

Continuous spectra in flames: the role of atomic oxygen in combustion

BY A. G. GAYDON, D.Sc., *Chemical Engineering Department,
Imperial College, London, S.W. 7*

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[Plate 2]

The causes and types of continuous spectra emitted by flames are discussed and their importance stressed. It is shown that the yellow-green continuous spectrum emitted by some flames containing oxides of nitrogen is probably identical with the spectrum of the air after-glow and is therefore due to a reaction between nitric oxide and atomic oxygen.

It thus becomes possible to test for the presence of atomic oxygen in a flame by admitting nitric oxide and observing if a yellow-green emission results. For the carbon monoxide flame there appears to be a high concentration of atomic oxygen, both for the dry and moist flame. The combustion mechanism is discussed in detail using this knowledge. For the hydrogen flame a little atomic oxygen is present, but results do not permit of definite conclusions. For hydrocarbon flames there is no sign of atomic oxygen in the inner cone, and this is taken as strong evidence in favour of a peroxidation rather than a hydroxylation mechanism.

INTRODUCTION

Of the three general classes of spectra observed in flames, line, band and continuous, the last have received least attention. Line spectra are, of course, due to electronic transitions between the quantized energy states of atoms; although of interest for the purpose of chemical analysis and in a few special cases such as the sodium-line reversal method of temperature measurement, line spectra are seldom of much importance in elucidating details of combustion mechanisms. Band spectra in the visible and ultra-violet regions correspond to similar transitions between quantized energy states of molecules; the emission and absorption of band spectra by flames have received a fair amount of attention in relation to combustion problems (for a general review see Gaydon 1942*a*). Continuous spectra (in gases) correspond to transitions in which at least one of the states involved is unquantized. Continua therefore correspond to *processes* such as dissociation, ionization, and association. Thus, while band spectra are of value in telling us what molecules and radicals are present under flame conditions, the examination of continuous spectra might be expected to give information of even greater value about the actual processes taking place during the combustion. Unfortunately, in practice, continuous spectra are difficult to identify with certainty owing to their characteristic lack of definite features. With band spectra, analysis of the structure gives precise information about certain molecular constants and so usually enables us to assign the bands to a

particular molecule. With continuous spectra this is not possible, and in only a few cases, such as the well-known hydrogen continuum corresponding to the process $H_2(^3\Sigma_g^+) \rightarrow$ unstable $H_2(^3\Sigma_u^+) \rightarrow H + H$, can details of the process be stated with certainty.

When alkali metals, or their salts, or, to a less extent, alkaline earth metals are introduced into a flame, strong continuous emission around the blue or violet region is obtained. Hartley (1894) reported observations of this type of continuum which has also been observed by the author when potassium or rubidium are introduced into either a hydrogen or a carbon monoxide flame. The position of the maximum of this continuum depends on the ionization potential of the alkali metal, moving to longer wave-lengths for metals with lower ionization potential. This and other types of continuum have been very fully reviewed and discussed by Finkelburg (1930, 1934, 1935) who has developed Stark's suggestion that the process responsible for this type of emission is the association of an electron and a positive ion to form a neutral molecule. Finkelburg has used the term 'electron radiation' to describe this process and has shown that it is quantitatively of the right magnitude to account for the strength of the continuum.

All flames show strong ionization, and, even when there is no evidence to show that the main constituents (e.g. H_2 or O_2) are ionized, it is possible that small traces of impurity may result in enough ionization to give some continuous emission of the 'electron radiation' type as a background to the main features of the spectrum.

Continua are also emitted when halogens are introduced into flames. Urey & Bates (1929) have examined these and concluded that they result from the reunion of an excited halogen atom and a normal atom to form a normal halogen molecule. Several other inorganic flames, such as those of phosphorus, arsenic and selenium, also give strong continuous emission (for references see Gaydon 1942*a*), although their cause is unknown.

The spectrum of the bright blue carbon monoxide flame appears under small dispersion to be continuous. More detailed examination (Weston 1925; Gaydon 1940) reveals a very complex band structure. This is particularly well developed in the flame at reduced pressure and also in the cool flame (Gaydon 1943). In hot flames at high pressure the structure is less outstanding, and the appearance differs little from that of a pure continuum. There is no doubt that the higher temperature increases the length of the branches of the rotational fine structure of the band system and so contributes to this change of appearance. Whether or not there is a genuine continuous emission as well as the complex band spectrum is uncertain. The maximum temperature for the $CO-O_2$ flame is, at least in theory, relatively high, and appreciable ionization and dissociation, both factors favouring the emission of continua, will result from this high temperature.

The continuous emission from luminous organic flames, which is due to thermal emission from hot carbon particles, falls outside the scope of this investigation.

CONTINUOUS EMISSION BY THE HYDROGEN FLAME

The simple flame of hydrogen burning in air is practically non-luminous. The spectrum shows the OH bands in the ultra-violet and the vibration-rotation spectrum of H_2O in the near infra-red. The flame normally appears faintly orange, this coloration being due to traces of impurities, chiefly Na and CaO. Higher temperature flames of hydrogen do, however, show appreciable luminosity. Finkelburg (1930) gives references to many old papers, some of which are not available to the author, as copies have been removed to safety for the duration of the war. Dibbits in 1864 found that hydrogen burning with air and other gases showed a weak continuum with maximum in the green. Frankland in 1868 observed that the spectrum of hydrogen burning in oxygen at ten atmospheres pressure was extremely bright and entirely continuous in the visible region, while Liveing & Dewar (1891) studied the rate of increase of the brightness of this continuum with pressure up to 40 atm.

The present experiments indicate that high-temperature flames of hydrogen burning with pure oxygen are blue, and that the pale yellowish green coloration only occurs in the presence of nitrogen. The blue luminosity is particularly well marked with a simple flame of oxygen burning in hydrogen at a quartz jet. This flame has a bright blue base, and is sometimes surrounded by a red outer mantle the colour of which is due to emission of the vibration-rotation bands of H_2O (Gaydon 1942*b*) which extend from the infra-red right up to the visible. A group of spectra of the blue part of this flame of oxygen burning in hydrogen is shown in the plate. There is strong emission throughout the blue, violet and near ultra-violet. The OH bands are very strong in this source and the very long branches of the rotational fine structure can be observed well down into the visible region, and there is some difficulty in distinguishing between true continuous emission and apparent continuum resulting from the unresolved fine structure of these OH bands. The blue colour is probably largely due to continuous emission, and this may be of the 'electron radiation' type. The possibility of association processes between free atoms present in these high-temperature flames cannot, however, be ruled out and may well contribute, along with other factors, to the blue colour.

The oxy-hydrogen blow-pipe flame burning in air has a blue core, but the outer part of the flame, especially the tip, shows a pale yellow or yellow-green luminosity. The colour is rather difficult to describe, and in this type of flame is usually confused by admixture with orange coloration due to the presence of Na and CaO as impurities; the true colour is probably best described as an unsaturated yellow-green, although it has on occasion been described as greyish green or brownish green or just as yellowish. It will be referred to as yellow-green throughout this paper. The same colour is produced when a trace of air or nitrogen is admitted to a flame of hydrogen burning in oxygen. Flames of hydrogen burning with nitrous oxide under suitable conditions show the yellow-green colour strongly. It was noticed that the oxy-hydrogen blow-pipe in air always smelt of oxides of nitrogen when the yellow-

green coloration was well developed, and it seemed that there must be some connexion between the emission of this yellow-green continuum and some reaction involving an oxide of nitrogen. The colour is very similar to that of the afterglow of air in an electric discharge at reduced pressure. The author has therefore carried out a number of experiments to compare the yellow-green continuum obtained by deliberately introducing oxides of nitrogen into flames with that emitted by the air afterglow.

EXPERIMENTAL

The spectrograph employed was a large aperture ($f/4$) glass prism instrument. This gave a visible spectrum about 5 cm. long, this moderate dispersion in the visible region combined with high speed making the instrument particularly suitable for the study of the yellow-green continuum emitted by the relatively weak flame sources.

The photographic plate characteristics desired were uniform sensitivity throughout the visible region combined with fairly high contrast and speed. Several makes and varieties of plates were tried, but no really satisfactory type was found. All the panchromatic or 'long-range' types showed low or irregular sensitivity in the green, while orthochromatic types failed, of course, at the red end. Ilford Rapid Process Panchromatic were actually used for all the investigations, although these show a double maximum of sensitivity in the red and not very high sensitivity in the green, as may be seen in the group of spectra of a luminous Bunsen flame in plate 2*g*.

Refined measurements of the continuous spectra emitted by flames appear to be of little value owing to the variations introduced by temperature and other factors. It was found sufficient for the present purpose to take a series of five exposures (by racking down the plate holder) for each source and to compare these visually. Exposures in the ratio $1:\sqrt{3}:3:3\sqrt{3}:9$ were found suitable. A neon lamp comparison spectrum, showing lines of Ne, He and H, was used to give an approximate wave-length scale.

Nitric oxide was prepared by dropping 50 % sulphuric acid on to a concentrated solution of sodium nitrite and potassium iodide, the gas being stored over water and used undried except where otherwise stated (i.e. for CO flames). Other gases were commercial products.

The flames studied were of three types: flames of premixed gases burning at a quartz jet, flames of one gas burning in an atmosphere of another (for brief description of apparatus see Gaydon 1942*b*), and flames of premixed gases burning at a Smithell's separator. This separator consisted of two concentric quartz or pyrex tubes about 1 and 1.5 cm. bore, a cork or similar fitting enabling the smaller tube to be slid gently down until its top was about 5 cm. below that of the outer tube. By adjustment of gas flow and mixture strength it thus became possible to separate the inner cone of hydrocarbon flames on to the top of the smaller tube, leaving the outer cone burning at the top of the larger tube.

The simple discharge tube used for the examination of the air or oxygen afterglow is shown diagrammatically in figure 1. It consisted of two pyrex tubes *A* and *B*, each 30 cm. long and 1 cm. bore, with viewing windows of quartz, W_1 , W_2 and W_3 , and steel electrodes E_1 and E_2 . Air or oxygen was admitted through a very fine capillary at the tap T_1 and was evacuated through tap T_3 . Nitric oxide could be admitted at T_2 when desired. The discharge in the tube *A* was maintained by an induction coil. It was found that stray weak discharges to the pump were reduced by connecting the electrode E_2 and the pump so that they were at the same potential. The afterglow in the tube *B* was viewed end-on through the window W_2 .

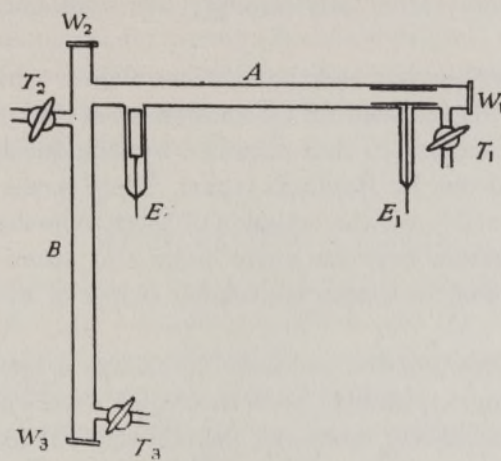


FIGURE 1. Discharge tube for afterglow.

THE YELLOW-GREEN CONTINUUM IN THE AFTERGLOW AND IN FLAMES

The yellow-green air, or so-called oxygen, afterglow, obtained when a discharge is passed through air or through oxygen containing a trace of nitrogen at a pressure of the order of a mm. of mercury, has been studied by a number of investigators (Rayleigh 1910; Stoddart 1934; Newman 1935), and Spealman & Rodebush (1935) have convincingly shown that the luminosity is due to a reaction between nitric oxide and atomic oxygen, this explanation fitting in well with the careful observations made earlier by Rayleigh. The spectrum is mainly continuous, extending throughout the visible region with a maximum somewhere in the green. Faint banded structure has also been observed, but it is very weak and features are difficult to measure.

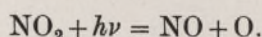
The spectrum of the afterglow of air and that of oxygen containing a little nitrogen have been photographed under similar conditions to the flame spectra. It has also been found that, when a very slow stream of nitric oxide is admitted at tap T_2 (figure 1) and fairly pure oxygen is used in the discharge, a bright glow is obtained at the point where the gases mix. A group of spectra of this glow, due to the reaction of atomic oxygen formed in the discharge with the nitric oxide, is shown in plate 2*f*. The

spectrum is continuous and of maximum intensity in the green; the double maxima in the red are due to plate sensitivity being high in these regions. There is some very faint banded structure, but even with the high contrast of the process plates this is not easy to see.

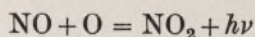
It has been remarked that some flames containing oxides of nitrogen show a yellow-green continuous emission. Plate 2*e* shows a group of spectra of the flame of nitrous oxide burning in hydrogen, which is of this type. It is also found that when nitric oxide is introduced into some, but not all, flames a strong yellow-green continuous emission results. This is true for carbon monoxide burning in oxygen (plate 2*d*) and, although rather less strongly, for hydrogen burning in oxygen (plate 2*c*).

The colour of the air afterglow and that of these flames containing nitric oxide is strikingly similar, and this is borne out by comparison of the spectra. The similarity of the colours of the afterglow to that obtained by introducing NO into a Bunsen flame was first pointed out by Rayleigh (1911). There seems no reason to doubt that the process responsible for the emission of these yellow-green continua is the same, namely, the reaction between nitric oxide and atomic oxygen. The cause of the yellow-green colour of flames containing oxides of nitrogen has thus been ascertained.

The absorption spectrum of the molecule NO₂ shows a banded structure in the visible region, indicating that absorption in this region results in the formation of an electronically excited stable NO₂ molecule. Beyond about 3700 Å the band structure merges into a continuum, indicating the process



There is thus the possibility that a collision between nitric oxide and atomic oxygen will result in the reverse process, the emission of a light quantum and the formation of a normal NO₂ molecule. This process would result, in the absence of appreciable thermal energy in the colliding particles, in a continuous emission with short-wave limit around 3700 Å. Assuming an electron transition probability of the order 10⁷ or 10⁸ per sec. and a duration of the order 10⁻¹² or 10⁻¹³ sec. for a collision, we obtain a probability of about the order 10⁻⁵ for the reaction



to occur as a bimolecular association. This seems to be of the right magnitude. In the afterglow each oxygen atom will make about 10⁷ collisions per sec., and, as only a small proportion of these collisions will be with nitric oxide molecules, this gives a reasonable duration for the afterglow, which in practice is usually of the order of a second, although much less if nitric oxide is admitted.

There is also a possibility of a triple collision between nitric oxide, an oxygen atom and a third body. In this case the third body might take up the rather large amount of energy set free by the formation of NO₂, or alternatively it might take up only a small part of this energy leaving the excess as electronic energy of excitation of the

newly formed NO_2 molecule. In this latter case the NO_2 molecule might then emit a banded spectrum. This would account for the faint banded emission superposed on the yellow-green continuum of the afterglow spectrum.

The majority of ordinary flames in air do not contain appreciable quantities of nitric oxide so that even if atomic oxygen is present the yellow-green continuum will not be emitted. For the very hot oxy-hydrogen flame, however, small quantities of nitric oxide may be formed if air is allowed to mix in with the flame, and so the flame shows the faintly luminous tip which has been commented on. Similarly, nitrous oxide usually breaks up into oxygen and molecular nitrogen rather than to oxides of nitrogen, and so the yellow-green continuum is not necessarily emitted even if atomic oxygen is present; under certain flame conditions, such as nitrous oxide burning in hydrogen, however, it seems that both nitric oxide and atomic oxygen are present, and so the flame shows the continuous emission; all flames of this type smell strongly of oxides of nitrogen.

NITRIC OXIDE IN FLAMES

The assignment of the yellow-green continuum to a reaction between nitric oxide and atomic oxygen gives us a simple qualitative test for the presence of atomic oxygen in a flame by introducing a little nitric oxide and observing whether or not the yellow-green continuous emission is then obtained. In this section the experimental results obtained by subjecting a number of flames to this test are described; application of the results to a discussion of the combustion mechanism is deferred to later sections.

Carbon monoxide. Flames, of all types, of carbon monoxide burning with air or oxygen are bright blue in colour. In all cases the addition of a little nitric oxide produces a marked change to a whitish yellow-green. The effect is particularly strong when the NO is added to a flame of CO burning in O_2 . Groups of spectra illustrating this are shown in plate 2*a* and *d*. It may be noted that the addition of a little nitrous oxide instead of nitric oxide does not produce the same effect.

The original experiments on CO flames were carried out with undried gases. In view of the importance of moisture in the combustion of CO , a flame of $\text{CO} + \text{NO}$ in O_2 in which the gases were carefully dried was also examined. The CO and O_2 were dried by slow passage through a liquid oxygen trap, and the NO was passed first through sulphuric acid and then through three U tubes packed with phosphorus pentoxide. The yellow-green colour was again produced with about the same intensity. These experiments cannot be compared with those on the combustion of intensively dried carbon monoxide, but they serve to show that moderate drying does not materially affect the concentration of atomic oxygen in the flame, which remains high.

Flames of carbon monoxide burning with nitrous oxide are bluish in colour and show a rather similar spectrum to that of flames with oxygen, but the blue shade is somewhat less intense, and this has already been commented on (Gaydon 1942*b*). This departure from the bright blue colour is particularly noticeable for the pre-

mixed CO-N₂O flame, and indicates some slight nitric oxide formation, the reaction of which with atomic oxygen leads to yellow-green emission which dulls the brightness of the blue colour of the flame. The addition of a very little nitric oxide to these flames supported by nitrous oxide produces a very marked intensification of the yellow-green colour.

Hydrogen. When a little nitric oxide is added to a flame of hydrogen burning in oxygen a definite, although not strong, coloration results. The colour is rather greyish green, the departure from the yellow-green shade being apparently the result of admixture with the natural blue shade of the untreated flame. With the flame of oxygen burning in hydrogen, which is quite a bright blue, the effect of adding nitric oxide is less marked. When the NO is admitted in the H₂ stream there does not appear to be any appreciable effect on the colour of the flame, which, however, enlarges slightly. When the NO is admitted in the O₂ stream there does appear to be a slight greenish coloration, but not very marked. In either case, however, there is a definite effect on the outer flame of the excess hydrogen burning in air, which becomes grey-green and shows the continuous emission spectrum. Groups of spectra of hydrogen burning in oxygen and the same with a little nitric oxide added are shown in plate 2*b* and *c*.

Flames of hydrogen burning with nitrous oxide are of rather varied type (Dixon & Higgins 1926). In some cases the spectrum shows NO, NH and the ammonia α bands (Fowler & Badami 1931) and in other cases, such as N₂O burning in H₂ or the premixed flame containing excess of N₂O, the yellow-green continuum is strong and dominates the spectrum.

Methane. Flames of methane in oxygen or air or vice versa are luminous (carbon deposition) and are not suitable for the nitric oxide test. The premixed CH₄-air flame, however, gives striking results. With a simple premixed flame of the Bunsen type it was observed that fairly strong yellowish green coloration was produced by the addition of nitric oxide, and that this colour was apparently restricted to the outer zone of the flame. This was confirmed by study of the separated cones in a Smithell's separator.

The methane-air flame in the Smithell's separator shows a bright blue-green inner cone and a very pale blue-violet outer cone. On admitting nitric oxide the inner cone turns bright violet and the outer cone shows the yellow-green colour strongly. This is a very simple and effective experiment.

The spectrum of the inner cone, before the admission of nitric oxide, shows the usual C₂ Swan and CH bands. When nitric oxide is present the CN Violet system comes up strongly, this accounting for the violet colour, and the C₂ Swan bands are partly suppressed; the CH bands do not appear to be affected (see plate 2*h*). With a steadily burning flame there is not the slightest trace of the yellow-green continuous emission in the inner cone. Only with an unsteady flame, or with excess air, does a slight evanescent yellow-green colour appear above and around the inner of the separated cones, and this is clearly due to incomplete separation of the two types of combustion occurring in the two cones.

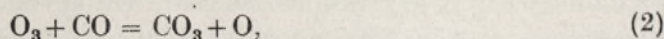
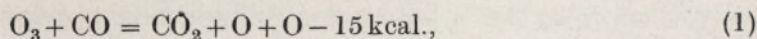
Ethylene. The results with ethylene are similar to those with methane, but the yellow-green coloration of the outer cone is rather less strong unless a fairly large amount of nitric oxide is present. This may be due to the partial decomposition of the nitric oxide in this very hot flame.

Butane. The results for butane are also similar to those for methane. In the Smithell's separator the inner cone changed from blue-green to violet when nitric oxide was added, while the outer cone changed from pale blue-violet to bright yellow-green.

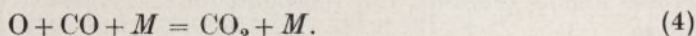
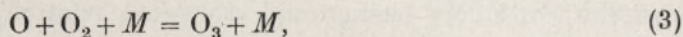
THE COMBUSTION OF CARBON MONOXIDE; THE ROLE OF ATOMIC OXYGEN

The experimental results detailed above serve as a qualitative test for the presence of atomic oxygen in the various flames studied. For the carbon monoxide flame it is clear that a considerable concentration of atomic oxygen exists, both for the dry and moist gases. Previously the author (Gaydon 1942*a*) has been sceptical of combustion mechanisms involving atomic oxygen, but it now seems that this attitude must be modified in discussing the carbon monoxide flame as there can be little doubt that the high concentration of atomic oxygen is the result of the combustion processes and is not merely thermal in origin. It should be remembered that the concentration of atomic oxygen will depend on the processes consuming the atoms as well as on those responsible for their liberation.

The several proposed combustion mechanisms for moist and dry CO have been dealt with in books by Hinshelwood (1933), Semenov (1935) and Lewis & von Elbe (1938). For the dry reaction it is very difficult to devise a mechanism involving only CO, O₂, O and CO₂ which will account satisfactorily for the chemical kinetics. Lewis & von Elbe have therefore supposed that ozone and a hypothetical carbon peroxide CO₃ may take part in the reactions. Of the reactions included as likely by them, the following lead to the formation of atomic oxygen:



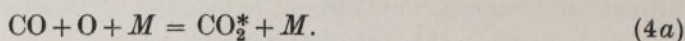
and the following to its removal:



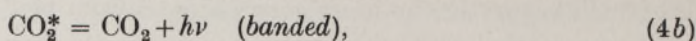
They rightly stress that at room temperature reaction (4) is at least 500 times slower than (3) and is therefore probably unimportant as a chain-breaking process.

The flame spectrum of CO shows a banded spectrum on a continuous background. This banded spectrum is believed (Gaydon 1940) to be emitted by CO₂. Kondratjewa & Kondratjew (1937) have shown that under favourable conditions at least one quantum of light is emitted by the flame for every 125 normal CO₂ molecules formed. This is vastly too much radiation to result from thermal causes, and in any case there is no evidence that this spectrum can be obtained from CO₂ molecules by either

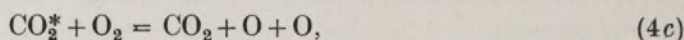
thermal or electrical excitation. Of the processes retained by Lewis & von Elbe, (4) is the only one liberating sufficient energy for the formation of electronically activated CO_2 molecules



This process is probably slightly endothermic. It might be followed by



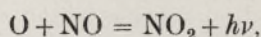
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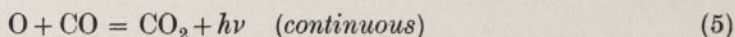
which is probably slightly exothermic, or by reactions involving the dissociation of the CO_2^* or another CO_2 molecule.

It has already been stressed by the author that there is no evidence that the electronically excited CO_2 molecules are metastable. Their life is probably between 10^{-8} and 10^{-5} sec. This would, however, allow for a fair number of collisions with oxygen molecules and, although sufficient radiation by process (4b) must take place to give the observed band spectrum, the majority of the excited molecules will probably end in reaction (4c). Thus reaction (4) should be regarded as *chain-branching* and not chain-breaking.

It is usual, in discussing combustion mechanisms, to disregard direct bimolecular associations because of the difficulty of removing the excess energy from the system. For the special case of the carbon monoxide flame, however, it is clear that the bimolecular association



resulting in the yellow-green continuous emission, is able to compete for atomic oxygen with the combustion processes, and therefore there seems no reason why the similar association

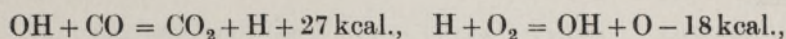


may not also have some probability. The reaction (5) probably requires some activation energy for a favourable collision accompanied by radiation, and the probability will in any case be less than 10^{-5} at each collision, but nevertheless the process may account for some of the continuous background to the flame spectrum. The existence of an activation energy for this reaction fits in with the observation that the continuous background is weaker, relative to the banded spectrum, for flames at low pressure and temperature and especially for the cool flame (Gaydon 1943).

It has been stressed (Gaydon 1942a) that normal carbon dioxide, CO_2 ($X^1\Sigma$), cannot be formed from normal CO ($X^1\Sigma$) and oxygen, O (3P), without electronic rearrangement. Thus reaction (1) probably requires a very high activation energy in addition to the 15 kcal. absorbed in the reaction, and may therefore be of little importance. These considerations also apply to reaction (4) but not to (4a). Little can be said about the hypothetical reaction (2). From a spectroscopic viewpoint it seems that reactions (4a), (4b), (4c) and (5) are required to account for the spectrum and the presence of atomic oxygen in the dry flame.

It should, however, be stressed that perfectly dry CO will not readily burn at all (Ubbelohde 1933), and that although the reactions listed above may serve to maintain combustion they do not account for its initiation. It is likely that for reaction (4a) to take place the third body M may have to fulfil special conditions and that water is particularly suitable.

For the moist reaction the concentration of atomic oxygen in the flame is also high. It seems likely, from the present study, that there is no essential difference in the combustion mechanism in the presence of a trace of water, but that its thermal decomposition may serve to initiate the reaction chains, and that by collisions the water molecules may quickly set free the vibrational energy of the newly formed CO_2 molecules so that this energy can thermally assist the further reaction instead of merely producing abnormal dissociation of the CO_2 in the flame products. However, the reaction chain

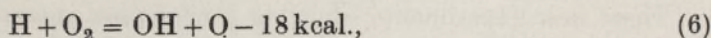


which could be initiated by thermal decomposition of H_2O to OH and H, would also lead to accumulation of atomic oxygen and may be important.

THE HYDROGEN FLAME

For flames in which oxygen is in excess, i.e. for hydrogen burning in oxygen or air, there is a moderate concentration of atomic oxygen, although not as high as that in the CO flame. When hydrogen is in excess, i.e. oxygen burning in hydrogen, the concentration of atomic oxygen appears to be small.

The results do not appear to be sufficiently definite to draw any certain conclusions. It seems that some atomic oxygen may be formed by the reaction



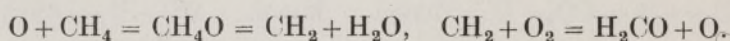
and that the removal of this atomic oxygen in the presence of an atmosphere of hydrogen may be more rapid than in an atmosphere of oxygen, but in the absence of quantitative data it cannot be said whether this reaction is of major importance in the combustion mechanism for hydrogen.

THE MECHANISM OF HYDROCARBON COMBUSTION

The experiments on methane, ethylene and butane in the Smithell's separator show clearly that in the outer cone, corresponding to the later stages of the combustion when hydrogen and carbon monoxide are the principal combustibles, there is a high concentration of atomic oxygen, but that in the inner cone, corresponding to the early stages of the combustion of the hydrocarbons, atomic oxygen is not present in sufficient quantity to give the slightest coloration with the nitric oxide test. It is known that for methane at room temperature there is practically no reaction with atomic oxygen and that methane does not show an 'atomic flame'

with oxygen. It therefore seems fairly certain that the negligible concentration of atomic oxygen in the early stages of the combustion must be due to its not being formed rather than to its very rapid removal. This receives experimental support from the observation that a flame of mixed carbon monoxide and butane (with a fairly high proportion of CO and air) burning in a Smithell's separator does show the yellow-green coloration in the inner cone, indicating presumably that the butane is not particularly effective in removing the atomic oxygen.

Two main types of mechanism, and a number of variants on these, have been suggested to explain the initial stages of hydrocarbon oxidation. These are usually referred to as the hydroxylation and peroxidation theories. The hydroxylation theory, put forward by the late Professor W. A. Bone, assumes the successive introduction of hydroxyl groups into the hydrocarbon molecule, and its most promising modification, that proposed by Norrish, makes use, for methane, of the chain process



According to the peroxidation theory as suggested by Engler and by Bach and applied to combustion processes by Callendar and by Sir Alfred Egerton and others, reaction occurs when a sufficiently energetic oxygen molecule combines momentarily with an energetic hydrocarbon molecule to form a temporary peroxide which subsequently breaks down to aldehyde and water, setting free energy to maintain the combustion. Variants on this theory proposed by Ubbelohde and by von Elbe & Lewis make use of reaction chains involving, for methane, the radical CH_3 and either another peroxidic radical or OH. These combustion mechanisms have been discussed elsewhere (Gaydon 1942*a*), and it has been shown that certain spectroscopic observations give some support for a peroxidation rather than a hydroxylation theory.

These new experiments, showing a negligible amount of atomic oxygen in the inner cone, appear to provide evidence against Norrish's modification of the hydroxylation theory which requires atomic oxygen for the chain reactions.

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For description of plate see page 124.

DESCRIPTION OF PLATE

Groups (a)–(g) each show at the top the spectrum of a neon glow lamp for approximate wavelength scale, and below five spectra of the various sources studied with exposures increasing in the ratio $1:\sqrt{3}:3:3\sqrt{3}:9$. Ilford Process Panchromatic plates were used, and conditions of development, etc., were maintained as constant as possible throughout.

- (a) Flame of CO burning in O_2 . Exposures 10–90 sec.
- (b) Flame of O_2 burning in H_2 . Exposures 2–18 min.
- (c) Flame of H_2 mixed with NO burning in O_2 . Exposures $\frac{1}{2}$ – $4\frac{1}{2}$ min.
- (d) Flame of CO mixed with NO burning in O_2 . Exposures 10–90 sec.
- (e) Flame of N_2O burning in H_2 . Exposures 1–9 min.
- (f) Glow produced by mixing nitric oxide with afterglowing oxygen from electric discharge. Exposures $6\frac{2}{3}$ –60 min.
- (g) Luminous Bunsen flame. Exposures 5–45 sec. This serves to illustrate photographic plate sensitivity.
- (h) Upper spectrum; inner cone of flame of premixed methane and air in Smithell's separator. Exposure 10 min. Lower spectrum; the same with nitric oxide added.

