Chemistry in Premixed Flames

C. P. FENIMORE

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BY

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BY

C. P. FENIMORE
GENERAL ELECTRIC RESEARCH LABORATORY
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INTRODUCTION

THE International Encyclopedia of Physical Chemistry and Chemical Physics is a comprehensive and modern account of all aspects of the domain of science between chemistry and physics, and is written primarily for the graduate and research worker. The Editors-in-Chief, Professor E. A. GUGGENHEIM, Professor J. E. MAYER and Professor F. C. TOMPKINS, have grouped the subject matter in some twenty groups (General Topics), each having its own editor. The complete work consists of about one hundred volumes, each volume being restricted to around two hundred pages and having a large measure of independence. Particular importance has been given to the exposition of the fundamental bases of each topic and to the development of the theoretical aspects; experimental details of an essentially practical nature are not emphasized although the theoretical background of techniques and procedures is fully developed.

The Encyclopedia is written throughout in English and the recommendations of the International Union of Pure and Applied Chemistry on notation and cognate matters in physical chemistry are adopted. Abbreviations for names of journals are in accordance with *The World List of Scientific Periodicals.*

CONTENTS

CHAPTER 1

FLAT PREMIXED FLAMES

EVERY flame is sustained by a complex reaction involving free radicals, as far as is known, and some of its elementary steps can often be followed more cleanly in other reacting systems. Radicals from discharges or photolyses may undergo the same elementary reactions at lower temperatures with less interference from unwanted species, and shock tubes which heat the gas mechanically may allow a desired step to be isolated at high temperatures in a way which would not be possible in a fire. Such considerations have suggested to some the paradox that flames are not very suitable objects of study in order to understand combustion. There is no reason why a chemist should not own both a discharge tube and a burner, however, and results by one technique may complement those by another.

Flames are called diffusion flames if the reactants must mix as they burn, and called premixed flames otherwise. Each kind can be either laminar or turbulent, depending on the character of the gas flow. All these types are dealt with in the books by Gaydon and Wolfhard[1] or by Lewis and von Elbe[2]; but the present treatment emphasizes the simplest burning possible, the steady, flat, pre-mixed flame, and only occasional reference is made to any other type of burning. The aim here is to discuss the chemistry, and flat flames are best for this purpose. In the arrangement envisaged, the motion of the gas is ideally in only one dimension, and one hopes to follow the course of the burning.

Figure 1.1 is a sketch of a water cooled, porous burner on which a flat flame can be burnt.[3,4] A laminar stream of reactants flows from the cooled surface into a reaction zone where the products are formed and accelerated downstream. There is a small pressure drop across the flame[2], but ordinarily it is of no consequence and the system can be taken to be a constant pressure one. As long as the gas flow is not too fast, the flame is stabilized above the burner by loss of heat to the cooled surface. If it could be displaced downstream while the gas flow remained unchanged, the flame would lose less heat to the burner and become hotter and faster burning, and recover its original position. It is also stable against displacement upstream which would cool it and make it slower burning. The steady burning velocity can be expressed either as a constant mass flow per unit of area or as a linear flow which increases as the gas warms up. When burning velocity is referred to without qualification, the linear velocity of the reactants is meant, measured before the gas has been warmed appreciably. In general usage, furthermore, the adiabatic burning velocity is meant; and although this is not achieved with a flat flame on a porous burner, it can be estimated in the following way.

If the gas flow is increased, the flame is blown a little farther off the burner until it is hot enough to burn at the faster velocity. It is possible to measure the decreased heat loss to the burner as the gas velocity is increased, and to extrapolate to an adiabatic burning velocity which is characteristic of the reactant composition and of its pressure and initial temperature. Measurements of the heat abstracted from flames by porous burners were first obtained by Botha and Spalding.[3] Their measurements have been criticized[5] and may have contained some errors,[6] but their extrapolation to zero heat abstraction seems valid.

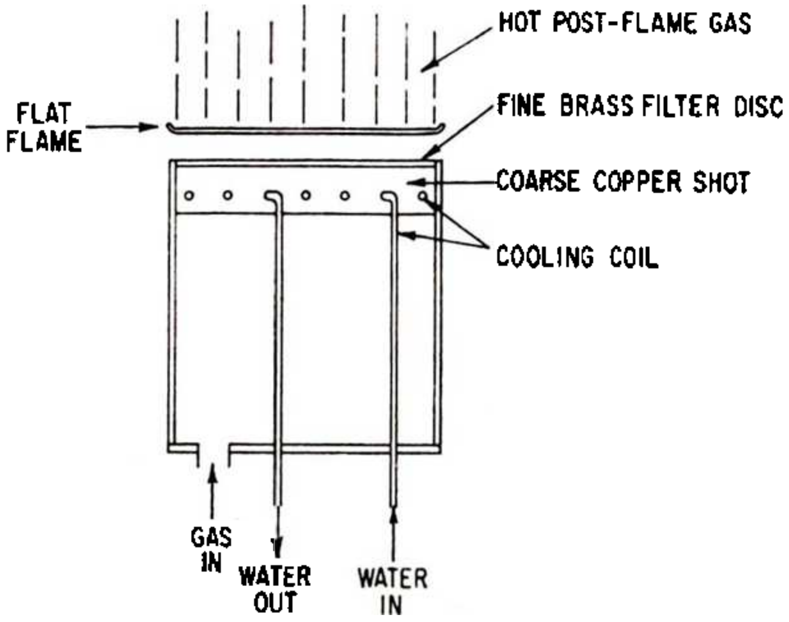


FIG. 1.1. Schematic flat flame burner, after Kaskan.[4]

Flames do not really burn without loss of heat to the surroundings, if only because of radiation. The notion of an adiabatic flame is an idealization, but it is usually a very good approximation.

Flat flames can be stabilized in other ways. The Powling burner[7] gives a flame nearer the ideal adiabatic one than a porous burner can. Instead of the cooled copper shot and porous surface shown in Fig. 1.1, the Powling burner possesses a honeycomb of columnar passages from which the gas issues with a flat velocity profile. A slight spreading of the flow occurs above the burner so that the flame can take a stable position where its burning velocity just equals the streaming velocity of the gas. A similar screen burner, in which a series of screens gives a uniform, approximately one dimensional flow, has also been used. The spreading of the gas above the burner can be measured by adding an inert dust of magnesium oxide and observing the paths of the particles. In a very fuel-lean methane flame burning as a flat, almost one dimensional flame at 1/10 atm, the spreading of the gas as it flowed from a screen burner to the downstream side of the reaction zone corresponded to a 10 per cent increase in area of a central stream tube.[8]

If the flow of gas through the burner of Fig. 1.1 is increased beyond the flat flame adiabatic burning velocity, the flame must become distorted. If the porous burner is replaced by a long open tube, a Bunsen burner, the flame remains attached to the rim of the tube and assumes a conical shape. The volume of gas supplied from the tube per second divided by the area of the flame surface is an average linear burning velocity. Such a premixed, laminar flame is still a flat flame locally, its thickness being small compared to the radius of curvature of its surface, and most published adiabatic burning velocities were measured on Bunsen type flames. Sometimes the total area of the flame is measured, sometimes the component of the flow normal to an especially suitable part of the cone.

A few experimental results may be quoted to give some feeling for the range of temperature and flammability. A stoichiometric, flat propane flame (4 per cent C_3H_8 in air) has an adiabatic burning velocity of 41·5 cm s^{-1}, measured at 289°K.[3] The velocity is slightly larger for a mixture containing a little excess fuel (4·2 per cent C_3H_8) but it decreases rapidly for compositions far from stoichiometric and is only 7 cm s^{-1} for either 2·13 or 7·1 per cent C_3H_8.[7] Linnett[9] reviewed the burning velocity measurements available for several fuels a few years ago, and discussed the errors in the various methods. His suggested values do not differ by more than about 5 per cent from some recent determinations by Scholte and Vaags,[10] obtained on Bunsen type burners, which are listed in Table 1.1. Agreement within 5 per cent is better than ought to be expected; the gas near the base of the cone is cooled by the burner wall, and that at the apex may be preheated in its passage, so the burning velocity is not really constant over the flame surface. Also the flame thickness while small is not negligible and this introduces some difficulty into determining its area. Flat flame burners possess fewer inherent sources of error, but these too always require correction or extrapolation to obtain the adiabatic velocity.

TABLE 1.1

Burning Velocities for the Fastest Burning Mixtures of Various Fuels with Air, from Scholte and Vaags[10]

Fuel	% Fuel by volume	Velocity cm s^{-1}
Hydrogen	42·4	280
Methane	10·5	40·0
Acetylene	9·45	150
Ethylene	7·3	70·0
Ethane	6·25	43·3
Propylene	4·95	45·0
Propane	4·3	41·4
But-1-ene	3·5	46·0
n-Butane	3·45	39·2

A few more burning velocities, those for the fastest burning mixtures of the five binary systems, are listed in Table 1.2. The pentaborane–air flame is the fastest burning fuel–air mixture reported so far. Its velocity was not determined on a burner, rather the growing shell of flame propagating out from a spark was photographed at various times and the burning velocity calculated from

$$\text{burning velocity} = (\mathrm{d}r/\mathrm{d}t)E$$

where $\mathrm{d}r/\mathrm{d}t$ is the rate of increase of radius of the shell with time and E a calculated expansion ratio of the burnt gas relative to the unburnt gas. The authors considered their value approximate, partly because the calculated E was used, partly because the flame front was cellular and not very well described as flat.

Hydrogen–fluorine is not listed among the halogen flames in Table 1.2 because the fastest burning mixtures cannot be burnt without detonations. Grosse and Kirschenbaum were able to mix fuel-rich compositions at 90°K which contained 6–25 per cent of F_2 and burnt about ten times faster than hydrogen–oxygen mixtures of the same initial temperature and fraction of stoichiometric strength.[256]

Fuel–air mixtures cannot burn if they contain too much of either constituent or have been diluted too much with inert gas. In general, the final flame temperature must be at least 1500°K for fuel-lean mixtures of light hydrocarbons and air to burn, and higher still for fuel-rich mixtures. Lean acetylene mixtures are exceptional in that they give flat flames with final temperatures of only around 1200°K, and both lean and rich hydrogen flames can burn with flame temperatures still lower.

There is no upper limit to flame temperatures. Among the hottest flames, that of $C_2N_2 + O_2$ is interesting because its temperature had some bearing on the estimation of the dissociation energy of molecular nitrogen. If the energy is taken as the accepted 225 kcal mole^{-1}, the calculated equilibrium flame temperature works out to 4850°K for products mostly of $N_2 + 2CO$ plus small amounts of NO, CN, N, and O. If the old abandoned value for the dissociation energy of N_2 had been correct, 170 kcal mole^{-1}, the easier formation of N atoms would have absorbed more of the heat of combustion and the flame temperature would have been only 4325°. Thomas and co-workers[21] measured the temperature as 4800 ± 200° at a time when the dissociation energy of N_2 was still in question, and their measurement suggested that 170 kcal could not be correct. Since the high temperature of the flame is partly a consequence of the stability of its main products, it will be appreciated that the addition of more oxygen to burn the CO to CO_2 would only cool the flame because of the easy dissociation of CO_2.

TABLE 1.2

Mixture	Initial T, °K	P, atm	Burning velocity cm s^{-1}	Ref
H_2–O_2, 73% H_2	room	1	~1180	a,b
H_2–Cl_2, 65% H_2	room	1	410	a
H_2–Br_2, 58% H_2	room	1	32	c
B_5H_9–air, 4% B_5H_9	room	1	540	d
H_2O–F_2, 52% H_2O	373	1	810	e
O_3	room	1	475	f
N_2H_4–H_2O, 3% H_2O	423	1	185	g
CH_3ONO	330–500	1	4–7	h
$C_2H_5ONO_2$	360	$<0{\cdot}2$	~13	i
C_2H_4O	365	0·2–1·5	~4	j

a, Bartholomé[11]; b, Senior[12]; c, Cooley *et al.*[13]; d, Berl *et al.*[14]; e, Streng[15]; f, Streng and von Grosse[16]; g, Murray and Hall[17]; h, Gray and Williams[18]; i, Hicks[19]; j, Friedman and Burke.[20]

The calculation of equilibrium adiabatic flame temperatures is easy in principle. A trial temperature is guessed, the equilibrium products for this temperature are calculated from thermodynamic data, and one checks that the heat released in forming the products is just sufficient to raise them to the trial temperature. If not, a new temperature is guessed and the process repeated.

Flame Equations

The equations describing steady, one dimensional flames have been formulated by Hirschfelder and co-workers[22] and by many others. They express the facts that the rate of mass flow is constant through the flame,

$$(\rho v)\ \mathrm{g\ cm^{-2}\ s^{-1}} = \text{constant}$$

$$\rho\ \mathrm{g\ cm^{-3}} = \text{density}$$

$$v\ \mathrm{cm\ s^{-1}} = \text{linear velocity}$$

Then ignoring radiation, the rate of heat evolution in a steady flame must be balanced by an increase in the heat flow due to the motion of the gas and to thermal conduction.

$$\dot{q}\ \mathrm{cal\ cm^{-3}\ s^{-1}} = \mathrm{d}/\mathrm{d}z \left\{ (\rho v) \int_{T_0}^{T} C_p \mathrm{d}T - \lambda \frac{\mathrm{d}T}{\mathrm{d}z} \right\} \tag{1.1}$$

$$C_p\ \mathrm{cal\ g^{-1}\ {}^\circ K^{-1}} = \text{specific heat at constant pressure}$$

$$T = \text{temperature}$$

$$\lambda\ \mathrm{cal\ cm^{-1}\ s^{-1}\ {}^\circ K^{-1}} = \text{thermal conductivity}$$

$$z\ \mathrm{cm} = \text{distance coordinate}$$

Finally, the rate of formation of any chemical species must also be balanced by an analogous increase in its flow due to the motion of the gas and to diffusion.

$$m_i R_i\ \mathrm{g\ cm^{-3}\ s^{-1}} = \mathrm{d}/\mathrm{d}z \left\{ (\rho v) M_i - \rho D_i \frac{\mathrm{d}[M_i]}{\mathrm{d}z} \right\} \tag{1.2}$$

$$m_i\ \mathrm{g\ mole^{-1}} = \text{molecular weight of the } i\text{th species}$$

$$R_i\ \mathrm{mole\ cm^{-3}\ s^{-1}} = \text{its chemical rate of formation}$$

$$M_i = \text{its mass fraction in the gas}$$

$$D_i\ \mathrm{cm^2\ s^{-1}} = \text{its diffusion coefficient.}$$

It is convenient to write equation (2) in terms of the mass fraction of the total flow carried by the ith species, G_i.

$$G_i = M_i(v + v_i)/v$$

v_i cm s^{-1} $= -D_i\,\mathrm{d}X_i/X_i\,\mathrm{d}z$ = diffusion velocity of the ith species

X_i = its mole fraction in the gas.

For then the content of equation (2) can be stated as follows: G_i is constant unless a chemical reaction involving the ith species occurs, and then the rate of reaction is given by

$$m_i R_i = (\rho v)\,\mathrm{d}G_i/\mathrm{d}z \tag{1.3}$$

Measurement in Flames

Equation (3) allows an estimate of R_i at any point in the flame if a profile of its mole fraction, X_i vs. z, can be obtained and if D_i and v are known through the same region. Similarly, $\dot{q}$ can be inferred from a temperature profile by equation (1). Except with unusually slow, thick flames, the required profiles cannot be obtained at atmospheric pressure because the reaction zone is too thin. But reduced pressures thicken flames. At 1/20 of an atmosphere pressure, the oxygen in a relatively low temperature hydrogen–oxygen flame requires about 0·3 cm of distance in order to react. This allows adequate resolution for good flame profiles.

Most composition traverses through flames have been obtained by probe methods. Microtechniques are necessary, and very small quartz probes have been developed[23] which give faithful samples of the partially reacted gas. Their important characteristic is that they should quench the gas quickly. The sample is drawn at sonic velocity through the small probe orifice and expanded and cooled. Little reaction of stable species seems to occur in these microprobes. Radicals in the sample ordinarily recombine in the probe, but Fristrom has reported[24] that one radical at least can be measured by a scavenger probe technique. Oxygen atoms in the gas were measured by rapidly mixing the sample with NO_2, introduced separately into the probe, and the NO formed via $O + NO_2 \rightarrow NO + O_2$ was measured. In the very fuel-lean flames used, the consumption of NO_2 by other radicals was judged to be small and could be corrected for.

Thermocouples of butt-welded Wollaston wires, quartz coated to reduce surface catalysis,[4] have been used to obtain temperature traverses through flames of up to around 2000°K. The usual optical temperature measurements by line reversal, or other methods involving emission from electronically excited species, depend on an equilibrium excitation of the emitters and are suspect in the reaction zone itself. The sodium D-line reversal temperature, for example, assumes that in gas coloured by a little added sodium the ratio of excited Na* in the upper states of the transiton to ground state Na is given by the equilibrium expression

$$[\mathrm{Na}^\star]/[\mathrm{Na}] = 3\,\mathrm{e}^{-h\nu/kT}.$$

A heated source of adjustable known temperature is viewed spectroscopically through the gas and the effective black body temperature of the source is the same as T in the expression when the D-lines are just reversed; that is, when seen neither in absorption nor emission. This is also the gas temperature if the sodium is equilibrated. It sometimes happens that the concentration of the excited species is much above its equilibrium value in the flame zone, and then a false "anomalous" temperature would be deduced if one supposed that the radiation reflected an equilibrium ratio of concentrations. In the post-flame gas the anomalies are rare and experience has shown that sodium D-line reversal temperatures are generally reliable. Optical temperatures can be obtained by absorption measurements of ground state OH radicals,[25,26] and these depend on the distribution of the OH among the rotational levels of the ground vibrational state. There is no reason why this distribution should not be thermally equilibrated. The temperature deduced from it is the same as a thermocouple temperature which has been properly corrected for heat loss.

The last paragraph is inexact because temperature is an equilibrium concept which is inexact in a reacting system. It can be reworded as follows: A thermocouple gives essentially a translational "temperature" of the bulk of the gas which is an appropriate T for equation (1) and (2). Measurements of the index of refraction[27] also give this "temperature", and OH rotational "temperatures" obtained in absorption are found to agree with it. But "temperatures" deduced from emission spectra are different unless the emitting species are distributed among their energy levels in accordance with the translational "temperature" of the bulk of the gas. In the post-flame gas equilibrium is approached and all "temperatures" converge on the translational "temperature".

Equation (2) neglects thermal diffusion due to the temperature gradient in the gas. Even with this simplification, the calculation of reaction rates is difficult enough because a general knowledge of the concentration diffusion coefficients does not exist. It is often possible to choose fairly reliable values in special cases. The temperature has not exceeded 2000°K in flames for which detailed composition traverses have been obtained so far, and experimenters have tried to work with mixtures in which one component made up the bulk of the gas, so that it was not unreasonable to treat it as a binary mixture of this main component with each of the other species in turn. A helpful summary of D and λ values exists with particular reference to flame studies,[28] and additional measurements for treating diffusion in fuel-lean methane–oxygen flames have been made by Walker and Westenberg. They added a flowing thread of some substance centrally to a stream of hot gas and measured its radial diffusion with time as the gas flowed downstream.[29] Ember and co-workers[30] have measured the self diffusion of carbon dioxide in this way to 1680°K by adding a stream of radioactive CO_2 to the post-flame CO_2 obtained by burning moist $CO–O_2–CO_2$ mixtures on a porous burner. It is possible sometimes to obtain D values from the profiles measured through flames because diffusion often changes the mole fraction of a particular species upstream of the reaction zone in a region where it is fairly certain that no chemical reaction involving it has yet occurred. If so, G_i remains unchanged for the species, and this fact together with a curve of X_i vs. z in the region in question defines D_i. If the temperature dependence of D_i can also be measured or assumed, the diffusion coefficient can be extrapolated everywhere through the flame.

The effect of erroneous transport data was discussed by Peacock and Weinberg[230] along the lines that equation (2) can be approximated by

$$R_i \sim \frac{(\rho v)}{\text{average mol. wt.}} \left\{ \frac{\mathrm{d}X_i}{\mathrm{d}z} - \frac{D_i}{v} \frac{\mathrm{d}^2 X_i}{\mathrm{d}z^2} \right\}$$

The term in $\mathrm{d}^2X_i/\mathrm{d}z^2$ is of opposite sign to $\mathrm{d}X_i/\mathrm{d}z$ upstream of the point where $\mathrm{d}^2X_i/\mathrm{d}z^2$ equals zero and of the same sign downstream of this point. Far upstream, an error in D_i leads to a greatly magnified error in R_i so it is impossible to state exactly where R_i first becomes appreciable. In the neighbourhood of the point where $\mathrm{d}^2X_i/\mathrm{d}z^2$ equals zero and farther downstream, however, errors in D_i do not give magnified errors in R_i.

In most of the flame studies published so far, thermal conductivities when needed were calculated by the method of Lindsay and Bromley[31] from the conductivities of the pure constituents.

Measurements of the detailed structure of flames have begun to appear in the literature only recently. Previously, the only experimental quantity was often a measurement of the adiabatic burning velocity and the use of equation (1) and (2) was different. It was supposed most often that the flame could be represented by some single reaction of rate R; and solutions were worked out to give the calculated burning velocity for various assumed R which could be compared with the measured burning velocity. In the absence of more experimental data, this was all that could be done. But the burning velocity is proportional to only the square root of some sort of an average reaction rate in such solutions; so it is an insensitive property for investigating flame reactions, and not much chemical insight can be expected from comparisons of calculated with measured burning velocities. The relation of burning velocity to reaction rate will be discussed in chapter 9.

The Post-Flame Region

Nothing has been said yet about the hot post-flame gas downstream of the thin flame proper. Gaydon and Wolfhard[1] call this region the "interconal gases" because it is terminated by a diffusion flame with the surrounding air when a fuel-rich Bunsen flame is burnt in the open. The post-flame gas is not always equilibrated thermodynamically and reactions of much interest may take place in it. Sufficient spatial resolution can generally be obtained to follow the reactions even at atmospheric pressure, and an approximate knowledge of the transport coefficients is adequate to correct for diffusion and thermal conductivity. In fact these corrections have often been omitted without introducing large errors, as could not possibly be done in the thin flame zone. Typically, the post-flame gas flows 100–1000 cm s^{-1} and reactions which go appreciably in times of the order of 10^{-3} s are easily followed by spectroscopic or by probe methods.

CHAPTER 2

THE POST-FLAME GAS FROM HYDROGEN–OXYGEN FLAMES

THE accepted reaction mechanism of hydrogen–oxygen mixtures at temperatures around 800°K [2,32,33] leads to a reasonable description of their burning at higher temperatures. If this extrapolation were not true, it would be much more difficult to understand flames. The mechanism is reviewed briefly below and its consequences are developed. The immediate goal is to deduce the expected state of the post-flame gas, but this requires some consideration of the vigorous reaction zone in which the gas is made.

The Mechanism at Around 800°K

The lower temperature mechanism was worked out to account for the observation that mixtures of the reactants when run into a heated vessel either explode or do not, depending on gas composition, temperature, pressure, and vessel size and surface. It is supposed that a few radicals are generated in some slow initiation process, and that these can multiply rapidly under isothermal conditions by the sequence of reactions

$$\mathrm{H} + \mathrm{O_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{OH} + \mathrm{O} \tag{2.1}$$

$$\mathrm{O} + \mathrm{H_2} \rightleftarrows \mathrm{OH} + \mathrm{H} \tag{2.2}$$

$$\mathrm{OH} + \mathrm{H_2} \rightleftarrows \mathrm{H_2O} + \mathrm{H}; \tag{2.3}$$

so that a steady, non-explosive system can exist only if terminating reactions also occur to cancel the multiplication of free radicals. k_1 cm^3 mole^{-1} s^{-1} is the rate constant for reaction (1) in the forward direction, k_{-1} the constant for the reverse, and analogous k's attach to the other reactions. The reverses are neglected in explosion limit studies where only the beginning of the consumption of oxygen and hydrogen is in question, but they must be included under more general circumstances.

The question investigated experimentally is whether the system is steady under essentially isothermal conditions, and an explosion indicates that a steady system was not obtained. If all experimental variables are held constant except pressure, the system is found to be steady above a certain pressure called the upper or second explosion limit. It is also steady below a lower or first explosion limit, but at intermediate pressures the gas explodes. In addition to this bounded explosive region, a third limit exists at higher pressures above which the system always explodes, but the third limit may not represent a purely isothermal branching chain and its study has not contributed to the simple mechanism being reviewed here. Qualitatively, the explosion limits for some particular composition at a fixed temperature can be represented by Fig. 2.1. Points A and B indicate the first and second explosion limits and at nearby pressures outside the explosive region the steady reaction rate is very small. At sufficiently high pressures the reaction rate increases so that it becomes difficult to maintain an approximately isothermal system. The third explosion limit occurs at C.

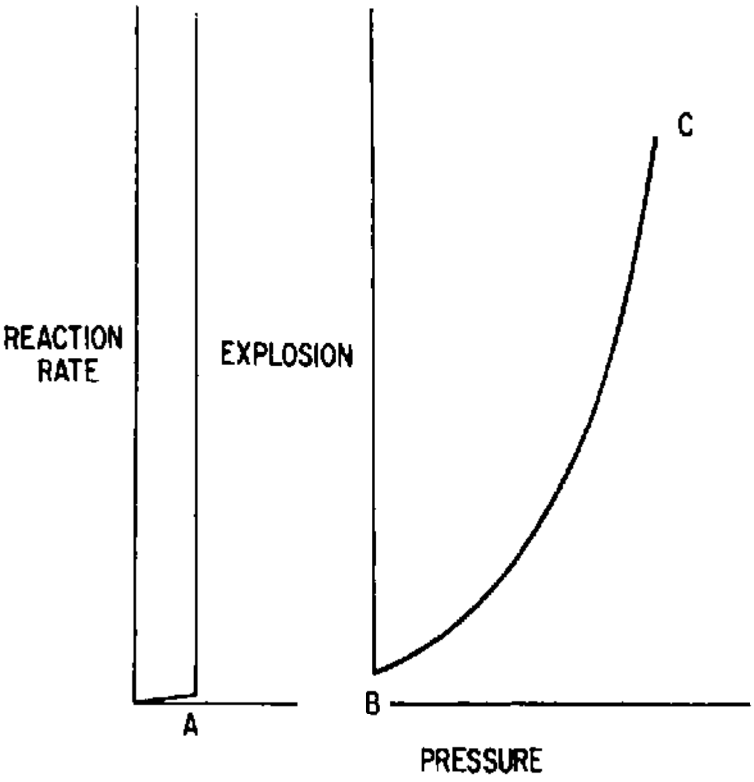


Fig. 2.1. Schematic plot of reaction rate, showing the bounded explosive region between A and B. Hinshelwood and Williamson.[34]

Two different terminating processes cancel the branching chains at the two lower limits. At the second limit, the terminating reaction is

$$H + O_2 + M \rightarrow HO_2 + M \qquad (2.4)$$

The collision complex of H and O_2 must lose part of its energy in order to form a stable entity, and M is any species which accepts the energy. The HO_2 is supposed not to regenerate an active free radical, so the branching is checked. Quantitatively, $2k_1 = k_4[M]$ at the second limit, and by varying other experimental parameters, the ratio k_1/k_4 can be determined as a function of temperature and of various M species.

At pressures below the second limit, termolecular reaction (4) is too slow to quench the branching, and fresh gas mixtures prepared at lower and lower pressures still explode until the chain branching is cancelled at the first limit by a new terminating reaction. The new reaction, favoured by low pressure, is the diffusion of active free radicals to the vessel wall and their destruction there,

$$\text{H or O} \rightarrow \text{destruction at the wall} \tag{2.5}$$

The evidence suggests that only H or O atoms are ordinarily destroyed in this way, OH radicals reacting too rapidly by (3) for many ever to reach the wall. Reactions (5) can be written formally as first order processes of rate equal to $k_5'[H]$ or $k_5''[O]$, and the ratios k_1/k_5' and k_2/k_5'' obtained for a particular reaction vessel from determinations of the first limit. In general, (5) depends on both the diffusion of atoms and on their accommodation at the wall; but if the vessel surface is sufficiently active in capturing the atoms which strike it, (5) is controlled by diffusion alone and absolute values of k_5' and k_5'' can be calculated. In this way, absolute values of k_1 and k_2 can be derived in the H_2–O_2 system[35] or in closely related systems.[36] A value of k_1 can also be obtained from measurements within the explosive region of the rate at which the chains develop.[37] These estimates and some others which will be discussed later are plotted in Fig. 4.1, chapter 4, where the data just discussed are the segments labelled a, b, and c.

Extension of Flames

Although radicals can diffuse from the region in which they are formed, wall reactions of type (5) are unimportant in flames where there are no walls. (4) might still be important, and if so, the HO_2 formed might no longer be effectively inert. Yet an extrapolation of k_1/k_4 from 800 to 1500°K shows that (4) cannot be as fast as (1). The most efficient M species in reaction (4) is the water molecule, and in a gas at atmospheric pressure, at 1500°, k_1 is expected to be about ten times larger than $k_4[H_2O]$ when the mole fraction of water is 0·25. The fastest flame reactions therefore should be (1), (2), and (3).

Sugden and his co-workers[38] developed the consequences to be expected. If the products from the forward reactions build up to considerable concentrations, the reverses of (1), (2), and (3) must become important. Also, since these three reactions and their reverses cannot give the final equilibrium products, recombination reactions are expected to occur in order to reach equilibrium eventually. The expected recombinations are such processes as

$$H + H + M \rightarrow H_2 + M \tag{2.6}$$

$$OH + H + M \rightarrow H_2O + M \text{ etc.} \tag{2.7}$$

and reaction (4) might also lead to recombination eventually. It is important that all the recombinations are strongly exothermal and require third bodies to accept part of their energies of reaction, because the expected state of the post-flame gas depends on the rates of the bimolecular as compared to the termolecular processes.

Following Sugden, a reaction equilibrated with its own reverse is called a balanced reaction, and at low enough pressure bimolecular (1), (2), and (3) will be balanced before termolecular (4), (6), (7), etc., can reduce the radical concentrations to values appropriate to equilibrium products. At low pressures, therefore, a hydrogen–oxygen flame is expected to contain a zone of vigorous net reaction before the bimolecular reactions become balanced—this will be the flame proper—followed by a post-flame gas in which the bimolecular reactions are balanced while the slower termolecular recombinations continue to reduce [H], [OH], and [O]. In the post-flame gas, the radicals are expected to be related by

$$\frac{[OH][O]}{[H][O_2]} = \frac{k_1}{k_{-1}} = K_1 = 300\, T^{-0{\cdot}372}\, e^{-17{\cdot}13\ \text{kcal}/RT} \tag{2.8}$$

$$\frac{[OH][H]}{[O][H_2]} = \frac{k_2}{k_{-2}} = K_2 = 2{\cdot}27\, e^{-1{\cdot}87/RT} \tag{2.9}$$

$$\frac{[H][H_2O]}{[OH][H_2]} = \frac{k_3}{k_{-3}} = K_3 = 0{\cdot}21\, e^{15{\cdot}19/RT} \tag{2.10}$$

The numerical values for the equilibrium constants are quoted from Kaufman and Del Greco[39] who offered them as good to within a few per cent at 300–2200°K. They are based on $\Delta H_{298} = 9{\cdot}33$ kcal mole^{-1} for the heat of formation of OH. This is the only quantity involved in the numerical values about which some doubt still exists, and if the choice is correct, the values are good to 3 per cent.

Experimental Tests

Schott[40] made a test of the concept of the quasi-equilibria by heating mixtures of H_2–O_2–Ar to temperatures of 1200–2800°K in a shock tube. He found that OH, measured by its ultraviolet absorption, rapidly developed to about the concentration expected on the basis of reversible reactions (1), (2), and (3) if no recombination took place at all. The recombination reactions were evidenced by a subsequent slower decay of [OH]. In the remainder of this section, the evidence from steady flames is reviewed.

Kondratiev and co-workers showed long ago that low pressure hydrogen flames at 0·3–2·5 cm of Hg pressure contained large [OH].[41,42] When gas of composition $2H_2$ plus O_2 was run through a vessel heated to 750–820°K, it burnt with the generation of much larger [OH] than corresponded to equilibrium in the products. The [OH] was estimated spectroscopically in absorption. These experiments did not differentiate between reaction zone and post-flame gas.

Sugden and co-workers[38] inferred large radical concentrations in fuel-rich post-flame gas even at atmospheric pressure by adding lithium salts to the reactants and determining [Li] in the products from the emitted resonance lines. The additive proved to be present mostly as a compound rather than as free metal atoms and by varying gas composition and temperature separately, [Li] at 2200–2400°K was found to agree with the assumed equilibrium

$$\mathrm{Li} + \mathrm{H_2O} = \mathrm{LiOH} + \mathrm{H_{equ}} \qquad (2.11)$$

where H_{equ} represents the calculated equilibrium H for the known composition and measured temperature. The temperature dependence of this equilibrium being known, the expected [Li] at any lower temperature could be calculated for a smaller $[H]_{equ}$, but the [Li] actually found in the gas from lower temperature flames was much larger than that calculated. The interpretation was that the equilibrium (11) was still maintained, but that $[H] > [H]_{equ}$ at lower temperatures. [H] could then be estimated from measurements of [Li]. In this way, and subsequently by other methods also, the decrease of [H] with increasing distance downstream into the post-flame gas could be measured and shown to conform to the expected occurrence of reactions (6) and (7), as far as this could be judged at a fixed pressure of one atmosphere.

The most direct proof that radicals in low temperature post-flame gases are much above their equilibrium concentrations comes from Kaskan's determination of [OH] by absorption in the ultraviolet.[25] At 1/2 and at 1 atm, he found that $[OH]/[OH]_{equ}$ just downstream of the flame varied from a few thousand at around 1340°K to a few hundred at around 1550°; which may be compared with the ratio from the lithium method, $[H]/[H]_{equ}$ having been found about 100 at 1600° and about 10 at 1850° in similar gas. The ratios follow a uniform trend with temperature, as they ought. In fuel-rich gas, the bulk products H_2O and H_2 cannot differ much from their equilibrium concentrations, and equation (10) implies therefore that

$$[OH]/[OH]_{equ} = [H]/[H]_{equ}$$

Accepting this relation, Kaskan estimated the decay rate of H atoms from the fall of [OH], and observed the characteristic pressure dependence expected for a termolecular recombination.

Fenimore and Jones[43] estimated [H] from measurements of the rate of formation of HD in rich post-flame gas containing added D_2O. It was supposed that the rate of exchange was determined by the reactions

$$H + D_2O \underset{\frac{1}{2}k_3}{\overset{k_{-3}}{\rightleftarrows}} HD + OD \underset{\frac{1}{2}k_{-3}}{\overset{\frac{1}{2}k_3}{\rightleftarrows}} HDO + D \underset{k_3}{\overset{\frac{1}{2}k_{-3}}{\rightleftarrows}} D_2 + OH$$

and also by the similar set obtained by exchanging H and D in these formulae. It could be shown that

$$H + D_2 = HD + D \text{ and } D + H_2 = HD + H$$

were equilibrated in the post-flame gas, and it was assumed that reactions of the type of (2) would not contribute much to the exchange in fuel-rich gas. Then $k_{-3}\,[H]$ should have been given by

$$k_{-3}[H] = \frac{-2[H_2]\,d\ln\{[D_2O]_O/[H_2]_O - [HD]/2[H_2]\}}{[H_2]_O\,dt} \qquad (2.12)$$

where $[H_2]/[H_2]_O$ was the fraction of hydrogen fed which remained unburnt, and $[D_2O]_O/[H_2]_O$ the ratio of added D_2O to the original H_2. Equation (12) could give only relative [H] until k_{-3} was known. It was found that the relative [H] was decreased strongly by the addition of simple hydrocarbons to fuel-rich H_2 flames; and in the post-flame gas from fuel-rich CH_4 or C_2H_2 flames, it varied over a small temperature range in the same way as the calculated $[H]_{equ}$ if k_{-3} was assumed to have an activation energy of about 25·5 kcal mole^{-1}. Supposing

$[H] = [H]_{equ}$ in these special cases, k_{-3} was obtained and estimates of [H] in the post-flame gas from pure fuel-rich H_2 flames agreed well with those by other methods. The activation energy assumed for k_{-3} has since been proved too large, 21·3 kcal mole^{-1} appears nearer the truth.[44] But all subsequent work has confirmed that [H] in post-flame gas containing hydrocarbons is approximately equal to $[H]_{equ}$, and the absolute value of k_{-3} at around 1600°K was not badly chosen.

From the experiments just described, it seems very probable that (3) is balanced in fuel-rich gas during the recombination processes. That it is also balanced in lean post-flame gas is more or less obvious in particular cases; with the approximate value of k_{-3}, it can be calculated that even the small equilibrium [H] in many hot lean gases would be enough to cause a very appreciable decrease in $[H_2O]$ unless (3) was at least approximately balanced.

Reactions (2) and (1) can be discussed more briefly. From equations (9) and (10)

$$[O] = K_3[OH]^2/K_2[H_2O] \tag{2.13}$$

and experimental evidence for this relation was obtained by Kaskan[45] in lean post-flame gas. [OH] was again measured by ultraviolet absorption. About one per cent of nitric oxide, known to be stable against decomposition to nitrogen and oxygen under the conditions used, was present in the gas; and by measuring the intensity of the greenish emission due to

$$O + NO \rightarrow NO_2 + h\nu$$

a quantity proportional to [O] could be obtained at each point where [OH] was measured. The form of equation (13) was satisfied experimentally, [O] was proportional to $[OH]^2$. By estimating the absolute intensity of the O + NO emission, a collision efficiency for radiation could be deduced which agreed moderately well with independent estimates. This indicates that the difference at least of (2) and (3) is balanced. A proportionality of the form of (13) was reported to hold in rich gas containing added nitric oxide at temperatures up to about 2100°K.[46]

Reaction (1) is almost obviously balanced in lean gas because the net $d[O_2]/dt$ is zero when some gross generation of oxygen must be occurring. In a typical one of Kaskan's lean gases just discussed, his measured [OH] and [O] would have formed by the reverse of reaction (1) more $[O_2]$ per millisecond than was present in the gas unless the reaction of (1) in the forward direction had cancelled it. In rich gas, of course, both [O_2] and [O] are small and it would be harder to prove (1) balanced.

To sum up: in the post-flame gas from hydrogen flames, [H], [OH], and [O] may be much above their equilibrium concentrations, and related to one another by the balanced reactions (1), (2), and (3) while they decay relatively slowly towards their equilibrium values. This behaviour is quite consistent with the lower temperature reaction mechanism. As the temperature of the post-flame gas is raised, equilibrium radical concentrations increase greatly but the actual radical concentrations do not increase very much; so that at sufficiently high temperatures, the radical concentrations no longer exceed equilibrium. In the post-flame gas from some H_2-rich flames at 1 atm, the concentrations approached equilibrium values at around 2200–2400°K.

As for the mechanism of balancing, equation (3) seems established in rich gas for [H] vs. [OH] by the tracer experiments. It is not certain that (2) and (3) need actually occur to maintain the balance of [O] vs. [OH] in lean gas, however, for they are equivalent to $2OH \rightleftarrows O + H_2O$ as far as the quasi-equilibria are concerned. This latter reaction is known to be very fast in the forward direction even at room temperature,[39] and it may maintain the balance in lean gas.

CHAPTER 3

REACTIONS IN THE POST-FLAME GAS FROM HYDROGEN FLAMES

A FEW years ago, Steacie[47] could say of flames, "The systems are so complex and our knowledge of them so slight that they cannot be used in practice as reliable sources of atoms and radicals." The last chapter showed that this statement is no longer altogether true, and some uses to which the post-flame gas has been put are now considered. The work to be described usually involves measuring the change in some property of the burnt gas as it flows downstream. The velocity of the gas is known, so the change of the property with time can be obtained.

Radical Recombinations

The radicals are related by the balanced reactions and decay as a pool. An expression to represent the pool can be obtained by noting that from equations (2.1), (2.2), and (2.3),

$$\mathrm{d}\{[\mathrm{H}] + [\mathrm{OH}] + 2[\mathrm{O}] + 2[\mathrm{O_2}]\}/\mathrm{d}t = \text{zero}$$

Therefore $\{[\mathrm{H}] + [\mathrm{OH}] + 2[\mathrm{O}] + 2[\mathrm{O_2}]\}$ is constant as far as the action of these reactions is concerned, and the recombinations must be supposed to decrease this sum rather than any single member of it. The species are all present in only small concentrations in fuel-rich gas, and the sum is a representation of the pool for rich gas.

The notion of a pool of species which decays towards equilibrium does not depend on the balancing reactions, however, and the expression just found can also be obtained by specifying which species are present and which are formed as the system approaches equilibrium. It was shown by Kaskan and Schott[48] that if a system containing H, OH, O, H_2, O_2, H_2O decays in such a way that H_2 and H_2O are formed, as should be the case in fuel-rich gas, the conservation of chemical elements requires that

$$-\mathrm{d}\{[\mathrm{H}] + [\mathrm{OH}] + 2[\mathrm{O}] + 2[\mathrm{O_2}]\}/\mathrm{d}t = \text{recombination rate} \quad (3.1)$$

If equilibrium is approached by a formation of O_2 and H_2O, as should be the case in fuel-lean gas, the corresponding equation is

$$-\mathrm{d}\{3[\mathrm{H}] + [\mathrm{OH}] + 2[\mathrm{O}] + 2[\mathrm{H_2}]\}/\mathrm{d}t = \text{recombination rate} \tag{3.2}$$

Equation (2) can be obtained from the balancing reactions, but it can also be considered a consequence of the stoichiometry and the requirement that the chemical elements cannot be formed or destroyed.

In studies of the recombination of radicals in fuel-rich gas it was supposed that the contributions of [O] and $[O_2]$ to the pool of radicals could be neglected and this assumption was justified by equations (2.8), (2.9), and (2.10). The recombination reactions considered were

$$\mathrm{H} + \mathrm{H} + \mathrm{M} \xrightarrow{k_6} \mathrm{H_2} + \mathrm{M} \tag{2.6}$$

$$\mathrm{OH} + \mathrm{H} + \mathrm{M} \xrightarrow{k_7} \mathrm{H_2O} + \mathrm{M} \tag{2.7}$$

so that equation (1) became

$$-\mathrm{d}\{[\mathrm{H}] + [\mathrm{OH}]\}/\mathrm{d}t = 2k_6\{[\mathrm{H}]^2[\mathrm{M}]\} + 2k_7[\mathrm{H}][\mathrm{OH}][\mathrm{M}] \tag{3.3}$$

The factors 2 are introduced in (3) because H atoms and OH radicals are consumed at twice the rate of the elementary processes. M was assumed to represent the same third body in both terms on the right side of (3). Writing [OH] as a function of [H] by equation (2.10), Bulewicz and Sugden[49] put (3) in the form

$$\frac{1}{[\mathrm{H}]} - \frac{1}{[\mathrm{H}]_0} = k'(t - t_0) \tag{3.4}$$

where

$$k' = \frac{2[\mathrm{M}]\{k_6 + k_7[\mathrm{H_2O}]/K_3[\mathrm{H_2}]\}}{\{1 + [\mathrm{H_2O}]/K_3[\mathrm{H_2}]\}}$$

Then estimating [H] as the gas flowed downstream by a method calibrated against their Li method, they could determine k' for various ratios of $[H_2O]/[H_2]$ and split k' between k_6 and k_7. They assumed that $[M] = [H_2O]$ and that no other species was nearly as efficient as a third body, to obtain at 1650°K

$$2k_6 = 2{\cdot}3 \times 10^{16}\ \mathrm{cm^6\ mole^{-2}\ s^{-1}}$$

if $[M] = [H_2O]$ only

$$2k_7 = 55 \times 10^{16}$$

A marked decrease in k_6 and k_7 at temperatures above 2000° was discounted as possibly due to $[H] - [H]_{equ}$ having become rather small.

Kaskan's[25] measurement of the same process, by OH absorption, gave approximately $2k_6 = 0{\cdot}4 \times 10^{16}$ cm^6 mole^{-2} s^{-1}, if $[M] =$ the whole gas and would have been about three times larger if he had supposed that $[M] = [H_2O]$ only. His data indicated that $k_7/k_6 > 1$ but were not extensive enough to give more than an approximate k_6. Dixon-Lewis and Williams[50] added water to various fuel-rich flames but found no special efficiency for this molecule as a third body and reported $2k_6 = 0{\cdot}6 \times 10^{16}$ for $[M] = [H_2]$, and $0{\cdot}4 \times 10^{16}$ when $[M] = [H_2O]$ or $[N_2]$. The estimates in flames are not inconsistent with the measurements of Farkas and Sachsse[51] who found $2k_6$ about 10 times larger near room temperature; nor with the smaller values from shock tube studies at 3000°K or more,[52–55] obtained by combining measured dissociation rates with equilibrium constants. The shock tube studies were interpreted to mean that k_6 varies inversely with temperature.

The decay of radicals in fuel-lean gas was investigated by Kaskan[45] under conditions where [OH] was considerably larger than any of [H], [O], or $[H_2]$. He simplified equation (2) to

$$-d[OH]/dt = \text{recombination rate},$$

and reported that

$$-d[OH]/dt \sim 4 \times 10^{10}[OH]^2 \text{ mole cm}^{-3}\text{ s}^{-1} \tag{3.5}$$

at 1 and at 0·45 atm. He could suggest no satisfactory interpretation for (5) and pointed out that a production of $O + H_2O$ or of $O_2 + H_2$ from 2OH is no recombination because it only exchanges species in the pool. Recently he remarked that a decay of [OH] proportional to $[OH]^3$ would also agree with his measurements. If the recombination had actually involved the process, known to occur at lower temperatures,

$$H + O_2 + H_2O \xrightarrow{k_4} HO_2 + H_2O \tag{2.4}$$

and if this had been followed by a destruction of HO_2 by any of

$$HO_2 + (O, OH, H) \rightarrow O_2 + (OH, H_2O, H_2)$$

or by

$$HO_2 + H \rightarrow 2OH$$

then

$$-d[OH]/dt = 4k_4[H][O_2][H_2O] = 4k_4\left\{\frac{K_3}{K_1K_2}\right\}[OH]^3 \tag{3.6}$$

The factor 4 is the number of OH radicals or the equivalent which are recombined for each occurrence of (2.4), and the equilibrium constants are from equations (2.8), (2.9), and (2.10). The reported values of the constant in equation (5) can be converted into values of k_4 since the range of [OH] was given for each run. Using the average [OH] in each of the 22 leanest runs to make this conversion, one finds that the data are consistent with

$$k_4 \sim 1 \text{ to } 2 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$$

which is some five times smaller than the known value of k_4 at 800°K.[56] The possible error in [OH] could give a compounded error in k_4 of a factor of five.

A value for k_4 of the same order can also be inferred from Fristrom's[24] work in the post-flame gas of a very fuel-lean CH_4–O_2 flame at 1/20 atm. This gas should not differ from the burnt gas of an H_2–CO–O_2 flame except for a lower level of radical concentrations and the possibility that the balancing reactions might become established more slowly. In particular, the CO analog of (2.3) which will be discussed in the next section,

$$CO + OH \rightleftarrows CO_2 + H$$

might balance more slowly. To estimate k_4 from his data, it must be supposed that [H], [OH], and [O] were related by the three balanced reactions (2.1), (2.2), and (2.3); and while Fristrom himself did not think these reactions balanced, they must not have been badly out of balance either. A really serious imbalance is equivalent to saying that O_2 or H_2O were still being rapidly formed or destroyed, and such was not observed. At 1600°K, he reported the measurements.

$$-d[O]/dt = 3{\cdot}7 \times 10^{-7} \text{ mole cm}^{-3} \text{ s}^{-1}$$
$$-d[H_2]/dt = 1{\cdot}7 \times 10^{-7}$$
$$-d[CO]/dt = 14 \times 10^{-7}$$

On the balancing assumption, it can be calculated that

$$-d[OH]/dt = 1{\cdot}7 \times 10^{-7}$$
$$-d[H]/dt = \text{zero}$$
$$[H][O_2][H_2O] = 9 \times 10^{-24} \text{ mole}^3 \text{ cm}^{-9}$$

For his gas, the data do not suggest that (2) can be simplified to $-d[OH]/dt$ only. Writing equation (2) as

$$-d\{[OH] + 2[O] + 2[H_2]\}/dt = 4k_4[H][O_2][H_2O]$$

the data give

$$k_4 = 3 \times 10^{16}\ \mathrm{cm^6\ mole^{-2}\ s^{-1}}$$

If the CO reaction had been balanced, $-2\,\mathrm{d[CO]/d}t$ would have had to be included in the pool, and k_4 would then have been 11×10^{16}. Probably the CO reaction was neither balanced nor yet irreversible, and k_4 lay between the extreme values. Fristrom's work therefore suggests a k_4 which agrees approximately with the recalculation of Kaskan's data, though it refers to a much leaner gas and to a pressure only 1/10 as large.

It is concluded that the radicals decay primarily by reactions (2.6) and (2.7) in H_2-rich gas and perhaps at a rate proportional to (2.4) in lean gas. For (2.4) to lead to recombination, however, it must be followed by another reaction which consumes the HO_2; and since such a process remains unproven in flames, the decay of the radicals in lean gas is uncertain.

Carbon Oxides in Post-Flame Gas

By adding CO_2 to fuel-rich H_2–O_2 flames of final temperature only 1200–1350°K, the water gas reaction

$$H_2 + CO_2 = H_2O + CO \tag{3.7}$$

was found not to be equilibrated in the post-flame gas, and the approach towards equilibrium could be followed by sampling the gas as it moved downstream.[57] If the mechanism of this reaction is a combination of

$$OH + H_2 \rightleftarrows H_2O + H \tag{2.3}$$

which is known to be balanced, at least over most of this temperature range, and of (8)

$$OH + CO \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} CO_2 + H \tag{3.8}$$

$$K_8 = k_8/k_{-8}$$

the establishment of the water gas equilibrium is only the establishment of a balance for (8), and can be represented by

$$-\mathrm{d[CO_2]/d}t = k_{-8}[\mathrm{H}][\mathrm{CO_2}]\left\{1 - \frac{K_8[\mathrm{CO}][\mathrm{H_2O}]}{K_3[\mathrm{H_2}][\mathrm{CO}]}\right\}$$

From measurements of all other quantities in this expression, Fenimore and Jones obtained $k_{-8}[\mathrm{H}]$, and from simultaneous determinations of k_{-3}[H] by equation (2.12) when heavy water was added to the reactants, the ratio was found

$$k_{-8}/k_{-3} \sim 0{\cdot}11\text{–}0{\cdot}17 \text{ at } 1200\text{–}1350°\text{K}$$

At temperatures above 1350°, the water gas equilibrium was established too quickly to be followed very conveniently at 1 atm, and it appeared that reaction (8) would always be quickly balanced in rich post-flame gas from H_2–O_2–CO_2 flames when the temperature was 1500°K or more.

The work of Friedman and Nugent[58] suggests that (8) also becomes balanced in lean gas at 1600–1800°K. They probed low pressure, lean CO–O_2–H_2 and CO–O_2–H_2O flames, and concluded,

> *The flame reaction consists of a rapid step associated with intense luminosity, followed by a much slower process in which the last of the* CO *is consumed. An assumption that the reaction rate decreases linearly with decreasing* [CO] *does not account for this effect. . . . Traverses show the temperature to be rising through the region in question, so the effect cannot be attributed to cooling. . . .*

This quotation describes very well the observations to be expected if (8), initially unbalanced, becomes balanced in the post-flame gas so that the last of the CO is a part of a pool of species decaying at a rate determined by the recombination of radicals.

In two papers Kaskan investigated carbon oxides in post-flame gas by optical methods, using the blue emission attributed to

$$CO + O \rightarrow CO_2 + h\nu$$

First[59] he measured [OH] in absorption in rich gas from H_2–CO–O_2 flames, and simultaneously measured the emitted intensity. [O] was calculable from

$$[O] = K_3[OH]^2/K_2[H_2O]$$

by virtue of (2.9) and (2.10). [CO] was calculated from the water gas equilibrium which must have held, the gas temperature being 1520–1880°. He could then compare the emitted intensity with the product [O][CO]. A very good proportionality was observed and, supposing that the total quanta emitted were twice those between 3500 Å and 6000 Å, he concluded that about 5×10^{-10} of the collisions of CO with O atoms radiated.

In a second paper,[60] he measured the intensity emitted from lean gas where CO was no longer a major constituent. If (8) were balanced,

$$[CO] = [CO_2][H]/K_8[OH] = \frac{K_3[CO_2][OH]^2}{K_1K_2K_8[O_2][H_2O]}$$

The intensity, being proportional to [CO][O], should now depend on $[OH]^4$ rather than on $[OH]^2$ as in fuel-rich gas. Measurements of intensity and of [OH] were in fact related in this way in lean gas from 1510 to 2000°K, 1/3–1 atm, and independently of whether the flame reactants were H_2–air–CO or H_2–air–CO_2. A gas at 1440°K did not fit the relation and might have reflected the incipient breakdown of the balance of (8) as the temperature became too low.

Estimates of the product [O][CO] by the emitted intensity have been used[61] to investigate the state of the gas behind detonations under more extreme conditions, to about 3400°K and 4 atm.

The work summarized above indicates that in the post-flame gas from H_2 flames containing CO or CO_2, (8) is quickly balanced at 1500°K or more, but not at somewhat lower temperatures. CO is a universal intermediate in hydrocarbon–oxygen flames, and it seems appropriate to add that radical concentrations are generally larger in gas from H_2 flames than in gas from hydrocarbon flames, so it is not necessarily true that a balance of (8) would be established as easily in the post-flame gas from hydrocarbon flames. It was mentioned above that Fristrom finds it unbalanced in gas from lean CH_4 flames.

In the studies of the O + CO radiation, it was not clear if the reaction involved a third body. Clyne and Thrush[62] investigated the emission at lower temperatures with particular reference to this point by mixing O atoms from a discharge with CO and various inert gases. The intensity was always proportional to [O][CO] and the proportionality constant was independent of the pressure of any particular inert gas, but different for different inert gases. The relative intensity was 1·0, 0·9, 0·7, or 0·5 when the inert gas was O_2, N_2, Ar, or He respectively. They concluded that the emission could be explained by

$$O + CO + M \xrightarrow{k'} CO_2^* + M$$

$$CO_2^* + M \xrightarrow{k''} CO_2 + M$$

$$CO_2^* \xrightarrow{k} CO_2 + h\nu;$$

and that the quenching of excited CO_2^* was always much more frequent than emission. Hence the emitted intensity

$$\mathrm{I} = k\left\{\frac{k'}{k''}\right\}[\mathrm{O}][\mathrm{CO}]$$

was independent of [M] for any particular species, but the ratio $\{k'/k''\}$ might change when [M] was changed from one species to another. Their intensities depended on temperature,

$$k\{k'/k''\} = 10^{6\cdot6\pm0\cdot4}\ \mathrm{e}^{-(3\cdot7\pm0\cdot5)\mathrm{kcal}/RT}\ \mathrm{cm^3\ mole^{-1}\ s^{-1}}$$

when $[\mathrm{M}] = [\mathrm{O_2}]$. An extrapolation of this expression to flame temperatures gives a rate constant of 10^6 as compared to Kaskan's observed value in flames of about 2×10^5 with different M species. The discrepancy is within the combined experimental error; but agreement between these estimates is meaningless unless the radiation has the same origin in both experiments. The blue radiation is a discrete system of "CO flame bands" at low temperatures, but is largely the "CO continuum" in flames on which the flame bands are merely superimposed; and the implication of agreement is that the continuum is an unresolved band system. Colloman and Gilby[270] have confirmed that this is so; under high resolution, the "CO continuum" in flames shows dense rotational fine structure with no evidence for a true continuum at all.

The overall process involves a spin reversal and Clyne and Thrush suggested that the CO_2^* is formed initially in a stable triplet state which undergoes a radiationless transition to an excited singlet CO_2^*. In the mechanism above, therefore, CO_2^* means two different things. In the stabilization of excited CO_2^* by a third body it is the stable triplet, but in the other two reactions it stands for excited singlet CO_2^*. The transition between the two multiplicities, though forbidden by the spin conservation rule, was thought to be easy and not rate determining.

Previous work on the radiation was discussed by Gaydon[63], who favoured the alternate interpretation that the spin reversal might occur at some other time than that proposed by Clyne and Thrush. He thought the emission might be a transition between a triplet state and the singlet ground electronic state of CO_2. The most recent study of the CO flame bands, however, suggests that the upper state of the transition is singlet.[271] It is a bent molecule of equilibrium angle 123 ± 3°, and of energy about 8 ± 1 kcal higher than the energy of $\mathrm{CO} + \mathrm{O}(^3\mathrm{P})$. The emission arises from transitions into high vibrational levels of the linear ground electronic state; and is associated with the absorption spectrum of carbon dioxide at about 1500 Å which occurs far in the ultraviolet because the absorption originates from low vibrational levels of the ground electronic state.

Nitrogen Oxides

The use of the greenish O + NO emission as a test for O atoms in flames was proposed by Gaydon, who has also described the qualitative observations.[63] Kaskan's work referred to in the last chapter[43] led to a rate constant for $I = k[\mathrm{O}][\mathrm{NO}]$ of about $1{\cdot}2 \times 10^6$ cm^3 mole^{-1} s^{-1}. This is twelve times smaller than the yield observed by Kaufman[64] at room temperature, but the difference may be partly explained by Clyne and Thrush's[62] finding that the emission from NO + O differed from that of CO + O chiefly in having a small negative activation energy of $-1{\cdot}2 \pm 0{\cdot}4$ kcal mole^{-1}. The pre-exponential factor for the emitted intensity was about the same as for CO + O and the emission was thought to go by the same kind of mechanism as that just outlined except that spin reversal was not necessary for NO + O.

Nitric oxide is very stable against decomposition to N_2 in the post-flame gas from hydrogen flames.[1,65] Even in the flames themselves, the evidence suggests that it decomposes only at high temperatures by a mechanism the same as or very similar to the thermal decomposition of pure nitric oxide.[65] The gas phase thermal decomposition of nitric oxide has been worked out by other means not involving flames; there are two mechanisms. One of these is[66,67,68]

$$\mathrm{O} + \mathrm{NO} \rightleftarrows \mathrm{N} + \mathrm{O_2} \tag{3.9}$$

$$\mathrm{N} + \mathrm{NO} \rightleftarrows \mathrm{O} + \mathrm{N_2} \tag{3.10}$$

the other is[69]

$$2\mathrm{NO} \rightarrow \ldots \rightarrow \text{eventually } \mathrm{N_2} + \mathrm{O_2} \tag{3.11}$$

which predominates at temperatures below about 1600°K when [N] is extremely small and (9) and (10) therefore unimportant. The detailed course of (11) will be discussed below. The reactions (9), in the reverse direction, and (10), as written, can be studied at low temperatures with N atoms generated in discharges. The over-all process represented by (11) can be studied in static systems. From such experiments, the expected rate of either mechanism can be calculated at flame temperatures and compared with the decomposition rate observed.

Small amounts of NO when present in post-flame gas at 2200°K or more suffer a slow decomposition[70] which is much faster, however, than that expected to occur by (11). The decomposition has the dependence on gas composition and about the rate expected if it could be supposed that (9), or some indistinguishable equivalent reaction such as $H + NO = N + OH$, was balanced; so that

$$[N] = K_9[O][NO]/[O_2]$$
$$-d[NO]/dt = 2k_{10}[N][NO]$$

There is considerable doubt, however, whether (9) or one of its variants could have been balanced in fuel-rich post-flame gas, and more work in such mixtures would be worthwhile.

Nitrous oxide cannot be obtained in the post-flame gas from fuel-rich mixtures, for it reacts in the flame about as quickly as molecular oxygen does. It can be readily obtained in moderately low temperature fuel-lean gas, however, where it decomposes partly by

$$O + N_2O \rightarrow 2NO \qquad (3.12)$$

and mostly by other reactions. (12) can be followed independently of the other processes because NO is inert under the conditions used. By measuring [O], $[N_2O]$, and d[NO]/dt, k_{12} can be obtained,

$$d[NO]/dt = 2k_{12}[O][N_2O]$$

The result was[71]

$$k_{12} = 1 \times 10^{14}\, e^{-28\,\text{kcal}/RT}\ \text{cm}^3\ \text{mole}^{-1}\ \text{s}^{-1}$$

with estimated uncertainties of about a factor of two in the absolute value of 1700°K, and ± 3 kcal in the activation energy. Reaction (12) has also been examined[72] by mixing O atoms from a discharge with N_2O and running the mixture through a furnace heated to various temperatures in the range 770–1070°K. The reaction was followed by the glow due to the interaction of $O + NO$. The experiment was considered inaccurate because of the many corrections required; and the 21 kcal mole^{-1} obtained for the activation energy was judged not to be inconsistent with the 28 ± 3 from flames.

The numerical value obtained for k_{12} has a bearing on the detailed mechanism of reaction (11). This bimolecular decomposition of nitric oxide might go either by a direct formation of the final products in a four-centre reaction, $2NO \rightarrow N_2 + O_2$, or might be controlled by the rate of the reverse of reaction (12), $2NO \rightarrow N_2O + O$, with a subsequent decomposition of N_2O and recombination of O atoms. In the latter case, the rate constant found experimentally[69] for (11) should also be calculable from the measured value of k_{12} and from the equilibrium constant k_{12}/k_{-12}. The experimental and calculated rate constants do agree and therefore it seems that the bimolecular NO decomposition goes at the rate of the reverse of reaction (12).

Some other Chemiluminescent Effects

When the radiation from flames is studied, the question comes up whether the emitting species are thermally equilibrated with species in the lower state of the transition or if the emitters are formed chemically in the excited state which then radiates; in short, whether the radiation is thermal or chemiluminescent. A decision is possible if the concentrations of the species in both states of the transition can be measured—for thermal excitation, the concentrations are related by the equilibrium constant. H_2–O_2 flames offer examples of both kinds of radiation. The emitters seem to be equilibrated[63] in the ultraviolet radiation from electronically excited O_2 and in the vibration–rotation infrared radiation from hot H_2O, both of which extend into the visible. But other radiations are observed which are not thermal.

The radiation of excited $OH^{*2}\Sigma^+$ in hydrogen flames is an example of non-thermal radiation. Charton and Gaydon[73] had suggested the association $O + H \rightarrow OH^*$ as a source of excitation of the $v' = 2$ and 3 vibrational states of the electronically excited level. Kaskan[74] attempted a quantitative test of the source of OH^* by measuring ground state $OH^2\pi$ in absorption and also the emission intensity from the first four vibrational levels of OH^*. In each case the intensity was found to be proportional to $[OH]^3$. A sample of his data in Fig. 3.1 shows the intensity of the O—O band as a function of ground state [OH] in nine flames. The post-flame gases were followed 0·5–1·5 cm downstream to get the variation in I_{00}/l as [OH] decayed. The temperatures were 1260–1610°K in these runs. The open symbols refer to measurements at 1 atm, the solid ones to 1/3–1/6 atm. The lines on the log–log plot are drawn with a slope of three, and it is seen how well the proportionality is obeyed. If OH^* had been thermally excited, the lines would have had a slope of one. Using the relations among the balanced radicals, [H], [OH], and [O], Kaskan could list all possible reactions which would be energetic enough to excite OH^* and would also be proportional to $[OH]^3$. He supposed that OH^* would be quenched by $OH^* + M \rightarrow OH + M$ much more often than it could radiate,[75] and could then write out the expected dependence of the emission on the concentrations of $[H_2]$ and $[H_2O]$ for each possible reaction. The expressions obtained were so much alike that a choice among them was impossible, except that definite evidence was obtained for an excitation by reaction (13) to the $v' = 2$ vibrational level. On the grounds that only the most exothermic reactions would give the non-equilibrium population ratios observed in the vibrational levels, reactions (14) and the odd looking (15) would be preferred; and it was suggested that (14) excites most of the emission except for that due to (13).

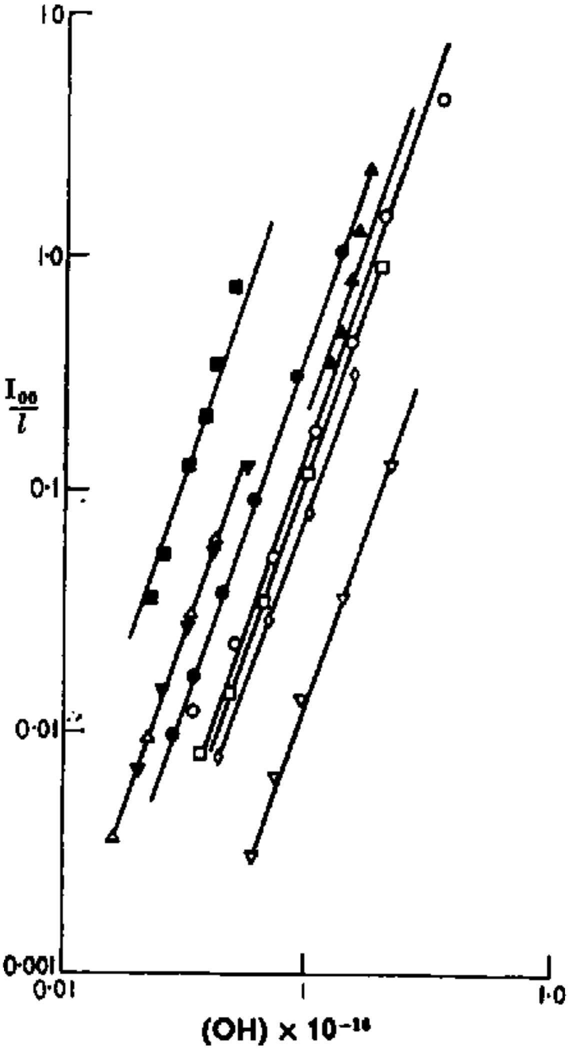


FIG. 3.1. Intensity of the $OH^* \rightarrow OH$, 0—0 band per unit of optical path as a function of ground state [OH], in molecules cm^{-3} (Kaskan[74]).

$$O + H \rightarrow OH^* \tag{3.13}$$

$$H + OH + OH \rightarrow OH^* + H_2O \tag{3.14}$$

$$O + H_2 + OH \rightarrow OH^* + H_2O \tag{3.15}$$

Another example of chemiluminescent radiation is the blue continuum of H_2–O_2 flames, investigated most recently by Padley.[272] It extends from about 2200–6000 Å with a broad maximum in intensity around 4500 Å. In a variety of fuel-rich post-flame gases, it decayed with time in the same way as $[H]^2$ did—or as quantities proportional to $[H]^2$. Its dependence on $[H_2]$ and $[H_2O]$ suggested that the intensity was proportional to $[OH][H]$ or to the indistinguishable $[O][H_2]$, of which the former was thought more reasonable. It was not determined if the preferred $H + OH \rightarrow H_2O + h\nu$ required a third body. Similar continua can be obtained[200] by adding small amounts of halogens to hydrogen flames; and if it is supposed that $H + HZ = H_2 + Z$ is balanced, where Z represents a halogen atom, the intensity is found to correlate with the product $[H][Z]$.

Examples of both thermal and chemiluminescent excitation are shown by Fig. 3.2 from Padley and Sugden[76] in which measurements

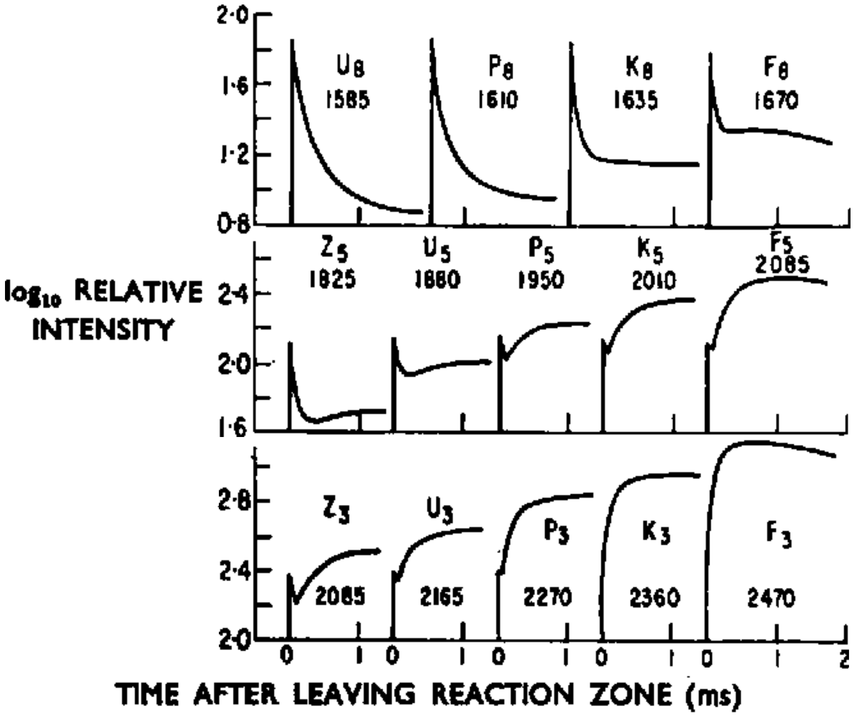


FIG. 3.2. Sodium D-line intensity vs. time for post-flame gases containing a constant trace amount of added NaCl. The reversal temperature for each flame is given, as estimated when the curve became horizontal. The letters and subscripts give the composition of the H_2–N_2–O_2 mixtures fed to the burner. For F, K, P, U, Z, H_2/O_2 fed was 2·5, 3·0, 3·5, 4·0, 4·5 respectively. The subscript gives the ratio of N_2/O_2 fed. From Padley and Sugden.[76]

of the intensity of the sodium D-lines in H_2-rich post-flame gas are plotted against time. About 1 ms from the reaction zone, a nearly steady intensity was reached and the reversal temperature measured at this time is quoted for each flame. This was considered the actual gas temperature as would be measured by a thermocouple. Before the steady intensities were reached, most flames showed a short region of increasing intensity which was attributed to heat evolved in exothermic radical recombinations. In the lower temperature flames, where the final thermal emission was small, strong spikes became predominant. These could scarcely arise from thermal excitation. The peak intensity of the spikes varied by a factor of less than four in all the flames, while the final thermal intensity varied by a factor of 400. The small change in the intensity of the spikes resembles the slight change in the actual radical concentrations in H_2 post-flame gas at various temperatures, and the authors showed that the spikes could be accounted for by the excitation processes,

$$H + H + Na \rightarrow H_2 + Na^* \tag{3.16}$$

$$OH + H + Na \rightarrow H_2O + Na^* \tag{3.17}$$

If [H] was balanced with [OH], the non-thermal radiation should have depended on $[H]^2$ for either process. Estimates of [H] and of the emitted intensity at low temperatures satisfied this proportionality. The relation (18) has been used to estimate relative [H] in some very low temperature flames where any thermal emission was negligible,[50]

$$I_{Na} \text{ proportional to } [H]^2 \tag{3.18}$$

In the experiments represented by Fig. 3.2, it was supposed that all the added NaCl was present as free metal atoms in the gas. Hence the thermal emission of the D-lines should depend only on temperature and not on the gas composition, as is shown for flames F_5 and Z_3 in the figure. Contrary evidence exists in the literature; Minkowski *et al.*[77] found that a part of added NaCl did not appear in rich gas as free Na atoms, though the fraction is not enough to call the interpretation of Fig. 3.2 into question. When lithium or gallium was added to fuel-rich flames under high temperature conditions where thermal excitation was probable, Sugden and his co-workers found that the intensity of the atomic lines depended markedly on gas composition and it was concluded that much of the metal was present as a compound. Thus as discussed in the last chapter, the variation of intensity of lithium lines was explained by the equilibrium

$$LiOH + H = Li + H_2O$$

In fuel-lean gas, even sodium must be mostly a compound; anyone who has measured reversal temperatures in lean gas from low temperature flames knows how difficult it is to get enough Na atoms to see the D-lines clearly.

Padley and Sugden suggested that processes analogous to (16) and (17) also accounted for the chemiluminescent excitation of other added metals. No energy level was excited, from iron for example, which required much more than the 118 kcal available from (17). The chemiluminescent excitation of low energy radiation was always swamped by equilibrium thermal excitation, as in Fig. 3.2, when the temperature was raised enough. But it was not possible to raise the temperature sufficiently if the excitation required nearly the whole 104–118 kcal available.

Molecular spectra obtained in emission when metals are added to H_2-rich flames often depend strongly on the gas composition and the probable nature of the emitter can be inferred from the dependence. The familiar flame colours, orange from added calcium, red from strontium, green from barium, were suggested to be due to triatomic CaOH, etc., on this basis,[78] and the suggestion was subsequently confirmed in other ways.[79] Also in this way, the green copper bands were identified as due to CuOH. The intensity of the CuH bands was found[49] to be proportional to the product [Cu][H], added Cu being considered present mostly as free atoms and [H] being determined by the Li method; and the CuH emission has been much used as a secondary means of estimating [H]. It was believed at first that the molecular spectra were thermally excited; but this notion has been abandoned. The spectra are considered to be excited by chemiluminescence and to have nothing to do with the amount of CuOH, CaOH, MnOH, etc., present in the gas.[80]

The Boron "Fluctuation" Bands

Kaskan and Millikan[81] demonstrated that the green bands characteristic of flames containing boron compounds are emitted by the BO_2 radical. In the post-flame gas from mixtures containing trimethyl borate, they could show by infrared emission spectra that most of the boron was present as HBO_2, with about 3 per cent present as B_2O_3 in typical cases, as would be expected from equilibrium considerations. This distribution of the bulk of the boron was almost independent of time as the gas flowed downstream, and was essentially the same in fuel-rich as in fuel-lean gas. The concentration of the emitter depended markedly on gas composition, however. It was measured by absorption in one of the stronger of the fluctuation bands, [OH] was measured by absorption also, and these two concentrations were always proportional to one another over the 50-fold or so change in [OH] which could be obtained in various post-flame gases. Changes of this magnitude in the concentration of the emitter were inconsistent with its identification as B_2O_3, but were compatible with its identification as BO_2 and the equilibrium

$$HBO_2 + OH = H_2O + BO_2 \tag{3.19}$$

or with indistinguishable variants of (19) such as $OH + B_2O_3 = HBO_2 + BO_2$ or $HBO_2 + H = H_2 + BO_2$. The assignment to BO_2 was checked by experiments in which the green bands were studied in the gas over molten, dry B_2O_3 in a furnace and shown to depend on the oxygen pressure according to[82, 83]

$$\tfrac{1}{2}B_2O_{3(\mathrm{liquid})} + \tfrac{1}{4}O_2 = BO_{2(\mathrm{gas})}$$

From the temperature dependence of BO_2, ΔH for reaction (19) was estimated to be roughly -16 kcal mole^{-1}, and therefore $\Delta H_{BO_2} \sim -84$ kcal mole^{-1}. From the furnace experiment,[82] $\Delta H_{BO_2} \sim -74$ kcal mole^{-1}. Johns[273] has presented a detailed analysis of the flame bands, obtained by flash photolysis of mixtures of boron trichloride and oxygen, and shown that they arise from two electronic transitions in the linear symetric BO_2 molecule.

The chemical applications of the post-flame gas from H_2–O_2 flames are due to its content of one or a few per cent of free radicals; to the balancing reactions which allow one radical concentration to be inferred from another, and also allows considerable variation in relative [H], [OH], and [O]; and to the possibility of controlling the temperature independently of the gas composition. The chief limitation is that one radical species cannot be obtained cleanly. Hence in studying the recombinations of H + H and H + OH, it was impossible to distinguish between

$$H + OH + H_2 \rightarrow H_2O + H_2$$

$$H + H + H_2O \rightarrow H_2O + H_2$$

because of the nature of the balancing reactions.[49] Also, a reaction such as

$$O + O + M \rightarrow O_2 + M$$

has not been measured in the post-flame gas, nor is it apt to be because of interference by the reactions of O atoms with other species present.

CHAPTER 4

RATE CONSTANTS IN HYDROGEN–OXYGEN FLAMES

THE constants for the elementary reactions in H_2–O_2 mixtures can be measured in flames. In this chapter, the values obtained are compared with those found by other techniques, and a list is given in Table 4.1 for occasional reference hereafter. The data for three of the constants are also plotted in Fig. 4.1 in Arrhenius form.

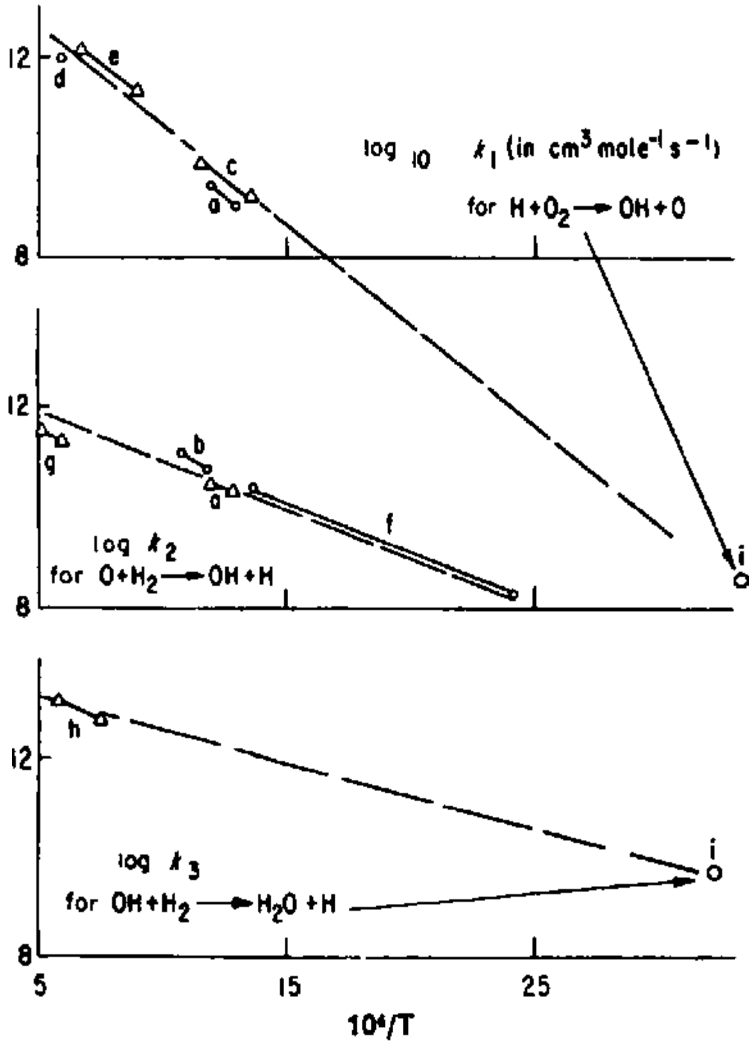


FIG. 4.1. Some recent estimates of rate constants. Key: a, Baldwin[35]; b, Azatian, Voevodskii, and Nalbandian[36]; c, Karmilova, Nalbandian, and Semenov[37]; d, Schott and Kinsey[38]; e, Fenimore and Jones[39]; f, Clyne and Thrush[40]; g, Fenimore and Jones[41]; h, Fenimore and Jones[42]; and i, Del Greco and Kaufman.[44]

Values of k_3

$$OH + H_2 \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} H_2O + H \tag{2.3}$$

Fenimore and Jones[43] measured the product $k_3[H]$ in the post-flame gas by the exchange of H_2 with D_2O as was described in chapter 2; the k_3 deduced from their k_{-3} when $[H] \sim [H]_{equ}$ is probably correct within the limits $k_3 = 1{\cdot}5 \pm 0{\cdot}8 \times 10^{13}$ cm^3 mole^{-1} s^{-1} at 1600°K. They did not determine the temperature dependence, but assumed $E_3 \sim 10$ kcal mole^{-1} from experiments at lower temperatures[34] in which OH from a discharge through water vapour was allowed to react with H_2. Del Greco and Kaufman[44] have proved the water discharge a treacherous source for OH, however, so $E_3 \sim 10$ kcal has no valid basis. These authors prepared OH in a dependable way, by mixing H atoms from a discharge with NO_2,

$$H + NO_2 \rightarrow NO + OH$$

and measured various reactions of OH near room temperature, reaction (2.3) among them. Their estimate of $k_3 = 4 \pm 1 \times 10^9$ at 310°K combines with the result near 1600° to give the rate constant listed in Table 4.1 which is probably good to a factor of two at flame

TABLE 4.1

Rate Constants, probably Valid within a Factor of Two at Flame Temperatures

$k = A\,e^{-E\,\text{kcal}/RT}$; units are mole cm^{-3} and s

Rate constant	Reaction	A	E
k_1	$H + O_2 \rightarrow OH + O$	4×10^{14}	18
k_2	$O + H_2 \rightarrow OH + H$	9×10^{12}	9
k_3	$OH + H_2 \rightarrow H_2O + H$	7×10^{13}	6·1
k_8	$OH + CO \rightarrow CO_2 + H$	$k_8 \sim 0{\cdot}08\, k_3$ at 1200–1350°K	
k_4*	$H + O_2 + H_2O \rightarrow HO_2 + H_2O$	$\sim 5 \times 10^{16}$	~ 0
k_6†	$H + H + M \rightarrow H_2 + M$	$\sim 0{\cdot}2 \times 10^{16}$	~ 0
k_7‡	$H + OH + M \rightarrow H_2O + M$	$\sim 5 \times 10^{16}$	~ 0
k_α	$H + N_2O \rightarrow N_2 + OH$	3×10^{14}	16

* This is of the order of k_4 at 800°,[58] and not incompatible with the rough value suggested in chapter 3. But it certainly might be worse than right to a factor of two.

† $-d[H]/dt = 2 \times k_6[H]^2[M]$. [M] is considered to be the whole gas concentration.

‡ $-d[H]/dt = -d[OH]/dt = k_7[H][OH][M]$. [M] considered to be the whole gas, and the constant taken to be $\sim 24 \times k_6$.

temperatures. Dixon-Lewis and Williams[50] also obtained an approximate estimate of k_{-3} at 1072°K. They measured k_{-3}[H] late in a flame by the exchange reaction with D_2O, and [H] early in the same flame from the exchange of H with D_2, the latter reaction having a known rate constant.[85] These two regions did not overlap, but were bridged by measuring relative [H] in both regions from the chemiluminescent excitation of sodium according to equation (3.18). Their value, $k_{-3} = 5 \times 10^9$, is consistent with the other data; although they thought this an upper limit, while from Table 4.1 and the equilibrium constant in equation (2.10), $k_{-3} = 8 \times 10^9$ at 1072°.

Values of k_1

$$H + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} OH + O \qquad (2.1)$$

The experimental data for k_1 in flames are temperature and composition profiles obtained by fairly standard methods,[23] and there is no difficulty in evaluating $-d[O_2]/dt$ and $[O_2]$. On the condition that only reaction (2.1) is important in consuming O_2 and that the reverse of (2.1) is negligible, as can be assured through most of the reaction zone by using fuel-rich mixtures, $-d[O_2]/dt = k_1[H][O_2]$ and k_1 can be inferred if [H] is known. In any estimate published so far, only approximate values of [H] have been obtained by assumptions which could not be strictly true. The assumption made here is that [H] is constant through the reaction zone of a low pressure H_2–O_2 flame.

This assumption is not a very bad one. Gaydon and Wolfhard[86] concluded that the diffusion of H atoms should be easy over distances of the order of the flame thickness though not over a much greater distance. Some experimental support for it can be obtained from estimates of [H] on both sides of the flame;[87] by the fast exchange of H with D_2 early in the reaction zone, and by the slow exchange with D_2O in the post-flame gas. The two [H] are not very different and a much greater value between the regions of measurement seems unlikely.

Figure 4.2 shows traverses through a fuel-rich H_2–N_2O–air flame containing added N_2, burnt at 6 cm of mercury pressure. A diffusion coefficient from Ref. 28 appropriate to a gas entirely of N_2 was used in calculating G_{N_2}, and one appropriate to a binary mixture of N_2–O_2 was used in calculating G_{O_2}. The G are plotted at the bottom of the figure, and $-d[O_2]/dt$ and $-d[N_2O]/dt \sim d[N_2]/dt$ were computed from them by equation (1.3). The curves for HD, which extend into the post-flame gas, gave k_{-3}[H] just downstream of the reaction zone; and by hypothesis [H] was the same in the flame zone also. The k_1 obtained for a k_{-3} which conforms to the k_3 of the last section are plotted as segment "*e*" at the top of Fig. 4.1.

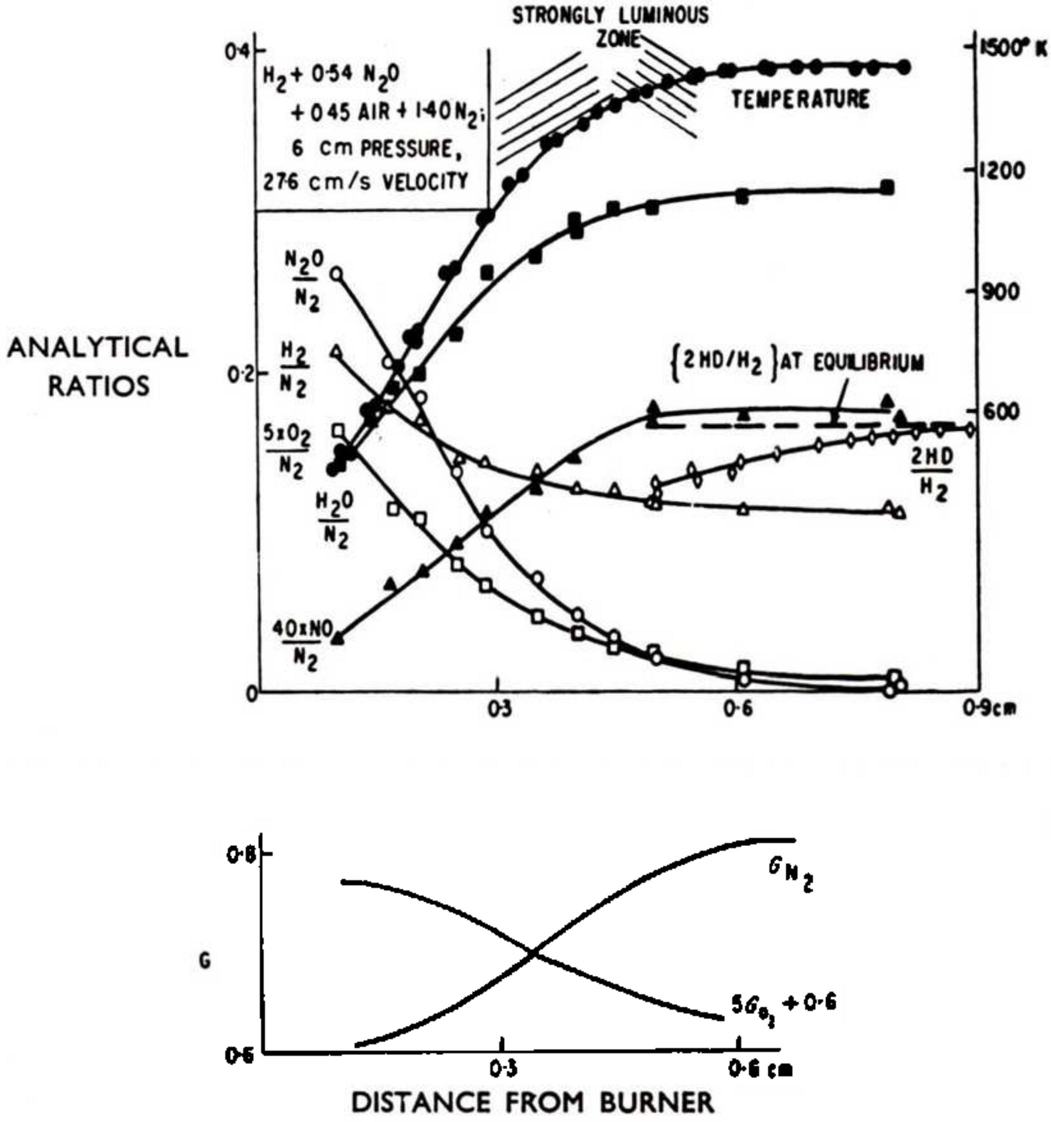


FIG. 4.2. Traverses through a low-pressure flame (Fenimore and Jones[87]).

A possible complication which was not considered is that reaction (2.4)

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad (2.4)$$

might also consume oxygen and lead to too large an estimate of k_1. However, if k_4 has a value of 5×10^{16} cm^6 mole^{-2} s^{-1} when $[M] = [H_2O]$, and is 1/10 as large for other [M], $k_4[M]$ would be negligible compared to k_1 at 1200° in the flame described by Fig. 4.2. At much lower temperatures or higher pressures, (2.4) would have to be taken into account.

Other estimates of k_1 are also plotted in Fig. 4.1. The segments labelled "*a*" and "*c*" were obtained from explosion studies and were discussed very briefly in chapter 2. "*d*" is from estimates of the rate of branching in H_2–O_2–Ar mixtures heated in a shock tube. Schott and Kinsey[88] found experimentally that the time required for [OH] to develop sufficiently in the heated gas to be detectable by ultraviolet absorption was related to $[O_2]$ and to temperature by the equation

$$[O_2]t = 2{\cdot}3 \times 10^{-14}\, e^{(18{\cdot}1 \pm 2{\cdot}9)\mathrm{kcal}/RT}\ \mathrm{mole\ cm^{-3}\ s} \tag{4.1}$$

Assuming that during this induction period, the chains developed by reactions (2.1), (2.2), and (2.3), of which the first was supposed to be much the slowest,

$$\mathrm{d[H]/d}t = 2k_1[\mathrm{H}][O_2]$$

This integrates to

$$2k_1[O_2]t = 2{\cdot}3 \log\left\{\frac{[\mathrm{H}]}{[\mathrm{H}]_0}\right\} \sim 2{\cdot}3 \log\left\{\frac{[\mathrm{OH}]}{[\mathrm{OH}]_0}\right\} \tag{4.2}$$

Where $[\mathrm{H}]_0$ is the concentration at zero time when the generation of radicals by reaction (2.1) was equal to their generation by some poorly understood initiation process. From (1) and (2),

$$k_1 = 0{\cdot}5 \times 10^{14}\, e^{-18{\cdot}1/RT} \times \log\left\{\frac{[\mathrm{H}]}{[\mathrm{H}]_0}\right\} \tag{4.3}$$

The measurements were made over the range 1100–2600°K. Those at 1650° were thought to be most free of complications; and the value plotted as "*d*" was obtained when $\log\{[\mathrm{H}]/[\mathrm{H}_0]\}$ was set equal to 7·1, this choice being more or less arbitrary. For an approximate estimate of k_1, however, any conceivable choice is all right; the k_1 would be unchanged within a factor of two if [H] or [OH] increased by any factor between 10^4 and 10^{14} during the induction period. The assumption $k_1 \ll k_2$, made to derive (2) is now known to be false at 1650° but k_1 should still be approximately correct.

The complication encountered by Schott and Kinsey was that at temperatures above 1700°K the values of $[O_2]t$ were not really independent of mixture composition as stated by (1). A partial explanation is that reaction (2.1) was not sufficiently slow compared to (2.2) at higher temperatures; but the authors suggested a more interesting origin since the complication appeared when the induction times were comparable to the times which might be required to excite molecular oxygen vibrationally. If oxygen must be excited to undergo (2.1), this would never be known under ordinary circumstances but the rate of reaction might become limited by vibrational relaxation of O_2 when reaction was sufficiently fast. While the shock tube results do not provide real evidence for it, the suggestion is interesting because it requires that the reverse of (2.1) be written as forming vibrationally excited oxygen, $O + OH \rightarrow O_2^* + H$; and a number of exothermal atom reactions of this type are known already where the energy released appears initially as vibrational excitation of the newly formed molecule.[89]

Schott's suggestion might possibly be proved by studying the reverse reaction as Del Greco and Kaufman did.[44] They prepared OH radicals, which were not vibrationally excited, from $H + NO_2$, mixed them with O atoms from a second discharge, and measured the reverse rate constant. The equilibrium constant being known, k_1 could be obtained at about 300°K. This estimate, indicated by "*i*" in Fig. 4.1, is smaller by a factor of 10^7 than any other, but is consistent with the rest. It would be interesting if the vibrational state of the O_2 formed could be determined.

The equation of the dashed line through the various results in Fig. 4.1 is given in Table 4.1. It would be possible to change E_1 by 2 kcal and still have as good agreement as that obtained with $E_1 = 18$ kcal.

Values of k_α

The rate of consumption of N_2O in various flames[87] of quite different [H], the flame portrayed by Fig. 4.2 is one example, could always be described by

$$-d[N_2O]/dt = k_\alpha[H][N_2O]$$

with k_α very near k_1 in magnitude. This was interpreted to mean that most of the N_2O decomposed by

$$H + N_2O \xrightarrow{k_\alpha} N_2 + OH$$

and that the rate constant had the value listed in Table 1.2 within a factor of two at flame temperatures. Pure N_2O–H_2 mixtures cannot be burnt at as low temperatures as O_2–H_2 because they do not involve rapidly branching reactions and therefore possess smaller radical concentrations. The reaction above, and also the formation of NO, N_2, and O_2 from $O + N_2O$, are not particularly slow reactions in flames, however, and there is no difficulty in burning N_2O–H_2 as there is in burning NO–H_2.

Value of k_2

$$O + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} OH + H \tag{2.2}$$

The rate constant has been determined in three different ways. Baldwin[35] found that at the lower explosion limit of H_2–O_2 mixtures, either the destruction of O atoms at the wall competed with (2.2) or the destruction of OH competed with (2.3). The ambiguity arose because (2.2) and (2.3) involve $[H_2]$ in the same way; but it is now known that (2.3) is too fast for much OH to have been destroyed at the wall under the conditions used, and his result is plotted in Fig. 4.1 as "*a*". Azatian and co-workers[36] replaced most of the $[H_2]$ by [CO]. The substitution does not affect the reactions of OH very much since $CO + OH \rightarrow CO_2 + H$, (3.8), duplicates reaction (2.3), though at a slower rate; but no reaction analogous to (2.2) was thought to exist for CO and, if so, the ambiguity which troubled Baldwin was removed. Their k_2 is plotted as "*b*".

Clyne and Thrush[90] mixed O atoms from a discharge with H_2 and used the O + NO emission to follow the decrease in [O]. This straightforward method gives the long segment "*f*".

The values "*g*" were obtained from profiles through H_2–N_2–O_2–N_2O flames, using the ratios of rate constants already determined.[91] It was supposed that the decomposition of N_2O could be adequately described by the processes

$$\begin{aligned} H + N_2O &\xrightarrow{k_\alpha} N_2 + OH \\ O + N_2O &\longrightarrow 2NO \\ M + N_2O &\xrightarrow[k_\beta]{} M + N_2 + O \end{aligned} \tag{3.12}$$

of which the reaction with H atoms was the fastest by far. The straight thermal decomposition of N_2O, the last reaction, was only important at the highest temperature, and the reaction $O + N_2O \rightarrow N_2 + O_2$ could be disregarded because this is known[72] to be slower than (12). In the region in which (2.2) was measured, its reverse could be shown to be small, although neither (2.1) nor (2.3) was irreversible. [O] was near its maximum value and its net rate of formation was approximately zero. The consumption of O atoms by reaction (2.2) could then be written in terms of the observed $-d[O_2]/dt$, $d[NO]/dt$, and the calculated thermal decomposition of nitrous oxide

$$\begin{aligned} d[O]/dt \sim \text{zero} = -d[O_2]/dt - k_2[O][H_2] \\ -d[NO]/2\,dt + k_\beta[M][N_2O]. \end{aligned} \tag{4.4}$$

Since k_α, k_1, and k_3 were known, equation (5), (6), and (7) could be solved in turn from the profiles of nitrous oxide, water, and molecular oxygen to get an independent value of [O]:

$$[\mathrm{H}] \sim -\mathrm{d}[\mathrm{N_2O}]/k_\alpha[\mathrm{N_2O}]\,\mathrm{d}t \qquad (4.5)$$

$$[\mathrm{OH}] = \frac{\{\mathrm{d}[\mathrm{H_2O}]/\mathrm{d}t + k_{-3}[\mathrm{H_2O}][\mathrm{H}]\}}{k_3\mathrm{H_2}} \qquad (4.6)$$

$$[\mathrm{O}] = \frac{\{k_1[\mathrm{H}][\mathrm{O_2}] - \mathrm{d}[\mathrm{O_2}]/\mathrm{d}t\}}{k_{-1}[\mathrm{OH}]} \qquad (4.7)$$

The [O] from (4) and (7) were equated to get the k_2 plotted as "*g*" in Fig. 4.1. The result does not depend on the absolute values of k_1, k_3, and k_α but only on their ratios.

Within a factor of about two, all estimates of k_2 agree with the dashed line drawn in Fig. 4.1. The equation of this line is given in Table 4.1.

Value of k_8

$$\mathrm{OH} + \mathrm{CO} \underset{k_{-8}}{\overset{k_8}{\rightleftarrows}} \mathrm{CO_2} + \mathrm{H} \qquad (3.8)$$

If it is accepted that $k_{-8}/k_{-3} = 0{\cdot}11$–$0{\cdot}17$ at 1200–1350°K, as stated in chapter 3, it follows that $k_8/k_3 \sim 0{\cdot}08$ in this temperature range with no marked dependence on temperature.

The simple Arrhenius expressions for the bimolecular constants in Table 4.1 might not be expected really to hold over the wide temperature ranges of Fig. 4.1 but within the scatter of the data they seem good enough.

CHAPTER 5

REACTIONS IN SIMPLE HYDROCARBON OXYGEN FLAMES

H_2–O_2 flames were discussed in terms of an accepted lower temperature mechanism, but a similar approach to hydrocarbon flames is opposed by much evidence. For example, hydrocarbons which differ by orders of magnitude in their rates of oxidation at around 500–700°K[92,93] have almost the same burning velocities.[94] The common opinion is that oxidation in a steady hydrocarbon flame differs in some fundamental way from the low temperature oxidation, and one had best study the flame directly to understand its reactions. In general, fuel-rich flames are more complex than lean ones. The fuel is consumed in the latter without any considerable formation of other hydrocarbons; but sufficiently rich flames are mixtures of oxidation and pyrolytic reactions which can give large yields of hydrocarbons not present in the original fuel. The oxidation of a hydrocarbon is studied most simply therefore in a lean flame. Under lean conditions, the relative radical concentrations favour large [OH] and [O] at the expense of [H], and it is difficult to deduce much about reactions involving H atoms. It is possible to burn fuel-rich flames of mixed H_2–hydrocarbon fuel in which large [H] can be obtained; and if only a little hydrocarbon is present, most of the complexities of pure hydrocarbon-rich mixtures are avoided. Thus in a CH_4-rich flame the oxidation of CH_3 radicals competes with a rapid formation of C_2 hydrocarbons presumably via $2CH_3 \rightarrow C_2H_6$ which is known to be a fast reaction.[95] But if only a little CH_4 is added to a fuel-rich H_2 flame, not much formation of C_2 hydrocarbons occurs.

Similarities of Hydrocarbon–O_2 to H_2–CO–O_2 Flames

The data of Fristrom and co-workers[96,97] furnish a good starting point for a discussion of hydrocarbon flames. Figure 5.1 shows a traverse for CH_4 through a very fuel-lean CH_4–O_2 flame burnt at 1/20 atm. M_{CH_4} is the measured mass fraction, G_{CH_4} the fraction of the mass flow carried by CH_4 as obtained after the diffusion correction was made. The slope of G is proportional to reaction rate; and while

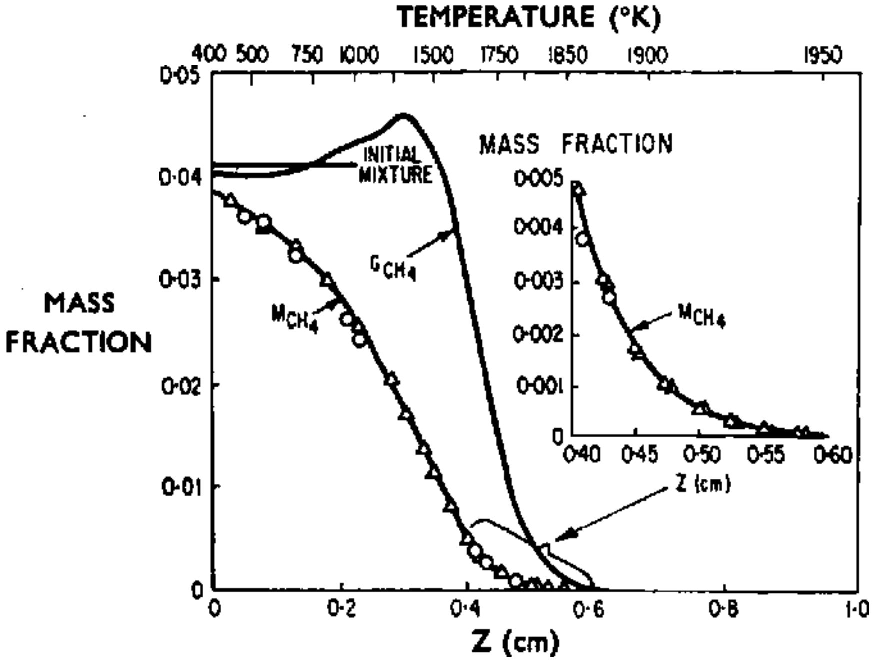


Fig. 5.1. Profile of the mass fraction of methane, M_{CH_4}, through a fuel-lean flame at 1/20 atm. The G_{CH_4} curve derived from the measurements is also shown (Fristrom[97]).

some uncertainties cloud the farthest upstream values of G, the difficulties are less later in the flame. From a set of curves such as Fig. 5.1, one for each constituent, the reaction rates of Fig. 5.2 were obtained by

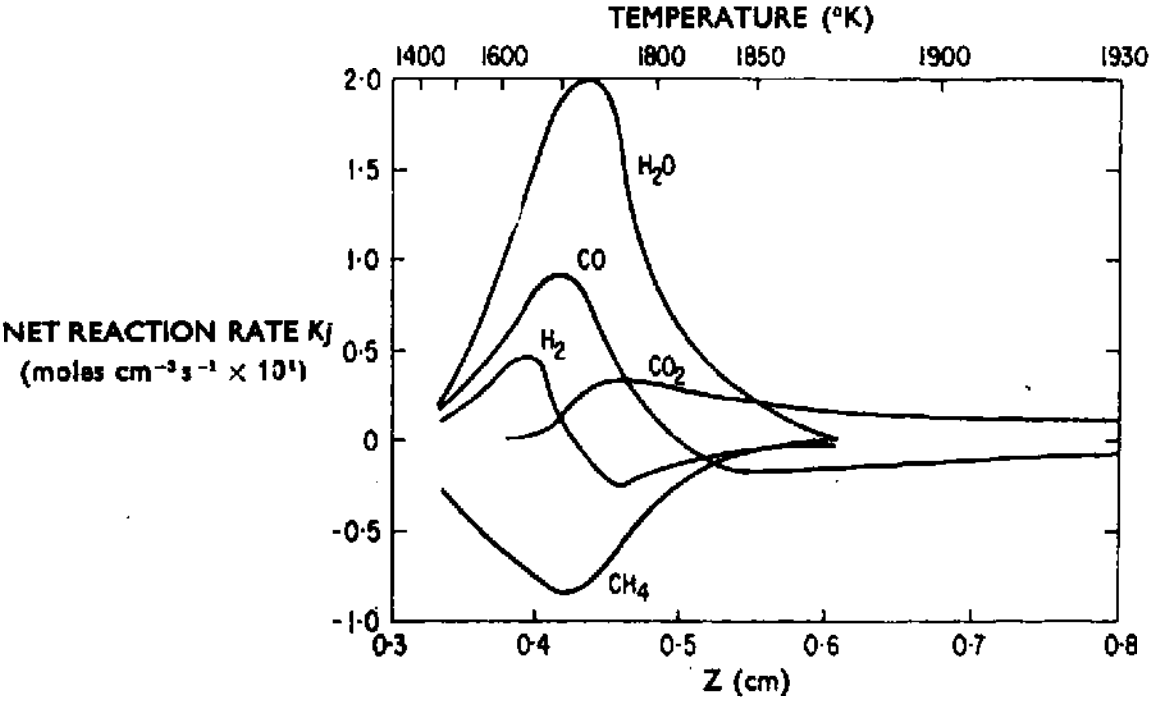


Fig. 5.2. Net reaction rates in CH_4–O_2 flame at 1/20 atm (Westenberg and Fristrom[97]).

equation (1.3). A curve for $-d[O_2]/dt$ is missing, but this was measured and was consistent with

$$-d[O_2]/dt = 1/2\{d[H_2O]/dt + d[CO]/dt\} + d[CO_2]/dt$$

as would be required by the conservation of atoms. The net rate measured for a little formaldehyde was too small to be shown in the figure. Table 5.1 lists the initial conditions and the final state of the gas when reaction had almost ceased. The column of observed mole fractions has vacancies because the radical concentrations were not determined.

It can be seen from Fig. 5.2 that CO was formed before CO_2 was. Much of the CO_2 must have been made by reaction (3.8), and it is generally supposed that all of it was,

$$CO + OH \underset{}{\overset{k_8}{\rightleftarrows}} CO_2 + H \tag{3.8}$$

Some but not all of the H_2O was formed from H_2 by

$$H_2 + OH \overset{k_3}{\rightleftarrows} H_2O + H \tag{2.3}$$

The presence of CO and H_2 had been observed before in fuel-lean mixtures of C_3H_8–air burning at low pressures;[98] and by now it has been confirmed repeatedly that the last stage of a hydrocarbon flame is a $CO–H_2–O_2$ flame. In fuel-lean gas, the H_2 is always rather small compared to CO, partly because k_3 is larger than k_8 and partly because not all the hydrogen in the hydrocarbon goes through a stage of H_2.

In the post-flame gas from $H_2–CO–O_2$ flames, [H], [OH], and [O] were balanced among themselves, and one naturally asks if this is true in the gas from hydrocarbon flames. Reaction (2.1) must have been balanced in the final gas described by Table 5.1,

$$H + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} OH + O \tag{2.1}$$

for taking k_1 from Table 4.1 and $[H]_{equ}$ and $[O_2]$ from Table 5.1, one finds that in the final gas $k_1[H][O_2]$ was about 3/4 of the maximum $-d[O_2]/dt$ observed in the reaction zone itself. Since $-d[O_2]/dt$ was really negligible in the final gas, the forward reaction of (2.1) must have been cancelled by the reverse. Similarly, $d[H_2]/dt \sim d[H_2O]/dt \sim$ zero in the final gas implies that (2.2) and (2.3) were balanced.

[H] may have been larger than $[H]_{equ}$ and therefore (2.1) faster than just estimated in both directions. According to Table 5.1, $[H_2]/[H_2]_{equ}$ was ~ 3 in the final gas; and since in a balanced lean gas,

$$[H]/[H]_{equ} = \{[H_2]/[H_2]_{equ}\}^{3/2}$$

$[H]/[H]_{equ}$ might have been about 5. Even without this factor of 5, [H] in the final gas was of the order required in the reaction zone to account for the consumption of O_2 at the rate of $k_1[H][O_2]$. The inference from these comparisons, that the O_2 may have been consumed mostly by H atoms, was shown to be true by direct measurements in other flames. Fenimore and Jones[99] probed a number of fuel-rich or only moderately lean flames where the reverse of (2.1) could be assumed small early in the reaction zone. The [H] was computed which would be required to make $k_1[H][O_2]$ equal to the observed $-d[O_2]/dt$, and this calculated [H] was compared with that measured by exchange reactions of H with added D_2 or D_2O. The two [H] agreed within about 30 per cent in various flames of CH_4, C_2H_4, and C_3H_8 over a 20-fold variation of [H].

TABLE 5.1

Initial and Final States of the Gas for the Flame Illustrated by Fig. 5.2

	Initial	Final	
		Calc*	Obs
T, °K	400†	1990	1980
V, cm s^{-1}	93†	323	312
X_{CH_4}	0·079	0	0
X_{O_2}	0·919	0·756	0·763
X_{H_2}	0	0·00023	0·0008
X_{H_2O}	0·0004	0·153	0·154
X_{CO}	0	0·00056	0·00305
X_{CO_2}	0·0015	0·0792	0·0788
X_H	0	0·00011	—
X_{OH}	0	0·00626	—
X_O	0	0·00285	—

* Calculated assuming the final equilibrium state.

† The flat flame was stabilized on a screen burner surface temperature 400°K.

The discussion to this point has shown that hydrocarbon flames are partly H_2–CO–O_2 flames, and that O_2 is consumed largely by reaction (2.1); these two conclusions being opposite sides of the same coin.

The Formation of CO in Methane Flames

From what was said above, the real problem in the methane flame is evidently to specify how the fuel is broken up to give CO and H_2 with more or less water. It is widely accepted that the only reactions of CH_4 itself are those forming a CH_3 radical,

$$CH_4 + X \rightleftarrows CH_3 + HX \qquad (5.1)$$

which is written as a reversible reaction because if X were H, it would be possible to reform CH_4 in the presence of much H_2; though if X were OH or O, the reverse would seem unlikely. The formation of CO in low temperature, slow oxidations has usually been ascribed to

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \rightarrow \ldots \rightarrow H_2CO + \ldots \qquad (5.2)$$

with a subsequent break up of the H_2CO to CO—and this has sometimes been suggested to account for the CO formed in CH_4 flames also, though without any evidence. In this section it will be suggested that the CO usually results from a reaction of CH_3 with O atoms rather than with O_2 molecules.

The formation of CO can be symbolized in a general way by

$$CH_3 + \text{oxidant} \rightarrow \ldots \rightarrow CO + (H_2 \text{ and/or } H_2O) \qquad (5.3)$$

Reaction (3) is considered irreversible because it forms a bond between the C atom in CH_3 and an O atom in the oxidant species, and the C—O bond is probably never broken once it is made. For example, no one has ever obtained appreciable hydrocarbons or soot by burning fuel-rich mixtures of methyl alcohol and O_2. Some information about the identification of the "oxidant" in (3) can be obtained by studying flames containing isotopically tagged atoms. On adding H_2O^{18} to the reactants of CH_4–O_2 flames,[100] it was found that the CO_2 formed contained considerable O^{18} but the CO did not. Since the CO_2 was supposed to be formed by reaction of CO with OH, the OH must have contained $O^{18}H$, and of course, the water contained H_2O^{18}. Therefore the CO did not derive its O atoms from either OH or H_2O. It can be concluded that if the "oxidant" in (3) is one of the species known to be present or formed in the flame, O_2, O, OH, H_2O, it must be O or O_2.

The $[O]_{equ}$ in the final products of a very lean flame, say that described in Table 5.1, was 0·38 per cent of $[O_2]$; the ratio $[H_2]/[H_2]_{equ}$ suggests that the actual [O] was about 1 per cent of $[O_2]$ in the final products, and [O] was perhaps of this order in the reaction zone too. In flames richer in fuel the ratio $[O]/[O_2]$ is generally larger than in very lean flames. Now the reaction of CH_3 with O_2 to form the methylperoxy radical is termolecular at 290 to 470°K,[101,102] with a rate constant of 2×10^{16} cm^6 $mole^{-2}$ s^{-1} when M in equation (2) is acetone or methyl iodide, and about 10 times smaller when M is CO_2. The constant has little temperature dependence and is roughly the same even at 1370°.[103] Reaction (2) is therefore a slow process for flame zones, being about as fast as other termolecular recombinations. It was found in the last two chapters that such termolecular processes often cannot keep up with the faster bimolecular reactions; and if CH_3 radicals reacted bimolecularly with O atoms with a collision efficiency of 10^{-3} or greater, it would outrun termolecular (2) even though [O] was only one per cent of $[O_2]$.

If CO was formed from CH_3 radicals at the rate of their reaction with O atoms,

$$CH_3 + O \xrightarrow{k_y} \ldots \rightarrow \text{eventually CO} \ldots \tag{5.4}$$

it should follow that

$$d[CO]/dt + d[CO_2]/dt = k_y[O][CH_3] \tag{5.5}$$

where the left side gives the total rate of formation of CO, as opposed to the net observed rate. Experiments have been made[100] to see if (5) applied to fuel-rich H_2–CH_4–O_2 flames containing a little added NO. The left side of (5) was measured from composition traverses, and [O] was approximated from an extension of equation (4.4). CH_3 was estimated from the partial decay of the added NO which is quite inert in H_2–CO–O_2 flames at the temperatures and pressures used. In the presence of reacting CH_4, however, NO decomposed with a roughly equivalent formation of HCN. It was supposed that the NO consumption was due to

$$CH_3 + NO \xrightarrow{k} CH_3NO \rightarrow \ldots \rightarrow HCN + \ldots$$

and that Christie's estimate[104] of the limiting value of the apparent second order constant, 7×10^{11} cm^3 mole^{-1} s^{-1}, could be used to infer $[CH_3]$ from $-d[NO]/dt$. The value of this constant is about the same at 1170°K[105] as at room temperature, so the assumption that it remains unchanged at temperatures a few hundred degrees higher seems reasonable.

Some profiles through a typical flame and the estimates of reaction rate derived from them are shown in Fig. 5.3. The fall in NO and the formation of HCN during the oxidation of the CH_4, and the stability of the remaining NO thereafter are obvious. The consumption of CH_3 by NO was only an indicator reaction, most of the CH_3 underwent the usual oxidation to give CO.

Supposing that [CH$_3$] of the right order at least had been measured, and substituting [O] and [CH$_3$] into equation (5), values of

$$k_\gamma \sim 4 \times 10^{13}\ \text{cm}^3\ \text{mole}^{-1}\ \text{s}^{-1}$$

were found in various flames at 1210–1560°K. The evidence for the oxidation of CH$_3$ by O atoms seemed fairly good, and since termolecular (3) could not have accounted for the observed formation of carbon oxides, it was concluded that CO was formed by reaction (4). The primary product was unproven; the obvious $O + CH_3 \rightarrow H + H_2CO$ would account for the little formaldehyde observed in the region where CH$_4$ was consumed.

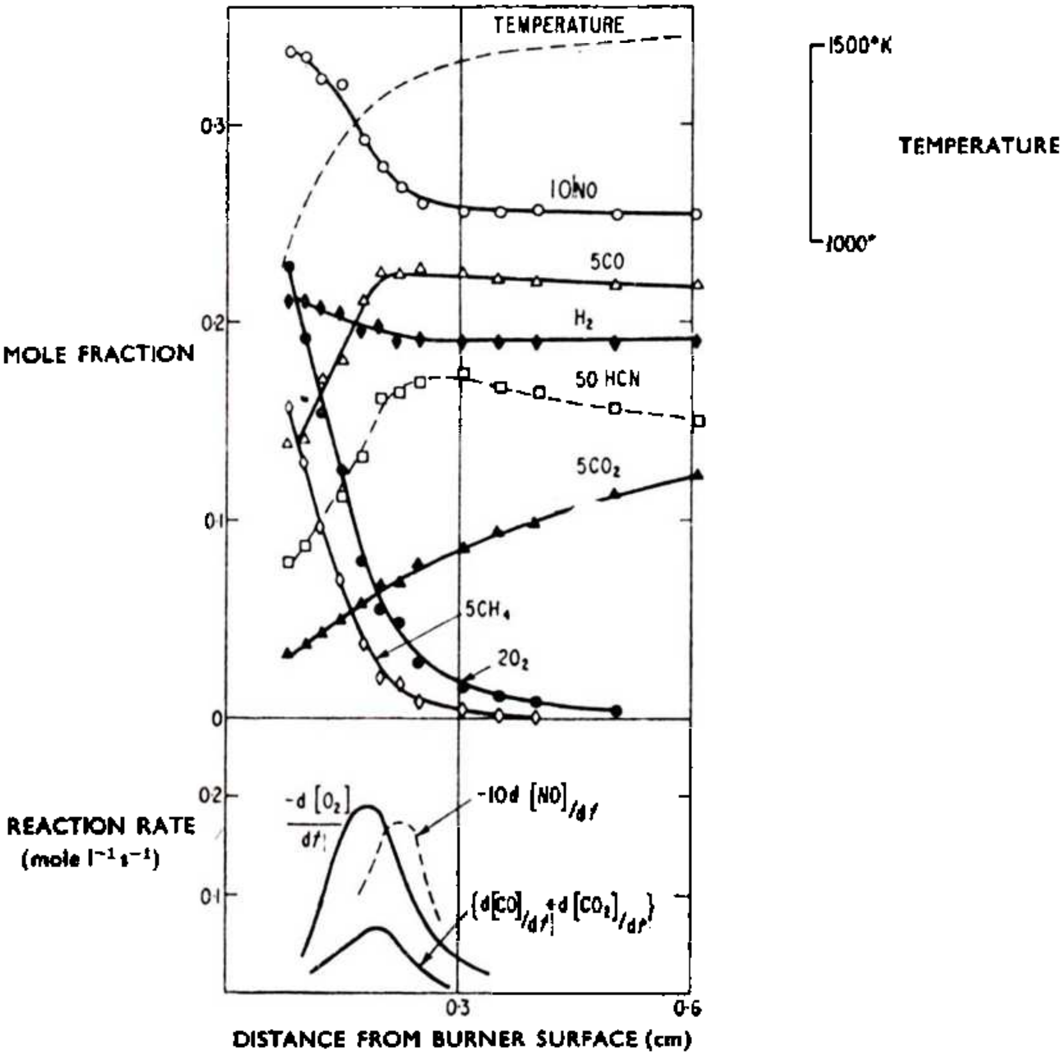


Fig. 5.3. Some traverses and calculated reaction rates in a flame of H$_2$ + 0·17 CH$_4$ + 0·54 O$_2$ + 0·105 NO + 1·05 Ar burnt at 8 cm of mercury P with a mass flow of 3·7 × 10^{-3} g cm^{-2} s^{-1} (Fenimore and Jones[109]).

Hoare[106] did not believe that the reaction of CH$_3$ + NO was a second order reaction. He thought it termolecular $CH_3 + NO + M \rightarrow CH_3NO + M$; whence the termolecular constant would be about

10^{18} cm^6 mole^{-2} s^{-1} in Christie's experiments at room temperature when M was CH_3I, or in Bryce and Ingold's experiments at 1170° when M was He. From his own work at 470°K, Hoare suggested a termolecular constant of $0{\cdot}3 \times 10^{18}$ when M was acetone. It should be added therefore that if the consumption of NO by CH_3 in the flames studied had been a termolecular process with rate constant 10^{18}, the $[CH_3]$ deduced would have been unchanged within 50 per cent and the conclusion unchanged.

The impression should not be left that general agreement exists about the fate of CH_3 radicals in methane flames. Fristrom[24] considers the question open whether the reaction is

$$CH_3 + O \rightarrow H + H_2CO$$

or

$$CH_3 + O_2 \rightarrow OH + H_2CO$$

or perhaps the former in moderately rich flames and the latter in very fuel-lean ones. McKellar and Norrish[107] flash photolysed CH_3I–O_2 mixtures and discussed their spectroscopic observations on OH and H_2CO in terms of the reaction of $CH_3 + O_2$, considered to be fast and bimolecular even when the combustion was explosive. If a fast bimolecular reaction does occur, it would obviously be wrong to reject $CH_3 + O_2$ on grounds that it was too slow. It is fair to add that no evidence for such a fast reaction has been presented as yet.

The Formation of CH_3 Radicals in Methane Flames

CH_3 radicals are formed as fast as CH_4 disappears. Westenberg and Fristrom[97] assumed that the process in very lean flames was the irreversible reaction,

$$CH_4 + OH \xrightarrow{k_6} CH_3 + H_2O \tag{5.6}$$

and supposed that the reverse of (3.8)

$$CO + OH \xrightarrow{k_8} CO_2 + H \tag{3.8}$$

could be neglected in regions where CH_4 reacted, as is certainly true. From the local measured ratios of $[CO]/[CH_4]$ and the ratios of $d[CO_2]/dt$ to $-d[CH_4]/dt$, read off Fig. 5.2, they obtained

$$k_6/k_8 \sim 15 \text{ at 1660–1840°K, 3·8 cm Hg pressure.}$$

A larger ratio of rate constants from another flame at twice the pressure was considered less accurate. Fenimore and Jones[108] confirmed the choice of equation (6) and found $k_\delta/k_8 \sim 22$ at 1450–1800°K, 5–14 cm Hg pressure. The k_8 in Table 4.1, chapter 4, does not differ significantly from the value assumed by Westenberg and Fristrom; it gives

$$k_\delta = 1 \text{ to } 2 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \text{ at } 1750^\circ$$

but the 9 kcal mole^{-1} activation energy reported by Fenimore and Jones is doubtless too large in view of the discussion of k_3 and k_8 in chapter 4. Table 4.1 implies $E_\delta \sim 6$ kcal, but this is based on very scanty evidence for E_8. It seems certain that the reactions of OH with CO and with CH_4 have nearly the same activation energies. Karmilova and co-workers[109] added isotopically tagged CO to slowly oxidizing CH_4–O_2 mixtures at 745°K and showed that CO_2 was mostly formed from CO, presumably by equation (3.8). Accepting that CH_4 is also destroyed by (6) under such circumstances, it follows from their observations that

$$k_\delta/k_8 \sim 30 \text{ at } 745^\circ\text{K};$$

so this ratio is nearly unchanged over an 1100° interval.

In fuel-rich H_2–CH_4–O_2–N_2O flames, [H]/[OH] is 30–100 times larger than in lean flames, and the k_δ just given cannot account for $-d[CH_4]/dt$. It was found[108] that the consumption could be correlated by

$$CH_4 + H \xrightarrow{k_\varepsilon} CH_3 + H_2 \qquad (5.7)$$

and that k_ε could be evaluated by comparison with

$$N_2O + H \xrightarrow{k_\alpha} N_2 + OH$$

if care was taken to avoid situations where the reverse of (7) was important. Accepting the k_α from Table 4.1, chapter 4,

$$k_\varepsilon = 1{\cdot}5 \times 10^{14}\, e^{-11 \text{ kcal}/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$$

at 1220–1790°K and 3–5 cm Hg pressure, but the 11 kcal could be changed by 2 or 3 kcal if compensating changes were made in the pre-exponential factor. k_ε has been measured often at lower temperatures. The earlier estimates[47] favoured an activation energy of 12–13 kcal and a pre-exponential factor of $\sim 10^{14}$ or larger, but more recent ones suggest an activation energy of about 8 kcal, or even less,[110–112] and a smaller pre-exponential factor, sometimes much smaller.[111] One cannot say much about the activation energy from work in flames alone when a difference of only a few kcal mole^{-1} is in question. If both the flame work and the lower temperature values are approximately correct in absolute magnitude, E is probably not less than 10 kcal and the pre-exponential factor is of order 10^{14}.

This concludes the description of the present situation for the burning mechanism of CH_4. The probable consumption of CH_3 by reaction with O atoms, and of O_2 by reaction with H atoms in flames contrasts with the low temperature oxidation of methane[113] when methyl radicals are thought to be oxidized by reaction with O_2 molecules. An important reason for the difference must be that reaction (2.1), $H + O_2 \rightarrow OH + O$, with its 18 kcal mole^{-1} of activation energy is 1000 times faster at 1500° than at 700°K, but the rate of $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ does not increase significantly with temperature. The products from $O + CH_3$ are uncertain but formaldehyde seems reasonable. If formed, its subsequent destruction should go very readily; for formaldehyde resembles a mixture of $H_2 + CO$ as a fuel and its breakup cannot be a difficult step in the overall oxidation. The ease of oxidation of formaldehyde will be commented on in chapter 8.

Radical Concentrations in Hydrocarbon Flames

Methane flames, particularly fuel-rich ones, possess smaller radical concentrations than do H_2–O_2 or H_2–CO–O_2 flames. The radicals recombine by termolecular processes in the absence of hydrocarbons, but methane flames may have a fast bimolecular reaction of $CH_3 + O$ which also terminates free valencies. Figure 5.4, which has not been published elsewhere, illustrates the point with some traverses through two H_2–O_2–Ar flames; one containing a little added CO, the other an equal concentration of CH_4. In the CO flame, the temperature continued to rise after the O_2 was all consumed because of the continued recombination of free radicals, as had been found before by Padley and Sugden.[114] In the gas from the CH_4 flame the radicals must have been considerably smaller because no continued large heat release is apparent. From the rates of consumption of oxygen in the two flames, assuming that the reverse of reaction (2.1) was negligible over most of the region where $-d[O_2]/dt$ is plotted, it can be inferred that [H] was about 4 times larger in the CO than in the CH_4 flame. If a ratio of this order holds in the post-flame gas also, the difference in the temperature traverses is very reasonable because the rate of heat release by recombination depends on the square of the radical concentrations.

Flames of other simple hydrocarbons resemble those of methane in that they too appear to be H_2–CO–O_2 flames fed by the breakup of the

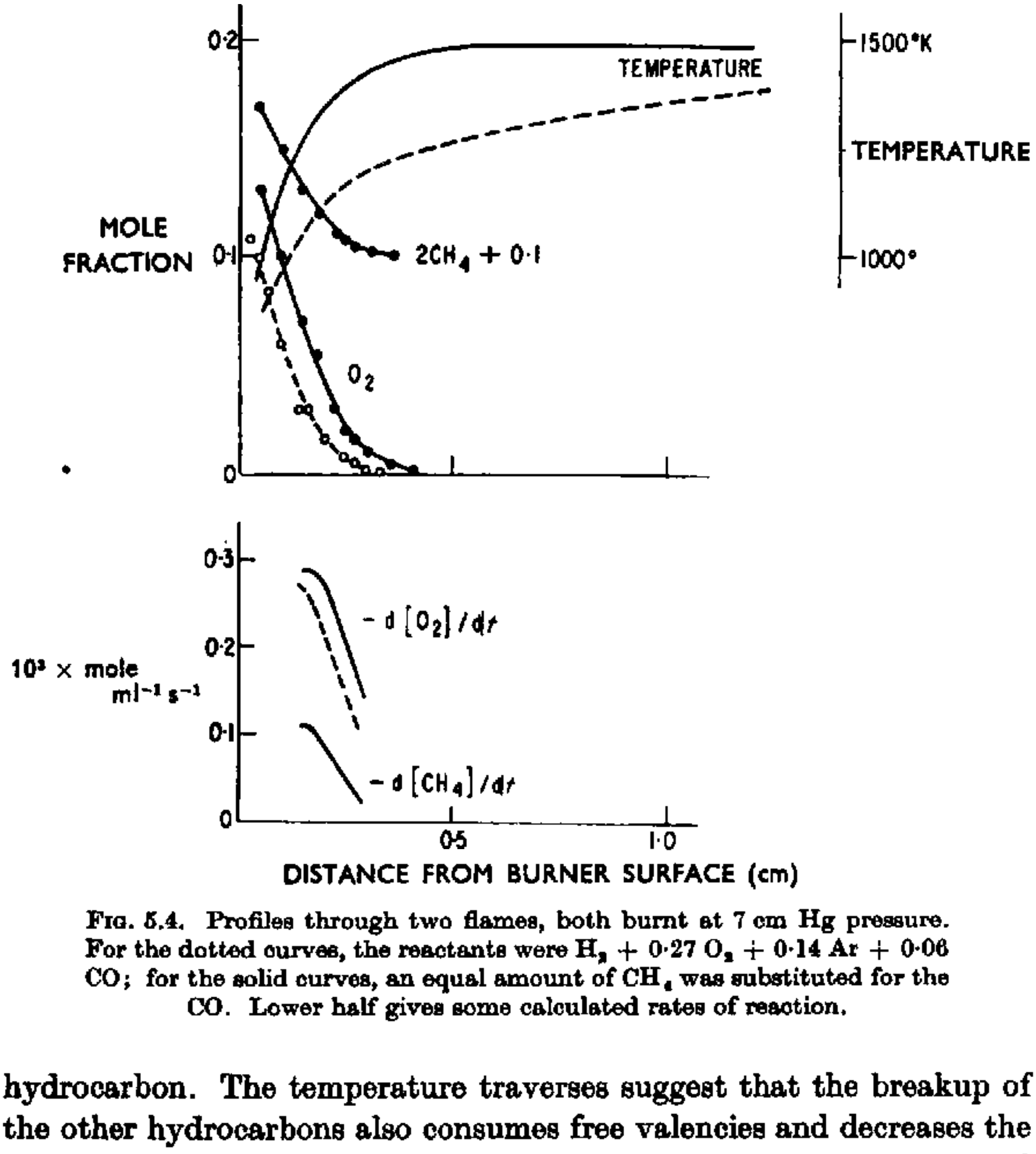


Fig. 5.4. Profiles through two flames, both burnt at 7 cm Hg pressure. For the dotted curves, the reactants were $H_2 + 0{\cdot}27\ O_2 + 0{\cdot}14$ Ar + 0·06 CO; for the solid curves, an equal amount of CH_4 was substituted for the CO. Lower half gives some calculated rates of reaction.

hydrocarbon. The temperature traverses suggest that the breakup of the other hydrocarbons also consumes free valencies and decreases the large excess radical concentrations which would otherwise be expected from the H_2–CO–O_2 flames. The effectiveness of hydrocarbons in decreasing excess radicals is most noticeable in fuel-rich gas, and [H] is near $[H]_{equ}$ whenever any hydrocarbon survives into the post-flame gas. This allowed a calibration in early determinations of [H] by exchange with added D_2O, as was mentioned in chapter 2, and it has been confirmed several times since then, e.g. by Reid and Wheeler in propane flames.[115]

The Decomposition of C_2H_6 in Flames

Much as with CH_4, the measured values of $-d[C_2H_6]/[C_2H_6]\,dt$ in fuel-lean C_2H_6–O_2 or fuel-rich C_2H_6–H_2–O_2 flames can be correlated with

[OH] and [H] respectively.[116] In neither type of flame is there evidence for a significant attack of O atoms on C_2H_6. In lean flames, the relative rates of

$$C_2H_6 + OH \xrightarrow{k_\delta} \text{presumably } C_2H_5 + H_2O \tag{5.8}$$

and

$$CO + OH \xrightarrow{k_8} CO_2 + H \tag{3.8}$$

gave

$$k'_\delta/k_8 \sim 34 \text{ at 1400–1600°K, 2–3 cm Hg pressure}$$

which is little different from the corresponding ratio for CH_4. In rich flames with small ratios of $[C_2H_6]/[H_2]$, the relative rates of

$$C_2H_6 + H \xrightarrow{k_\varepsilon} \text{presumably } C_2H_5 + H_2 \tag{5.9}$$

and

$$O_2 + H \xrightarrow{k_1} OH + O \tag{2.1}$$

when measured in regions where the reverse of (2.1) could be assumed negligible, and interpreted by the k_1 from Table 4.1, gave

$$k'_\varepsilon \sim 1 \times 10^{14}\, e^{-9\cdot7/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \text{ at 1000–1400°K}$$
$$\text{3–5 cm Hg pressure.}$$

This agrees very well with the estimate by Darwent and Roberts[117] at 300–580°, but not so well with that of Berlie and LeRoy[118] who interpreted their results at 250–430° by a 30-fold smaller pre-exponential factor and a 3 kcal smaller activation energy. The ratio k'_ε/k_1 has also been estimated at 793° [119] and at 753° [120] from shifts of the explosion limit of H_2–O_2 mixtures. A little added C_2H_6 shrank the bounded explosion region, and the additional chain terminating reaction was found to be proportional to $[C_2H_6]$ and probably to [H] by consideration of the reasonable kinetic possibilities. By identifying the new terminating reaction with (9), the ratio of k'_ε/k_1 could be obtained. The two determinations from explosion limits agreed with each other and with an extrapolation of the ratio from flames.

Baldwin[121] has carried out additional work at 813°K to obtain from explosion limits an absolute value of k_1 and then of k'_ε, and has also recalculated the experiments of Darwent and Roberts using more recent estimates for the velocity of exchange of D + H_2 which was involved in their calculation. He plotted the results of the various investigations over the temperature range 300–1500°K, reproduced as Fig. 5.5, and concluded that

$$\log_{10} k'_s = 14{\cdot}0 \pm 0{\cdot}4 - 9{\cdot}5 \pm 1{\cdot}0\ \text{kcal}/2{\cdot}3\ RT.$$

It is probable that in flames the subsequent reactions of C_2H_5 radicals include bimolecular processes which terminate free valencies, analogous to and even the same as those of CH_3—but they have not been worked out.

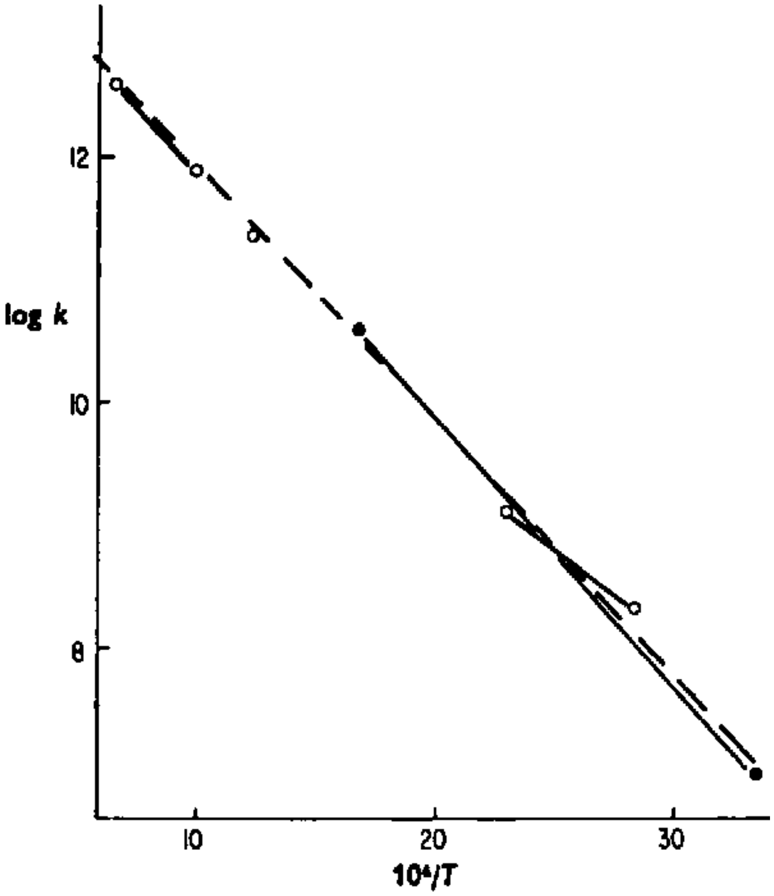


FIG. 5.5. Estimates of the rate constant, in cm³ mole⁻¹ s⁻¹, for H + $C_2H_6 \rightarrow C_2H_5 + H_2$. From the top of the curve downwards, the data are: the flame results; Baldwin's estimate at 813°K; his recalculation of Darwent and Roberts' results; Berlie and LeRoy's results. The equation of the dotted line is given in the text.

Decomposition of C_2H_4 in Flames

By probing a number of ethylene flames,[116] the specific decay rate of this fuel was measured in mixtures containing various concentrations of [H], [OH], and [O]. The radical concentrations were approximated in ways already discussed, using the constants from Table 4.1 of chapter 4 and supposing that molecular oxygen and carbon monoxide were consumed only by reactions with H and OH radicals respectively. The specific decay rate of the fuel was found to increase markedly towards the downstream end of the reaction zone: [H] and [OH] did not increase in the same region, but [O] did. This suggested that C_2H_4 was destroyed mostly at the rate of its reaction with O atoms,

$$C_2H_4 + O \xrightarrow{k''} C_2H_4O^\star \rightarrow . . . \qquad (5.10)$$

and if so, the data for all flames would be consistent with

$$k'' = 2\text{–}3 \times 10^{13}\ \text{cm}^3\ \text{mole}^{-1}\ \text{s}^{-1}\ \text{at}\ 1400\text{–}1600°\text{K}$$

The k'' from flames would then be of the same order as the constant obtained at much lower temperatures for reaction (10); agreeing moderately well with Ford and Endow's[122] calculation of Cvetanovic's[123] photolytic work, or with Elias and Schiff's[124] estimates by discharge tube methods. A partial consumption of C_2H_4 by reaction with OH could not be excluded, however, in the flame work.

At low temperatures, the excited $C_2H_4O^\star$ formed in (10) are thought to break up partly to give CH_3 radicals,[125] and these may well have formed in flames too. Fuel-rich mixtures of a little C_2H_4 in much H_2 gave a transient yield of CH_4 in the reaction zone which was compatible with the occurrence of

$$H + CH_4 \rightleftarrows CH_3 + H_2 \qquad (5.7)$$

if it was supposed that CH_3, formed at the rate of $k''[O][C_2H_4]$ and destroyed just as in methane flames at the rate $k_y[O][CH_3]$, could also undergo a transient formation of CH_4 by the reversible reaction (7). The transient CH_4 was only large in the presence of much added H_2 and therefore was thought not to have been formed directly in the destruction of C_2H_4.

Studies of Acetylene Flames

When a little fuel-rich C_2H_2–O_2 mixture in much inert gas was heated suddenly in a shock tube, Kistiakowsky and co-workers[126,127,128,128a] observed that the induction time until appreciable reaction began was the same function of temperature and $[O_2]$ as had been reported when H_2–O_2 was heated, equation (4.1). They concluded that the branching reaction

$$H + O_2 \rightarrow OH + O \qquad (2.1)$$

which controls the build up of free radicals for H_2–O_2 did so for C_2H_2–O_2

also. In H_2–O_2, O atoms and OH radicals were supposed to react rapidly with hydrogen by (2.2) and (2.3) to regenerate the H atom consumed in (2.1) and to form two new H atoms besides. The subsequent reactions must be different in rich acetylene mixtures where much carbon monoxide and smaller amounts of water, diacetylene, and doubtlessly other products are formed,[128] but these must also make two new H atoms per molecule of oxygen consumed by (2.1) if branching is to be equally rapid. Bradley and Kistiakowsky[128] were primarily interested in the diacetylene. They suggested it was formed by

$$O + C_2H_2 \rightarrow C_2H + OH$$
$$OH + C_2H_2 \rightarrow C_2H + H_2O$$
$$C_2H + C_2H_2 \rightarrow C_4H_2 + H,$$

and noted that if all the O and OH radicals formed in (2.1) reacted this way, two new H atoms would be returned to the system per molecule of oxygen consumed in (2.1). However, the fraction of acetylene which simultaneously formed carbon monoxide was much larger than that forming diacetylene; so if the build up of free valencies is attributed to (2.1) plus the equivalent occurrence of reactions forming diacetylene, it must also be supposed that much more oxygen is consumed simultaneously in some other way to form carbon monoxide from acetylene. This is unlikely; in steady flames at least molecular oxygen is mainly consumed by (2.1).[99] If it is mainly consumed by (2.1) in shock tubes also, the bulk of the O and OH formed must react with acetylene, or with intermediates derived from it, to give carbon monoxide from its carbon. There is no obvious reason why the induction times should not still conform approximately to equation (4.1)—but this point of view relegates diacetylene formation to an unessential side reaction as far as the main branching mechanism is concerned. The importance of diacetylene is that it suggests the presence of C_2H radicals which may be important in processes of electronic excitation[127] and ionization,[128a] though of little importance in the development of the bulk of the free radicals.

That acetylene does not react mainly with OH radicals in some mixtures at least was shown[274] by probing low pressure flames of CO–O_2–Ar–C_2H_2 and comparing the rate of disappearance of the hydrocarbon with the formation of carbon dioxide. In one example it was found that the ratio of the specific rate of consumption of acetylene, $-d[C_2H_2]/[C_2H_2]\,dt$, to the specific rate of formation of carbon dioxide.

$d[CO_2]/[CO]\,dt$, increased from 30 at 1150° to 300 at 1380°K. If both processes were irreversible reactions with OH radicals,

$$OH + CO \xrightarrow{k_9} CO_2 + H$$
$$OH + C_2H_2 \xrightarrow{k'} \text{products},$$

k' must have had around 30 kcal more of activation energy than k_9 and a pre-exponential factor about 10^6 times larger—which is judged to be impossible. An analogous comparison with $-d[O_2]/[O_2]\,dt$ in regions where the oxygen consumption could be considered unaffected by the reverse of (2.1) showed that acetylene could not have been mainly destroyed by an irreversible reaction with H atoms either. Crude estimates of [O] were possible in a narrow region of the reaction zone, similar to those obtained in ethylene flames, and these [O] were proportional to $-d[C_2H_2]/[C_2H_2]\,dt$; so acetylene is probably destroyed in such flames by reaction with O atoms. The rate constant for the attack of O on acetylene was estimated to be 1 to 2×10^{13} cm^3 mole^{-1} s^{-1} and of essentially zero temperature dependence. The value is near that found for the attack of O on ethylene.

It is interesting that ethylene and acetylene both seem to be destroyed by O atoms. Methane and ethane are not, but are attacked by H atoms and OH radicals which doubtlessly abstract H from the saturated fuels. A plausible reason for the difference is that carbon is attacked directly in the unsaturated fuels; and such an attack on carbon has been directly demonstrated by Haller and Pimentel,[129] though under conditions about as different from flames as could be imagined. They photolysed a solid argon matrix containing nitrous oxide and acetylene, and found that the O atoms from nitrous oxide formed ketene. Ketene was not observed in samples probed from flames, but has been reported formed when a mixture of acetylene plus about 1·5 per cent of oxygen was run through a tube heated to 750°K.[130]

The course of reaction in flames is unknown. The formation of methylene or a ketyl radical is not unlikely,

$$O + C_2H_2 \rightarrow CH_2 + CO, \text{ or } HCCO + H,$$

but other suggestions might be advanced. Whatever the primary products, other than H atoms, they should not react largely with molecular oxygen if this is mostly consumed by (2.1). At lower temperatures methylene reacts considerably faster with many other species than with molecular oxygen;[275,276] and if it reacted 100 times or so faster with O or OH than with oxygen molecules, it need not consume much molecular oxygen in flames either.

Cool Flames

Steady reactions in a flow system can be obtained in fuel-rich mixtures of oxygen with higher hydrocarbons, or with ethers, alcohols, aldehydes, etc., which have a much smaller temperature rise across the reaction zone than the flames just described. These cool flames occur spontaneously[92] with most higher hydrocarbons at around 500–700°K and at pressures which depend on the particular fuel molecule. Townend and co-workers[131,132] stabilized the flame in a mixture of ether and oxygen flowing in a diverging conical tube, and Bailey and Norrish[133] using a similar tube heated to 528–538°K stabilized a cool flame of n-hexane–O_2–N_2. Similar flames of ether-air fed at room temperature[134,135] or of pre-heated n-hexane–air and n-heptane–air[134] have also been stabilized on a Powling burner.

These low temperature flames are very different from the hot ones described above. The emitted light from them is the same as from fluorescing formaldehyde.[136] The flame temperatures of various stabilized $(C_2H_5)_2O$–O_2 cool flames lies in the range 600–800°K.[131,134] The intermediate reaction products include aldehydes, etc., most of which, except for formaldehyde, may be destroyed again with the formation of considerable unsaturated hydrocarbons. They are certainly not associated with H_2–CO–O_2 flames, and the O_2 in them doubtlessly reacts with larger radicals and molecules rather than with H atoms. In unsteady systems, however, and in the presence of enough oxygen they sometimes ignite the hot flame.[3]

CHAPTER 6

IONIZATION AND ELECTRONIC EXCITATION IN HYDROCARBON FLAMES

ELECTRONICALLY excited molecules are the most obvious species in the visible reaction zone of hydrocarbon flames. They decay rapidly and do not persist into the post-flame gas. It was conceivable once that they might be accounted for on equilibrium considerations; that in some instances, an excited molecule A^* might be thermally equilibrated with ground state A which was formed and then burnt up in the reaction zone. The A^* have been found too numerous for this interpretation, however, and the excited species are now thought to originate in chemiluminescent or chemi-ionization processes. Though too many to be accounted for on equilibrium considerations, they are too few to affect the main course of the combustion.

The excitation processes are quite energetic in hydrocarbon flames. When a little iron carbonyl is added to hydrogen, the most energetic line excited requires 122 kcal,[76] very near the 118 kcal available from the recombination of H + OH; but a line requiring 174 kcal is excited in hydrocarbon flames.[137] The larger energy must often derive from forming in some way the strong C–O bond from species like C, CH, etc.;[137] and it may be that a process of this kind is directly visible in the emission from the excited HCO^* radical.[138] More often the excited species which is observed does not contain the C—O group.

It is difficult to get quantitative evidence about excitation processes in hydrocarbon flames because the species suspected to be involved are only present in small concentrations. The way in which these are formed is unknown, though of course it is not unreasonable that hydrocarbon radicals should include traces of C_2 and CH, for example. Only traces are involved; until recently, neither of these species could be measured in steady flames. Both of them have now been found by absorption spectroscopy.[139] Yet no reaction attributed to the species C_2, CH, etc., has been shown to depend on the concentrations $[C_2]$, [CH], etc.; and the chemiluminescent and chemi-ionization processes in hydrocarbon flames are therefore not understood very well.

Ions in Flames

Ions have been studied by Langmuir probes, by the effect of free electrons on high frequency circuits, and by mass spectroscopy. In the probe method[140,141] a fine wire is introduced in the flame and the current to it measured as a function of applied voltage. The other, non-saturating, grounded electrode is the burner itself and a screen placed above the flat flame. At sufficiently negative voltages the electrons are repelled and all the positive ions diffusing to the wire are captured.

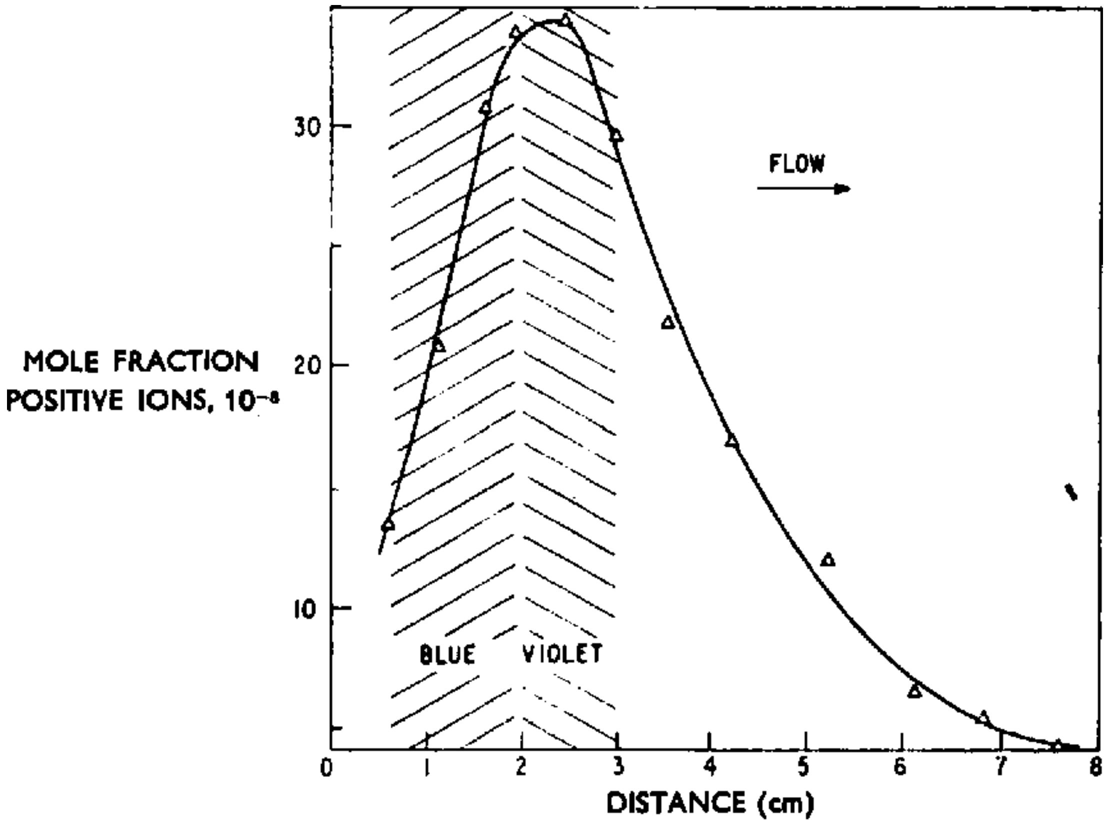


FIG. 6.1. Variation of positive ions through a C_2H_4–O_2 flame burning at 0·3 cm Hg (Calcote[141]).

The method can be checked by measurements in post-flame gas containing easily ionizable alkali metals, when the calculable equilibrium ionization swamps any residual ionization of the pure flame. Probes cannot identify ion species but can give the total ion concentration with high spatial resolution.

Figure 6.1 from Calcote[141] shows the mole fraction of positive ions through a low pressure C_2H_4–O_2 flame. There is no species known to be present in such a flame which would have a sufficiently low ionization potential to account for the peak value by the equilibrium process,

$$A \rightleftharpoons A^+ + e^-$$

When mixture strength was varied, the greatest ion concentration occurred in the neighbourhood of stoichiometric mixtures. When pressure was varied the mole fraction of ions was essentially constant between 10 cm Hg and atmospheric pressure.[142] CH_4, C_3H_8, and C_2H_4 fuels gave about the same mole fraction of ions in their flames, but C_2H_2 gave more.[141]

Measurements by high frequency methods of the concentration of electrons in fuel-rich hydrogen flames containing added cesium showed that negative ions were not very numerous compared to electrons.[143] Some probe measurements which imply that negative ions are important in stoichiometric and lean flames have not been confirmed by the mass spectrometer,[144] and the weight of the evidence is that $[e^-]$ is about the same as the concentration of positive ions in the flame itself and immediately downstream of it.

By mass spectroscopy, Van Tiggelen and co-workers[145,146] and Knewstubb and Sugden[147] proved that the principal ion in hydrocarbon flames was H_3O^+, although a large number of other species also exist in smaller concentrations. The preponderance of H_3O^+ was confirmed in other studies[144,148] and the disappearance of ions in Fig. 6.1 must have been chiefly a disappearance of H_3O^+ and may have involved the dissociative recombination

$$H_3O^+ + e^- \rightarrow H_2O + H \tag{6.1}$$

If it was supposed that only recombination was significant along the descending curve downstream of the flame zone, Fig. 6.1 could be corrected for diffusion and fitted to the expression

$$-d[n^+]/dt \sim 1 \times 10^{17}[n^+]^2 \text{ mole cm}^{-3} \text{ s}^{-1}\cdot$$

which conforms to (1) if $[n^+] = [H_3O^+] = [e^-]$. A diffusion coefficient appropriate to the neutral N_2 molecule was used in the correction, the electrons being constrained by electrical forces from diffusing faster than the heavy positive ions. About the same rate constant was observed in the pressure range, 3 cm Hg to atmospheric pressure.[141] Since ion recombination was a second order reaction and the maximum mole fraction of ions independent of pressure, it is probable that the formation of ions was second order also. The assumption in this conclusion is that the mole fractions of ion precursors were independent of pressure. Considering the possible reactions among species known to be present in the reaction zone, Calcote[141] suggested that the ionization might be explained by such reactions as

$$O + CH \xrightarrow{k} HCO^+ + e^-, \qquad \Delta H = 0 \qquad (6.2)$$

$$H_2O + HCO^+ \xrightarrow{k'} H_3O^+ + CO \qquad \Delta H = -34 \text{ kcal} \qquad (6.3)$$

$$e^- + H_3O^+ \xrightarrow{k''} H_2O + H \qquad \Delta H = -145 \qquad (6.1)$$

with a formation of other ions by charge transfer from the HCO^+ or H_3O^+. The ΔH are quoted from Green and Sugden[148] who used the same reactions to interpret a study of fuel-rich H_2–N_2–O_2 flames containing 1 per cent or less of added acetylene. In their work at atmospheric pressure, a flame of purified H_2 gave an insignificant yield of ions but added C_2H_2 caused much ionization. $[HCO^+]$ and $[H_3O^+]$ were the smallest and largest ion concentrations observed by mass spectroscopy, $[H_3O^+]/[HCO^+] = 4 \times 10^5$ for 1 per cent acetylene. When ion concentrations were varied by changing the added acetylene, $[HCO^+]$ was proportional to $[H_3O^+]^2$ in the region of maximum ionization—as would be consistent with reactions (3) and (1) if $d[H_3O^+]/dt$ were zero in this region. No other ion was found with concentration proportional to $[H_3O^+]^2$, and this was taken to support (3) and (1) as written. If the $k'' \sim 10^{17}$ cm^3 mole^{-1} s^{-1} is accepted from Fig. 6.1, the observed ion ratios give k' of order 10^{15} to 10^{16}. The evidence so far is consistent with (3) and (1), but there is no experimental evidence yet for equation (2) for the [CH] in the flames studied was unknown. The reason for proposing it is that few other reactions can be imagined which would be sufficiently energetic, and none which also involve species definitely known to be present in the flame.

Kistiakowsky and co-workers[126–128a] have studied ionization in shock heated C_2H_2–O_2–A_r mixtures. Their mass spectrometric results led them to propose that C_2H was a major intermediate under the conditions used and that it was partly oxidized according to $C_2H + O \rightarrow CO + CH$, where the CH might well be formed as electronically excited $CH^\star$. CH (or excited $CH^\star$) was considered to react with O to form ions, equation (6.2), or to form electronically excited $CO^\star$ which gave the short ultraviolet radiation observed. The yield of short UV photons was estimated as about 10^{-5}, and of ion pairs as about 10^{-6} of the acetylene molecules reacting.

A charge exchange from the flame ions to added metals was proposed[143] as the most reasonable explanation for the ionization of lead in acetylene flames to a greater extent than corresponded to equilibrium. The ionization of the metals persisted into the post-flame gas because no fast recombination process such as (1) could operate; and this differentiated it from the ionization of the pure flame. An exchange process was also thought to contribute to the ionization of sodium in flames, which did not ionize above equilibrium but reached equilibrium faster in hydrogen flames containing one per cent of acetylene than in nominally pure hydrogen flames. Other data from the same school are plotted in Fig. 6.2, which gives the degree of ionization, relative to equilibrium, for various metals added in traces to acetylene flames. The extent of non-equilibrium ionization evidently depends on the ionization potential of the metal and is consistent with the ΔH quoted for (2), (3), and (1), which could give as much as 7·8 eV.

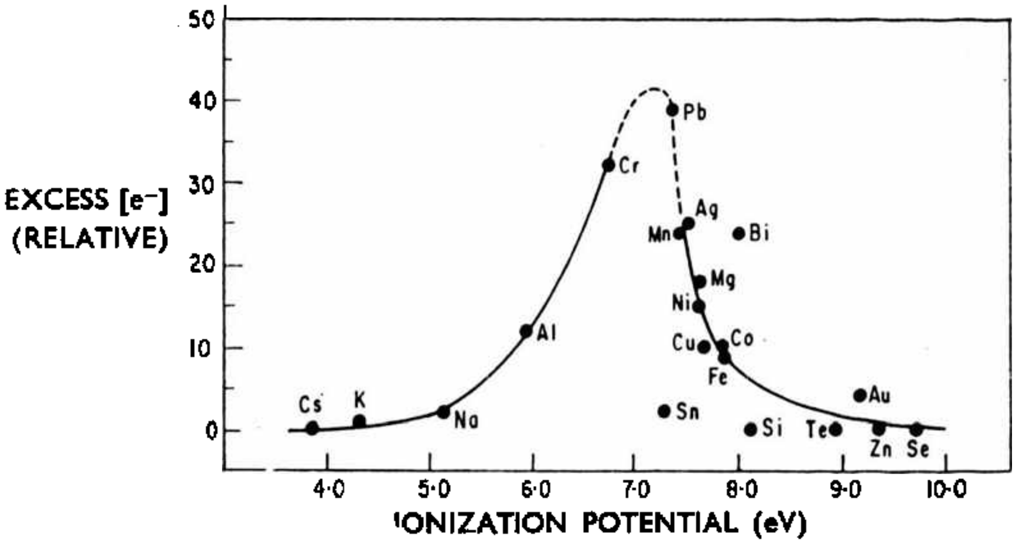


FIG. 6.2. $[e^-]/[e^-]_{equ}$ for various metals in a fuel-rich acetylene flame at 2500°K (Bulewicz and Padley[138]).

Electronically Excited Species

Added lead and iron[137] and probably chromium[149] undergo a non-equilibrium excitation in the reaction zone of hydrocarbon flames. The effect is described sometimes by quoting the excitation temperature which would be required to give the populations observed in the excited levels if these conformed to an equilibrium distribution. The excitation temperature is often higher than the calculated adiabatic flame temperature. Gaydon and Wolfhard[1] commented on the parallel between the ionization of pure hydrocarbon flames and the non-thermal excitation of metals added to them, and King[150] and then in more detail Bulewicz and Padley[138] have shown that the correlation is very good indeed.

An excitation deriving its energy from the reaction partners, O + CH,[151] could parallel ionization via reaction (2).[152]

The visible and ultraviolet radiation from the reaction zone of hydrocarbon flames free of added metals is mostly due to excited $OH^\star$, $CH^\star$, $C_2^\star$, and sometimes to $HCO^\star$.[63] Bands of $CO^\star$ are also obtained in the far ultraviolet which require over 8 eV for their excitation. The origin of none of these species is established, though plausible conjectures can be put forward for some.

Ground state [OH] is smaller in low pressure stoichiometric CH_4–O_2 flames than in H_2–O_2, yet the peak $[OH^\star]$ is some hundreds of times larger.[26] Furthermore, the OH formed in H_2–O_2 has a rotational energy distribution more or less appropriate to the gas temperature; but that in hydrocarbon flames has a distribution appropriate to a temperature several times higher than the actual gas temperature. The exchange of rotational energy with other molecules is very rapid for $OH^\star$, as Carrington[153] showed by exciting a single rotational level and studying the fluorescence from this and from nearby rotational levels populated from the level excited. Despite the rapid rotational exchange, the electronic quenching by $OH^\star + M \rightarrow OH + M$ is also so fast that no very large shift of energy occurs, and the emission from $OH^\star$ is a fairly faithful representation of the states in which it is made. Gaydon[63] is of the opinion that the formation of $OH^\star$ in hydrocarbon flames requires the presence of ground state CH radicals. If the recently proposed ionization mechanism (2) and (3) is correct, the hints linking $OH^\star$ to CH might link it just as well to H_3O^+; and oddly enough, a marked similarity exists between the rotational energy distribution of $OH^\star$ in hydrocarbon flames and in discharges through water vapour.[154]

The emission from $C_2^\star$ and $CH^\star$ has been studied for its dependence on mixture strength, pressure, and the fuel burnt.[63] Both molecules in their ground states have been observed weakly in absorption in an equimolecular C_2H_2–O_2 flame at 0·4 cm Hg pressure.[139] $[C_2^\star]/[C_2]$ was about 70 times the equilibrium ratio. The CH absorption was not found in the stronger emission bands of $CH^\star$ at 4315 and 3900 Å but in the 3143 Å band which is only weakly emitted by $CH^\star$; and this is evidence that $CH^\star$ is not thermally excited since the lower state for all three systems is the ground state of CH.[63] Absorption by these molecules can also be observed in the products obtained by flash photolysing C_2H_2–O_2 mixtures [155] and in those behind detonation waves.[156]

Using acetylene with isotopically tagged carbon atoms, Ferguson showed that excited $C_2^\star$ in C_2H_2–O_2 flames did not preserve the pairing of C atoms in the fuel[157]. The formation of $C_2^\star$ in other systems also seems to involve carbon atoms in separate entities. Miller and Palmer[158] swept various organic halides by a carrier gas into an atmosphere of potassium vapour at 670°K and observed $C_2^\star$ radiation in the resulting diffusion flame. From $CHCl_3$ or $CHBr_3$ plus K, the $C_2^\star$ was found preferentially in the $v' = 1$ and 2 vibrational levels of the excited electronic state. They suggested the reactions

$$2CH \rightarrow C + CH_2$$
$$C + CH \rightarrow C_2^\star + H$$

the second of which is energetic enough to give $C_2^\star$ in $v' = 1$ of the excited state. Conceivably the same process could take place in flames, though the distribution of $C_2^\star$ among its vibrational levels is not the same for the halogen diffusion flames as it is for premixed hydrocarbon flames. The reactants $CFCl_3$–K, CCl_4–K, and CCl_4–Na all gave $C_2^\star$ excited preferentially into higher vibrational states, $v' = 7$ and 8, and were thought to involve analogous reactions of CCl radicals. From a diffusion flame of C_2Cl_4–K, $C_2^\star$ was not observed.

In diffusion flames of ClF_3 + (CH_4 or C_2H_2), $CH^\star$ was not found when oxygen was rigorously excluded, but was obtained otherwise.[159] Its excitation is therefore presumed to require oxygen and probably to involve the simultaneous formation of CO. Such possibilities as $C_2 + OH \rightarrow CO + CH^\star$, favoured by Gaydon,[63] or $O + C_2H \rightarrow CO + CH^\star$ by Hand and Kistiakowsky,[128a] would satisfy the facts known at present. The former suggestion uses only species known to be present but is a four-centre reaction which are rare among fast gas phase processes. While C_2H has not been identified in flames, its existence is suggested by the interpretation of the reaction of fuel-rich C_2H_2–O_2–Ar mixtures heated in shock tubes.

$HCO^\star$ radiation is said[63] not to occur as commonly in flames as that from $OH^\star$, $C_2^\star$, or $CH^\star$. The spectrum can also be obtained in fluorescence by illuminating formaldehyde vapour with light in the far ultraviolet, the exciting wave lengths possibly lying in absorption bands of H_2CO at 1287 and 1223 Å.[160]

The ultraviolet radiation from CO occurs in hot C_2H_2–O_2 flames and is almost certainly the same as the far ultraviolet radiation observed from C_2H_2–O_2 or from CH_4–O_2 mixtures heated by shocks[127]. In shock tubes, the radiation intensity was slight from CH_4 and much larger in the C_2H_2 mixtures where it developed with about the same exponential time constant as characterized the development of the branching chains during the induction period. The formation of CO was appealed to for the excitation of this high energy radiation; and the same reactants as those for equation (2), O + CH, are plausible.

Although the hints reviewed above suggest that the electronic excitation, including ionization, in hydrocarbon flames depends fundamentally on only a few radical–radical interactions, the particular processes involved are not identified very well. This state of affairs may not be true for long, however, because the subject interests a number of active investigators.

CHAPTER 7

SOOT IN PREMIXED FLAMES

THE formation of soot in the gas from a premixed flame is usually a form of disequilibrium. Solid carbon could not exist under equilibrium conditions unless the over-all atom ratio of the reactants, O/C, was about unity or less, and while soot contains a large proportion of H atoms and some O and is not solid carbon, bodies of its composition should not exist either. Street and Thomas[161] determined the critical O/C ratios at which many fuel–air mixtures would just form a luminous carbon zone in Bunsen burner flames at atmospheric pressure. They observed soot when the over-all atom ratio was $O/C < 1{\cdot}2$ for acetylene fuel; when $O/C < 1{\cdot}7$–$1{\cdot}9$ for C_2H_4, C_3H_6, or C_4H_8; or when $O/C < 2{\cdot}2$ for C_2 to C_4 paraffins.

Figure 7.1, taken from Macfarlane,[162] shows how the soot yield in premixed flames varies with wide changes in burning conditions. If equilibrium had obtained for these flames, soot should not have

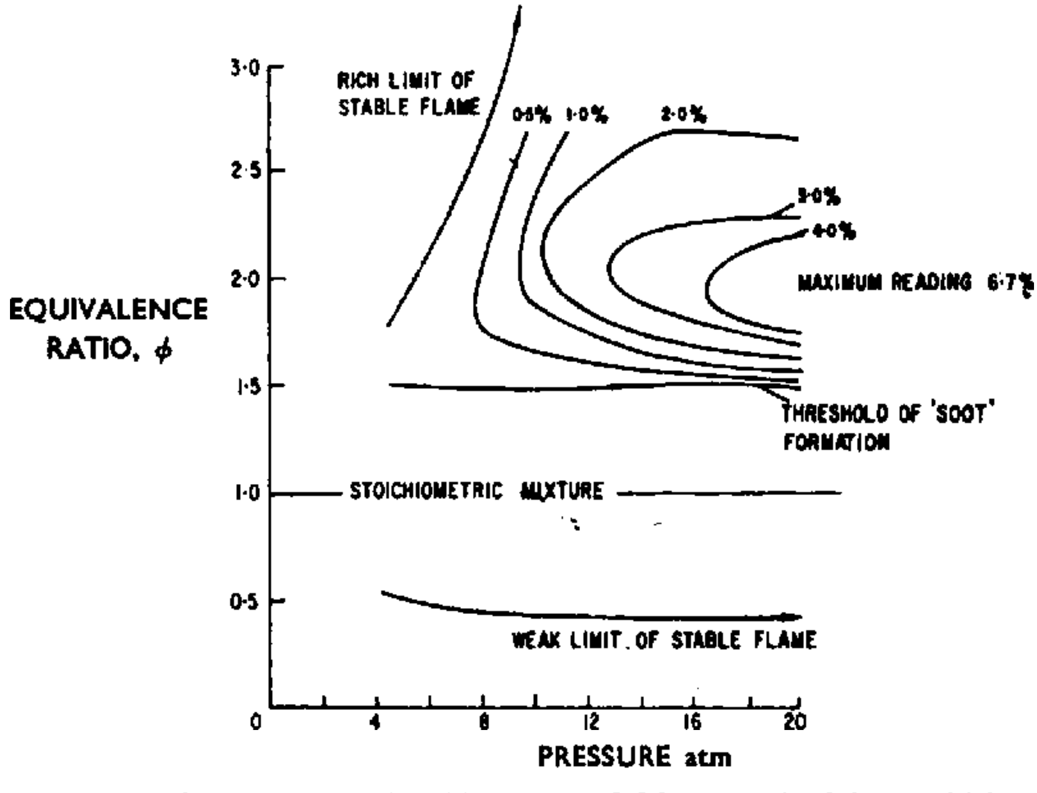


FIG. 7.1. Percent by weight of isopentane fed in a premixed flame which was recovered in the product as filterable solids and tars (Macfarlane[162]).

separated until an equivalence ratio of nearly 3·2 was reached; but the threshold occurs at much leaner mixtures, at an equivalence ratio of about 1·5 or for atom ratios of $O/C < 2{\cdot}1$. As the mixtures are made richer at constant pressure, the soot yield goes through a maximum and decreases again in the cooler flames near the rich limit. The region of very rich flames has not been investigated much by other experimenters—most have worked nearer the threshold of soot formation.

The ratios quoted above and Fig. 7.1 prove the lack of equilibrium, but the different tendencies of various fuels to give soot in their flames is not very direct information, because the soot need not form from the original fuel. When fuels containing 1–4 carbon atoms are burnt, the blue-green flame is followed by a clear non-luminous space of thickness comparable to the flame thickness; and the soot condenses downstream of the clear space. Aromatic fuels do not possess a clear space, in Bunsen flames at least[161], and the soot region follows directly on the flame proper. In either case, the soot forms in the post-flame gas and it is the conditions here which are really relevant. Some attempts to correlate conditions in the post-flame gas with the presence of soot will be described.

Most of the carbon fed in the fuel is present as CO in rich post-flame gas and does not participate in soot formation. Ferguson[163] exploded rich mixtures of $C^{13}O$–C_3H_8–O_2 and found that no significant amount of C from the $C^{13}O$ was incorporated in the soot.

The post-flame gas from sooty flames often contains hydrocarbons equivalent to 10 per cent or more of the carbon fed, though the original fuel may no longer be an important constituent.[164,165] The rapid formation of CO in the flame involves species such as O atoms and is much slower once these active oxidants are exhausted. The hydrocarbons in the post-flame gas are themselves non-equilibrium species, and in view of its hydrogen content, the soot can also be considered a hydrocarbon of sorts. Acetylene is the hydrocarbon present in largest concentration in the burnt gas from most flames, methane flames excepted; and Porter[265] suggested that soot forms directly from acetylene in most flames.

Millikan[166] studied the conditions when soot first appeared in the post-flame gas from C_2H_4–air flames burning at atmospheric pressure on a porous burner. The [OH] in the reaction zone was about 5 times $[OH]_{equ}$ calculated for the post-flame gas and decayed rapidly through the clear region between the flame proper and the carbon zone. It was found that soot, deposited on a small wire immersed in the carbon zone, would burn off when the wire was moved upstream into the clear space. The clear space was therefore an oxidizing region which terminated when [OH] had decayed to its equilibrium value and only then could soot deposit. [C_2H_2], which was 2–3 times greater than [CH_4], was measured by infrared absorption, the necessary corrections for the underlying water bands and the absorption coefficient for C_2H_2 at flame temperatures having been worked out previously[167]. The gases contained at most only a thin cloud of carbon particles, and the temperature from the spectral distribution of its emissivity was proved the same as the gas temperature by sodium D-line reversal.[168] Since OH radicals in the clear zone seemed to oppose soot growth, it was postulated that the visible onset of soot farther downstream was opposed by oxidation processes (assumed proportional to $k_{\mathrm{ox}}[\mathrm{OH}]_{\mathrm{equ}}$) and made possible by growth processes (proportional to $k_g[C_2H_2]$); and that soot appeared when

$$\frac{[C_2H_2]}{[\mathrm{OH}]_{\mathrm{equ}}} > \frac{k_{\mathrm{ox}}}{k_g} = 0{\cdot}05 \times e^{34\ \mathrm{kcal}/RT} \tag{7.1}$$

The numerical constant was determined to fit the data at 1720–1820°K. It may be that at lower temperatures (1) would not fit as well, for the heterogeneous deposition of soot from hydrocarbons on to a carbon surface, and its consumption by O_2 or CO_2, cannot be expressed by an Arrhenius equation at 1000–1500°K.[169] The particle or precursor which is supposed to grow or to be destroyed, depending on [C_2H_2]/[OH] and the temperature, was not identified. If it were some sort of a nucleus, such identification would be very difficult for the nucleus need be only a small part of the soot particle.

There is evidence that moderately short polymers of C_2H_2 may be intermediates in soot formation from acetylene. Aten and Greene[170] found diacetylene, C_4H_2, and vinyl acetylene, C_4H_4, along with higher boiling unidentified materials, in C_2H_2–Ar mixtures which had been heated briefly in reflected shock waves to 1400–2500°K; and Bradley and Kistiakowsky showed by sampling into a time-of-flight mass spectrometer that C_4, C_6, and C_8 hydrocarbons were present in the hot gas itself.[128] In the latter work, the concentration of polymers decreased at about the same time that appreciable quantities of soot should have appeared according to Hooker's[171] measurements of the time lag for carbon deposition in similar shocked gas. The question whether such precursors are necessary intermediates or if acetylene itself deposits directly on a growing soot particle has not been answered conclusively.

The choice of OH and C_2H_2 as the chief species to consider was reasonable for Millikan's C_2H_4 flame where acetylene was the principal hydrocarbon species present. For other flames, it is possible that other hydrocarbons could be important. Fenimore, Jones, and Moore[164] also used the notion that the onset of soot in premixed flames might be determined by a balance between processes of growth (proportional to one or more hydrocarbons) and oxidation processes (proportional to $[H_2O]/[H_2]^{\frac{1}{2}} = [OH]_{equ}$). If so, it was necessary to suppose that not only $[C_2H_2]$ contributed to soot growth, as was assumed in equation (1), but that $[CH_4]$ could also make some smaller contribution, and that whenever it was present, $[C_6H_6]$ in the post-flame gas was around 50 times as effective as $[C_2H_2]$ in causing the onset of visible soot. $[C_6H_6]$ was always very small in the post-flame gas from simple hydrocarbon fuels, however, unless it was added in the fuel. Such experiments suggest that the importance of acetylene to soot growth is that it is often the most plentiful hydrocarbon species present. Other hydrocarbons may be as important if present in large amounts, or even certain ones in small amounts. In diffusion flames of light paraffins or ethylene, Cole and Minkoff[172] found no correlation between soot formation and acetylene in the reaction zone. But in such flames, C_2H_2 would not have been the chief hydrocarbon present in the region of soot growth; as was proved for methane flames at least by Gordon and co-workers.[173] No correlation should have been found if other hydrocarbons than acetylene could deposit soot.

When the soot formed in premixed flames is examined in the electron microscope[165], it is found to be filaments if caught on metal grids, or sometimes aggregates of various sizes if caught on quartz or mica slips. These may be artifacts of the mode of collection. Samples obtained by sucking a slightly sooty gas through a probe[168] contained no filaments and were rather uniform in size—about 400 Å in diameter collected well out in the soot zone and considerably smaller when collected some 10 ms earlier, farther upstream, from an ethylene–air post-flame gas at about 1800°K. As estimated by the extinction of light at the two levels, about 3 times as much soot was in the cloud at the downstream as at the upstream station. If a given number of particles had grown to contain 3 times as much soot, the particle diameter should have increased by only $^3\sqrt{3} = 1{\cdot}4$–$1{\cdot}5$, but it appeared that the particle diameter increased several times between the two stations; so some of the particle growth may have been an aggregation of small particles into fewer large ones. Particles of the order of a few hundred angstroms diameter are the most frequently observed size in other premixed flames and even in diffusion flames.[174] Streznewski and Turkevitch[175] found that soot from a benzene diffusion flame had an average diameter of 450 Å and a size distribution agreeing with a symmetrical Gaussian curve of half width 195 Å.

The extinction of a beam of light by a cloud of particles is partly due to scattering, partly to absorption. For soot particles smaller than about 600 Å, the extinction by scattering of light of 6000 Å or more is not important compared to absorption. The extinction can be expressed empirically[176] as a function of wavelength of the light by

$$\log (I_0/I) = C/\lambda^n \tag{7.2}$$

where C depends on the concentration of carbon in the cloud but n does not. n can be determined either in the flame or by catching a thin soot deposit on a cooled glass plate.[177] If the plate is allowed to become hot as the soot is collected, the n value subsequently measured is decreased. The value of n was found to be quite variable, 0·7–1·43 for a variety of fuels,[178] and not constant even for the same fuel. Millikan[177] then found that n depended on the composition of the soot, and increased about linearly with the H/C atom ratio from $n = 0{\cdot}66$ for H/C = zero (carbon evaporated in a vacuum from a spectroscopic electrode) to $n = 1{\cdot}9$ for H/C = 0·53 (soot from a low temperature C_2H_4–air flame). A measurement of C and n from extinction curves of the soot cloud at various levels in a post-flame gas may tell something about the soot. The estimate given in the last paragraph, that the total concentration of carbon in the cloud increased threefold between two stations was read from Millikan's data.[166] At the same time, n in equation (2) decreased from about 2·4 to $1{\cdot}8 \pm 0{\cdot}2$; which implies that the H/C ratio in the soot decreased from around 0·7 to around 0·5. The soot, initially containing 2/3 or more of the hydrogen in the C_2H_2, must have changed in composition by stewing out hydrogen as it flowed downstream.

Hydrocarbon flames are not the only ones which can form a condensed phase, of course. The post-flame gas from trimethyl borate–air flame[179] was found to contain boric oxide droplets of about 1200 Å diameter when first observed by light scattering experiments. They grew as the gas flowed downstream to about 1800 Å in 30 ms or so, mostly by aggregation of smaller into larger droplets. This condensation resembles soot formation in that a gas, H_2O in this instance, was presumably lost at some point of the process. In the vapour phase, most of the boron was present as HBO_2; but the condensed phase must have been nearer B_2O_3 in composition.

CHAPTER 8

FLAME INHIBITION

Flammability Limits

A CH_4–air mixture containing about 10 per cent of fuel burns faster than any other composition of these reactants. If the mixture is diluted by air or fuel, compositions are reached while the burning velocity is still a few cm s^{-1} which no longer propagate flame. These flammability limits occur at about 5 and 14 per cent of CH_4, and corresponding limits are found with other fuels. The standard method[180] of measuring them is to attempt to ignite a large volume of quiescent gas in a long tube of 5 cm or more diameter, open at the lower end so that the gas remains at atmospheric pressure during the upward passage of the flame. If the flame travels the length of the tube, the mixture is called flammable. It is specified that the flame should propagate upwards because many mixtures will burn upwards but not downwards. Fuel-rich hydrocarbon flames are notably sensitive to the direction of flame propagation, though CH_4–air is an exception with rich limits about 14 per cent CH_4 for upwards burning and about 13 per cent for downwards. The ethylene–air rich limit occurs at 28–32 per cent C_2H_4 for upward burning but only 15 per cent for downwards.

Egerton and co-workers[7,181] found that they could burn leaner mixtures on flat flame Powling burners than were flammable in tubes. Fuel-rich flames were difficult to stabilize and rich mixtures, flammable by the standard test, could not be burnt as steady flat flames.[7] Table 8.1 gives some limits determined by flat flames and in tubes.

There are two notions at present why limits occur. One view is that the limit is an inherent property of a one dimensional flat flame and that diluting the reactants to slower burning and cooler compositions eventually brings one to some catastrophic point where flame propagation breaks down. The catastrophe suggested by Van Tiggelen[182] and by Burden *et al.*[183] was that the generation of free radicals in branching chain reactions could no longer outrun their consumption in terminating reactions. Spalding[184] and Mayer,[185] independently, based a more general theory of inherent limits on the consideration that a strictly adiabatic flame is an idealization. They considered that

TABLE 8.1

Flammability Limits and Burning Velocities at the Limits of some Fuel–Air Mixtures

Fuel	% H_2O in mix	Flat flames*		Upward propagation† in tubes	
		% fuel at lean limit	Burning velocity cms s^{-1}	% fuel at lean limit	% fuel at rich limit
CH_4	—	5·31	3·40	5·4	14·0
C_2H_6	—	2·53	3·50	3·0	12·5
C_3H_8	—	1·89	3·82	2·2	9·5
C_4H_{10}	—	1·40	3·72	1·9	8·5
C_2H_4	—	2·72	3·74	3·1	32·0
CO	0·12	15·89	3·12	—	—
	0·50	14·18	4·20	—	—
	1·35	12·79	3·52	—	—
	2·1	—	—	12·5	74·0
$(CN)_2$	1·90	5·05	3·38	6	32·0

* From Badami and Egerton.[181]

† From Coward and Jones.[180]

the hot gas radiates and consequently possesses a falling temperature gradient in the post-flame region which cools the reaction zone the more the smaller the burning velocity. But a cooler reaction zone gives a slower burning rate and therefore the temperature of the reaction zone might be lowered still more. The reciprocal action of a greater fraction of heat lost as radiation and of slower burning velocity becomes catastrophic at a low enough flame temperature for simple theoretical reaction models, and a flammability limit is predicted at a finite burning velocity.

It is probable that inherent limits exist, and an example will be given presently in which it was supposed that they were approximated experimentally. The observed limit need not necessarily be an inherent one, however, as was pointed out by Linnett and Simpson.[186] These authors noted that Egerton's work had extended the lean limits found in tubes, and that the burning velocities in Table 8.1 were approximately constant. They inferred that the observed limit might be fixed by the least burning velocity which was stable under the conditions used. Recalling how it is necessary to pay attention to suppressing instabilities in order to establish a slow flame at all, they thought that convective effects might blow out the flames at flows of 3–4 cm s^{-1}.

Their opinion that a limit mixture is just a slowly burning one which is easily extinguished by convective forces or perhaps by heat losses to the apparatus used was also favoured by Dixon-Lewis and Isles.[187]

How close an observed limit is to an inherent theoretical one need not be specified in order to use the observation as an indication of the ease of the overall reaction. Limits obtained by diluting stoichiometric mixtures with inert nitrogen, until they will only just propagate flames have been used for this purpose. A "limiting oxygen index of combustion" was defined as $[O_2]/([O_2] + [N_2])$ in a mixture containing the maximum of added nitrogen which will burn. Hall and co-workers[188] quoted some of these indices; 0·056 for H_2, 0·069 for moist CO, 0·130 for CH_4, 0·118 for C_2H_6. They inferred from the values that hydrocarbons inhibit their own combustion in a way which hydrogen and carbon monoxide do not, and went on to show that the index for formaldehyde was about the same as for moist CO and therefore this substance did not inhibit its own combustion either. The conclusion is borne out by the observations of Legrand *et al.*[189] that the flammability limits of H_2CO–air mixtures are about as wide as those of H_2–CO–air.

The same point about the self inhibition of hydrocarbons is suggested by the calculated adiabatic flame temperature of 1500°K for lean limit mixtures of CH_4–air or for other light saturated hydrocarbons; this temperature is about 1600° for the hexanes and octanes.[190] By contrast, 10 per cent of H_2 in air, with an adiabatic flame temperature of less than 1100°K, propagates a coherent flame.[180] Even leaner H_2–air mixtures burn, but the light H_2 molecules diffuse preferentially into regions where burning occurs and the flame is not a flat flame in any approximation. At the H_2-rich limit, a similar preferential diffusion would have to be by the heavier O_2 molecule, and it does not occur noticeably. The rich H_2–air limit mixture has a low flame temperature, only about half the 1800°K of the rich CH_4–air limit. The self inhibition of the hydrocarbons is probably to be attributed to the fewer free valencies present in their flames than in H_2–CO flames. It has been already remarked in chapter 5 that this is particularly true of the rich hydrocarbon flames. In rich CH_4 mixtures, more than in lean ones, the generation of O atoms and of free valencies by $H + O_2 \rightarrow OH + O$ is more nearly equal to their consumption by $O + CH_3 \rightarrow \ldots \rightarrow CO + \ldots$, and a greater fraction of the free valencies is necessarily consumed in the burning. An equality between the rate of formation of O atoms and their rate of consumption by CH_3 radicals might give a fundamental limit of the sort envisaged by Van Tiggelen.

A characteristic of hydrocarbon–air limits is that, while the lean limit is not very dependent on pressure, the fuel-rich limit is displaced strongly towards richer mixtures by increasing pressures; e.g. the isopentane limits in Fig. 7.1 in the last chapter. Such a displacement does not occur for H_2–air limits. The rich limit of CH_4–air, about 14 per cent CH_4 at 1 atm, is displaced to 35–40 per cent CH_4 at 100 atm[180]. This shift is not understood, though one may suspect that something like a cool flame is being approached which involves reactions of hydrocarbon radicals with O_2 molecules in very fuel-rich mixtures. For CH_4, it is possible that at high pressures there might be an increasing role of termolecular $CH_3 + O_2 + M$ (rate constant $= 2 \times 10^{15}$ $cm^6\,mole^{-2}\,s^{-1}$) as compared to $CH_3 + O$ (rate constant $= 4 \times 10^{13}$ $cm^3\,mole^{-1}\,s^{-1}$), the constants being taken from chapter 5 with M assumed to be CO_2. If [O] were 1 per cent of $[O_2]$, the two reactions would be comparable at 10 atm.

In addition to composition limits at fixed pressure, flames of fixed composition can be extinguished by reducing the pressure sufficiently in a given apparatus. Although the radiation theory predicts an intrinsic limit at low enough pressures, the extinction of flames of hydrocarbons with air or oxygen are probably quenching effects which can be avoided, as far as is known, by scaling up the dimensions of the apparatus as the pressure is reduced. The special case of the decomposition flame of acetylene may be an exception; Cummings and coworkers[191] thought that a limit might be approached for this flame because of radiation losses. When ignited in tubes, acetylene propagated flame upwards with burning velocities of 2·8–8·5 cm s^{-1} at pressures of 2·02–10·2 atm respectively and with measured brightness temperatures of the hot soot of 1620–2140°K. In the faster flame, about 2 per cent of the C_2H_2 remained undecomposed; in the slower about 28 per cent. It was considered that at still lower pressures, a flammability limit was encountered because the slower flames lost more of their energy by radiation. The more usual non-sooty flames are less luminous, and the radiation losses are much smaller. Wolfhard[192] has stressed that an intrinsic limit due to increased radiation losses at decreasing pressures has never been observed for near stoichiometric flames of hydrocarbons with air or oxygen.

Le Chatelier's Rule

The rule states that mixtures of lean or of rich limit mixtures are themselves limit mixtures. A numerical example is given in the next paragraph. The rule is often obeyed fairly well by the common fuels, quantitatively by the flat flame hydrocarbon limit mixtures in Table 8.1. When it is not obeyed, the separate limit mixtures are inferred to possess strong mutual interaction. Thus mixtures of the hydrocarbon-air with the CO-air mixtures in Table 3.1 do not obey it very well,[181] and this is explained by the assumption that CO flames require H atoms to consume the O_2 molecules and OH radicals to form CO_2. Another example of mutual interaction is Simmons and Wolfhard's[193] observation that the H_2–air limits are contracted much more sharply by added Br_2 than corresponds to the rule. Le Chatelier's rule is not a very sensitive criterion for mutual interaction of two reacting systems, however; because even when it is approximately obeyed, the systems may still interact. For example, fuel-rich H_2–air and CH_4–air limit mixtures obey it approximately,[180] but CH_4 is considered to inhibit H_2 burning as will now be discussed.

Inhibition of Burning Velocity

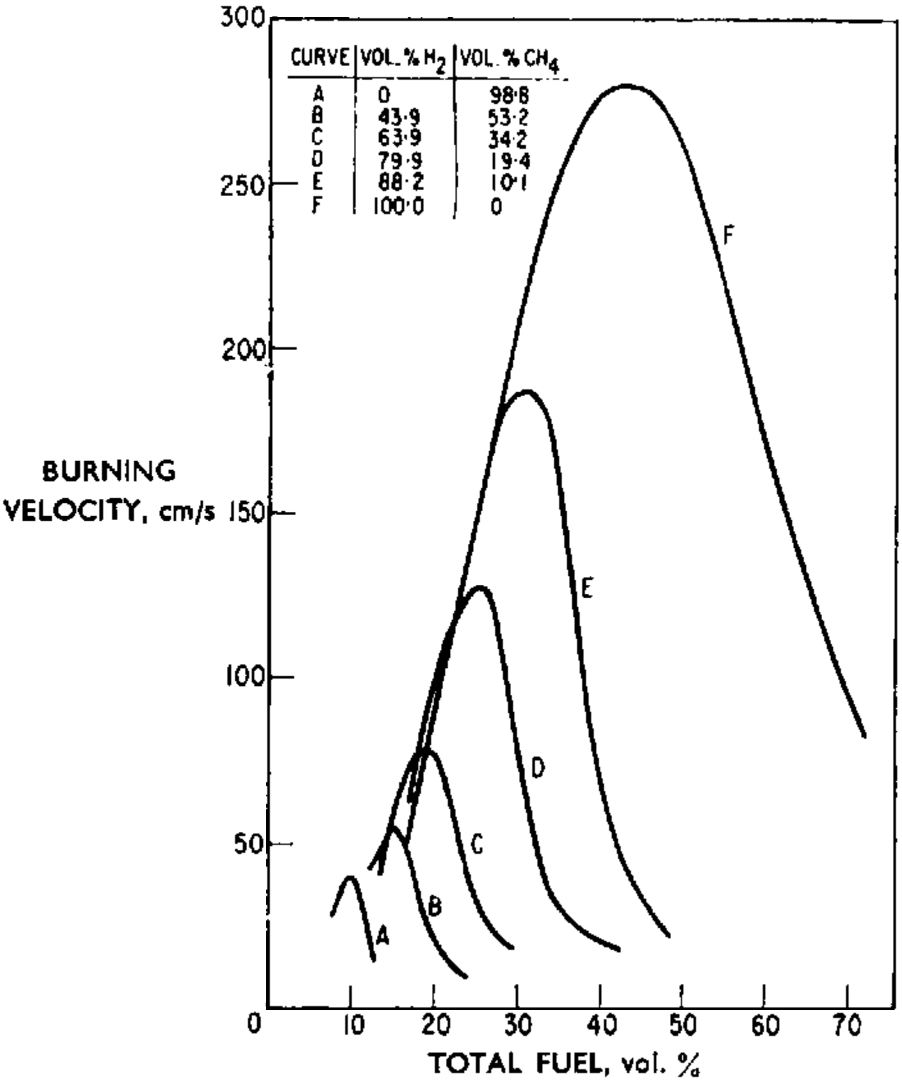
Figure 8.1 from Scholte and Vaags[194] shows some burning velocities for various H_2–CH_4–air mixtures at room temperature and atmospheric pressure. The fuel mixture for curve *E* is composed of 0·101 CH_4, for which the rich fuel–air limit is 14 per cent fuel, and 0·882 H_2 for which the fuel–air limit mixture is 75 per cent fuel. According to Le Chatelier's rule, the percentage of mixed fuel, *L*, in the limit mixture is given by

$$\frac{1}{L} = \frac{0{\cdot}101}{14} + \frac{0{\cdot}882}{75} = \frac{1}{53}$$

and in Fig. 8.1, it looks possible that curve *E* would approach its rich limit at 53 per cent fuel. It is not very surprising therefore that the burning velocity of very rich H_2–air flames should be reduced by the addition of CH_4.

The maximum of curve *E* is near the maximum burning velocity for any CH_4–H_2–air mixture which contains 3·1 per cent of CH_4; and its burning velocity, 2/3 of the maximum burning velocity of pure H_2–air mixture, can be viewed as an inhibition of H_2 burning by CH_4. Lask and Wagner[195] showed that the same reduction could be obtained by a smaller addition of bromine; 1·5 per cent of Br_2 added to H_2–air mixtures reduces the maximum burning velocity to 2/3 of the uninhibited maximum.

Methyl bromide, a combination of both inhibitors just mentioned, was studied by Burden and co-workers[183] who did not measure burning



CURVE	VOL. % H_2	VOL. % CH_4
A	0	98·8
B	43·9	53·2
C	63·9	34·2
D	79·9	19·4
E	88·2	10·1
F	100·0	0

FIG. 8.1. Burning velocities of CH_4–H_2–air mixtures (Scholte and Vaags[194]).

velocities but only the flammability limits of H_2–air–CH_3Br mixtures. They found that the initial ratios of $[O_2]/[CH_3Br]$ in near limit mixtures were related to the calculated adiabatic temperature, T_{ad}, by:

$$[O_2]/[CH_3Br] = 0{\cdot}05\ e^{14\ \text{kcal}/RT_{ad}}$$

and proposed that the branching reaction of H atoms with O_2 was opposed by terminating processes which occurred at the rate of:

$$H + CH_3Br \xrightarrow{k} CH_3 + HBr$$

Then the branching chains could only develop when:

$$k_1[H][O_2] \gg k[H][CH_3Br]$$

and the ratio $[O_2]/[CH_3Br]$ at the limit was roughly k/k_1 at T_{ad}. The actual inhibition by added methyl bromide was perhaps due to the consumption of free valencies by the methyl radical, and to the action of HBr in ways not yet understood; but the sum of these was supposed to equal the rate of formation of methyl radicals. The interpretation could be only roughly true because the ratio of reactants in the cold gas could not have been the mean ratio in the flame, nor could T_{ad} have been a mean reaction temperature. Furthermore, it may be only approximately true that the limit was an inherent property of the reaction. The competing rates of branching and terminating reactions may have needed to be only roughly equal for extinction of the flame. Despite these reservations, the interpretation seems valid. If one accepts the k_1 from Table 4.1 of chapter 4, Burdon's treatment gives a rate constant for the reaction of H atoms with methyl bromide which is not inconsistent with the observations at much lower temperatures.[47] In unpublished work, the writer has checked the rate constant by probing some H_2–NO–N_2O flames containing a little added CH_3Br. [H] was estimated from the nitrous oxide profile, using the k_α of Table 4.1, and the rate constant determined from $-d[CH_3Br]/[CH_3Br]dt = k[H]$ was found to have only a small temperature dependence and to equal $1{\cdot}4 \times 10^{13}$ cm^3 mole^{-1} s^{-1} at 1900°K. This is twice the value deduced from the data of Burdon and co-workers—and the agreement is good enough to suggest their view is essentially correct.

When CH_4 or Br_2 are added to CO flames, the effects induced depend on the moisture or H_2 content of the CO. CH_4 added to quite dry CO–air increases the burning rate until the ratio of $CH_4/CO = 1/10$; further additions inhibit.[194] Doubtlessly, this reflects a need for H and OH radicals for CO to burn with air. When Br_2 is added to stoichiometric CO–O_2 of uninhibited burning velocity 20 cm s^{-1}, it has little effect.[196] Such a mixture contains only a few hundredths of 1 per cent of H_2 as judged by the effect of traces of H_2 on the burning velocity.[197] The inhibition of the burning velocity by added Br_2 is pronounced, however, if the CO contains 0·75 or 4·5 per cent H_2 and is faster burning initially.[196,198] When only one part in 10^4 or so of hydrogen containing substance, say $[H_2O]_O$, is present, it seems likely that the level of [OH] depends more on $[H_2O]_O$ than on the total free radicals present, which are mostly [O] atoms in any case. If added Br_2 inhibits by decreasing the concentration of free valencies, the inhibition does not affect [H] and [OH] very much when $[H_2O]_O$ is small enough. Consider as an illustration the equilibrium $H_2O + O = 2\,OH$ at 2000°K and ignore all other radicals except O and OH; so that $[H_2O] = [H_2O]_O - [OH]/2$. When $[H_2O]_O$ is 1 per cent or so of the total gas, [OH] is proportional to $[O]^{1/2}$ and decreasing the total free valencies by a factor of four essentially decreases [O] by a factor of four and [OH] by a factor of two. But if $[H_2O]_0$ is only 0·01 per cent of the total gas, most of the $[H_2O]_0$ is present as OH and remains so despite large changes in [O]. If [O] is now decreased by a factor of four, say from 2 to 0·5 per cent, [OH] decreases by only 20 per cent of its original value. The assumption in this illustration, that $O + H_2O = 2OH$ is equilibrated, was believed to be true by Semenov; it will be discussed further in the next chapter.

The effect of CH_3Br in inhibiting CH_4–air flames resembles that of an equivalent amount of Br_2,[193] about 2·4 per cent of Br_2 or twice as much CH_3Br being required to suppress flammability altogether. Rosser, Wise, and Miller[199] found the same effect to hold when smaller amounts of inhibitors were added; the addition of equal small mole fractions of molecules containing 1, 2, or 3 Br atoms (HBr, CH_3Br, CH_2ClBr, CF_3Br), (Br_2, CH_2Br_2, CF_2BR_2), or $CHBr_3$ decreased the burning velocity of a CH_4–air flame containing 10 per cent fuel in the ratio of approximately 1 : 2 : 3. For CH_4–air compositions other than 10 per cent CH_4, the proportionality of inhibition to bromine content of the additive did not hold. This was ascribed to the non-bromine moiety of the inhibitors; for example, CH_3 from CH_3Br exercises its own inhibition in fuel-rich mixtures. The effectiveness of a little added Br_2 or HBr was reported not to change markedly with changes in mixture strength of the CH_4–air flame, and the effect of halogen on radical concentrations could perhaps be studied best with added Br_2 or HBr. No such studies have been reported so far. In connection with other work, Phillips and Sugden[200] found that 1/4 of 1 per cent of added Br_2 did not significantly affect radical concentrations in a fuel-rich H_2–O_2–N_2 flame; but this was not enough to inhibit H_2–air flames very decidedly anyway.

It is not certain why added bromine compounds inhibit—Wise and Rosser[201] discussed how the addition of any Br compound might decrease the rate of reaction in oxygen flames by substituting inactive atoms for part of the active free radicals. The partial substitution of H by Br would hinder the branching reaction, $H + O_2 \rightarrow OH + O$, of O by Br would hinder the oxidation of CH_3 radicals, etc. A considerable effect is expected because a branching reaction is among those hindered, and a non-branching mechanism should not be so susceptible.

More effective inhibitors have been reported than the substances discussed above, but they are even less understood. Lask and Wagner[193] stated that 0·02 per cent or less of added $Fe(CO)_5$, CrO_2Cl_2, or $Pb(C_2H_5)_4$ was as effective as 0·7 per cent of Br_2 in decreasing the burning velocity of stoichiometric n-hexane–air mixtures at atmospheric pressure. Bonne, Jost, and Wagner[202] attempted to study the effect of $Fe(CO)_5$ on temperature and OH traverses in low pressure CH_4 flames; but it was found that the inhibiting action of a constant mole fraction of $Fe(CO)_5$ decreased markedly as the pressure was lowered, and at pressures low enough for a detailed investigation of the reaction zone of the flame, its effect was very small. The [OH] and the temperature in the reaction zone were then little different with or without added $Fe(CO)_5$.

Miller and co-workers[283] have measured the burning velocity of the fastest burning hydrogen–air mixture when small amounts of eighty different substances were added. For this flame, hydrocarbons as a group were comparable to brominated hydrocarbons as inhibitors, and even iron carbonyl was not tremendously more effective. They suggested that the destruction of radicals by methane was due to

$$2CH_3 \rightarrow C_2H_6,$$

rather than to the reaction of methyl radicals with O atoms as was suggested earlier in this chapter and in chapter 5. The rate constants are about the same[95,100] and either reaction destroys two free valencies in fuel-rich flames. The relative importance should depend on the relative concentrations of CH_3 vs. O; and the first process be more important the more the added methane.

CHAPTER 9

SOME FLAME CALCULATIONS

It is debatable if measurements of burning velocity alone can give enough information to establish a conclusion of much chemical interest. Even so, people have wanted to know if a measured burning velocity was consistent with one or another suspected reaction mechanism. For a simple enough mechanism, the question can be answered by calculating the mass burning velocity (ρv) from equation (1.1) and (1.2),

$$\dot{q}\ \mathrm{cal\ cm^{-3}\ s^{-1}} = (\rho v)C_p\mathrm{d}T/\mathrm{d}z - \mathrm{d}(\lambda \mathrm{d}T/\mathrm{d}z)/\mathrm{d}z \tag{1.1}$$

$$m_iR_i\ \mathrm{g\ cm^{-3}\ s^{-1}} = (\rho v)\mathrm{d}M_i/\mathrm{d}z - \mathrm{d}(\rho D_i\mathrm{d}M_i/\mathrm{d}z)/\mathrm{d}z \tag{1.2}$$

If the generation of heat and products can be represented by a single chemical process of known dependence on temperature and on one reactant, the equations can be solved as accurately as one pleases. Hirschfelder and co-workers[22] obtained solutions for such cases, by numerical integration. These seem to be accepted as standards for checking simpler approximations. Their treatment does not give an explicit relation between reaction rate and burning velocity; and when something is suggested about the reactions merely from a knowledge of the burning velocity, it can be brought out by explicit approximations of which the most commonly used has been the Zeldovich, Frank–Kamenetsky, Semenov equation.[203]

The Zeldovich equation is an approximate solution for equation (1.1) when $\dot{q}$ is assumed to depend so strongly on temperature that it can be neglected between the initial temperature, T_0, and some intermediate T_1 which is supposed to be near to the final temperature, T_f. The temperature gradient is zero both at T_0 and at T_f. It can be obtained at T_1 either by integrating equation (1.1) from T_0 up to T_1, or by integrating from T_1 on up to T_f. The solution is obtained by equating the two estimates of the temperature gradient at T_1. Thus in the region from T_0 to T_1, where $\dot{q}$ = zero, (1.1) gives

$$(\mathrm{d}T/\mathrm{d}z)_{T_1} = \overline{C}_p(\rho v)(T_1 - T_0)/\lambda_1 \tag{9.1}$$

$\overline{C}_p$ = mean specific heat from T_0 to T_i, or approximately from T_0 to T_f

λ_f = value of λ at T_i, or approximately the value at T_f.

In the region from T_i on up to T_f, the first term on the right side of equation (1.1) is less important, compared to the second term, the nearer T_i is to T_f. If the first term is omitted altogether in this region

$$\int_{T_\mathrm{i}}^{T_\mathrm{f}} \dot{q}\,\mathrm{d}T = \int_{T_0}^{T_\mathrm{f}} \dot{q}\,\mathrm{d}T = \frac{\lambda_\mathrm{f}}{2}\,(\mathrm{d}T/\mathrm{d}z)^2 T_\mathrm{i} \tag{9.2}$$

From (1) and (2), one gets for the constant mass flow

$$(\rho v)^2 = \frac{2\lambda_\mathrm{f}\displaystyle\int_{T_0}^{T_\mathrm{f}} \dot{q}\,\mathrm{d}T}{\overline{C}_p^2\,(T_\mathrm{f} - T_0)^2} \tag{9.3}$$

Equation (3) is a limiting law, valid when $\dot{q}$ is appreciable only near T_f. Spalding[204] has shown, however, that even if $\dot{q}$ is appreciable over a larger temperature interval, the equation is still useful. He examined several forms of $\dot{q}$ for which equation (1.1) could be solved exactly and concluded that for any probable curve of $\dot{q}$ vs. T, $(\rho v)^2$ calculated from (3) would be correct to within a factor of three. He gave a modification of (3) which should be more accurate, the modified version being

$$(\rho v)^2 = \frac{\displaystyle\int_{T_0}^{T_\mathrm{f}} \lambda\dot{q}\,\mathrm{d}T}{\beta\overline{C}_p^2\,(T_\mathrm{f} - T_0)^2} \tag{9.4}$$

λ is now the local value, a function of T

$$\beta = 1/2 - 0{\cdot}6604(1 - \tau) - 0{\cdot}4823(1 - \tau)^2$$

$$\tau = \frac{\displaystyle\int_{T_0}^{T_\mathrm{f}} (T - T_0)\lambda\dot{q}\,\mathrm{d}T}{(T_\mathrm{f} - T_0)\displaystyle\int_{T_0}^{T_\mathrm{f}} \lambda\dot{q}\,\mathrm{d}T}$$

In simple cases, the local rate of heat evolution, $\dot{q}$, can be written in terms of the initial reactants. The simplest case of all is when an initial concentration of $[a]_0$ moles cm^{-3}, and of initial mass fraction $(M_a)_0$, is consumed in the flame and $\dot{q}$ is proportional to its rate of reaction. Any other reactant, say species b, is present in excess and is supposed to be related to a by the stoichiometry. The mass fraction, M_a, is obtained from equation (1.2) at any point; but if

$$\rho D_a C_p/\lambda = \delta_a = 1 \tag{9.5}$$

(1.2) gives the same description of the decrease of M_a as (1.1) does of the increase of T, and (1.2) merely states that M_a decreases linearly with increasing temperature,

$$M_a = (M_a)_0 \frac{(T_f - T)}{(T_f - T_0)} \tag{9.6}$$

Equation (5) is a fairly good approximation unless species a is relatively light or heavy; but δ_a equals about 3·3 for H_2 in air, and about 1/2 for C_3H_8 in air[204]. If (6) is true and $[b]$ calculable, $\dot{q}$ can be evaluated,

$$\dot{q} = Q[a][b]k_0\,e^{-E/RT} \tag{9.7}$$

Q = heat released by the reaction per mole of species a

$k_0\,e^{-E/RT}$ = rate constant

and the integration in (3) or (4) can be performed graphically. Finally, if the rate constant is not known, it might be evaluated from an explicit solution of the integral in (3). For example, if in equation (7)

$$Q = \bar{C}_p\rho_0(T_f - T_0)/[a]_0$$

$$[a] = [a]_0\left(\frac{T_0}{T}\right)\left(\frac{T_f - T}{T_f - T_0}\right)$$

$[b] \sim$ unconsumed excess in the burnt gas.

an approximate integration of equation (3) is[203]

$$(\rho v)^2 = \frac{2\lambda_f\rho_0[b]k_0\,e^{-E/RT_f}\left(\dfrac{T_0}{T_f}\right)\left(\dfrac{RT_f^2}{E}\right)^2}{\bar{C}_p(T_f - T_0)^2} \tag{9.8}$$

When one speaks of getting a rate constant by applying the Zeldovich equation to measurements of burning velocity, what is meant is that the measurements as a function of flame temperature have been fitted to equation (8), or to a similar equation appropriate to the assumed order of the reaction, and k_0 and E inferred. The variation in flame temperature is often obtained by adding diluents, or changing T_0.

An Application of the Foregoing Equations

Levy and Weinberg[27] used the equations to discuss temperature profiles through lean, flat C_2H_4–air flames at atmospheric pressure. T was deduced from measurements of the index of refraction, and then $\dot{q}$ calculated from equation (1.1). Substitution of the experimental $\dot{q}$ into (3) gave (ρv) too small by 30 per cent. The use of (4) decreased the discrepancy to only 8 per cent. The authors then[205] used their local values of $\dot{q}$ to consider the following question. If some species, $[x]$ was present which reacted with C_2H_4 at the rate of

$$\dot{q} = \text{constant}\ [C_2H_4][x]\, e^{-E/RT} \qquad (9.9)$$

what must the profile of $[x]$ have been through the reaction zone? Supposing that $M_{C_2H_4}$ and hence $[C_2H_4]$ could be obtained from (6) at each point where T and $\dot{q}$ was known, they could solve for a quantity proportional to $[x]\, e^{-E/RT}$. It then appeared that if E was large, about 40 kcal mole^{-1}, $[x]$ must have decreased far too drastically for it to have been $[O_2]$. If E was small, about 5 kcal mole^{-1}, $[x]$ must have increased markedly through the reaction zone. For intermediate E, $[x]$ must have gone through a minimum. They could not choose among these possibilities, or even decide if (9) were approximately true. In view of the subsequent work on hydrocarbon flames, already described in chapter 5, (9) could have been only approximately true. The lagging oxidation of the CO would have supplied more heat towards the downstream side of the reaction zone than would have been expected according to (9), although most of the heat would have been evolved at about the rate of the destruction of the hydrocarbon. It is interesting that one of their possibilities, E small and $[x]$ increasing through the reaction zone, agrees qualitatively with the more detailed studies; and this is the only one of their three possibilities which is very reasonable chemically. The identification of the O atom as the chief reactant for C_2H_4 in chapter 5 was based on the observation that the species which reacted with the hydrocarbon must have increased its concentration rapidly in the reaction zone, and [O] was the radical concentration which did so most markedly.

Burning velocities are easy to correlate by an incorrect assumption about the chemistry and give less reliable information than can be deduced from temperature traverses. Levy and Weinberg went on to show this by fitting their (ρv) values to an equation of the type of (8) with $[a] = [C_2H_4]$, $[b] = [O_2]$, $E = 42$ to 49 kcal mole^{-1} over the range in T_f available with Powling burners.[205] That is, they showed that

(ρv) could be fitted very well by a fundamentally meaningless correlation because their local values of $\dot{q}$ in the same flames proved that the C_2H_4 did not disappear by a reaction with O_2 of activation energy around 40 kcal. Many correlations of just this kind have been made for hydrocarbon flames, and doubtlessly none of them has any more fundamental significance than the one proved meaningless by Levy and Weinberg.

Such correlations may have practical utility; Brokaw and Gerstein[257] showed how burning velocities of hydrocarbon–air flames, or properties depending on burning velocity such as the quenching distance, could be expressed by equations resembling (8) with activation energies around 40 kcal mole^{-1}. The concentration terms were varied in order to get the best empirical fit, and no fundamental significance was attached to the correlations.

Moist CO–O_2 Flames

CO flames tell something of their chemistry from their burning velocities alone; namely, that pure CO–O_2 or CO–air mixtures may not be able to maintain a steady flame. The burning velocity of stoichiometric CO–O_2 at one atmosphere pressure has been reported[197] to be less than 3 cm s^{-1}; and even this was considered characteristic of mixtures containing less than one part in 10^5 of H_2, rather than of pure mixtures. A little added H_2 or H_2O greatly speeds the burning and furnishes good evidence that the chief oxidation process is not a reaction of CO with O_2. It is assumed here that the main process is

$$\mathrm{d}[CO_2]/\mathrm{d}t = k_8[CO][OH] - k_{-8}[CO_2][H] \qquad (9.10)$$

and the flame work is examined from this point of view.

In the flame studies it was supposed from theory that

$$(\rho v)^2 \text{ was proportional to } \int_{T_0}^{T_f}\left(\frac{\mathrm{d}[CO_2]}{\mathrm{d}t}\right)\mathrm{d}T$$

and the aim of the experiment was to determine the reaction rate, $\mathrm{d}[CO_2]/\mathrm{d}t$, as a function of [CO], [O_2], [H_2O], and the temperature. The reaction rate was expressed

$$\mathrm{d}[CO_2]/\mathrm{d}t = \text{constant } [CO]^s[O_2]^u[H_2O]^w\, e^{-E/RT}$$

and the coefficient for each concentration term was estimated in flames of constant T_f in which that species was present in excess. In this way in fuel-rich flames, s was found to be one;[206,207] in fuel-lean flames,

u was zero[206,208] or perhaps 0·25;[207] and w was 1/2–1 according to various workers with the lower values seemingly determined most reliably.[208] If it is postulated, as Semenov did twenty years ago,[203] that equation (2.2) and (2.3) are balanced,

$$\mathrm{O + H_2 = OH + H} \tag{2.2}$$

$$\mathrm{OH + H_2 = H_2O + H} \tag{2.3}$$

and if the reverse reaction in equation (10) is neglected; one can re-write (10) as

$$\mathrm{d[CO_2]/d}t = k_8 \left(\frac{K_2}{K_3}\right)^{1/4} [\mathrm{CO}][\mathrm{O}]^{1/4}[\mathrm{H_2O}]^{1/4} \tag{9.11}$$

Semenov also assumed that the rate of (2.1), $\mathrm{H + O_2 \rightarrow OH + O}$, was equal to that of both $\mathrm{O + CO \rightarrow CO_2}$ and of the reaction of OH with CO; so that steady state concentrations of the radicals existed. Then [O] in (11) could be written in terms of the initial reactants. The new expression for (11) was multiplied by the heat released per mole of $\mathrm{CO_2}$ formed and substituted into the Zeldovich equation to get the burning velocity of carbon monoxide flames. The process destroying O atoms, $\mathrm{O + CO \rightarrow CO_2}$, would not be considered very important nowadays; if it is omitted, (11) remains but [O] can no longer be written in terms of the initial reactants. One can ask from experiment, however, what the order of [OH] or [O] in a typical moist flame must be, relative to $[\mathrm{OH}]_{\mathrm{equ}}$ or $[\mathrm{O}]_{\mathrm{equ}}$, if (11) is true. Writing $[\mathrm{O}]^{1/4}$ as a multiple of the equilibrium $[\mathrm{O}]^{1/4}{}_{\mathrm{equ}}$ in the post-flame gas, one has

$$[\mathrm{O}]^{1/4} = \alpha[\mathrm{O}]^{1/4}{}_{\mathrm{equ}} = \alpha 2{\cdot}2\, \mathrm{e}^{29\cdot 7\ \mathrm{kcal}/RT}[\mathrm{O_2}]^{1/4}$$

the equilibrium constant being known. Substituting this in (11) along with the equilibrium constants K_2 and K_3 from equation (2.9) and (2.10), and with the approximate value of k_8 from Table 4.1 of chapter 4,

$$\mathrm{d[CO_2]/d}t = 4 \times 10^{13}\, \mathrm{e}^{-44/RT} \alpha[\mathrm{CO}][\mathrm{O_2}]^{1/4}[\mathrm{H_2O}]^{1/4} \tag{9.12}$$

The right side of (12) is of course only $k_8\alpha[\mathrm{CO}][\mathrm{OH}]_{\mathrm{equ}}$—but it shows the temperature and composition dependence expected if α were constant. The order of α can be obtained by comparison with Sobolev's[207] result by the Zeldovich equation. For fuel-lean mixtures containing 2 per cent moisture, burnt at one atmosphere with measured flame temperatures of 1900–2400°K, he obtained

$$\mathrm{d[CO_2]/d}t = 9{\cdot}5 \times 10^{7}\, \mathrm{e}^{-(30\pm 4)/RT}[\mathrm{CO}]$$

where the concentrations of O_2 and H_2O were absorbed into the constant. A smaller activation energy than 44 kcal is expected because the ratio $\alpha = [OH]/[OH]_{equ}$ decreases with rising temperature. His absolute value of $d[CO_2]/[CO]\,dt$ was about 10^5 s^{-1} at 2200°K, and if this is substituted in (12) and $[O_2]^{1/4}$ and $[H_2O]^{1/4}$ inserted, α comes out around 10 which seems a reasonable value.

Sobolev probed the post-flame gas downstream of the flame and found $d[CO_2]/[CO]\,dt$ a few hundred times smaller than he had deduced it from burning velocity in the flame. Friedman and Nugent[58] observed at lower temperatures about a ten-fold decrease in the specific rate of consumption of CO between a flame at 3 cm Hg and its post-flame gas. As was explained in chapter 3, most of this decrease was due to the growth of the second term on the right side of (10)—the decrease being more sharply defined for Sobolev at higher temperatures and pressures.

Flames of cyanogen–oxygen–inert gas resemble carbon monoxide in their sensitivity to moisture. Despite a calculated flame temperature of 2600°K, the stoichiometric mixture with air burns at only around 10 cm s^{-1} when prepared as free as it can be of H-containing compounds. Addition of moisture or hydrogen increases this velocity markedly—for all mixture strengths according to Brokaw and Pease[269] but not for very fuel-rich mixtures according to Rutner and co-workers.[268] From rich flames the products are mostly $CO + N_2$, and it is plausible that CO is an intermediate in lean flames. The mode of consumption of the cyanogen is unknown and one cannot say whether it is directly catalysed by H compounds or if only CO oxidation and the consumption of O_2 are.

Burning Velocity and Radical Concentrations

In the examples above, the rate of reaction and hence approximately the square of the burning velocity was thought to be proportional to $[C_2H_4][O]$ in ethylene flames or to $[CO][OH]$ in carbon monoxide flames. It was impossible to test this dependence by measurements of burning velocity alone because the radical concentrations were not expressed in terms of the initial reactants and the temperature. The failing is usual in flames which are all radical reactions as far as it known. Some years ago, Tanford and Pease[258] attempted to circumvent the problem. They proposed that radicals were present in equilibrium concentrations in the burnt gas, and diffused upstream into the reaction zone where they attacked the species fed initially. The chief result of Tanford and

Pease was the suggestion that if the reaction depended on the concentration of some radical to the first power, the burning velocity would be proportional to the square root of the equilibrium concentration of this species as calculated in the burnt gas. It is now known that the proposed radical concentrations and distribution do not occur generally, so their suggestion cannot be generally true. For very hot flames, however, the equilibrium concentrations are so large that they might approach the actual values—and burning velocity might then correlate with the equilibrium concentration of a radical on which the reaction rate depends.

The moist carbon monoxide–air flame was a favourite reaction for attempting such correlations because $[H]_{equ}$ and $[OH]_{equ}$ can be varied by adding water while maintaining a fixed ratio of $[CO]/[O_2]$ in the reactants and a fixed flame temperature. For many studies, however, the temperature must have been too low for [H] and [OH] to be approximated by the equilibrium values. It may be remembered from chapter 2 that temperatures of 2200–2400°K were necessary for $[OH]_{equ}$ to approximate the actual [OH] in the post-flame gas from fuel-rich hydrogen flames; and higher temperatures would be necessary for the same approximation to be reasonable in the reaction zone. According to the last section, [OH] was about $10[OH]_{equ}$ in the reaction zone of moist carbon monoxide flames at 2200°.

Pickering and Linnett[259] found for approximately constant temperature fuel-lean C_2H_4–O_2–N_2 flames that burning velocities increased with $[O]_{equ}$ or $[OH]_{equ}$, but did not correlate with $[H]_{equ}$. In mixtures containing 30–60 per cent of oxygen initially, $[O]_{equ}$ increased from 0·84 to 1·84 per cent of the post-flame gas, thus by a factor of $(1{\cdot}48)^2$, as $[OH]_{equ}$ increased by a factor of $(1{\cdot}19)^2$ and burning velocity by a factor of 1·50. The result could be consistent with an attack of O atoms on ethylene; and the approximately constant flame temperature of 2690°K may have been high enough for $[O]_{equ}$ to approach the actual [O].

A more reasonable way of writing radical concentrations in terms of the initial reactants is by means of the hypothesis of the chemical steady state. The reaction mechanism is supposed to be known, and the radicals are assumed to be destroyed chemically as fast as formed, or almost as fast, at every point in the reaction zone. The chemical steady state could hardly apply everywhere throughout flames involving rapid branching processes. But flames are known which are believed to react by non-branching processes, and the hypothesis has been applied to these as will be discussed below.

The Hydrazine Decomposition Flame

Murray and Hall[17] measured the steady burning velocity at atmospheric pressure for N_2H_4 vapour containing 3 per cent H_2O. At 423°K, it was about 185 cm s^{-1}. The flame products corresponded to the over-all reaction

$$2N_2H_4 \rightarrow 2NH_3 + H_2 + N_2$$

with a calculated adiabatic temperature of about 1900°K as was also roughly measured. If equilibrium products had been formed, all N_2 plus H_2, the temperature would have been only 1340°. Gray and coworkers[209] and Hall and Wolfhard[210] measured the burning velocity at lower pressures and proved (ρv) proportional to P. A flame can also be obtained above liquid N_2H_4 in glass tubes and (ρv) estimated by the rate at which the liquid burns down. When the results are corrected for quenching by the walls, this (ρv) is also proportional to P up to 1 atm.

The pressure dependence of (ρv) suggests that the rate of the reactions in the flame depends on the square of the pressure. In equation (3) the integral of $\dot{q}$ should vary with pressure in the same way that $(\rho v)^2$ does, and the reaction rates should also vary as $(\rho v)^2$ if corresponding mass fractions and temperatures occur at corresponding points when the pressure is changed. Indeed if these conditions are satisfied, it can be shown[22] from the form of equation (1.1) and (1.2) that if all the R_i vary as P^{2n}, (ρv) and $1/z$ both vary as P^n—which is the reason why low pressure thickens flames. The difficulty with determining reaction order from the pressure dependence of the burning rate is that it is not known if the conditions for a valid test are satisfied. By traverses through the reaction zone, it can be determined if the conditions are met: but then one has better evidence about the reactions than can be inferred from the pressure dependence of (ρv) and the test is no longer needed.

The suggestion for hydrazine is that since (ρv) varies with P, the decomposition may be controlled by second order reactions. The temperature dependence[209,211] implies from the Zeldovich equation an over-all activation energy of 30–45 kcal $mole^{-1}$ for the flame decomposition, with a value of 36 kcal most probable. If a steady state concentration of radicals can be assumed, the observations would be consistent with a second order initiation process,

$$N_2H_4 + M \rightarrow 2R + M \qquad (9.13)$$

followed by a decomposition of most of the N_2H_4 in non-branching chain reactions, and terminated by second order processes. Assuming all propagating and terminating reactions to have identical rate constants, $k \sim 10^{13} e^{-7/RT}$, Gilbert[213] deduced from the burning velocity that the constant for (9.13) should be about $3 \times 10^{18} e^{-60/RT}$ cm^3 mole^{-1} s^{-1}. An apparent difficulty for this interpretation was that the gas phase decomposition of N_2H_4 at lower temperatures had been reported to be first order.[212] But Gilbert re-examined the lower temperature data and showed that they could be interpreted better as evidence for a second order reaction of rate constant just quoted than for the original interpretation of a first order decomposition. Profiles of species or temperatures have not been obtained, however, and the general type of mechanism cannot be considered settled.

The rate constant assumed by Gilbert for all propagating and terminating reactions was Birse and Melville's[260] measured value for the attack on H atoms on hydrazine at 400–500°K. A more recent measurement by Schiavello and Volpi[261] does not agree very well with the older work. In neither study was any evidence found for chain decomposition reactions of considerable length. Indeed, Schiavello and Volpi claimed a quantitative titration of H atoms according to the overall reaction, $H + N_2H_4 \rightarrow NH_3 + \frac{1}{2}N_2 + H_2$. The long chains which are the heart of the proposed flame mechanism seem to have been found at higher temperatures by Michel and Wagner[277] who heated a little hydrazine in much argon in a shock tube to 1100–1400°K, 3–7 atm pressure, and followed its decay by absorption spectroscopy. The time for half the initial hydrazine, $[N_2H_4]_0$ in mole cm^{-3}, to decompose was approximately

$$t_{½} = \frac{10^{-14.4} e^{40\text{kcal}/RT}}{[N_2H_4]_0^{½}} \text{ seconds}$$

which suggests chain reactions of overall 3/2 order in hydrazine and independent of argon. This does not confirm the overall second order decomposition inferred from steady flames at low pressures; but it is very possible that steady flames at 3–7 atm possess a smaller pressure dependence.

The radicals involved are unknown. Lord and Sederholm[278] studied the infrared emission from the hydrazine flame under high resolution and observed many lines which could be assigned neither to N_2H_4 nor NH_3—nor to any other definite species because of the many possibilities all containing only N and H atoms and hence having their infrared bands in the same region. Lines observed in the hot ammonia of NH_3–O_2 diffusion flames and assigned tentatively to the NH_2 radical were not observed in the N_2H_4 decomposition flame, so $[NH_2]$ was perhaps smaller in the latter.

The Hydrogen–Bromine Flame

The classical reaction law for hydrogen and bromine is[262]:

$$\mathrm{d[HBr]/d}t = \frac{2kK^{1/2}[H_2][Br_2]^{1/2}}{1 + k''[HBr]/k'[Br_2]}$$

where a steady state of [H] and [Br] is assumed and the constants refer to the elementary steps:

$$Br_2 \rightleftharpoons 2Br, \; K = [Br]^2_{equ}/[Br_2]_{equ}$$

$$Br + H_2 \xrightarrow{k} HBr + H$$

$$H + Br_2 \xrightarrow{k'} HBr + Br$$

$$H + HBr \xrightarrow{k''} H_2 + Br.$$

This has been confirmed repeatedly in studies not involving flames, most recently by Britton and Cole.[229] Steady state concentrations of chain carriers were also predicted to be a fairly good assumption in flames by Gilbert and Altman[263] who compared the expected time to establish them with the residence time of the gas in the flame. This was disputed by Campbell, however.[279] The mass burning velocity of mixtures containing 45–60 per cent of bromine gives (ρv) proportional to about $P^{0\cdot73}$ and therefore the reaction may be of about $1\cdot46 \sim 1\cdot5$ order as would be consistent with the slow reaction.[264]

Peacock and Weinberg[230] obtained preliminary traverses of temperature and of Br_2 through slowly burning mixtures at atmospheric pressure by optical methods but considered them of limited value because the transport properties necessary to interpret them could not be confidently assigned. With the values they did choose, and assuming steady state [Br], they worked out $[H_2]$ and [HBr] from their data and then calculated the rate of heat release if d[HBr]/dt was given by the classical expression. The rate of heat release could also be calculated from the temperature traverse by equation (1.1), but the two $\dot{q}$ disagreed rather badly. Wehner and Frazier[231] examined the flame at lower pressure with thermocouples and quartz probes to obtain profiles of temperature, $[H_2]$, $[Br_2]$, and [HBr]. They treated their measurements as Peacock and Weinberg had done to get $\dot{q}$ by substituting their measured concentrations into the assumed rate law. The values were again in poor agreement with $\dot{q}$ from the temperature traverse. The $\dot{q}$ from the temperature traverse, when integrated through the flame, accounted adequately for the enthalpy difference of products and reactants, so the cause of the disagreement lay probably with the $d[HBr]/dt$ assumed. More interesting results will probably be obtained when more measurements have been made in various flames, e.g. $d[HBr]/dt$ from the HBr traverse itself, and when the preoccupation is dropped with merely checking extrapolations of the lower temperature kinetic data.

Decomposition Flames of Nitrate Esters

It was found by Belayev[217] that glycol dinitrate, $(H_2CONO_2)_2$, which decomposed at moderate temperatures and low pressures with a first order rate constant of $\sim 10^{14}\,e^{-35\ \mathrm{kcal}/RT}\ s^{-1}$; burnt as a steady flame above its liquid with a temperature dependence still appropriate to an activation energy of about 35 kcal, but with (ρv) proportional to pressure and therefore possibly with a second order reaction in the flame. The interpretation was that the ester decomposed under both circumstances by the mechanism

$$(H_2CONO_2)_2 + M \underset{k'}{\overset{k}{\rightleftarrows}} (H_2CONO_2)_2^{\star} + M \qquad (9.14)$$

$$(H_2CONO_2)_2^{\star} \xrightarrow{k''} \text{products} \qquad (9.15)$$

but that at lower temperatures the activation step (14) was balanced so that $-d[(H_2CONO_2)_2]/dt = (k''k/k')[(H_2CONO_2)_2]$; while in the flame, the formation of the activated $(H_2CONO_2)_2^{\star}$ controlled the rate and a second order reaction was therefore observed. This interpretation is not inconsistent with unimolecular reaction theories;[218] according to which the transition pressure where the decomposition changes from more-or-less second order to first order ought to increase with rising temperature for complex molecules. Not enough is really known about any nitrate ester flame, however, for the interpretation to carry much conviction. It is not certain that the reaction rate really was second order in the flame—first order in the ester and first order in M—because the conditions may not have been satisfied for the reaction order to be reflected accurately by the pressure dependence of the burning rate.

The steady decomposition flame of methyl nitrate was observed by Gray, Hall, and Wolfhard at 1·3 cm Hg pressure.[219] It consisted of a blue zone about 0·1 cm thick emitting formaldehyde bands followed by a thin dark gap and then an orange red region emitting continuous radiation. Adams and Scrivener[220] measured its burning velocity by photographing the growing shell of primary flame in a closed vessel after igniting the reactant by a central spark. The primary flame was followed by a secondary burning of the initial products, NO, CO, H_2CO, etc., and their conclusions about the primary decomposition were necessarily indirect.

More has been learned about ethyl nitrate. Wolfhard[221] found (ρv) proportional to P for this flame at 0·6–20 cm Hg pressure. Needham and Powling[222] probed the steady flame at one atmosphere pressure; and Hicks[19] did the same with the greater resolution afforded by low pressures. At 3·5 cm Hg pressure, only a trivial reduction of NO formed in the reaction took place and the final measured temperature was 800°K. Ethyl nitrite to the extent of 10 per cent of the nitrate fed was observed as an intermediate, which is also a major product in the slower thermal decomposition at lower temperatures. The final flame products per mole of $C_2H_5ONO_2$ included 0·85 NO, 0·8 H_2CO, 0·35 H_2O, 0·2 CO, 0·2 CH_3CHO, 0·14 CH_3OH, 0·1 C_2H_5OH, plus smaller amounts of other species.

Hicks made no use of his composition traverses except to show that the mass fraction of $C_2H_5ONO_2$ varied inversely with the fractional increase in temperature through the flame; that is, that equation (6) applied. Thereafter he worked only with the temperature traverse to calculate $\dot{q}$ from equation (1.1) and inferred the rate of consumption of $C_2H_5ONO_2$ from $\dot{q}$. The maximum rate of heat release occurred at 750°K; and if the reactions were assumed to be controlled by

$$C_2H_5ONO_2 + M \rightarrow C_2H_5O + NO_2 + M \qquad (9.16)$$

$$-d[C_2H_5ONO_2]/dt = k[M][C_2H_5ONO_2]$$

where [M] = total gas concentration, the temperature traverse gave

$$k = 4 \times 10^9 \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1} \text{ at } 750°\text{K}$$

or

$$k[M] = 3 \times 10^3 \text{ s}^{-1}.$$

The temperature dependence was consistent with the process envisaged, corresponding to an activation energy of $\sim$38 kcal mole^{-1}. The mass burning velocity was proportional to P; and assuming the reaction to be of the form of (16), the same rate constant and temperature dependence as the values just stated could also be inferred from the Zeldovich equation.

In isothermal decomposition studies at temperatures 300° lower, the decomposition of $C_2H_5ONO_2$ is believed to measure the same process; and here the decomposition is first order in the pressure range used by Hicks. A long extrapolation of these lower temperature results to 750° would predict specific decomposition rates of

$$-d[C_2H_5ONO_2]/[C_2H_5ONO_2]\,dt = 16 \times 10^3\ s^{-1} \qquad \text{Adams and Bawn}^{223}$$
$$68 \times 10^3 \qquad \text{Levy}^{224}$$

The difference between these figures is that Adams and Bawn did not correct for any re-association of the $C_2H_5O + NO_2$ fragments into which the molecules split, but Levy aimed to get the true value of the breakup free of any re-association. The observed rate in the flame was smaller than those extrapolations by a factor of 5–23. If the flame was controlled by a bimolecular activation process, it ought to have exhibited a slower decomposition rate than the extrapolated values of the high pressure limiting rate; so as far as the evidence goes, it is consistent with the assumption of reaction (16). Furthermore, above 15 cm Hg pressure, at which point $k[M]$ would presumably have been about $13 \times 10^3\ s^{-1}$, the pressure dependence of (ρv) decreased considerably according to Hicks; so the flame may have been controlled by a bimolecular activation process only as long as the specific decay rate was smaller than the expected high pressure limiting rate. This seems very reasonable. Yet the evidence for reaction order comes entirely from the pressure dependence of burning velocity, and one wishes that it had come from measurements of $-d[C_2H_5ONO_2]/dt$ from profiles of the ester in a variety of flames.

Some Other Flames

A few other types of premixed or decomposition flames have been studied but in less detail than those discussed above. Flames known to require a reduction of nitric oxide are put off to the next chapter.

It is known that N_2O decomposes by a thermal explosion when it is quickly heated in a static system to 1100–1300°K, the temperature required depending on pressure.[214] Brandt and Rozlovskii[215] investigated what pressure was necessary to obtain flame propagation through

N_2O initially at room temperature. It was found that flame would propagate upwards in a cylindrical bomb 6 cm diameter by 54 cm long when the initial pressure was 1·6 atm, and downwards when the pressure was 10 atm; but flames would not propagate at lower pressures. If it was supposed that (ρv) must be about 5×10^{-3} g cm^{-2} s^{-1} in order to have a flame at all; that is, that the linear burning velocity must be about 3 cm s^{-1} at atmospheric pressure, but less at higher pressures, then it could be calculated from the Zeldovich equation that the required (ρv) would have been expected to occur at 1·2–3·1 atm, depending on whose low temperature kinetics were used in the calculation. A critical (ρv) was considered to define the limit because of the notion that it was determined by radiation losses—but the same criterion could have been suggested on other grounds. For example, a criterion for quenching a flame by heat losses to the wall of a tube of diameter d, that

$$(\rho v) = 30 \text{ to } 50 \times \lambda/dC_p$$ [266]

would also give a critical (ρv) of the same order.

Rozlovskii[216] has calculated the expected yield of NO in this flame, formed by reaction (3.12), $O + N_2O \rightarrow 2NO$. Under a number of assumptions, he concludes that the measured yield is probably too small to be consistent with the rate constant given in chapter 3 for (3.12) and that a smaller constant which he quotes is more probable. It seems unlikely that the calculation could do more than suggest the order of magnitude of the NO yield; and the constant rejected and that preferred predict yields of the same order. The smaller constant is no longer favoured by Kaufman[72] who determined it.

The burning velocity of hydrogen peroxide vapour was measured by Satterfield and Kehat[225] for mixtures of 0·45–0·6 mole fraction of H_2O_2 with H_2O; the results seem to be consistent with the lower temperature decomposition studies. The temperature dependence of the burning velocity was estimated to be rather smaller than that expected from work on the slow isothermal decomposition, but the difference was within the error of the flame result. The pressure dependence of the burning rate was not positively determined.

Luft[280] maintained a yellow orange decomposition flame over a concentrated aqueous solution of hydroxylamine, 0·6 mole fraction of NH_2OH. The flame products included ammonia but not nitric oxide. The liquid burnt back about 0·1 cm s^{-1}, faster than liquid hydrazine or hydrogen peroxide do even when more nearly anhydrous. He commented on the possible relation of the decomposition of NH_2OH to those of N_2H_4 and H_2O_2—and the series may prove an interesting one when more experimental data are gathered.

A flat decomposition flame of ethylene oxide was studied by Friedman and Burke[20] over the pressure range 0·2–1·5 atm. The decomposition products at 1 atm were 44 per cent CO, 26 per cent CH_4, 20 per cent H_2, 10 per cent unsaturates. The flame temperature was about 1200°K when the reactant was initially at 365°. The linear burning velocity was only around 4 cm s^{-1}, and not very dependent on pressure; that is, (ρv) varied as P^n where n was less than but almost equal to one. Increasing the initial temperature of the reactant by 30° gave a very moderate activation energy by the Zeldovich equation, 14 kcal $mole^{-1}$. The authors mistrusted the pressure dependence as evidence for a second order reaction and the temperature dependence as a measure of the activation energy of the propagating reactions; and showed how a small increase in the final temperature with pressure might have given an apparent dependence of (ρv) on P appropriate to a second order reaction even though the reactions had really been controlled by a first order process. Nothing could be positively inferred about the flame reactions from measurements of burning velocity.

The slow decomposition rate of ozone has been measured[226] as has the burning velocity at atmospheric pressure for a wide range of O_2–O_3 mixtures.[16] Hirschfelder and co-workers,[227] by numerical integration, and Von Karman and Penner,[228] by an elaboration of the Zeldovich equation equivalent to (4), computed velocities which agreed closely with experiment; and there is general agreement that the burning rate is consistent with the reaction rate, $-d[O_3]/dt = 2k[O_3]M$, where k is the rate constant for the reaction

$$O_3 + M \rightarrow O_2 + O + M$$

The computations were made with a value of k about ten times smaller, for $M = O_3$, and five times smaller, for $M = O_2$, than the more recent value quoted by Benson.[226] If the larger k is correct, the agreement of calculated with measured velocities is within a factor of two or three rather than within the stated 20 per cent. No chemical conclusions need follow if this discrepancy exists. Perfect agreement does not prove the mechanism and disagreement by a factor of two or three need not disprove it. If reasons for or against it are sought from flames, a more intimate knowledge of the reaction zone is required than has yet been obtained.

Low Temperature Hydrogen Flames at Atmospheric Pressure

The possible formation of HO_2 by reaction (2.4),

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \tag{2.4}$$

was touched on in chapter 3 where it was shown that (2.4) might determine the rate of the recombination of radicals in the post-flame gas of fuel-lean flames if the HO_2 reacted subsequently with some other radical, no matter which. At low pressures, or in moderately hot gas even at atmospheric pressure, (2.4) is expected to be slow compared to (2.1) in the forward direction

$$H + O_2 \xrightarrow{k_1} OH + O \tag{2.1}$$

but this is not so at low enough temperatures and at atmospheric pressure. Furthermore if (2.4) occurs in the reaction zone at a rate comparable to (2.1), the subsequent fate of the HO_2 matters a great deal; a reaction with O or OH would terminate free valencies but a formation of 2OH from $HO_2 + H$, which was also a terminating reaction in the post-flame gas from lean flames, need not terminate free valencies in the reaction zone of fuel-rich flames. Dixon-Lewis and Williams[50] attempted to test two plausible fates for HO_2 by calculating the profiles of [H] and of the temperature for different reaction schemes involving HO_2 and comparing the calculated profiles with experiment. The calculation was done by the arduous method[232–234] of setting up unsteady, time-dependent equations corresponding to (1.1) and (1.2), one for temperature and one for each species considered. Starting from some arbitrary distribution of temperature and of the mass fractions, the equations were integrated numerically until the steady state profiles and burning velocity were reached.

A fuel-rich near limit H_2–O_2–N_2 flame was burnt at one atmosphere pressure on a Powling burner; burning velocity 9·2 cm s^{-1}, measured flame temperature 1072°K. By methods discussed previously, traverses were obtained for stable species, H atoms, and temperature. It was supposed that reaction (2.1) would always be followed by the reactions of O and of OH with H_2, so that (2.1), (2.2), and (2.3) could be combined into

$$H + O_2 + 3H_2 \rightarrow 2H_2O + 3H, \quad -\Delta H = 11{\cdot}4 \text{ kcal} \tag{9.17}$$

$$\text{rate} = k_1[H][O_2]$$

Among H, OH, and O, the most important recombination was assumed to be

$$2H + M \xrightarrow{k_6} H_2 + M. \quad -\Delta H = 104 \text{ kcal} \tag{2.6}$$

With values of k_1 and k_6 about the same as those listed in Table 4.1 of chapter 4, a mechanism composed of (17) and (6) was integrated repeatedly until the steady state was obtained. The work was lightened by assuming $\rho D_{O_2} C_p = \lambda$ so that the profile of O_2 was equivalent to the temperature profile. The steady state arrived at gave a maximum rate of heat release about 1/3 of that observed experimentally, a calculated burning velocity 2/3 of that observed, and a calculated maximum [H] about 5/2 of that observed. The general shape of the calculated traverses was consistent with those observed.

The agreement between observed and calculated traverses when HO_2 was omitted from consideration altogether was probably as good as ought to have been expected for a complete mechanism. Omitting HO_2 from consideration, however, ignores the implication of the relative size of $k_4[M]$ vs. k_1, that considerable HO_2 should have formed. An attempt was therefore made to include HO_2 in the reaction scheme. Two cases were considered: first that the HO_2 reacted with H atoms with no net consumption of free valencies,

$$H + O_2 + M \rightarrow HO_2 + M$$
$$H + HO_2 \rightarrow 2OH$$
$$2(OH + H_2 \rightarrow H_2O + H)$$

which were summed up as

$$H + O_2 + 2H_2 \rightarrow H + 2H_2O$$
$$\text{rate} = k_4[H][O_2][M] \tag{9.18}$$

The second case was to suppose that the formation of HO_2 was a terminating reaction,

$$2H + O_2 + H_2 \rightarrow 2H_2O$$
$$\text{rate} = k_4[H][O_2][M]/2 \tag{9.19}$$

It was found that the addition of (9.19) to the previously assumed mechanism of (9.17) and (2.6) led to a calculated burning velocity of almost zero, which seems to assert that (9.19) cannot be the only important course of reaction for HO_2. Addition of (9.18) did not look very promising either; for it gave 9 times too fast a burning velocity and 6 times too great a maximum rate of heat release. However, it is impossible to say how badly such a calculation must disagree with experiment before its proposed mechanism can be reliably abandoned. When the authors took a more direct approach,[281] accepting their experimental profile for [H] rather than calculating it, they concluded that the addition of (9.18) to (9.17) and (2.6) was more consistent with the observed rate of heat release than was (9.17) and (2.6) alone. There seems to be little merit in *ab initio* calculations of burning velocities and profiles through the reaction zone as compared to observations of the local rates of reactions as functions of the locally observed concentrations.

CHAPTER 10

DECOMPOSITION OF NITRIC OXIDE IN FLAMES

FLAMES of hydrogen, moist carbon monoxide, hydrocarbons, and probably ammonia burning with oxygen all have a family resemblance because the oxidant is destroyed in every case by the same fairly easy reaction with H atoms. H atoms do not destroy nitric oxide as easily and a similar family resemblance is not easy to see among the more difficult nitric oxide flames.

Three types of behaviour can be recognized when nitric oxide is mixed with H atoms or H_2 molecules. (i) Clyne and Thrush[235] found that NO was merely a recombination catalyst when mixed with H atoms at low temperatures, $H + NO + M \rightarrow HNO + M$, $H + HNO \rightarrow H_2 + NO$. (ii) At 1100–1400°K, NO–H_2 mixtures undergo a slow reaction which was originally believed[236] to be termolecular, involving binary collision complexes of different lives, but which has since been found to be of fractional order in $[H_2]$ and almost certainly in [NO] also.[237,238] It is possible that this reaction may involve HNO and reactions such as $NO + HNO \rightarrow N_2O + OH$, but the interpretation of the experimental results is uncertain.[238] (iii) At much higher temperatures around 3100°K, the H_2–NO flame resembles the decomposition flame of preheated NO so much that nitric oxide was thought to disappear by very similar mechanisms in both.[65] If so, there are at least two types of decomposition which might occur in flames.

The more reasonable path is a decomposition by

$$O + NO \rightarrow N + O_2 \tag{3.9}$$

$$N + NO \rightarrow O + N_2 \tag{3.10}$$

or by some variant of (3.9) in the presence of H atoms such as $H + NO \rightarrow N + OH$, which is indistinguishable whenever $H + O_2 = OH + O$ is balanced. Gaydon and Wolfhard[1] rejected this path, for NO–H_2 flames at least, because they thought that electronically excited NH^* should be formed if the flames contained free N atoms; and NH^* is absent. However, Garvin and Broida[239] found that NH^* was not formed when N atoms from a discharge were run into mixtures of H, H_2, and

NO_2 at room temperature and low pressures so the absence of NH^* in flames may not be a very strong objection. The probably less reasonable path for NO decomposition is the second order process which was formulated in chapter 3 as

$$2NO \rightarrow N_2O + O \qquad \text{reverse of (3.12)}$$

followed by a decomposition of the N_2O and recombination of the O atoms. Since small additions of N_2O cause emission of NH^* from $NO–H_2$ flames,[65] the absence of NH^* from pure $NO–H_2$ flames would seem a better argument against the reverse of (3.12) than against (3.9) or its variants and (3.10). The reverse of (3.12) is too slow to account for the decomposition of NO in hot post-flame gas and might be too slow in flames too.

Ammonia Flames

Adams, Parker, and Wolfhard[65] found that the burning velocity of the stoichiometric $NH_3–NO$ mixture is twice as large as the 30 cm s^{-1} of $H_2–NO$. The flame temperature is 170° less for NH_3. This implies a faster decomposition in the NH_3 flame, and since NO reacts rapidly with NH_2 radicals even at room temperature[240,241] by

$$NO + NH_2 \xrightarrow{k} . \quad . \rightarrow N_2 + H_2O \qquad (10.1)$$

they suggested that the same process occurs in flames, or that NH radicals which were also present in the flame might react with NO. NH_2 radicals would be expected to be formed more readily in flames of $NH_3–NO$ than N atoms in $H_2–NO$ flames, and the ammonia mixture might therefore burn faster.

The reaction of ammonia with nitric oxide has been studied by mixing these species into the reactants of low pressure, fuel-rich $H_2–N_2O$ flames, and obtaining traverses through the reaction zones.[242] The flames had final temperatures of 1700–1900°K, under which conditions all of the N_2O reacted with part of the H_2 but any added NO was stable. If a little NH_3 was also added, it was rapidly destroyed with the simultaneous consumption of an equimolecular amount of NO. The destruction of NO ceased when NH_3 was consumed; and it seemed very likely that NO reacted with some radical derived from NH_3, though it was not possible to measure the concentrations of these radicals. It was assumed that NH_2 radicals and H atoms were equilibrated according to

$$H + NH_3 = NH_2 + H_2 \qquad (10.2)$$

$$[NH_2] = K[H][NH_3]/[H_2]$$

[H] could be estimated from the N_2O profile by means of the known k_α from Table 4.1 in chapter 4, or in other ways. The consumption of NO in flames of varying [H], and therefore of varying [NH_2] if (2) was true, could be correlated by

$$-d[NO]/dt = k[NO][NH_2] = kK[NO][H][NH_3]/[H_2]$$
$$kK = 5 \times 10^{13}\ \text{cm}^3\ \text{mole}^{-1}\ \text{s}^{-1}\ \text{at } 1700\text{–}1900°\text{K}$$

The correlation is evidence, though not proof, for the truth of (2). The equilibrium constant, K, is expected to be of order unity and to have little temperature dependence, so the interpretation suggests that k is a large constant with little temperature dependence, as of course it must be in view of the results at room temperature. No other literature value of k exists with which to compare the numerical estimate from flames.

Because NO decomposes faster in flames with NH_3 than in flames with H_2 or in its decomposition flame, it is possible to obtain a set of reaction zones on a porous burner of 30 cm^2 area when a mix of $NH_3 + 2{\cdot}6NO + 1{\cdot}2Ar$ is burnt at one atmosphere pressure with a burning velocity of about 9 cm s^{-1}. Close to the burner surface, the NH_3 plus about one mole of NO are consumed in a zone coloured yellow by emission from the bands of excited NH_2^*. Downstream of this, a colourless region extends to about 0·5 cm from the burner until [H_2] falls to a low value and [O_2] begins to rise. At this point a bluish-white emission sets in as the remaining NO continues to decompose and [O_2] builds up. Corresponding multiple reaction zones are better known in flames of hydrocarbons with nitrogen oxides.

Reaction (1), or whatever reaction consumes NO in NO–NH_3 flames, is also important in NH_3–O_2 flames, the NO then being generated by oxidation of part of the NH_3. By probing relatively low temperature NH_3–H_2–O_2 flames,[242] it was found that the values of [H], [O_2], and of $-d[O_2]/dt$ were consistent with the notion that all the O_2 was consumed by reaction (2.1), $H + O_2 \rightarrow OH + O$; and therefore there was no considerable reaction of O_2 with NH_3 or with N-containing radicals derived from NH_3. NO was always found in the reaction zone, formed possibly by the attack of O atoms on NH_3 since this occurs at room temperature when O atoms from a discharge are mixed with NH_3.[243] If a large excess of NH_3 was fed in the reactants, NO was only a transient species which was quickly destroyed again and the excess NH_3 in the fuel-rich post-flame gas was relatively stable. When small ratios of [NH_3]/[O_2] were fed, more NO was formed in the flame than could be consumed, and the excess NO was stable at the temperatures used. It was concluded that the NH_3–O_2 flame was a combination of the H_2–O_2 and the NH_3–NO flames, coupled through a fast formation of NO by attack of O atoms on NH_3. The nature of the reaction of O with NH_3 is unknown, however.

The interpretation of the NH_3–O_2 flame does not agree with Husain and Norrish's views of the high temperature reaction.[282] They flash photolysed equimolecular or leaner NH_3–O_2 mixtures at about 2 cm of mercury pressure; the main function of the flash being to heat the gas to a temperature which was undetermined but less than 1500°K, the upper limit for the NH vibrational temperature. About 0·5 milliseconds after the flash, OH and NH radicals became visible in absorption; and a few milliseconds later, NH disappeared again and NH_3 disappeared with the onset of strong absorption by NO. They believed that oxygen was mostly consumed by the reaction of $NH_2 + O_2$, not by $H + O_2$ as in steady flames; and believed that nitric oxide was also formed eventually in consequence of $NH_2 + O_2$, not in consequence of $NH_3 + O$ as suggested in the last paragraph. Neither $[NH_2]$ nor [H] were estimated in the flash photolysis, however, so no real evidence was possible for the mode of consumption of O_2. The eventual formation of much nitric oxide and a little nitrous oxide resembles the products from fuel-lean steady flames, but flames also form considerable nitrogen by the partial consumption of NO before the ammonia is exhausted. The yield of nitrogen in the photolysis was not stated; if it was very small, as was implied, there must be a real difference between flash photolyses and steady flames.

Hydrazine–NO flames resemble NH_3–NO in giving an easy reduction of nitric oxide. By contrast with ammonia, the decomposition of hydrazine is fast at flame temperatures; and a hydrazine flame containing only a little added O_2 may be essentially a hydrazine decomposition flame still.[244] Larger additions of O_2 cause a marked formation of NO—as seems reasonable because O atoms at room temperature give NO more readily from N_2H_4 than from NH_3.[243]

Hydrocarbon Flames

In low temperature, fuel-rich flames of H_2–CH_4–O_2–NO, CH_3 radicals react in part with NO and a roughly equivalent formation of HCN is observed as is shown in Fig. 5.3 of chapter 5. HCN is also formed in hotter flames but decays again. A similar consumption of NO with formation of transient HCN can be observed by probing fuel-rich flames of C_2H_4 or C_2H_2 containing some O_2. Pure hydrocarbon–NO flames have not been probed and there is nothing to add to Wolfhard and Parker's[245] accounts of their qualitative features—that NO is reduced by hydrocarbon radicals, and perhaps by other species generated in the flame, and that any excess NO may decompose more slowly in a subsequent second reaction zone if the flame is hot enough. NO_2 is easily reduced to NO, and fuel-rich flames of NO_2 may possess an additional reaction zone, upstream of the NO-radical reaction zone, in which the easy reduction takes place. Otherwise, NO_2 flames seem to differ little from NO flames.

Nitric acid–hydrocarbon mixtures burn to give most of their nitrogen as NO; butane–nitric acid flames so rich that the NO would have to be reduced in order to consume the hydrocarbon are not stable.[246] The flames, on small burners at least where cooling by the surroundings is easy, seem not quite hot enough to decompose NO at atmospheric pressure. Propane–nitric acid mixtures preheated to 400°K give most of the nitrogen as NO, but if the reactants are preheated to 600° a secondary reaction zone appears in which additional NO is thought to be decomposed.[247]

Methyl Nitrite Decomposition

The decomposition flame of this substance cannot give a hot gas except by reducing much of its nitrogen to N_2O or N_2. The flame temperature is low even when about half the nitrogen is reduced, and the path by which the easy reduction occurs is a puzzle.

Gray, Hall, and Wolfhard[219] established a steady decomposition flame in CH_3ONO at one atmosphere pressure. Moderate preheating[18] increased the burning velocity from 3·2 cm s^{-1} when the reactant was initially at 288°K to 7 cm s^{-1} at 483°. On preheating to 550°, most of the reactant was decomposed before it reached the flame, and a little stronger preheating extinguished the fire because the pyrolysis products cannot support a similar flame. Arden and Powling[248] found that half of the nitrogen remained as NO in the products at the flame temperature of about 1370°K, the rest having been reduced mostly to N_2 and partly to N_2O. In the reaction zone, more of the nitrogen was present as NO and large quantities of H_2CO and CH_3OH were present. The fraction of nitrogen reduced past the stage of NO was no larger in flames of 80 per cent CH_3ONO plus 20 per cent of either H_2CO or CH_3OH than in a flame of the pure ester; but addition of NO caused a greater reduction of nitrogen.

The main point of interest is the path by which N_2O or N_2 is formed at so low a temperature. This has not been found out. It has been assumed with some evidence[18] that the flame reactions are very much like the slow decomposition reactions of the ester at lower temperatures. According to Phillips[249] and by analogy with Levy's[250] work with ethyl nitrite, this mechanism as far as nitrogen is concerned is

$$CH_3ONO \rightleftarrows CH_3O + NO \qquad (10.3)$$

$$NO + CH_3O \rightarrow H_2CO + HNO \qquad (10.4)$$

$$HNO + CH_3O \rightarrow CH_3OH + NO \qquad (10.5)$$

or

$$2CH_3O \rightarrow CH_3OH + H_2CO \qquad (10.6)$$

$$2HNO \rightarrow N_2O + H_2O \qquad (10.7)$$

or

$$NO + HNO \rightarrow N_2O + OH \qquad (10.8)$$

and some thermal decomposition of various species might occur and lead to $H + N_2O \rightarrow N_2 + OH$. Good evidence exists for (3) and its reverse:[251] but there is no evidence as yet for (7) or (8). At lower temperatures, the work of Clyne and Thrush[235] indicates that the HNO formed when H atoms are mixed with NO reacts much faster with H to regenerate $NO + H_2$ than with NO or with another HNO molecule to form N_2O. At higher temperatures, some unpublished work by W. E. Kaskan shows that HNO is also formed when much NO is added to fuel-rich H_2–air flames burning on porous burners. The HNO was identified by comparison of its red emission with the spectrum given by Dalby.[252] No significant reduction of NO occurs in these flames either, though the concentration of HNO was unknown and probably small. Other modes of reduction than (7) and (8) have been suggested. Arden and Phillips[267] believed that at low temperatures

$$HNO + 2NO \rightleftarrows HN(NO)ONO \rightarrow H + N_2 + NO_3$$

where the first stage was supposed to be a reversible equilibrium which was strongly displaced to the left with rising temperature. The process presumably would not have been observed by Clyne and Thrush at their lower pressures. The yield of N_2 was considerable at 368°K, but very small at temperatures only 40° hotter and the scheme would not seem important therefore in the decomposition flame of methyl nitrite.

It is not ruled out that the reduction of the nitrogen in flames may involve reactions of the nitrite ester itself with nitric oxide. Kuhn and

Günthard[253] proposed the exchange process for primary nitrite esters labelled by N^{15}

$$N^{14}O + RON^{15}O \rightleftarrows RON^{15}(N^{14}O)O \rightleftarrows RON^{14}(N^{15}O) \rightleftarrows N^{15}O + RON^{14}O$$

and such an intermediate compound might react at higher temperatures to give N_2O or N_2.

Other flames exist which involve easy reduction of NO, but by unknown mechanisms. Mixtures of $CS_2 + 3NO$[254] ignite spontaneously at 45 cm Hg pressure when run into a 5 cm diameter vessel at 1070°K; at 18 cm pressure, ignition occurs at 1170°. The steady flame burns readily, velocity about 45 cm s^{-1} at 5 cm pressure, and its colour consists mainly of S_2 bands.[245] B_2H_6–NO mixtures[255] are readily ignited by sparking and NO present in excess of the stoichiometric ratio is largely decomposed, possibly because of the high temperature. The radiation includes BO_2 bands and, if $[NO]/[B_2H_6) > 3$, OH bands.

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* The late George William Jones is not the same man as the co-author of several papers with C. P. Fenimore, George Wallace Jones.

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AUTHOR INDEX

SUBJECT INDEX

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