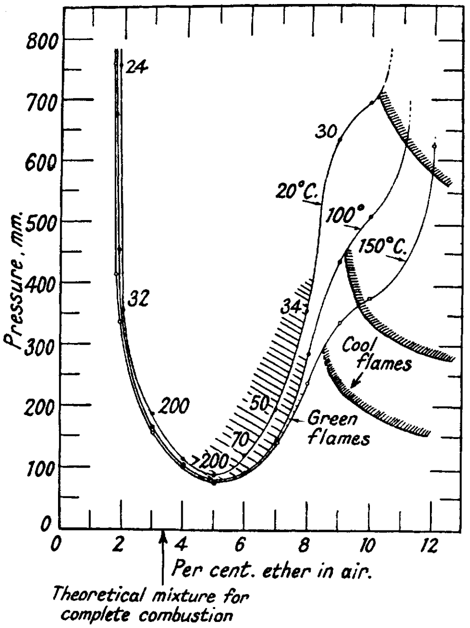
Results.

The Inflammable Ranges of Ether–Air Mixtures.—A careful redetermination of the inflammable ranges of ether–air mixtures for horizontal propagation of flame was made at temperatures of 20°, 100°, and 150°. The new experiments (Fig. 1) showed that, although the influence of temperature on the actual inflammability limits was quite small, particularly at the lower limits and at the upper limits between 100° and 150°, yet it was such as would be predicted from the thermal theory of flame propagation, the higher the initial temperature the wider the limits. The widening of the upper limit, however, was marked at pressures above that at which the "normal" and "cool" flame ranges become superposed and the curves in this range showed close agreement with those of Townend and Chamberlain.

The values at the lower limits at atmospheric pressure (*i.e.*, 1·85% at 20°, 1·78% at 100°, and 1·70% at 150°) also agreed well with those of previous workers. For instance, White (J., 1927, 498) gave a value of 1·88% for horizontal propagation in a 5-cm. closed tube at 20°; Coward and Jones (*Bureau of Mines*, Bulletin No. 279, 1931, p. 74) gave 1·85% for upward propagation in a 5-cm. tube open at the firing end; and Tanaka and Nagai (*Proc. Imp. Acad. Tokyo*, 1928, **4**, 154) gave 1·89% for downward propagation in 5-cm. closed tube. The curves are also in general agreement with the results of Berl and Hartmann (*Z. physikal. Chem.*, 1930, *A*, **146**, 281) and of Berl and Barth (*ibid.*, 1931, Bodenstein Festband, 211) except that ignition was found to occur at lower pressures than in their experiments.

A matter of interest is that the mixture giving rise to ignition at the lowest critical pressure (*i.e.*, 90 mm. at 20°, 80 mm. at 100°, and 78 mm. at 150°) contains about 5% of ether compared with the 3·35% ether content of the theoretical mixture; this is no doubt attributable in part to suppression of dissociation, which would be appreciable at low pressures, and in part also, in conformity with spontaneous-ignition experiments, to the probable greater reactivity of the medium ahead of the flame front in the case of the richer mixtures. Another observation of interest is that, whereas at atmospheric pressure the flame speeds at the limits (20°) approximate to 30 cm./sec. (see figures against the curve), yet as the pressure is lowered the corresponding speeds increase until at the minimum pressures they exceed 200 cm./sec.; when it is remembered that the relative heat losses increase as the pressure is reduced, it would be expected on thermal grounds that the flame velocity at the limiting composition would be increased, complete flame propagation along the tube being now only possible by a reduction of the time of contact with the walls of the tube.

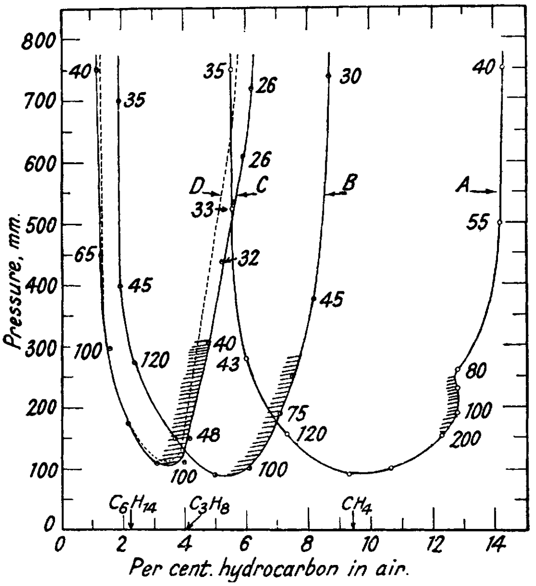
FIG. 1.



The Inflammable Ranges for Normal Flames of Ether–Air Mixtures at Reduced Pressures.

Figures along curves (20°) *denote speeds* (*cm./sec.*) *of flames through the mixtures of limit composition.*

FIG. 2.



The Inflammable Ranges for Normal Flames of Hexane– (*C, D*)*, Propane*(*B*)*– and Methane*(*A*)*–Air Mixtures at Reduced Pressures.*

(*Mixtures of " theoretical " composition are denoted by the arrows.*)

Figures along curves denote speeds (*cm./sec.*) *of flames through the mixtures of limit composition.*

" Green " Flames.—In the new experiments it was found that the green flames were readily reproducible; they were most intense at the lowest pressures where the higher and the lower limits coincide; the approximate limits for mixtures giving rise to these flames are shown by the diagonal shading (Fig. 1); at 20° they were observable up to about 400 mm., but at 100° the upper limit was about 300 mm. and at 150° 240 mm. The flames are very striking, as noted by White (*loc. cit.*). Berl and Hartmann, who employed a small glass sphere as an explosion vessel in a thermostat, seem also to have been aware of an unusual appearance of the flames for they said :" Längs der obern Grenze und in Nachbarschaft des kritischen Zündungsdruckes befindet man sich in einem Gebiet, in dem die Gemische nur noch unvollkommen verbrennen. Man beobachtet ein langsames Abbrenen und Auftreten von Aureolen."

A matter of importance was whether the flames were in any way peculiar to ether–air mixtures or whether they are common to combustibles generally, for there is little record in the literature of observations of flame propagation at reduced pressures other than with methane–air mixtures (Burrell and Robertson, *U.S. Bureau of Mines*, Tech. Paper, No. 121, 1916; Mason and Wheeler, J., 1918, **113**, 45). On this account it was decided to examine under the same conditions the flames of mixtures with air of other representative hydrocarbons, and if possible to examine the emission spectra of the green flames.

n-*Hexane–Air Mixtures.*—Curves *C* and *D* (Fig. 2) show the influence of pressure on the inflammability ranges of *n*-hexane–air mixtures at initial temperatures of 100° and 20°, respectively. The lower limit was scarcely influenced by raising the temperature from 20° to 100°, but the upper limit was definitely widened, as had been observed with the ether–air mixtures. Moreover, the flames for the mixtures and over the pressure range covered by the shaded area, curve *C*, were of the same bright green appearance as had been found with the ether–air mixtures. The mixture ignitable at the minimum ignition pressure contained about 3·5% of hexane compared with the 2·16% hexane content of the theoretical mixture, and the flame speeds at the limits also varied in much the same way as those for the ether–air mixtures.

Propane–Air Mixtures.—As the typical green flames were found with both ether- and hexane–air mixtures, it was of interest to find whether they were in some way common to those combustibles exhibiting a low-temperature cool-flame system or to combustibles generally. Accordingly, the behaviour of propane–air mixtures was examined as representing the simplest paraffin member of the former group, and also methane–air mixtures which, as far as is now known, do not give rise to cool flames. Curve *B* (Fig. 2) shows that the behaviour of propane is in keeping with that of ether and hexane and no further comment is therefore necessary. Recently, Hoeven (*Ind. Eng. Chem.*, 1937, **29**, 445) has published a similar determination of the inflammable ranges of propane–air mixtures at reduced pressures with results showing close agreement with those illustrated by curve *B*.

Methane–Air Mixtures.—Curve *A* (Fig. 2) shows the results obtained with methane–air mixtures at 20°, an interesting observation being that with the 12·8% mixture there were three pressure limits of inflammability, *viz.*, at 190 mm., 230 mm., and 270 mm. This effect was probably observable with only a very narrow range of mixtures; it was repeated many times with the 12·8% mixture but was not found with either the 12·3% or the 13·6% mixtures. While our work was in progress we found that a similar observation had been made by Lavrov and Bastchastry (*Acta Physicochim. U.S.S.R.*, 1935, **1**, 975), who found the lower-pressure limits to be widened somewhat by increased spark intensity so that under the conditions of the present experiments the phenomenon, though a real one, is not as striking as might be observed with less intense igniting sources.

The mixture range showing the pressure limits approximates to that in which Neumann and Serbinoff (*J. Physical Chem. Russia*, 1933, **4**, 41) observed the phenomenon of low-pressure *spontaneous* ignition limits with methane–oxygen mixtures; Lavrov and Bastchastry regard the fact that such limits can be observed by spark ignition in the cold to be against any view ascribing the second pressure limit in *spontaneous* ignition work to surface deactivating effects at a critical pressure (cf. Haber and Alyea, *J. Physical Chem.*, 1930, *B*, **10**, 193), but in favour of the Hinshelwood–Semenoff view that a chain deactivation in the gas phase occurs which is probably attributable at a critical pressure to the incidence of triple collisions.

As far as our experiments on the inflammable ranges induced by spark ignition at reduced pressures have proceeded, the phenomenon of three pressure limits has not been observed with explosive media other than methane and air; and although in *spontaneous* ignition experiments the phenomenon is well established with such combustibles as hydrogen, carbon monoxide, phosphine, and carbon disulphide, there are no recorded observations of its occurrence with hydrocarbons higher than ethane.

The mixture exhibiting the minimum ignition pressure has a methane content of between about 9 and 10%, which compares with the 9·4% content of the theoretical mixture for complete combustion. In this respect methane–air mixtures differ from those of ether, hexane, and propane, for, as already pointed out in the case of the last-named, the mixtures ignitable at the minimum ignition pressures all contain a large excess of combustible. Reference to flame-speed–composition curves at atmospheric pressure (Payman, J., 1919, **115**, 1446) also shows a similar difference in behaviour in that, although the maximum speed mixtures contain approximately the theoretical combustible content in the case of methane, yet with propane an excess of combustible is required; on thermal considerations it is likely, therefore, that the mixture giving complete propagation of flame at the lowest pressure will be that exhibiting the greatest flame speed and hence having least contact with the walls of the tube. The essential known relevant difference between the respective behaviours of mixtures with air of methane and of higher hydrocarbons or ether is that at the pressures under consideration, whereas with the first the mixtures most easily spontaneously ignitable contained an excess of air, with the last two the reverse is true; it would therefore appear that the rate of slow combustion leading to spontaneous ignition in the gases ahead of the flame is a factor of great importance in regard to flame phenomena generally, in accord with the general principle of the Le Chatelier view.

By comparison with the other combustibles examined, the green flames could be observed only over very narrow ranges of mixtures and pressures; *e.g.*, with the 12·8% mixture they ceased at about 240 mm. pressure, and with the 12·3% mixture they occurred only at the limiting pressure. There could be no doubt as to their identity, however, and it may be concluded, therefore, that the emission is common to all hydrocarbon flames under suitable experimental conditions.

At pressures above the green flame range, the flames usually exhibited a greenish-blue front and a luminous tail. As the air contents of the mixtures were increased towards the theoretical composition, the flames became very luminous, indicative of the emisson from carbon aggregates; and when the mixtures contained an excess of air the flames were, of course, free from incandescent carbon, and deep blue in colour.

Origin of the Green Emission.—It seemed likely, as a result of the experiments as a whole, that the green emission is probably common to the flames of specific mixtures of all hydrocarbons with air when burning under the suitable conditions of pressure and flame temperature described herein. Although it is probably always present to some extent, it is not usually apparent to the eye on account of " masking " by the continuous emission from incandescent free carbon, by the emission from burning carbon monoxide, or by other processes giving rise to excited radicals which emit in the visible region of the spectrum. Reference has often been made to the fact that the inner cone of the Bunsen flame possesses a greenish tinge, and particularly by Smithells and Dent (J., 1894, **65**, 603) in their classical flame-separation experiments with cyanogen, but it is perhaps curious that no previous record appears to have been made of the striking effect of reduction of pressure in producing intense green flames, particularly with higher hydrocarbons.

Previous spectrographic investigations of the emission in the visible and the ultraviolet region of the spectrum from the inner conal flames of burning hydrocarbons have established the presence of (i) OH bands at 2608, 2811, and 3064 A., (ii) CH bands at 3143, 3900, and 4300 A., and (iii) C_2 bands at 4737, 5165, and 5635 A. (cf. Bonhoeffer and Haber, *Z. physikal. Chem.*, 1928, *A*, **137**, 243; Laurer, *Z. Physik*, 1933, **82**, 178). Vaidya (*Proc. Roy. Soc.*, 1934, *A*, **147**, 513) has also identified a band system, extending from 4100 to 2500 A., which he refers to as the " ethylene flame " bands and ascribes them to the emission from " CHO " radicals. In the outer cone the continuous and banded emission characteristic of the carbon monoxide flame is also usually observed.

An attempt was made to examine the green flames of ether spectrographically, but a number of explosions failed to give a good plate, partly owing to the lack of sensitiveness of the photographic emulsion in this region of the spectrum. We were fortunate at this juncture, however, in securing the collaboration of Mr. E. C. W. Smith, Radiation Fellow in the Bone Research Laboratories at the Imperial College, who had been examining the influence of high pressure on the emission from stationary ethylene–oxygen flames of controlled composition and in the course of his work was extending these experiments so as to include observations at reduced pressures. He has definitely established for us that the green flames are attributable to the Swan bands now known to arise from C_2 molecules, which emit at 4381 and 4737 A. in the green region of the spectrum; the results of his own extensive observations on the subject are now being prepared for publication. It is of interest to recall in this connexion the experiments of Bonhoeffer and Harteck (*Z. physikal. Chem.*, 1928, **139**, 64), who showed with hydrocarbons higher than methane that under suitable conditions, collisions with hydrogen atoms may successively strip those of the hydrocarbon so that ultimately a predominance of CH radicals, which emit in the violet, and subsequently of C_2 molecules, which emit in the green, is produced in the tube.

The work as a whole has opened up an interesting field of enquiry directly concerning the influence of pressure on the mechanism of flame propagation. For, although it is generally known that temperature, pressure, and mixture composition directly influence the emission from flames particularly in regard to (*a*) the degree of excitation and (*b*) the absolute concentration of an emitting species by virtue of changes in degree of dissociation into radicals or of secondary processes such as interaction between carbon and steam (cf. Bone and Outridge, *Proc. Roy. Soc.*, 1936, *A*, **157**, 234), yet an interesting new possibility arises when the attainment of a critical change in pressure or mixture composition may effect an abrupt change in the nature of the slow combustion processes ahead of the flame, as, for example, would seem probable in the region where in any particular case the cool-flame range overlaps the normal-flame range.

In general, with regard to the green flames, our experiments and Mr. Smith's spectrographic examination of them indicate that: (1) The emission is due to the excitation of C_2 molecules, and apparently it becomes predominant under the conditions indicated, the most important of which is deficit of oxygen. (2) The emission is favoured by reduced pressure. (3) The C_2 molecules are present in an excited state at temperatures and/or pressures below which there is any evidence of aggregated carbon. (4) The processes by which they arise remain a matter for further investigation, but spontaneous ignition experiments (cf. Townend and Chamberlain, *loc. cit.*, and recent unpublished results) indicate that they may be related to the nature of initial oxidation or reduction processes during slow combustion.

The presence of the " green " emission in the flames of methane, which contains but one atom of carbon in the molecule, is also a matter of great interest (cf. also Bell's recent observations on the methane flame, *Proc. Roy. Soc.*, 1937, *A*, **158**, 429).

We are greatly indebted to Mr. E. C. W. Smith for his valuable collaboration in identifying the green emission with that of the C_2 bands, and 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.

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

UNIVERSITY OF LEEDS. [*Received, December* 29*th*, 1938.]