THE COMBUSTION AND OXIDATION OF ACETYLENE

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Received August 11, 1969

Contents

I. Introduction

The oxidation and combustion of acetylene are of considerable chemical and industrial interest and importance.[1,2] The reasons for this largely arise from its unique molecular structure. In particular, because of its triple bond and resultant high enthalpy of formation, combustion of acetylene results in flame temperatures higher than those normally obtained from other hydrocarbon fuels. Thus acetylene finds wide usage[1,2] in industrial welding and cutting and also in other applications where high-temperature flames are required,[3] such as flame photometry and atomic absorption. The combustion reactions of acetylene are of wider significance than this, however, since acetylene is formed as an intermediate in the combustion of fuel-rich mixtures of other hydrocarbons and plays an important role in soot formation.[4,5] A knowledge of acetylene combustion is important also with respect to industrial hazards presented during acetylene manufacture and its wide use for chemical synthesis.[1,2,6] This is particularly so since acetylene is capable of sustaining a self-decomposition flame, while in mixtures with oxygen it readily detonates.

The thermodynamic and physical properties of acetylene have been listed and discussed in a number of reference books.[1,2,6–8] Some relevant points are listed in Table I.

Acetylene is a linear molecule and its structure is best described in terms of sp hybridization. The bond lengths are short and bond strengths high, but the enthalpy of formation is also high, resulting in the unstable nature of acetylene. Acetylene is a gas under normal ambient conditions, and the oxidation reactions are usually studied in the gas phase. Some studies of acetylene decomposition in the liquid phase have been reported,[2] but this aspect is not considered here.

Although acetylene is the simplest stable bicarbon molecule, its oxidative chemistry is complicated and little of its detailed

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(1) W. F. Tiedge and F. E. Caskey, *Encycl. Ind. Chem. Anal.*, 4, 126 (1967).

(2) S. A. Miller "Acetylene: Its Properties, Manufacture and Uses," 2 vol., Benn, London, 1965–1966.

(3) R. Mavrodineanu and H. Boiteux, "Flame Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1965.

(4) K. H. Homann, *Combust. Flame*, 11, 265 (1967).

(5) A. G. Gaydon and H. G. Wolfhard, "Flames, Their Structure, Radiation and Temperature," 2nd ed, Chapman and Hall, London, 1960.

(6) D. W. F. Hardie, "Acetylene: Manufacture and Uses," Oxford University Press, London, 1965.

(7) "JANAF Thermochemical Tables," The Dow Chemical Co., Midland, Mich.

(8) F. Din, "Thermodynamic Functions of Gases," Vol. 2, Butterworth & Co., Ltd., London, 1956, p 56.

Table I
Properties of Acetylene

Boiling (sublimation) point	189.1°K
Enthalpy of formation (298°K)	54.19 ± 0.19 kcal mole^{-1}
Enthalpy of combustion (298°K, 1 atm)	−300.10 ± 0.2 kcal mole^{-1}
Bond dissociation energy (H—C_2H)	114 ± 7 kcal mole^{-1}
Bond dissociation energy (HC≡CH)	230 ± 2 kcal mole^{-1}

oxidative mechanism has been elucidated.[9–14] This is partly a consequence of the fact that little is known[15] about the reactions of the ethynyl radical (C_2H). Studies at low temperatures indicate[15] that the hybridization state of the C–H bond changes during fission and resonance presumably occurs between the two states.

$$HC{\equiv}\dot{C} \longleftrightarrow H\dot{C}{=}C:$$

It has been suggested[16] that the ethynyl radical, in common with other σ radicals, should show low reactivity toward molecular oxygen, but more readily undergo hydrogen abstraction reactions. A further complication results from the absence of information concerning possible association reactions of acetylene directly with molecular oxygen.

In contrast to this lack of detailed chemical knowledge, there is a considerable bulk of experimental information concerning the macroscopic properties of the combustion and oxidation of acetylene with air, oxygen, or other oxidizers. Most of these data are of technical or commercial interest and concern burning velocities, flame temperatures, minimum ignition energies, flammability and explosion limits, quenching distances, etc. Although acetylene was first synthesized in 1836, the first practical combustion applications were not known until the 1890's, when it became widely used for illumination purposes. In 1895, the oxyacetylene flame was developed. The first measurement of the burning velocity of an acetylene–air mixture was made by le Chatelier[17] in 1895; the first flame temperature measurement was made[18] in 1902 and the first combustion product analysis in 1909.[19] Extensive investigations of acetylene–air and acetylene–oxygen flames followed. However, little was learned about the chemistry of the oxidation processes, although a number of theories were advanced.[9,10,13] Only in the last half-decade or so have real advances been made in the understanding of the reaction mechanisms.

The combustion and oxidation of acetylene may proceed in a number of ways, namely slow reaction, low-temperature combustion (spontaneous ignition and cool-flame phenomena), high-temperature ignition and combustion (hot flames), and detonation. Although some aspects of this subject have been surveyed in recent years,[2,10,11] no comprehensive review has appeared. This review includes a phenomenological description of the various modes of combustion and, wherever possible, an interpretation in terms of the reaction mechanism.

II. Low-Temperature Oxidation and Combustion

Studies of the low-temperature thermal oxidation of acetylene–oxygen mixtures have generally been confined to the temperature range 200–450°, although, in certain cases, studies at lower temperatures have been carried out, with initiation assisted by chemical initiators (*e.g.*, NO_2) or photochemical means. At temperatures higher than about 450°, spontaneous ignition may occur. Extensive work has been carried out on both spontaneous ignition and the isothermal reaction. In contrast, little is known about cool-flame behavior.

A. ISOTHERMAL REACTION

The work up to 1961 has been reviewed by Minkoff and Tipper[11] and by Lewis and von Elbe.[10] At that time many important points were unresolved. In these earlier investigations,[20–26] the rate of chemical reaction was followed by observing the pressure change accompanying the reaction and by simple product analysis. The major products of the acetylene–oxygen reaction were carbon monoxide, carbon dioxide, and water together with small yields of hydrogen, ethylene, ethane, glyoxal, formaldehyde, formic acid, acetaldehyde, and hydrogen peroxide. Measurements of this sort showed that the reaction was second order with respect to acetylene and zero order with respect to oxygen. The temperature variation of reaction rate corresponded to an overall activation energy of 33–35 kcal mole^{-1}.

Semenov[27] suggested that the reaction mechanism was a degenerate branched-chain reaction. Lewis and von Elbe[10] concurred with this and proposed glyoxal as the degenerate chain center. In contrast, Minkoff and Tipper postulated[11] a straight-chain process, involving OH and HO_2 radicals, with degenerate branching playing only a minor role.

Recently, two further investigations of low-temperature acetylene oxidation have been undertaken,[28,29] using more sophisticated analytical procedures allowing the reaction product concentrations to be followed throughout the course of the reaction. In the first of these, Hay and Norrish followed[28] the reaction in a static system in the range 300–400°, both manometrically and by detailed product analysis. A typical set of results is shown in Figure 1. In agreement with previous

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[9] W. A. Bone and D. T. A. Townend, "Flame and Combustion in Gases," Longmans, London, 1927.

[10] B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," 2nd ed, Academic Press, New York, N. Y., 1961.

[11] G. F. Minkoff and C. F. H. Tipper, "Chemistry of Combustion Reactions," Butterworth & Co., Ltd., London, 1962.

[12] C. P. Fenimore, "Chemistry in Premixed Flames," Pergamon Press, New York, N. Y., 1964.

[13] R. M. Fristrom and A. A. Westenberg, "Flame Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[14] A. G. Gaydon, "The Spectroscopy of Flames," Chapman and Hall, London, 1957.

[15] A. M. Tarr, O. P. Strausz, and H. E. Gunning, *Trans. Faraday Soc.*, **61**, 1946 (1965).

[16] J. M. Hay, *Combust. Flame*, **11**, 83 (1967).

[17] H. le Chatelier, *C. R. Acad. Sci., Paris*, **121**, 1144 (1895).

[18] V. F. Kurlbaum, *Phys. Z.*, **3**, 187, 332 (1902).

[19] F. Haber and H. J. Hodsman, *Z. Physik. Chem.*, **67**, 343 (1909).

[20] W. A. Bone and G. W. Andrew, *J. Chem. Soc.*, 1232 (1905).

[21] G. B. Kistiakowsky and S. Lehner, *J. Amer. Chem. Soc.*, **52**, 3785 (1930).

[22] R. Spence and G. B. Kistiakowsky, *ibid.*, **52**, 4837 (1930).

[23] R. Spence, *J. Chem. Soc.*, 686 (1932).

[24] E. W. R. Steacie and R. D. McDonald, *J. Chem. Phys.*, **4**, 75 (1936).

[25] R. G. W. Norrish and J. D. Reagh, *Proc. Roy. Soc., Ser. A*, **176**, 429 (1940).

[26] Z. G. Szabo and B. Gal, *Acta Chim. Acad. Sci. Hung.*, **11**, 263 (1957).

[27] N. N. Semenov, "Chain Reactions," Oxford University Press, Oxford, 1935.

[28] J. M. Hay and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **288**, 17 (1965).

[29] T. M. Stevenson and C. F. H. Tipper, *Combust. Flame*, **11**, 35 (1967).

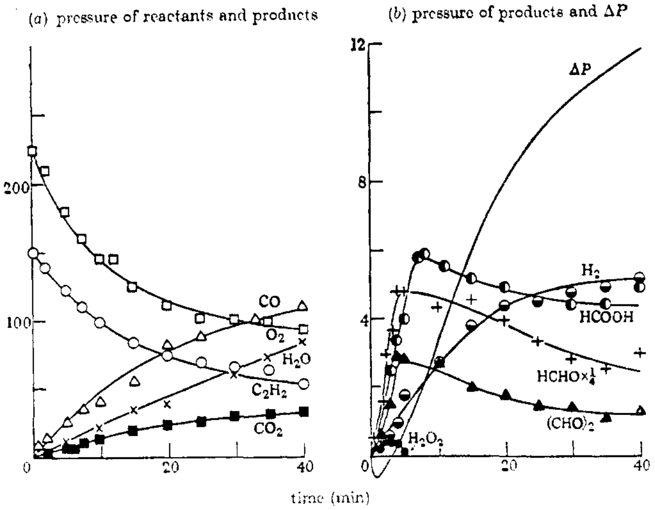


Figure 1. Variation of reactants and products during the reaction between 150 mm of acetylene and 225 mm of oxygen at 330°: ○, pressure of acetylene; □, pressure of oxygen; △, pressure of carbon monoxide; ×, pressure of water; ■, pressure of carbon dioxide; +, pressure of formaldehyde × ¼; ◒, pressure of hydrogen; ◐, pressure of formic acid; ●, pressure of hydrogen peroxide; ▲, pressure of glyoxal; —, pressure–time curve (after Hay and Norrish[28]).

investigations, they observed a reaction order of two with respect to acetylene, but this order tended to zero at high acetylene pressures. Increasing oxygen concentrations retarded the reaction rate, when the oxygen to acetylene ratio was greater than unity. The overall activation energies at high and low acetylene concentrations were 33.4 and 33.2 kcal mole^{-1}, respectively, in agreement with earlier values.[22,24] Addition of the intermediate products, glyoxal and formaldehyde, to the initial mixture had a significant effect on the course of the reaction. Increasing quantities of glyoxal first reduced and then eliminated the induction period. The effect of formaldehyde was more complex. In a clean reaction vessel, acceleration of the reaction occurred, whereas in a carbon-coated vessel inhibition resulted.

Hay and Norrish concluded from this evidence that the isothermal oxidation of acetylene proceeded by a degenerate branching chain mechanism involving glyoxal. The major reaction steps suggested by them to describe the course of the oxidation were

Initiation and branching

$$C_2H_2 + O_2 \longrightarrow (C_2H_2O_2) \longrightarrow (CHO)_2 \qquad (1)$$

$$(CHO)_2 + O_2 \longrightarrow CO + CHO + HO_2 \qquad (2)$$

Propagation

$$C_2H_2 + OH \longrightarrow HC{=}CH(OH) \rightleftharpoons CH_2CHO \qquad (3)$$

$$\xrightarrow{RH} H_2C{=}CH(OH) \qquad (4)$$

$$CH_2CHO + O_2 \longrightarrow (CHO)_2 + OH \qquad (5)$$

Aldehyde oxidation

$$CHO + O_2 \longrightarrow CO + HO_2^* \qquad (6)$$

$$(CHO)_2 + HO_2^* \longrightarrow 2CO + H_2O + OH \qquad (7)$$

$$(CHO)_2 + OH \longrightarrow CO + H_2O + CHO \qquad (8)$$

followed by termination steps. Here HO_2^* represents an energized HO_2 radical. Evidence for reactions 3 and 4 leading to the formation of vinyl alcohol has been recently obtained by a mass spectrometric analysis of the oxidation of acetylene and dideuterioacetylene.[30]

At about the same time as the work of Hay and Norrish, Stevenson and Tipper[29] studied the oxidation of acetylene between 190 and 250° in a static system. Most of the data obtained by them was for a system in which initiation resulted from the photolysis of acetone, although some results were obtained for the thermally initiated reaction. In general, the results of both the photoinduced and uncatalyzed reactions confirm the results of Hay and Norrish[28] and earlier workers.[20-26] The activation energy of the uncatalyzed reaction was 30–34 kcal mole^{-1}, but for the catalyzed reaction the Arrhenius plots were generally curved, with activation energies in the range 12–18 kcal mole^{-1}. Addition of formaldehyde was found to retard the photoinduced oxidation, but addition of glyoxal, contrary to the experience of Hay and Norrish,[28] had little effect on the reaction. From their results, Stevenson and Tipper concluded that a straight-chain process was dominant. The major steps were thought to be

$$OH + C_2H_2 \longrightarrow C_2H + H_2O \qquad (9)$$

$$OH + C_2H_2 \longrightarrow CH{=}CH(OH) \qquad (3)$$

$$C_2H + O_2 \longrightarrow CO{\cdot}CHO \longrightarrow CO + CHO \qquad (10)$$

$$\xrightarrow{O_2} CO_2 + HCO_2$$

$$CH{=}CH(OH) + O_2 \longrightarrow CO + HCHO + OH \qquad (11)$$

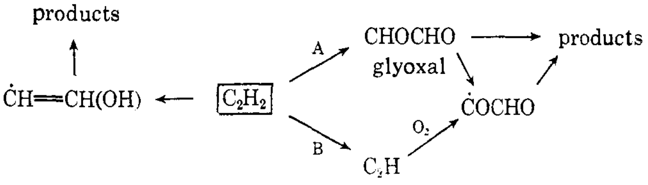
$$HO_2 + C_2H_2 \longrightarrow CH{=}CH(OOH) \xrightarrow{O_2} (CHO)_2 + HO_2 \qquad (12)$$

The propagation reactions were summarized as

$$\dot{X} + C_2H_2 \longrightarrow \dot{X} \xrightarrow{O_2} \text{products} + \dot{X}$$

and termination was assumed to be by radical–radical reactions and to give inert products.

The main aspects of the mechanism of the slow reaction can thus be summarized as follows.



The initiation reactions are either by the addition of molecular oxygen to acetylene (path A) or by hydrogen abstraction (path B). The relative importance of these two paths is determined by the composition and reaction conditions.

Two possible reactions are

$$C_2H_2 + O_2 \longrightarrow C_2H + HO_2 \qquad E \sim 65 \text{ kcal mole}^{-1} \qquad (13)$$

or

$$C_2H_2 + C_2H_2 \longrightarrow C_4H_3 + H \qquad E \sim 46 \text{ kcal mole}^{-1} \qquad (14)$$

The second reaction is more probable in rich mixtures.

There are few reports of the isothermal oxidation of acetylene by oxidizers other than oxygen. Thomas examined[31] the reaction between acetylene and nitrogen dioxide. The major products were glyoxal, oxides of carbon, and nitric oxide. The reaction was first order in acetylene and nitrogen dioxide,

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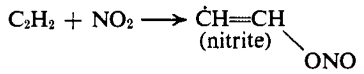
(30) J. M. Hay and D. Lyon, *Nature*, **216**, 790 (1967).

(31) J. H. Thomas, *Trans. Faraday Soc.*, 48, 1142 (1952).

with a rate constant $k = 1.3 \times 10^{12} \exp(-15{,}000/RT)$ cm^3 mole^{-1} sec^{-1}. The suggested mechanism was



$$C_2H_2 + NO_2 \longrightarrow \underset{\text{(nitrite)}}{\dot{C}H{=}CH}\!\!\diagdown_{ONO} \qquad (15)$$

$$CH{=}CH(NO_2) + NO_2 \longrightarrow (CHO)_2 + 2NO \qquad (16)$$

The measured activation energy was thought to apply to reaction 15.

Oxidation of acetylene at low temperatures may also be achieved by reaction with atomic oxygen. The products formed and the reactions that occur are unlike those discussed above and are much more closely akin to those found in high-temperature oxidation. Indeed, the O + C_2H_2 reaction was initially examined[32] to gain insight into the high-temperature reaction. Most of these studies have been carried out in rapid flow systems at or near room temperature. The major oxidation products are carbon monoxide, hydrogen, and small amounts of water. The reaction is first order in acetylene and oxygen atoms, and two oxygen atoms are consumed for each acetylene molecule. The initial reaction is almost certainly

$$O + C_2H_2 \longrightarrow CO + CH_2 \qquad \Delta H = -45 \text{ kcal mole}^{-1} \qquad (17)$$

which may proceed *via* the formation of ketene[33] as an intermediate. The rate constant for this reaction is well established. At 298°K, values of $(5.3 \pm 1.7) \times 10^{10}$, $(6.9 \pm 2.0) \times 10^{10}$, $(9 \pm 2) \times 10^{10}$, $(9.2 \pm 0.4) \times 10^{10}$, 9.6×10^{10}, and $(11 \pm 1) \times 10^{10}$ cm^3 mole^{-1} sec^{-1} have been reported.[32,34-38] Activation energies of 3150 ± 200 and 3200 ± 900 cal mole^{-1} over the temperature ranges 273–729 and 297–398°K, respectively, have been obtained.[34,38]

Arrington, Brennen, Glass, Michael, and Niki proposed[32] the subsequent steps

$$O + CH_2 \longrightarrow CHO + H \qquad \Delta H = -89 \text{ kcal mole}^{-1} \qquad (18)$$

$$O + CH_2 \longrightarrow H_2 + CO \qquad \Delta H = -180 \text{ kcal mole}^{-1} \qquad (19)$$

Brown and Thrush have suggested[36] the scheme

$$O + CH_2 \longrightarrow CO + 2H \qquad \Delta H = -77 \text{ kcal mole}^{-1} \qquad (20)$$

$$CH_2 + C_2H_2 \longrightarrow CH_3C{\equiv}CH \text{ or } H_2C{=}C{=}CH_2 \qquad (21)$$

with a rate constant ratio of 2.7 ± 1.0 at 298°K. This scheme seems more plausible, in view of the instability of the formyl radical (CHO) and the high exothermicity of the reaction in which it is formed.

B. SPONTANEOUS IGNITION AT LOW TEMPERATURES

Mixtures of acetylene and oxidants will, under suitable environmental conditions, undergo spontaneous ignition. This mode of combustion has been extensively studied, although surprisingly little work has been carried out in recent years.

The technique involves a measurement of the ignition temperature of the mixture. This may be defined as the minimum temperature of the mixture at which rapid combustion, usually accompanied by flame, becomes independent of the external source of heat. In practice, ignition temperatures are somewhat dependent on the experimental technique used, but it is nonetheless a useful criterion since overall trends can be compared.

1. *Effect of Composition on Ignition Temperature*

The variation of ignition temperature with composition for mixtures of acetylene with oxygen or air has been determined[39-45] by a number of investigators. These results are summarized in Figure 2. Ignition temperatures have been measured over a wide composition range for the acetylene–air system, but generally only fuel-rich acetylene–oxygen mixtures have been studied, because of the violence of the combustion of near stoichiometric mixtures.

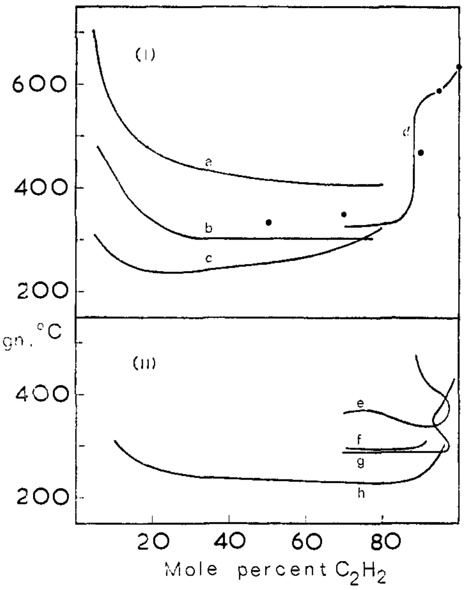


Figure 2. Dependence of spontaneous ignition temperature (T_{ign}, °C) on composition for (I) acetylene–air, and (II) acetylene–oxygen mixtures; pressures at 1 atm unless otherwise stated: (a) ref 41; (b) ref 40; (c) (10 kg cm^{-2}) ref 42; (d) ref 41; (e) (300 Torr) ref 45; (f) ref 40; (g) ref 44; (h) (10 kg cm^{-2}) ref 42; ●, ref 39.

Ignition temperatures are markedly dependent on the mixture composition at both high and low acetylene concentration, but almost independent of mixture composition in the range 30–80% C_2H_2. However, there is one exception in that high-pressure acetylene–air mixtures do show[42] an increase in ignition temperature as the acetylene concentration increases. At high acetylene concentrations (*ca.* 90% acetylene)

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(32) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *J. Chem. Phys.*, **43**, 525 (1965).

(33) I. Haller and G. C. Pimental, *J. Amer. Chem. Soc.*, **84**, 2855 (1962).

(34) G. S. James and G. P. Glass, *J. Chem. Phys.*, **50**, 2268 (1969).

(35) J. O. Sullivan and P. Warneck, *J. Phys. Chem.*, **69**, 1749 (1965).

(36) J. M. Brown and B. A. Thrush, *Trans. Faraday Soc.*, **63**, 630 (1967).

(37) K. Hoyerman, H. G. Wagner, and J. Wolfrum, *Z. Phys. Chem.* (Frankfurt am Main), **55**, 72 (1967).

(38) D. Saunders and J. Heincklen, *J. Phys. Chem.*, **70**, 1950 (1966).

(39) P. Schläpfer and M. Brunner, *Helv. Chim. Acta*, **13**, 1125 (1930).

(40) G. W. Jones and W. E. Miller, *U. S. Bur. Mines, Rept. Invest.*, 3567 (1941).

(41) G. W. Jones and R. E. Kennedy, *ibid.*, 3809 (1945).

(42) R. Kiyama, J. Osugi, and M. Teranishi, *Rev. Phys. Chem. Jap.*, **25**, 58 (1955).

(43) T. A. Ponizko and A. I. Rozlovskii, *Dokl. Akad. Nauk SSSR*, **160**, 94 (1965).

(44) W. W. Robertson and F. A. Matsen, *Combust. Flame*, **1**, 97 (1957).

(45) R. Kiyama, J. Osugi, and S. Kusuhara, *Rev. Phys. Chem. Jap.*, **27**, 22 (1951).

the ignition temperature very rapidly rises with decreasing oxidant concentration.

2. *Effect of Pressure on Ignition Temperature*

The effect of pressure on the ignition temperature for acetylene decomposition or combustion with air or oxygen is summarized in Figures 3 and 4. In general, an increase in pressure reduces the ignition temperature. However, at pressures in the range 200–400 Torr and with high (90–95%) acetylene concentrations, it has been found[45] that there are two ignition temperatures, as shown in Figure 4. Cool flames also occur in this region. The same behavior has been indicated by the results of Schläpfer and Brunner[39] for mixtures containing 70% acetylene, and also possibly 50% acetylene.

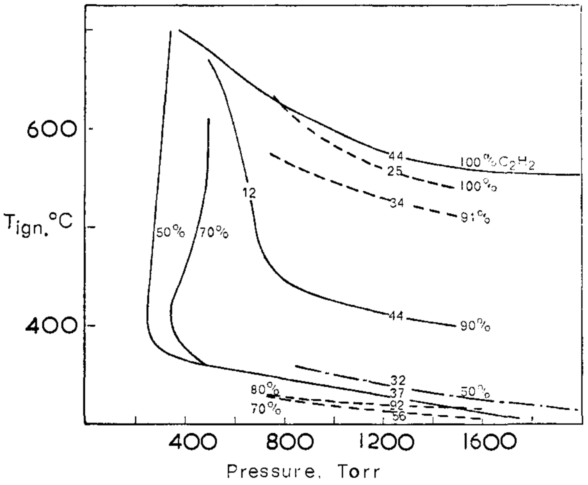

Figure 3. Dependence of spontaneous ignition temperature (T_{ign} °C) on initial pressure for acetylene–air mixtures. Acetylene percentages are indicated for each curve and also the corresponding activation energies (kcal mole^{-1}): —, Schläpfer and Brunner;[39] - - -, Jones and Kennedy;[41] — — — —, Kiyama, Osugi, and Teranishi.[42]

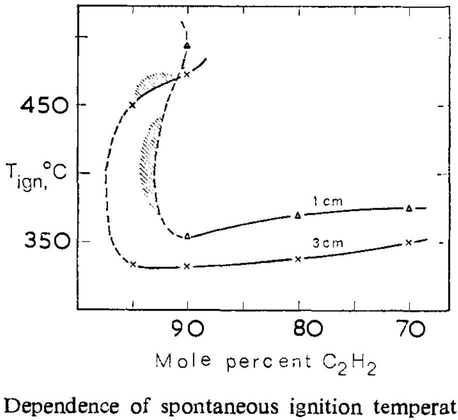

Figure 4. Dependence of spontaneous ignition temperature (T_{ign}, °C) on composition for acetylene–oxygen mixtures at 300 Torr in vessels of 1 cm and 3 cm diameter. Cool flame regions indicated by hatched lines.

If ignition of acetylene–oxidant mixtures occurs by means of a thermal explosion mechanism, then the Frank-Kamenetskii expression

$$\log (P^n/T_{ign}^{n+2}) = \text{constant} + E/RT_{ign}$$

should hold. Here P is the pressure, n the order of reaction, T_{ign} the ignition temperature, and E the activation energy. For the results given in Figure 3, it is possible to obtain good linear plots for most of the results if n is given the value of 2. The values obtained are indicated in Figure 3, and it is obvious that there is considerable variation in the values obtained. It is thus difficult to attach any great significance to them except that they probably indicate that the spontaneous ignition of acetylene mixtures is not a pure thermal explosion and that chain reactions are involved. Their relative contributions and mechanism will also change with the mixture strength.

C. COOL FLAMES

There are few reports of cool-flame phenomena in acetylene oxidation systems. Robertson and Matsen observed[44] cool flames when they passed mixtures of acetylene and a little oxygen (*ca.* 3% O_2) at atmospheric pressures through a heated tube, but this only occurred if the tube was coated with freshly deposited carbon. The cool flames were observed in the range 300–400°, as periodic, vigorous pressure pulses accompanied by rises in temperature. At 450 and 500° these changed to single or double weaker pulses. They concluded that the reactive intermediate responsible for the cool-flame behavior was formed only at low temperatures and high acetylene concentrations, and that this intermediate was destroyed on a clean surface. Kiyama, Osugi, and Kusuhara also observed[45] cool flames in rich (90–95%) acetylene–oxygen mixtures at temperatures between 360 and 470° and at pressures of about 0.5 atm. The cool-flame regimes are indicated by the hatched lines in Figure 4. The fact that cool-flame behavior only occurs in very rich mixtures and not in other regimes is most unusual. This may indicate that the reactive intermediate is a hydrocarbon radical (*e.g.*, $C_2H_3\cdot$), but the increased yields of glyoxal found[44] as a result of cool-flame behavior also suggest that the radicals $\cdot$CHCHO or $\cdot$CHO are involved.

D. IGNITION DELAY

When a gaseous mixture undergoes spontaneous ignition, there is a delay in time (ignition delay or induction time) between the sudden heating of the gas mixture and the onset of explosion. Few studies have been made of such ignition delays in acetylene combustion. The first measurements were reported by Dixon,[46] who used a concentric tube technique. Early measurements were also obtained by Fenning and Cotton.[47] More recently, Mullins[48] has used a flow technique in which the fuel was injected into a high-velocity hot air stream.

The variations of ignition delay with temperature for acetylene–air mixtures, obtained by these three techniques, are compared in Figure 5. An overall activation energy (E) for the chemical reactions involved can be estimated from ignition delay measurements for a fixed mixture composition using the relationship

$$\ln \tau_i = \text{constant} + (E/RT)$$

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(46) H. B. Dixon in H. F. Coward, *J. Chem. Soc.*, 1382 (1934).

(47) R. W. Fenning and F. T. Cotton, *Aeronaut. Res. Council R. M.*, No. 1324 (1929).

(48) B. P. Mullins, *Fuel*, 32, 343 (1953).

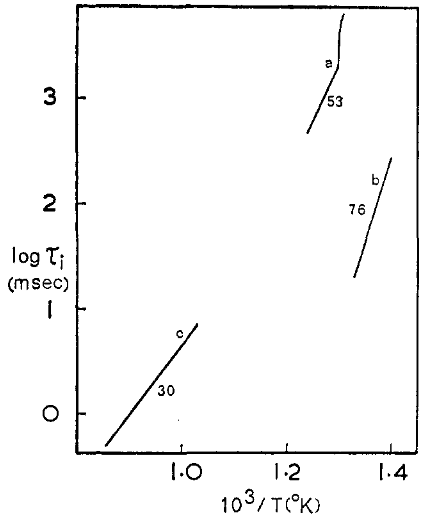

Figure 5. Variation of ignition delay (τ_i, msec) with temperature for the spontaneous ignition of acetylene–air mixtures. The corresponding activation energies (kcal mole^{-1}) are indicated on each curve: (a) Dixon;[46] (b) Fenning and Cotton[47] (c) Mullins.[48]

where τ_i is the ignition delay. The values of E obtained are included in Figure 5.

Dixon[46] observed ignition delays of up to 10 sec at relatively low temperatures (425–580°) over a pressure range 50–760 Torr. Fenning and Cotton[47] also used low temperatures (440–470°), but ignition delays were much shorter (up to 0.3 sec), probably due to the higher pressures used. The greater temperatures (700–900°) used by Mullins[48] resulted in delays of only a few milliseconds. Mullins' work is the most recent and reliable. Activation energies of *ca.* 30 kcal mole^{-1} were obtained for acetylene–air mixtures over a pressure range 0.3–0.9 atm and composition range of $C_2H_2/O_2 = 0.022$ to 0.066. This value for the activation energy agrees with that found in the isothermal oxidation of acetylene (*ca.* 33 kcal mole^{-1}) and suggests that a similar reaction mechanism may be operative in both regimes. The activation energies are, however, lower than those found in the high-temperature studies of shock-heated gases, which are discussed in the next section.

III. High-Temperature Ignition and Combustion. Shock-Tube and Flash Photolysis Studies

The only experimental tool extensively employed to study high-temperature ignition phenomena of acetylene is the shock tube. To a certain extent these studies have been complimented by investigations using the technique of flash photolysis.

A. SHOCK-TUBE STUDIES

Shock-tube techniques permit investigations of the high-temperature ignition and combustion of acetylene–oxidant mixtures under a variety of reactant conditions, although it is common practice in such studies to add large quantities of inert diluent to maintain the shocked gas temperatures as nearly isothermal as possible.

The first studies were by Kistiakowsky and his collaborators, who, in a series of papers published from 1960 onwards, described their extensive studies of the acetylene–oxygen system in shock waves.[49-56] They used a wide variety of techniques, namely vacuum ultraviolet chemiluminescence,[49] X-ray densitometry,[50] mass spectrometry,[51-53] Langmuir probes,[54] and ultraviolet, visible, and infrared emission.[53-56] More recent studies by other workers have also utilized the techniques of emission spectroscopy,[57-61] hydroxyl-absorption spectroscopy,[57-61] pressure measurements,[60,61] interferometry,[62] laser schlieren,[59] mass spectrometry,[63] and microwave attenuation.[64]

1. Ignition-Delay Measurements

Measurements of ignition delays (or induction periods) of inert-gas diluted mixtures of acetylene and oxygen have shown that they exhibit similar values over a wide temperature range to those of equivalent hydrogen–oxygen mixtures. The first measurements were made by Kistiakowsky and Richards,[49] using the vacuum ultraviolet chemiluminescence to follow ignition. The ignition delay data obtained in the range 1300–2200°K was presented in the form $\log \{t_i[O_2]\}$ mole sec l.$^{-1}$ $= -10.57 \pm 0.15 + (17{,}100 \pm 1200/4.58T)$, where t_i is the ignition delay time and $[O_2]$ the oxygen concentration in the shock-heated but unignited mixture. They concluded from the value of the overall activation energy that the dominant branching chain reaction process is the reaction of hydrogen atoms with oxygen molecules.

$$H + O_2 \longrightarrow OH + O \qquad (22)$$

The general validity of the ignition delay expression obtained by Kistiakowsky and Richards[49] was confirmed by the use of a number of other experimental techniques to follow ignition. These include Gardiner[50] using X-ray densitometry, Bradley and Kistiakowsky[51] and Dove and Moulton[63] using mass spectrometry, and Hand and Kistiakowsky[54] using an ionization technique. In all these experiments only one property was used to follow the course of the reaction. More recently investigators have simultaneously monitored several properties and have observed that the exact onset of ignition, and thus the reported ignition delay, is dependent upon the variable chosen. Thus Stubbeman and Gardiner[57,58] found that in high-temperature, low-pressure, incident shock systems the

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(49) G. B. Kistiakowsky and L. W. Richards, *J. Chem. Phys.*, **36**, 1707 (1962).

(50) W. C. Gardiner, Jr., *ibid.*, **35**, 2252 (1961).

(51) J. N. Bradley and G. B. Kistiakowsky, *ibid.*, **35**, 264 (1961).

(52) G. P. Glass, G. B. Kistiakowsky, J. V. Michael, and H. Niki, *ibid.*, **42**, 608 (1965).

(53) G. P. Glass, G. B. Kistiakowsky, J. V. Michael, and H. Niki, "Proceedings of the Tenth Symposium (International) on Combustion, University of Cambridge, Cambridge, England, 1964," The Combustion Institute, Pittsburgh, Pa., 1965, p 513.

(54) C. W. Hand and G. B. Kistiakowsky, *J. Chem. Phys.*, **37**, 1239 (1962).

(55) J. B. Homer and G. B. Kistiakowsky, *ibid.*, **45**, 1359 (1966).

(56) J. B. Homer and G. B. Kistiakowsky, *ibid.*, **46**, 4213 (1967).

(57) R. F. Stubbeman and W. C. Gardiner, Jr., *ibid.*, **40**, 1771 (1964).

(58) R. F. Stubbeman and W. C. Gardiner, Jr., *J. Phys. Chem.*, **68**, 3169 (1964).

(59) W. C. Gardiner, Jr., W. G. Mallard, K. Moringa, D. L. Ripley, and B. F. Walker, "Proceedings of Eleventh Symposium (International) on Combustion, University of California, Berkeley, Calif., 1966," The Combustion Institute, Pittsburgh, Pa., 1967, p 1151.

(60) T. Takeyama and H. Miyama, *Bull. Chem. Soc. Jap.*, **38**, 936 (1965).

(61) T. Takeyama and H. Miyama, *J. Chem. Phys.*, **42**, 2636 (1965).

(62) D. R. White, ref 59, p 147.

(63) J. E. Dove and D. M. Moulton, *Proc. Roy. Soc.*, **A283**, 216 (1965).

(64) L. N. Wilson and E. W. Evans, *J. Chem. Phys.*, **46**, 859 (1967).

ground-state hydroxyl concentration appears much later than the emission pulse due to excited CH. Thus ignition delays based on hydroxy concentrations are longer than those based on CH chemiluminescence. In further studies,[59,65] simultaneous measurements of OH emission, CH emission, and density profiles obtained by a schlieren method were observed. The early part of the exponential increase of emission preceded the heat release, the CH* intensity continued to rise exponentially past the maximum heat-release point, but the OH* intensity fell off from the initial exponential growth rate about when the heat release became appreciable. A recent study[66] has established that the density profiles obtained by the laser–schlieren method are not influenced by electron concentration gradients.

Measurements of induction periods for the appearance of ground-state hydroxyl radicals, the onset of visible emission, and the increase in pressure in incident and reflected shock waves at low temperature and high pressure were made by Takeyama and Miyama.[60,61] In contrast to Stubbeman and Gardiner,[57,58] they observed simultaneous increases in hydroxyl concentration, visible emission (CH*), and pressure over the range of conditions studied. There may be differences in mechanism in the high-temperature, low-pressure and the low-temperature, high-pressure regions.[60,65] In the temperature range of 820–1520°K and for acetylene/oxygen ratios of 0.4 to 1.5, they also found a linear relationship between log $\{t_i[O_2]\}$ and reciprocal temperature, this being log $\{t_i[O_2]\}$ mole sec l.$^{-1}$ $= -10.16 \pm 0.15 + (19{,}050 \pm 641/4.58T)$. This apparent activation energy is similar to the value of 18.9 kcal mole^{-1} obtained by these investigators for hydrogen–oxygen ignition, although the induction periods are about half those of the corresponding hydrogen–oxygen mixtures.

White[62] measured density induction times for lean acetylene–oxygen mixtures over the range $1100 < T < 2200$°K. Ignition was defined as the first sign of exothermic reaction as evidenced by a decrease of gas density, this being measured by an interferometric technique. The data were correlated best by the expression log $\{[O_2]^{1/2}[C_2H_2]^{2/3}t_i\} = -10.81 + (17{,}300/4.58T)$. These induction times are also about half those of the corresponding hydrogen–oxygen mixtures.

2. *The Reaction Mechanism*

The work of Kistiakowsky and Richards[49] combined with the mass spectrometric study[51] of Bradley and Kistiakowsky led to the proposal that for rich mixtures, the major branching chain mechanism of the induction period involved the reactions

$$H + O_2 \longrightarrow OH + O \qquad (22)$$

$$OH + C_2H_2 \longrightarrow H_2O + C_2H \qquad (9)$$

$$O + C_2H_2 \longrightarrow OH + C_2H \qquad (23)$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad (24)$$

The principal arguments advanced to support this mechanism were the similarity of the induction period behavior to that in the hydrogen–oxygen system and the presence of diacetylene in the mass spectrum of the shocked mixture. Miyama and Takeyama also agreed[60] that the rate-controlling reaction was reaction 22.

Later mass spectrometric experiments[52,53,63] confirmed the presence of diacetylene in rich mixtures but showed that carbon monoxide was formed instead in lean mixtures. Dove and Moulton[63] also showed mass spectrometrically that for lean mixtures in the range 1300–1870°K, carbon monoxide and water were formed simultaneously. Under these conditions diacetylene is only a minor product. Thus for lean mixtures, reaction 25 predominates over reaction 24, although

$$C_2H + O_2 \longrightarrow 2CO + H \qquad (25)$$

this reaction may proceed by more than one stage *via* an excited CHO radical.

The formation of carbon dioxide was shown by Dove and Moulton[63] to occur concurrently with the other oxidation products while the ratio of $[CO] + [CO_2]$ to $[H_2O]$ remained approximately constant throughout the reaction.

The production of carbon dioxide during the oxidation of acetylene has been generally attributed to reaction 26. However, a comparison[52,53] of the exponential rise of carbon monoxide to carbon dioxide indicated that reaction 26 cannot solely account for the appearance of carbon dioxide in the initial stages of the acetylene–oxygen reaction. A further investigation[56] of the rates of formation of carbon monoxide and carbon dioxide by means of an infrared technique confirmed this, and also that the time constants of carbon monoxide and carbon dioxide formation are identical in the early stages of reaction. It was suggested that the reaction responsible might be

$$CO + OH \longrightarrow CO_2 + H \qquad (26)$$

$$C_2H + O_2 \longrightarrow CO_2 + CH \qquad (27)$$

although it must play only a minor role in the overall reaction scheme.

Some uncertainty surrounds the mode of reaction of oxygen atoms with acetylene. Although Kistiakowsky and Richards[49] proposed the hydrogen abstraction reaction 23 as the major path, more recent work[34–38] has indicated that, except at very high temperatures (>2000°K), the methylene-forming reaction 17 is predominant. A rate expression for reaction 17 of

$$O + C_2H_2 \longrightarrow CH_2 + CO \qquad (17)$$

$k_{17} = (1.43 \pm 0.50) \times 10^{13} \exp(-3150 \pm 200/RT)$ cm^3 mole^{-1} sec^{-1} in the temperature range 273–729°K has been reported.[34] In contrast, rate constants for the hydrogen abstraction reaction of $k_{23} = 2 \times 10^{14} \exp(-14{,}000/RT)$ and $3.2 \times 10^{15}T^{-0.6} \exp(-17{,}000/RT)$ cm^3 mole^{-1} sec^{-1} have been estimated.[34,67]

The fate of the methylene produced in reaction 17 is uncertain, but possible reactions are

$$CH_2 + O \longrightarrow H + (H + CO) \qquad (18)$$

$$CH_2 + O_2 \longrightarrow CO_2 + (H + H) \qquad (28)$$

Reaction 28 may be an alternative to reaction 27 for the production of CO_2 in the initial stages of reaction.[56]

No experimental information is available on the initiation step at high temperatures. However, the proposed acetylene pyrolysis reactions[68] may occur

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(65) W. C. Gardiner, Jr., W. G. Mallard, and K. Moringa, *J. Chem. Phys.*, 44, 4653 (1966).

(66) W. C. Gardiner, Jr., and B. F. Walker, *ibid.*, 48, 5279 (1968).

(67) W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clark, "Proceedings of the Twelfth Symposium (International) on Combustion, University of Poitiers, Poitiers, France," The Combustion Institute, Pittsburgh, Pa., 1969, p 1035.

(68) I. D. Gay, G. B. Kistiakowsky, J. V. Michael, and H. Niki, *J. Chem. Phys.*, 43, 1720 (1965).

$$C_2H_2 + M \longrightarrow C_2H + H + M \qquad (29)$$

$$C_2H_2 + C_2H_2 \longrightarrow C_4H_3 + H \qquad (14)$$

followed by

$$C_4H_3 \longrightarrow C_4H_2 + H$$

and probably predominate at high temperatures over the reaction of molecular oxygen with acetylene.

$$C_2H_2 + O_2 \longrightarrow [\mathrm{CHO\ CHO}] \longrightarrow 2CO + 2H \qquad (30)$$

This reaction, however, may be significant at all temperatures. Using reaction schemes based on these major acetylene oxidation reactions, together with the appropriate hydrogen–oxygen radical reactions and the water gas reactions, it has proved possible to compute by numerical integration methods the ignition delays and composition profiles during the induction period and during ignition.[66,69] A compilation of pertinent reaction rate data is given in the Appendix.

3. *Chemiluminescence and Chemiionization*

Associated with the oxidation reactions of acetylene are a number of important chemiluminescence and chemiionization effects. Of particular interest has been the chemiluminescence from CH, from the fourth positive band of CO, from the blue CO_2 emission, and from OH. The OH emission is much weaker than the CH emission but is nevertheless approximately three orders of magnitude greater than the OH emission from comparable hydrogen–oxygen–argon mixtures. Because of their extensive use in induction-time experiments, there is considerable interest in the chemical mechanism leading to their formation, particularly to the stage in the reaction in which they are formed.

The mechanistic interpretation of the phenomena of visible and ultraviolet chemiluminescence and chemiionization must account for the facts that they grow exponentially with time and with the same time constants in the initial stages of the reaction. Furthermore, the two effects are most pronounced in nearstoichiometric mixtures. Thus it has been suggested[52] that both phenomena are the result of the reaction of two intermediates of the branching cycle.

The first observations of vacuum ultraviolet chemiluminescence in shocked acetylene–oxygen mixtures were by Kistiakowsky and Richards.[49] They inferred that the maximum intensity of emission was in the region 1500–1770 Å. The emitter was later identified[70] as the CO fourth positive system. Similar vacuum ultraviolet chemiluminescence has been observed in acetylene–oxygen flames (see section IV.C) and in the low-temperature reaction of acetylene and atomic oxygen.[71–73] The process resulting in this chemiluminescence is almost certainly second order. Furthermore, since the intensity ratio of CO* to CH* is almost independent of the oxygen concentration,[55] then reactions such as (31) and (32) can be ruled out.

$$CH^* + O_2 \longrightarrow CO^* + OH \qquad (31)$$

$$CH^* + O \longrightarrow CO^* + H \qquad (32)$$

Evidence[72,73] from the low-temperature studies of the atomic oxygen and acetylene reaction suggests that the precursor to excited carbon monoxide is almost certainly carbon suboxide, the reaction sequence being

$$C_2H_2 + O \longrightarrow C_2O + H_2 \qquad (33)$$

$$C_2O + O \longrightarrow CO^*(A^1\pi) + CO(X^1\Sigma) \qquad (34)$$

The reactions leading to excited CH and OH are not well established, and probably a number of reactions are involved. Excited hydroxyl is almost certainly produced by the association reaction[59]

$$O + H(+M) \longrightarrow OH^*(+M) \qquad (35)$$

but to explain the high intensities of emission in acetylene–oxygen flames compared to equivalent hydrogen–oxygen mixtures, it is necessary to postulate additional reactions. The present evidence[14,74,75] indicates that reaction 36 is important

$$CH + O_2 \longrightarrow CO + OH^* \qquad (36)$$

and also possibly[59]

$$CH_2 + O_2 \longrightarrow CHO + OH^* \qquad (37)$$

A number of reactions have been suggested as the source of CH*, but the choice of reaction must be consistent with the experimental facts that the rate of reaction must go through a maximum when the $[O_2]/[C_2H_2]$ ratio is increased from lean to rich,[52] and also that the ratio of intensities of CH* to CO* is independent of the oxygen concentration.[53] A likely reaction on this basis[52,55] is

$$C_2H + O \longrightarrow CO + CH^*(A^2\Delta) \qquad (38)$$

$$\Delta H = 8 \pm 8 \text{ kcal mole}^{-1}$$

However, to be fully acceptable[76] the C_2H radicals would have to be vibrationally excited.

Other energetically favorable reactions include the reaction of the C_2 radical[14,55,74,76]

$$C_2 + OH \longrightarrow CH^* + CO \qquad (39)$$

and possibly

$$C_2H + O_2 \longrightarrow CH^* + CO_2 \qquad (27)$$

$$C_2O + OH \longrightarrow CH^* + CO_2 \qquad (40)$$

Chemiionization in acetylene–oxygen ignition parallels in many respects the processes of chemiluminescence. After an induction period, it rises exponentially to a maximum and then decays. In particular, it has been shown that ion formation and CO* chemiluminescence are closely related to OH* emission.[52,64] The first investigation[64] utilized a probe technique to follow ionization, and it was established that this method gave similar induction periods to those obtained using vacuum uv chemiluminescence.[49] More recent microwave electron concentration measurements[64] have shown that the absolute values of maximum electron concentrations and rates of decay of ionization were not correct, but nevertheless this investigation gave valuable insight into the importance of this process in acetylene combustion.

Mass spectroscopic studies[52,53,77] of chemiions have shown that during ignition, the cyclopropenyl ion ($C_3H_3^+$) appears first and is gradually replaced by other ions, the most prominent being H_3O^+. The overall concentration of ions was

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(69) D. J. Seery, personal communication, 1968.

(70) C. W. Hand, *J. Chem. Phys.*, **36**, 2521 (1962).

(71) C. A. Arrington, W. Brennen, G. P. Glass, J. V. Michael, and H. Niki, *ibid.*, **43**, 1489 (1965).

(72) K. H. Becker and K. D. Bayes, *ibid.*, **48**, 653 (1968).

(73) F. F. Marmo, J. P. Padur, and P. Warneck, *ibid.*, **47**, 1438 (1967).

(74) A. Fontijn, W. J. Miller, and J. M. Hogan, ref 53, p 545.

(75) K. H. Becker, D. Kley, and R. J. Norström, ref 67, p 405.

(76) W. Brennen and T. Carrington, *J. Chem. Phys.*, **46**, 7 (1967).

(77) G. B. Kistiakowsky and J. V. Michael, *ibid.*, **40**, 1447 (1964).

greatest in stoichiometric mixtures and at higher temperatures. Under the latter condition the $C_3H_3^+$ decayed more rapidly to give larger H_3O^+ concentrations. Other ions present included $C_2H_3^+$, CH_3O^+, $C_4H_3^+$, $C_2H_3O^+$, and $C_5H_3^+$.

At present, there is considerable uncertainty about the formation of the $C_3H_3^+$ ion. Initially, its formation was attributed[53] to reaction 41 and later to reaction 42.[52] Recent evidence[52,78,79] has eliminated reaction 41. The ratio of ion formation to CH* chemiluminescence should be linearly dependent on acetylene concentration, since this reaction competes with reaction 36; this was not found experimentally.[52] However. $C_3H_3^+$ may be formed as a primary ion by reaction 42 or by some other reaction[34,52] such as

$$CH^* + C_2H_2 \longrightarrow C_3H_3^+ + e \qquad (41)$$
$$CH + C_2H_2 \longrightarrow C_3H_3^+ + e \qquad (42)$$

$$CH_2 + C_2H \longrightarrow C_3H_3^+ + e \qquad (43)$$

For either of these reactions to be thermodynamically acceptable, $\Delta H_f(C_3H_3^+)$ must be considerably lower than the reported value[80] of 265 kcal mole^{-1}. Alternatively, $C_3H_3^+$ may be a secondary ion,[52] produced in an ion–molecule reaction. A possible reaction sequence is

$$CH + O \longrightarrow CHO^+ + e \qquad (44)$$
$$CHO^+ + C_2H_2 \longrightarrow C_3H_3^+ + O \qquad (45)$$

Here the primary ion is CHO^+, which, although not detected in shock-tube studies,[52,53] is known[79] to be formed in flames. The $C_3H_3^+$ ion is then produced by CH^+ transfer. Reaction 45 also requires a lower value of $\Delta H_f(C_3H_3^+)$ before it is acceptable. Once combustion commences the acetylene concentration falls and the $C_3H_3^+$ ion decays resulting in the predominance of H_3O^+ which is formed by the reaction

$$CHO^+ + H_2O \longrightarrow H_3O^+ + CO \qquad (46)$$

The oxygenated ions are presumably produced by reactions of the (O + C_2H_2) adduct, for example[79]

$$C_2H_2 + O \longrightarrow C_2H_2O \qquad (47)$$
$$C_2H_2O + CHO^+ \longrightarrow C_2H_3O^+ + CO \qquad (48)$$

B. FLASH PHOTOLYSIS

A number of investigations have been made of the flash photolysis of acetylene–oxygen mixtures. In fact, the oxidation of acetylene was one of the first systems to be studied by this technique. The reaction is usually initiated by the photolytic decomposition of a sensitizer, this commonly being a small amount of NO_2. Radical concentrations in the reacting gas have been determined[81–83] by absorption spectroscopy. In mixtures where $C_2H_2/O_2 < 1$, the hydroxyl radical was predominant, whereas in mixtures where $C_2H_2/O_2 > 1$, the hydroxyl concentration was negligible, and the carbon radicals CH, C_2, and C_3 predominated. After an initial period of about 0.5 msec, high concentrations of radicals were attained, and these then decayed relatively slowly. Norrish, Porter, and Thrush concluded[82,84] that the main explosion occurred in the initial period prior to the onset of radical formation and that the radicals were formed only as a result of the explosion: carbon radicals from the photolysis of excess acetylene, and hydroxyl from the afterburning of hydrogen liberated in the reaction. However, hydroxyl radicals were always present before carbon radicals, suggesting that hydroxyl is an important chain carrier.

Takahashi, Yoshida, and Masuko[85] monitored pressure changes in flash-photolyzed $C_2H_2 + O_2 + NO_2$ mixtures. With high flash energies, the induction period before explosion was very short, and almost independent of the mixture composition, amount of sensitizer, and total pressure. With lower flash energies, however, the induction period was markedly increased and was dependent on the initial mixture parameters. Wadsworth[86] used a flash photolytic technique to initiate detonations in $C_2H_2 + O_2 + NO_2$ mixtures. The ignition delay between the first appearance of the photolytic flash and the onset of detonation was also found to be dependent on the initial mixture parameters.

Kinbara and Noda recently studied[83] the mechanism of ionization in $C_2H_2 + O_2 + NO_2$ mixtures by the simultaneous recording of absorption spectra and the ion current through the reacting gas. In acetylene-rich mixtures, there was a correlation between the time dependences of radical concentrations and ion current. This was taken as evidence for ionization by the reactions

$$CH + O \longrightarrow CHO^+ + e \qquad (43)$$
$$CHO^+ + H_2O \longrightarrow H_3O^+ + CO \qquad (46)$$

In acetylene-lean mixtures, however, no correlation existed between radical concentration and ion current. It was considered that the ionization could be of a thermal nature, or due to photoionization caused by the luminosity behind the shock waves which are known[85,87] to occur in flash photolysis systems.

IV. High-Temperature Flames

Studies of the high-temperature combustion of mixtures of acetylene with various oxidants have essentially covered four aspects: (i) parameters associated with ignition and extinction, particularly minimum ignition requirements, flammability limits, and quenching diameters; (ii) investigations of macroscopic properties, such as burning velocity and flame temperature measurements; (iii) microscopic examination of flame structure and chemical mechanism by spectroscopic or flame analysis techniques; and (iv) investigation of chemiluminescence and ionization phenomena.

A. IGNITION AND EXTINCTION PARAMETERS

1. Minimum Ignition Energy

Most of the investigations into the minimum ignition requirements for acetylene combustion have employed spark ignition, although other methods of ignition have also been used. The minimum energies for spark ignition of many acetylene–oxidant mixtures are extremely low: for a stoichiometric

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(78) W. J. Miller, ref 59, p 311.
(79) W. J. Miller, *Oxid. Combust. Rev.*, 3, 98 (1968).
(80) R. R. Bernecker and F. A. Long, *J. Phys. Chem.*, 65, 1565 (1961).
(81) R. G. W. Norrish, G. Porter, and B. A. Thrush. *Proc. Roy. Soc.*, A216. 165 (1953).
(82) R. G. W. Norrish, G. Porter, and B. A. Thrush, *ibid.*, A227, 423 (1955).
(83) T. Kinbara and K. Noda, ref 67, p 395.
(84) R. G. W. Norrish, ref 53, p 1.
(85) T. Takahashi, E. Yoshida, and A. Masuko, *Kogyo Kagaku Zasshi*, 63, 1364, 2130 (1960).
(86) J. Wadsworth, *Nature*, 190, 623 (1961).
(87) B. A. Thrush, *Proc. Roy. Soc.*, A233, 147 (1955).

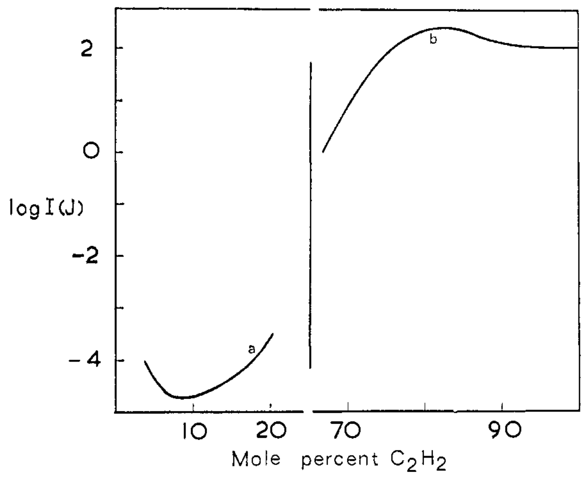

Figure 6. Plot of minimum ignition energy (I, joules) against composition for acetylene–air mixtures: (a) Calcote, Gregory, Barnett, and Gilmer[88], and Fenn[89]; (b) Ivanov and Kogarko.[90]

acetylene–air mixture,[88,89] the value is only 2×10^{-5} J. The minimum energy does not vary greatly with composition,[88,89] except in very rich mixtures, as shown in Figure 6. The ignition of pure acetylene requires[90] an energy of several hundred joules, while acetylene–air mixtures containing up to 18% air are even more difficult to ignite.

The influence of initial pressure on ignition has been investigated for acetylene–air mixtures.[89,91] The data of Fenn[89] for a stoichiometric mixture in the pressure range 0.1–1 atm can be expressed as $I = 5.4 \times 10^{-4}P^{-2.12}$ J, where I is the minimum ignition energy and P the pressure, while for a mixture containing 17% air at pressures between 2 and 13 atm, Ivanov and Kogarko[91] have reported the relationship $I = 24.5P^{-3.66}$ J.

The absolute values of the minimum ignition energies have been shown[88,92] to depend also on the electrode geometry and spark gap.

2. *Limits of Flammability*

There exists a wide range of composition over which acetylene–oxidant mixtures can be ignited, and the extent of this range of flammability has been widely investigated, particularly for acetylene–air mixtures. Such investigations are of obvious importance in assessing the industrial hazards that arise with the use of acetylene.

Extensive compilations of flammability data have been given by Coward and Jones[93] and by Miller.[2] At atmospheric pressure acetylene forms flammable mixtures with air in the composition range 2.5 to *ca.* 80% acetylene, although the actual limits depend somewhat on the experimental conditions used. Mixtures with up to 100% acetylene can be ignited, although large ignition energies are required.[90]

Fewer measurements have been reported for acetylene–oxygen mixtures. The limits of flammability at atmospheric pressure are 2.0 to *ca.* 95% acetylene,[92] again dependent on the ignition energy. The effect of reducing the initial pressure has been investigated by Ivanov and Kogarko.[92] The upper limit was almost unaffected, although the lower limit was considerably reduced at lower pressures. No acetylene–oxygen mixtures could be ignited at pressures below 1.4 mm.

Very little work has been reported for the limits of flammability of acetylene with an oxidant other than air or oxygen, although limits of 2.2 and 67.0% acetylene have been determined[93] for acetylene–nitrous oxide mixtures.

3. *Quenching Parameters*

There are two parameters that have commonly been used to characterize the quenching of flames. The first is the quenching distance, and refers to the minimum separation of parallel plates for a flame to propagate between them. The other, quenching diameter, refers to the critical diameter for quenching on a cylindrical burner. The two parameters have been shown[94] to be related.

Few determinations of quenching distance have been made for acetylene flames, although a value of 1.68 mm at a pressure of 11 mm of mercury has been reported[95] for stoichiometric acetylene–oxygen. However, quenching diameters have been more extensively studied. Anagnostou and Potter[96] examined the effect of initial pressure on quenching diameter by determining whether a flame stabilized on a burner flashed back or was quenched when the flow to the burner was interrupted. For stoichiometric acetylene–oxygen flames in the pressure range 0.06–0.35 atm, the data fitted an expression of the form $d = aP^{-n}$, where d is the quenching diameter in millimeters, P is the pressure in atmospheres, and a and n are constants, equal to 0.16 and 1.06, respectively. The results were thought to indicate an overall reaction order of two.

Gaydon and Wolfhard[5] determined quenching diameters by measuring the minimum pressures at which flames could be maintained on burners of known diameters. For stoichiometric acetylene–oxygen flames at pressures from 0.01 to 0.3 atm, $a = 0.12$ and $n = 1.07$, while for stoichiometric acetylene–air flames, $a = 0.77$ and $n = 1.07$.

Thus, for stoichiometric oxyacetylene flames at atmospheric pressure, the quenching diameter is only 0.12 to 0.16 mm. Indeed, it has been observed[97] that even sintered metal plugs are not totally effective in quenching these flames.

B. MACROSCOPIC FLAME PARAMETERS

1. *Laminar Burning Velocity*

The laminar burning velocity S_u is a fundamental property of a flammable mixture under a particular set of initial conditions and is defined as the rate at which the flame front moves through and relative to the unburnt gas. Burning velocity measurements may be made by a variety of experimental methods: by measuring the flame propagation along a tube,

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(88) H. F. Calcote, C. A. Gregory, C. M. Barnett, and R. B. Gilmer, *Ind. Eng. Chem.*, **44**, 2656 (1952).

(89) J. B. Fenn, *ibid.*, **43**, 2865 (1951).

(90) B. A. Ivanov and S. M. Kogarko, *Dokl. Akad. Nauk. SSSR*, **145**, 1308 (1962).

(91) B. A. Ivanov and S. M. Kogarko, *Combust. Explos. Shock Waves*, **1** (2), 73 (1965).

(92) B. A. Ivanov and S. M. Kogarko, *ibid.*, **1** (4), 51 (1965).

(93) H. F. Coward and G. W. Jones, *U. S. Bur. Mines Bull.*, No. 503 1952.

(94) A. L. Berlad and A. E. Potter, "Proceedings of the Fifth Symposium (International) on Combustion, University of Pittsburgh, Pittsburgh, Pa., 1954," Reinhold Publishing Corp., New York, N. Y., 1955, p 728.

(95) A. L. Berlad, R. D. Rowe, and C. H. Yang, *Combust. Flame*, **3**, 477 (1959).

(96) E. Anagnostou and A. E. Potter, *ibid.*, **3**, 453 (1959).

(97) A. C. Egerton, A. J. Everett, and P. Moore, "Proceedings of the Fourth Symposium (International) on Combustion, Massachusetts Institute of Technology, Cambridge, Mass., 1952," Williams and Wilkins, Baltimore, Md., 1953, p 689.

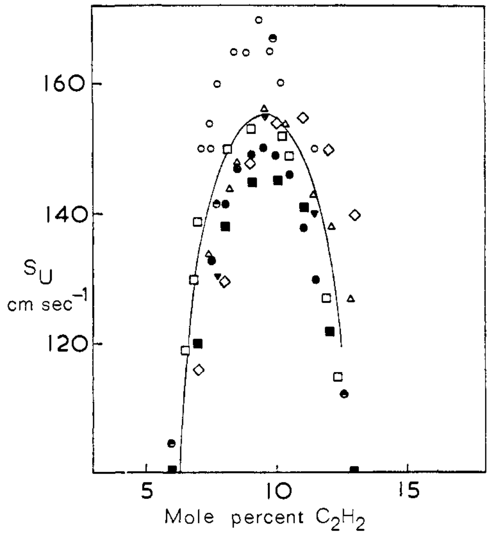

Figure 7. Dependence of burning velocity (S_u, cm sec^{-1}) on composition for acetylene–air mixtures at 1 atm pressure: ○, ref 98; ◓, ref 99; △, ref 100; ▼, ref 102; ◇, ref 103; □, ref 104; ●, ref 105; ■, ref 106; —, ref 101.

in a spherical bomb, in a soap bubble, or on a burner. All these techniques have been used for acetylene flames.

Burning velocity data obtained[98–106] over a range of composition for acetylene–air mixtures initially at 1 atm pressure and 298°K are displayed in Figure 7. In common with other hydrocarbon–air flames, the maximum velocity occurs in a fuel-rich mixture, in this particular case at an equivalence ratio of 1.23 (9.5% C_2H_2). The equivalence ratio is defined as $\{[C_2H_2]/[\text{air}]\}/\{[C_2H_2]/[\text{air}]\}_{\text{stoichiometric}}$. The differences in the experimental values are caused by several factors. The experimental error associated with some measuring techniques is fairly high, and it has also been demonstrated[101] that systematic differences arise in the data obtained by different procedures. However, at 298°K the maximum burning velocity is fairly well established to be 153 cm sec^{-1}, this occurring at an equivalence ratio of 1.23.

There are a few reports[98,107–110] of burning velocity data for acetylene–oxygen flames. The results that have been obtained are displayed in Figure 8. The lack of data and the extremely poor agreement in the reported values can be partially accounted for by the very rapid combustion of acetylene–oxygen mixtures, which causes severe experimental difficulties. For instance, if burner methods are adopted, the high flow rates required to prevent flash-back mean that very narrow tubes (diameter <1 mm) must be used to preserve laminar flow. Such small flames involve high curvature and render accurate measurements on the cone extremely difficult. The rate of propagation of a flame in a combustible mixture is primarily determined by its chemical composition, but it is also influenced by experimental conditions such as initial pressure and initial temperature. This latter factor is instrumental in determining the final flame temperature (T_f) as well as the temperatures at which the maximum rate of chemical reaction occurs (~0.7 to $0.8T_f$). These changes can also be brought about by the use of inert diluents.

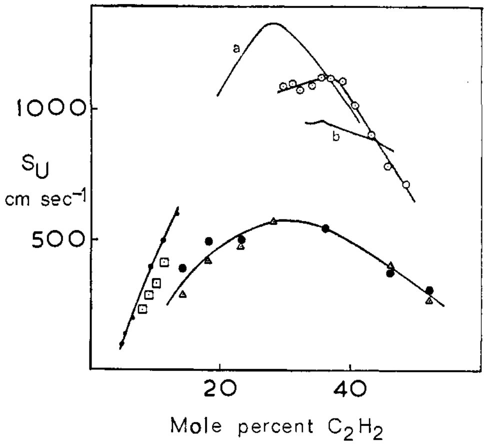

Figure 8. Dependence of burning velocity (S_u, cm sec^{-1}) on composition for acetylene–oxygen mixtures at 1 atm pressure: (a) ref 107; (b) ref 108; ⊙, ref 98; •, ref 100; ⊡, ref 103; ◬, ●, ref 109.

Early theories (for reviews, see ref 111 and 112) of flame propagation have attempted to derive expressions relating burning velocity to kinetic parameters, such as activation energy and reaction order. In one approach the flame is assumed to be controlled by a single overall reaction obeying the simple Arrhenius rate expression; thus for a reaction of order n

$$\text{reaction rate} = AC_r^n \exp(-E/RT)$$

Here A and E are the Arrhenius parameters and C_r is the reaction concentration. By means of various assumptions, it can be shown that

$$S_u^2 = \text{constant} \exp(-E/RT_f)$$

where the constant involves terms such as thermal conductivity, heat of reaction, etc. This analysis also indicates that $S_u^2 \propto P^{n-2}$, where P is the total pressure. However, any data obtained in this way need careful interpretation, particularly for a system as complex as the combustion of acetylene. With the advent in recent years of modern experimental techniques enabling the flame structure to be examined, these approaches are now little used.

The influence of initial pressure on burning velocities has been investigated by many researchers. An extensive compilation of data has been given[2] by Miller. The data show that for both acetylene–air and acetylene–oxygen flames, burning

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(98) E. Bartholomé, *Z. Elektrochem.*, **54**, 169 (1950).

(99) C. J. Rallis, A. M. Garforth, and J. A. Steinz, *Combust. Flame*, **9**, 345 (1965).

(100) M. Gilbert, "Proceedings of Sixth Symposium (International) on Combustion, Yale University, New Haven, Conn., 1956," Reinhold Publishing Corp., New York, N. Y., 1957, p 174.

(101) C. J. Gibbs and H. F. Calcote, *J. Chem. Eng. Data*, **4**, 226 (1959).

(102) J. Manton and B. B. Milliken, "Proceedings of the Gas Dynamics Symposium on Aerothermochemistry, Northwestern, University, Evanston, Ill., 1955," 1956, p 151.

(103) J. W. Linnett, H. S. Pickering, and P. J. Wheatley, *Trans. Faraday Soc.*, **47**, 974 (1951).

(104) R. Friedman and E. Burke, *Ind. Eng. Chem.*, **43**, 2772 (1951).

(105) T. G. Scholte and P. B. Vaags, *Combust. Flame*, **3**, 495 (1959).

(106) F. A. Smith, *Chem. Rev.*, **21**, 389 (1937).

(107) H. Brückner, W. Becher, and E. Manthey, *Schweissen Schneiden*, **12**, 92 (1937).

(108) G. M. Skinner and J. M. Gaines, quoted by ref 2.

(109) G. von Elbe and M. Menster, *J. Chem. Phys.*, **13**, 89 (1945).

(110) J. W. Linnett and P. J. Wheatley, *Trans. Faraday Soc.*, **48**, 338 (1952).

(111) S. S. Penner, "Chemistry Problems in Jet Propulsion," Pergamon, London, 1957, Chapter 24.

(112) M. W. Evans, *Chem. Rev.*, **51**, 363 (1952).

velocities are almost independent of pressure over the pressure range of 0.01 to 10 atm and over a wide range of initial mixture composition. More recently it has been suggested[99] that there is a complex variation of burning velocity with pressure for stoichiometric acetylene–air flames, the burning velocity first increasing, then decreasing, and finally increasing again with increase in pressure. However, the bulk of the evidence indicates that burning velocity varies little with pressure, suggesting, from the relationship $S_u^2 \propto P^{n-2}$, a reaction order of two.

Relatively few studies have been made of the effect on the burning velocity of an increase in the initial mixture temperature (T_i). Friedman and Burke[104] obtained the expression $S_u \propto (T_i)^{0.84}$ and more recently, results have been obtained[99] which yield a temperature exponent of 0.85. The variation of burning velocity and of final flame temperature by the addition of inert diluents has also been examined, allowing overall activation energies to be estimated. Kaskan, using nitrogen and helium, obtained[113] an activation energy of *ca.* 44 kcal mole^{-1}. Likewise, van Wonterghem and van Tiggelen obtained[114] *ca.* 32 kcal mole^{-1}, but in this analysis an estimated reaction zone temperature was used rather than the final flame temperature. The activation energy obtained in this way was similar with that derived from the variation of intensity of hydroxyl radical emission with diluent concentration.

2. *Calculation of Flame Temperatures and Burnt Gas Compositions*

A knowledge of the temperature attained in a flame is of considerable importance in industrial and scientific applications. However, the high temperatures associated with acetylene–oxidant flames render experimental determinations difficult, and errors in the flame temperatures so obtained may be several hundred degrees. Consequently, flame temperatures and the corresponding chemical composition of the burnt gas are frequently calculated from the appropriate thermochemical data. Such calculations assume that complete chemical equilibrium exists in the combusted gaseous mixture and that there are no heat losses from the flame or burnt gases. Calculations of this type are most conveniently executed by means of a digital computer, and a number of suitable methods have been described.[115,116]

Computed flame temperatures of a range of acetylene–oxygen mixtures are given in Figure 9. These values refer to combustion at 1 atm and at constant pressure. The maximum temperature attained[117] is 3430°K, this occurring in a mixture containing 40% acetylene. It is interesting to note that the theoretical temperature of 3430°K obtained for the reaction

$$C_2H_2 + 1.5O_2 \longrightarrow \text{dissociation products of } (2CO + H_2O)$$

is higher than the temperature of 3341°K resulting from the complete combustion to carbon dioxide and water

$$C_2H_2 + 2.5O_2 \longrightarrow \text{dissociation products of } (2CO_2 + H_2O)$$

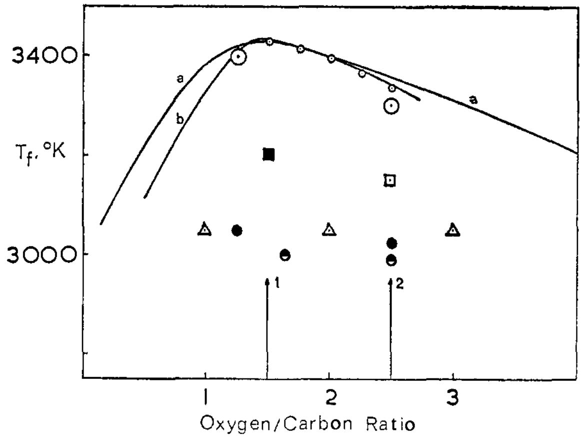

Figure 9. Dependence of the flame temperature (T_f, °K) on composition for acetylene–oxygen mixtures. Calculated values: (a) ref 119; (b) ref 120; ⊙, ref 117. Experimental values: ⊙, ref 133; ⊡, ref 130; ■, ref 143; △, ref 131; ●, ref 124; ◒, ref 128. The compositions corresponding to the first and second stoichiometric compositions (combustion leading to CO and CO$_2$, respectively) are indicated by 1 and 2, respectively.

This difference results from the higher bond dissociation energy of carbon monoxide which is manifest in less dissociation of the products of combustion and consequent higher flame temperature. Since the maximum temperature obtained during combustion is limited by the dissociation of the products, higher temperatures can be reached by the use of elevated pressure to diminish dissociation. This is only of limited usefulness, however, since the temperature is a function of log (pressure). For example, the temperature of 3430°K for combustion at 1 atm is raised to 3737°K at 10 atm, but at 100 atm it only becomes 4199°K.[118]

Values of the calculated equilibrium compositions[117] for acetylene–oxygen combustion at 1 atm are given in Table II. These values have been obtained using the recent thermochemical data given in the JANAF Tables[7] and they are in substantial agreement with earlier published results[119] based on the use of less reliable thermochemical data. In the case of combustion of rich mixtures, the situation is complicated by the possible formation of solid carbon. Calculations have been performed[120] in which allowance was made for the presence of the hydrocarbon species C_2H_2, C_2H_4, and CH_4, as well as for polyatomic carbon in the burnt gas.

Calculated flame temperatures and equilibrium compositions have been reported[121] for acetylene–air mixtures and also for other acetylene–oxygen–nitrogen mixtures.[122] In the case of combustion with air the maximum flame temperature is 2604°K for a mixture with 9.29% acetylene content. These data are shown in Figure 10.

There is little published information for flames supported by oxidants other than air or oxygen although such data could readily be computed if needed. A temperature of 3152°K has

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(113) W. E. Kaskan, ref 100, p 134.

(114) J. van Wonterghem and A. van Tiggelen, ref 94, p 637.

(115) F. J. Weinberg, *Proc. Roy. Soc.*, A241, 132 (1957).

(116) G. S. Bahn and E. E. Zukoski, Ed., "Kinetics, Equilibria and Performance of High Temperature Systems," Butterworth & Co., Ltd., London, 1960, Chapters 10–23.

(117) D. N. Baxendale and A. Williams, unpublished data, 1968.

(118) R. L. Browne, D. A. Everest, J. D. Lewis, and A. Williams. *J. Inst. Fuel*, **41**, 433 (1968).

(119) H. E. Edwards, R. W. Smith, Jr., and S. R. Brinkley, Jr.. *U. S. Bur. Mines, Rept. Invest.*, 4958 (1953).

(120) N. R. Gay, J. T. Agnew, O. W. Witzell, and C. E. Karabell, *Combust. Flame*, **5**, 257 (1961).

(121) R. W. Smith, Jr., J. Manton, and S. R. Brinkley, *U. S. Bur. Mines, Rept. Invest.*, 5035 (1954).

(122) W. Malaerts, G. de Soete, J. N. Bertrand, and A. van Tiggelen, *Bull. Soc. Chim. Belg.*, **69**, 95 (1960).

Table II

Calculated Flame Temperature and Burnt Gas Compositions for Acetylene–Oxygen Mixtures at Atmospheric Pressure

O/C ratio	*Flame temp, °K*	*Equilibrium composition, mole fraction*							
		CO_2	CO	H_2O	H_2	O_2	H	O	OH
1.25	3420	0.0277	0.5500	0.0521_5	0.1320	0.0039	0.1770	0.0247	0.0322
1.50	3430	0.0512	0.4974	0.0761	0.0930	0.0124_5	0.1525	0.0539	0.0575
1.75	3416	0.0718	0.4494	0.0890	0.0703	0.0388	0.1280	0.0776	0.0742_5
2.00	3394	0.0892	0.4062	0.0960	0.0555	0.0653	0.1080	0.0948	0.0846_5
2.25	3367	0.1052	0.3670	0.1000	0.0452_5	0.0942	0.0914	0.1060	0.0903
2.50	3339	0.1188	0.3323	0.1026	0.1375_5	0.1246	0.0777	0.1128	0.0930

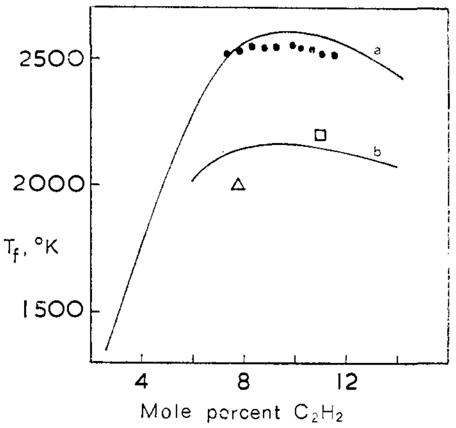

Figure 10. Dependence of flame temperature (T_f, °K) on composition for acetylene–air mixtures. Calculated values: (a) ref 121; (b) ref 114. Experimental values: ●, ref 136; □, ref 129; △, ref 137.

been calculated[118] for a stoichiometric (based on combustion to CO_2) acetylene–nitrous oxide flame and 3363°K for a stoichiometric acetylene–nitric oxide flame.[123]

3. Experimental Determination of Flame Temperatures

In a classical thermodynamic sense, a system may be said to have a temperature only if it is in a state of complete equilibrium. The very rapid chemical changes occurring in flames may lead to nonequilibrium distributions of chemical species and consequently to difficulties in defining temperature in a strict sense. As a result of this, special definitions of temperature have been adopted, based on the average energy of the chemical species or, more usually, on the relative population of species in the various internal energy states. Population temperatures are designated rotational, vibrational, or electronic, depending on the mode of internal energy.

A variety of spectroscopic techniques have been developed to measure population temperatures.[124–136] For acetylene flames, rotational temperatures have most commonly been measured. The intensity I of a line in the rotational fine structure of an emission band is given by

$$I = CP\nu^4 \exp(-E_r/kT)$$

where C is a constant for all lines in the same band, P the rotational transition probability, ν the wave number, E_r the rotational energy of the upper state, k the Boltzmann constant, and T the temperature. By measuring the relative intensities of rotational lines, the temperature may be determined. The $^2\Sigma^+–^2\Pi$ transition of the OH radical at 3064 Å is most suitable,[124] although CH,[125] C_2,[126] and NH[5] bands have also been used.

Vibrational temperatures may be determined in a similar way from the intensity distribution of the vibrational bands in a system. However, the practical difficulties are more severe. The greater wavelength range over which the emission occurs increases the significance of the response characteristics of the detector changing with wavelength. Vibrational temperatures have been obtained for the OH,[127,128] C_2,[129] and BaO[129] species.

Electronic temperatures have been determined by the two-line method.[130–132] The ratio of the intensities of any two lines in the emission spectrum of an element introduced into the flame is given by

$$\frac{I_1}{I_2} = \frac{P_1 \exp(-E_1/kT)}{P_2 \exp(-E_2/kT)}$$

where P is the transition probability and E the excitation energy of the line. If P and E are known, the temperature can be established. Iron, introduced into the flame as ferrocene[130] or ferric chloride,[131,132] has been used in studies of acetylene flames.

In addition to the methods described above, radiance methods, particularly line reversal,[114,132–134] and line-broadening measurements[125] have yielded flame temperatures. Nonoptical methods have also been employed. The degree of equilibrium ionization in the burnt gas region of a flame is

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(123) H. G. Wolfhard and W. G. Parker, ref 94, p 718.

(124) H. P. Broida and G. T. Lalos, *J. Chem. Phys.*, **20**, 1466 (1952).

(125) A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc.*, **A199**, 89 (1949).

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(127) K. E. Shuler, *J. Chem. Phys.*, **18**, 1221 (1950).

(128) L. de Galan and J. D. Winefordner, *J. Quant. Spectrosc. Radiat. Transfer*, **7**, 703 (1967).

(129) E. S. Ortenberg and N. A. Nesterko, *Opt. Spectrosc.* (USSR), **10**, 136 (1961).

(130) H. P. Broida and K. E. Shuler, *J. Chem. Phys.*, **27**, 933 (1957).

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(133) H. H. Lurie and G. W. Sherman, *Ind. Eng. Chem.*, **25**, 404 (1933).

(134) V. S. Rossikhin and N. A. Nesterko, *Zh. Fiz. Khim.*, **33**, 665 (1959).

(135) P. F. Jessen and A. G. Gaydon, ref 67, p 481.

(136) W. Snelleman and J. A. Smit, *Metrologia*, **4**, 123 (1968).

a function of temperature, and from ionization data free-electron temperatures have been obtained.[137,138]

The temperature determinations for acetylene flames fall into two categories. The first consists of the experimental temperatures[114,124,128–138] determined under conditions where equilibrium is fairly well established. These results are displayed in Figures 9 and 10. The measured temperatures are lower than calculated by up to several hundred degrees, due to heat losses by radiation and also by air entrainment, as the flames are generally burned unenclosed in the atmosphere.

In contrast to these temperatures are the anomalously high values, which form the second category.[125–127,139,140] These high values may be caused by experimental factors, particularly self-absorption, or by genuine chemical effects. The role of self-absorption in flame-temperature measurement by emission spectroscopy has been fully discussed[141] by Penner, who has shown that much of the early data were wrongly interpreted because self-absorption was ignored. The effects of self-absorption may be minimized by the use of the "iso-intensity" technique,[142] in which lines of equal intensity are compared.

A more important reason for the abnormally high-temperature measurements is the lack of equilibrium in certain regions of flames. Many of the emitting species in a flame are produced by chemiluminescent reactions, such as the highly exothermic reaction

$$\mathrm{CH} + \mathrm{O_2} \longrightarrow \mathrm{CO} + \mathrm{OH^*} \qquad (36)$$

The OH radicals initially formed in such a process may have electronic, vibrational, and rotational energy distributions corresponding to very high temperatures. The equilibrium distribution is then attained by collisions with other molecules. When equilibrium is not attained, for example, in the reaction zone of flames or in flames burning at low pressure, emission spectroscopic techniques lead to high values for the temperature of the flame. These effects are discussed more fully in a later section (III.D).

There have been several recent reports of temperature measurements in acetylene flames burning at atmospheric pressure. Janin, Roux, and d'Incan established[143] the temperature profile of an acetylene–oxygen flame, containing 40% acetylene, from the (1, 0) band of the rotational-vibration spectrum of OH in the wavelength range 3.5–3.9 μ. A maximum temperature of 3200°K was observed about 2 mm downstream from the oxidation zone. OH radical concentrations were also determined, using the $^2\Sigma^+$–Π^2 transition. The experimental values were in agreement with calculated values, indicating that equilibrium was rapidly attained outside the oxidation zone. Rotational temperatures of oxy-acetylene flames have been determined[144] by Takai and Ariyasu from the OH($^2\Sigma^+$–$^2\Pi$) and CH($^2\Sigma$–$^2\Pi$) transitions. Unusual temperature profiles were obtained. In flames of equimolar mixtures, a maximum temperature of 3750°K was obtained 11 mm downstream from the main reaction zone; 1 mm downstream from the reaction zone, the temperature was 3650°K.

These previous reports all refer to premixed flames. Measurements have also been made[128] on turbulent, diffusion flames by de Galan and Winefordner. It was found that temperatures obtained by a variety of techniques were in good agreement, with values around 2900°K, suggesting that thermal equilibrium existed in the flame.

Temperature measurements have also been reported[132] for premixed acetylene–nitrous oxide flames, using the sodium line-reversal and iron two-line methods. Values of about 3050°K were obtained by both methods. The agreement between experimental and theoretical temperatures again indicates the attainment of at least partial equilibrium in flames burning at atmospheric pressure.

C. STRUCTURE AND REACTION MECHANISM OF ACETYLENE-OXYGEN FLAMES

Investigations of the structure and reaction mechanism of acetylene flames have been confined almost exclusively to premixed flames, with little detailed work being carried out using diffusion flames. A detailed interpretation of the structure of a premixed laminar flame in terms of the elementary chemical kinetic steps requires a knowledge of the concentrations of the chemical species through the flame so that their rates of appearance or disappearance may be calculated. In order to make a complete analysis of the flame, it is also necessary to know the burning velocity (which sets the time scale) and the temperature profile. In the last decade or so a number of experimental techniques have been developed to permit measurements to be made of composition and temperature in flames. However, two restrictions to their application exist: the flame must usually be laminar or one-dimensional, and secondly the reaction zone studied must be sufficiently wide to permit adequate spatial resolution. As a consequence of the latter requirement, flame-structure studies are carried out with low-pressure flames, or with flames heavily diluted with nitrogen to reduce the burning velocity, or in the burnt gas region.

A number of investigations have been made of the structure of acetylene–oxygen flames. Since only relatively few species are involved, the basic mechanism involved in the combustion of lean mixtures is fairly well understood, although many points remain to be resolved. In the case of rich mixtures, however, where a considerable number of transient species participate, the mechanism is far less well understood.

1. *Lean and Stoichiometric Flames*

The first experimental investigation of the structure of the reaction zone of a lean acetylene–oxygen flame was reported[145] in 1958. A low-pressure flame was used so that microprobe sampling could be employed. Mass spectrometric analysis of the products indicated the buildup of carbon monoxide, hydrogen, and formaldehyde in the reaction zone, these

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(137) B. E. L. Travers and H. Williams, ref 53, p 657.

(138) V. I. Tverdokhlebov and M. E. Tretenko, *Zh. Tekh. Fiz.*, **35**, 1044 (1965); *Chem. Abstr.*, **63**, 10720*a* (1965).

(139) A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc.*, **A205**, 118 (1951).

(140) W. R. Kane and H. P. Broida, *J. Chem. Phys.*, 21. 347 (1953).

(141) S. S. Penner, "Quantitative Molecular Spectroscopy and Gas Emissivities," Addison Wesley Publishing Co., Inc., Reading, Mass., 1959, Chapter 17–4.

(142) G. H. Dieke and H. M. Crosswhite, Bumble Bee Report No. 87, Johns Hopkins University, Baltimore, Md., 1948; *J. Quant. Spectrosc. Radiat. Transfer*, 2, 97 (1962).

(143) J. Janin, F. Roux, and J. d'Incan, *Spectrochim. Acta*, **23A**, 2939 (1967).

(144) M. Takai and T. Ariyasu, *Technol. Rept. Kansai Univ.*, No. 8, 23 (1966).

(145) R. M. Fristrom, W. H. Avery, and C. Grunfelder, "Proceedings of the Seventh Symposium (International) on Combustion, London and Oxford, 1958," Butterworth and Co., Ltd., London, 1959, p 304.

being mainly converted to carbon dioxide and water in the burnt gas region. It was also observed that the maximum flame luminosity occurred at the point of disappearance of the acetylene.

Fenimore and Jones, also using microprobe sampling of low-pressure fuel-lean flames, studied[146] the combustion of acetylene–oxygen flames diluted with argon to which trace amounts (indicators) of carbon monoxide and nitrous oxide were added. The hydroxyl radical and hydrogen and oxygen atom concentrations in the reaction zones were estimated by the rates of the reactions

$$OH + CO \rightleftharpoons CO_2 + H$$

$$H + N_2O \longrightarrow OH + N_2$$

$$O + OH \rightleftharpoons O_2 + H$$

The authors suggested that acetylene was consumed exclusively by the reaction

$$O + C_2H_2 \longrightarrow [C_2H_2O]^* \longrightarrow CH_2 + CO \qquad (17)$$

$$\text{or } H_2 + C_2O \qquad (33)$$

and that molecular oxygen was mostly consumed by the step

$$H + O_2 \rightleftharpoons OH + O \qquad (22)$$

However, it was later suggested[147] that the exclusive destruction of acetylene by oxygen atoms occurred in the particular flame studied only because the added carbon monoxide suppressed the hydroxyl radical concentration, and that in general, other radicals (*e.g.*, OH) can react with acetylene under suitable flame conditions. Some support for this has been obtained[148] from esr measurements of hydrogen and oxygen atom concentrations through a very acetylene-lean, low-pressure flame. Although there may have been considerable errors[149] in the measured radical concentrations, it was concluded[148] that hydroxyl reacted with acetylene

$$OH + C_2H_2 \longrightarrow C_2H + H_2O \qquad (9)$$

followed by

$$C_2H + O_2 \longrightarrow HCO + CO \qquad (10)$$

$$HCO + \left\{\begin{matrix} O \\ OH \end{matrix}\right. \longrightarrow CO + \left\{\begin{matrix} OH \\ H_2O \end{matrix}\right. \qquad (49)$$

However, in general, it seems likely that the major reaction paths are determined largely by the acetylene to oxygen ratio in the initial mixture, since this determines the relative concentrations of hydrogen and oxygen atoms and of hydroxyl. More recently, two reports of detailed examinations[67,150] of low-pressure acetylene–oxygen flames have been made. In the first of these studies,[150] composition profiles of the reactants and stable products through the flame were made by microprobe sampling, while the concentrations of the radicals OH, CH, and C_2 were determined by absorption spectroscopy. Oxygen atom concentrations were inferred from the intensity of emission of the CO + O reaction continuum at 4450 Å. These experimental data were later analyzed[67] in detail by integrating numerically the one-dimensional flame equations, and incorporating the experimental temperature and hydroxyl concentration profile into the analysis. A reaction scheme was postulated which apparently explained the major experimental facts, and the rate coefficients of this scheme were adjusted until the experimental and computed concentration profiles of the species C_2H_2, O_2, H_2, H_2O, CO, and CO_2 were in agreement.

For a lean acetylene–oxygen–argon flame ($C_2H_2/O_2 = 0.167$), oxygen-atom attack on the acetylene by reaction 17 accounted for 80% of the total acetylene consumption.

$$O + C_2H_2 \longrightarrow CO + CH_2 \qquad (17)$$

In less lean flames ($C_2H_2/O_2 = 0.309$), the acetylene was attacked at approximately equal rates by O, OH, and H *via* reactions 17, 9, and 50, respectively.

$$OH + C_2H_2 \longrightarrow C_2H + H_2O \qquad (9)$$

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad (50)$$

Little is known about the oxidation reactions of the methylene (CH_2) or ethynyl (C_2H) radicals. Methylene was assumed to react only by reactions 18 and 51, which are both exothermic.

$$CH_2 + O \longrightarrow HCO + H \qquad (18)$$

$$CH_2 + OH \longrightarrow HCO + H_2 \qquad (51)$$

Ethynyl may react with molecular oxygen or atomic oxygen.

$$C_2H + O_2 \longrightarrow HCO + CO \qquad (10)$$

$$C_2H + O \longrightarrow CO + CH \qquad (38)$$

The consumption of molecular oxygen in the flames was thought to be primarily due to the reaction

$$H + O_2 \longrightarrow OH + O \qquad (22)$$

with reaction 10 only playing a relatively small role. The direct formation of carbon dioxide from ethynyl

$$C_2H + O_2 \longrightarrow CO_2 + CH \qquad (27)$$

only makes a very small contribution in the temperature range of 1000–1500°K. At higher temperatures, however, both reactions 27 and 25 may be of greater significance.

$$C_2H + O_2 \longrightarrow 2CO + H \qquad (25)$$

The formyl radical produced in these reactions decomposed by reaction 52 or reacted with atoms or free radicals, resulting

$$HCO + M \longrightarrow CO + H + M \qquad E \sim 12 \text{ kcal mole}^{-1} \qquad (52)$$

in the loss of a hydrogen atom to give carbon monoxide. The carbon dioxide yields could be interpreted in terms of the single reaction

$$CO + OH \rightleftharpoons CO_2 + H \qquad (26)$$

The mechanism given here is capable of explaining the basic phenomenological aspects of the combustion of lean acetylene–oxygen flames and is broadly consistent with the mechanism proposed for oxidation in shock-heated mixtures. The available estimates of the rate expressions for the reactions involved in this scheme are given in the Appendix.

2. *Fuel-Rich Flames*

Fuel-rich flames of acetylene and oxygen are more complex than lean flames since a large number of hydrocarbon species may be formed. The formation of carbon particles (or soot) may be a further complication. Thus the reaction mechanism is more obscure than is the case for lean flames. However,

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[146] C. P. Fenimore and G. W. Jones, *J. Chem. Phys.*, **39**, 1514 (1963).

[147] W. C. Gardiner, Jr., *ibid.*, **40**, 2410 (1964).

[148] A. A. Westenberg and R. M. Fristrom, ref 53, p 473.

[149] F. Kaufman, P. H. Kydd, *et al.*, ref 53, p 483.

[150] R. P. Porter, A. H. Clark, W. E. Kaskan, and W. G. Browne, ref 59, p 907.

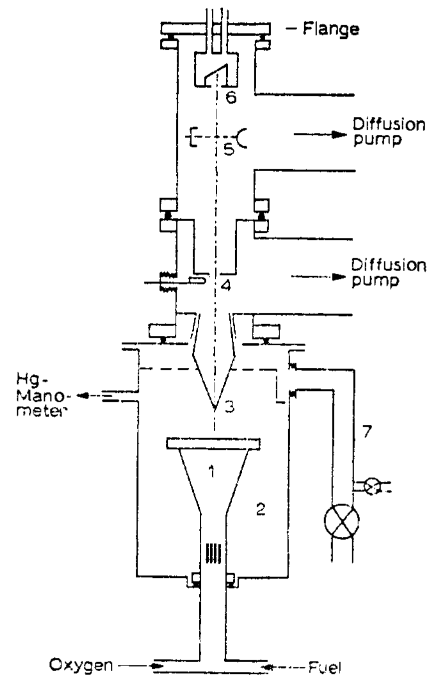

Figure 11. Molecular beam sampling system for low-pressure flames: (1) burner for flat flames; (2) burner housing; (3) nozzle probe; (4) collimating slit; (5) ion source; (6) cooled baffle. The direction of the ion beam is perpendicular to the plane of the paper (after Homann[158]).

since the concentrations of hydrocarbon radicals are sufficiently high to be measured, important information about individual reactions has been deduced.

The first examination of the flame structure of such flames was made by Fenimore and Jones, who studied[151] a number of acetylene–oxygen–nitrogen flames at low pressures. The compositions of the flames were such that in the burnt gas [H] > [OH] ≫ [O] > [O$_2$]. It was concluded that in the temperature range 1700–2000°K acetylene was only consumed by reaction with hydroxyl

$$OH + C_2H_2 \longrightarrow C_2H + H_2O \qquad (9)$$

rather than by reaction with hydrogen atoms. On this basis the rate constant for the reaction over the range 1700–2000°K was deduced to be about 2×10^{12} cm^3 mole^{-1} sec^{-1}, with a possible activation energy of about 7 kcal mole^{-1}. In a more recent study[67] Browne, Porter, Verlin, and Clark concluded that for fuel-rich flames with temperatures 1500–1600°K, the predominant mode of attack was *via* hydrogen atoms

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad (50)$$

and deduced rate expressions for reactions 9 and 50 of $6 \times 10^{12} \exp(-7000/RT)$ and $2 \times 10^{14} \exp(-19000/RT)$ cm^3 mole^{-1} sec^{-1}, respectively. Since there are few other kinetic data available for these reactions, it is not possible at this time to establish their relative rates accurately. However, it is likely that both reactions 9 and 50 contribute in fuel-rich flames, their relative importance being determined by flame conditions. An approximate value for k_9 of 6×10^{11} cm^3 mole^{-1} sec^{-1} at room temperature has also been reported.[152] When combined with the high-temperature values, this suggests an activation energy for reaction 9 of only about 1 kcal mole^{-1}.

The ethynyl radical (C$_2$H) once formed is capable of undergoing either oxidation reactions or addition reactions with acetylene or other hydrocarbon species to give polyacetylenes. The most comprehensive investigations of this latter class of reactions have been carried out by Wagner, Homann, and their collaborators,[153–157] who were primarily interested in the mechanism of carbon formation. Flame gas compositions were obtained by sampling from low-pressure flames by means of a molecular beam mass spectrometric technique;[158] a diagram of the apparatus used is shown in Figure 11. The profiles obtained for a typical flame are displayed in Figure 12. In this flame, which had a fuel/oxygen ratio of 0.95 and was slightly carbon forming, it was found that the species CH$_4$, C$_2$H, CH$_2$O, and HCO did not survive the main reaction zone.[156] A further feature was the presence of polyacetylenes in the reaction zone and their subsequent decay in the burnt gas region. The formation of the polyacetylenes was explained by the following mechanism

$$\begin{tikzcd} & C_4H_2 & & \\ C_2H + C_2H_2 \arrow[r] & C_4H_3 \arrow[u] \arrow[d] \arrow[r, "+C_2H_2"] & C_6H_3\ (+H_2) \arrow[r, "+C_2H_2"] & C_8H_3 \\ & C_4H_4 & & \end{tikzcd}$$

The concentration profiles of C$_4$H$_4$ and C$_4$H$_2$ in acetylene flames indicate that the C$_4$H$_3$ species reacts to give C$_4$H$_4$ at lower temperatures and C$_4$H$_2$ at high temperatures.

Spectroscopic studies of low-pressure flames[135,159–161] have also established by absorption techniques that radicals such as C$_2$ and CH are present in the reaction zone in concentrations greatly above their equilibrium values. The C$_3$ radical is also present in very rich flames.[135]

3. *Formation of Carbon in Acetylene Flames*

The mechanism leading to the formation of carbon (or soot) in flames is extremely complicated, although considerable advances have recently been made in this aspect of combustion.

Acetylene flames readily produce carbon.[5] The onset of carbon formation in the burnt gases is indicated by a yellow luminosity due to the radiating carbon particles. The critical limit for carbon formation in premixed flames at atmospheric pressure corresponds[4] to a C/O ratio of 0.8 to 0.9. This ratio, however, is dependent upon the experimental conditions and on the criterion used to determine the onset of carbon formation. Increasing the flame temperature increases the ratio, but it is largely independent of pressure if the linear gas velocity is kept constant.

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(151) C. P. Fenimore and G. W. Jones, *J. Chem. Phys.*, **41**, 1887 (1964).

(152) W. E. Wilson and A. A. Westenberg, ref 59, p 1143.

(153) K. H. Homann and H. G. Wagner, *Ber. Bunsenges. Phys. Chem.*, **69**, 20 (1965).

(154) U. Bonne and H. G. Wagner, *ibid.*, **69**, 35 (1965).

(155) K. H. Homann, M. Mochizuki, and H. G. Wagner, *Z. Phys. Chem.* (Frankfurt am Main), **37**, 299 (1963).

(156) U. Bonne, K. H. Homann, and H. G. Wagner, ref 53, p 503.

(157) K. H. Homann and H. G. Wagner, ref 59, p 371.

(158) K. H. Homann, *Oxid. Combust. Rev.*, **2**, 230 (1967).

(159) P. F. Jessen and A. G. Gaydon, *Combust. Flame*, **11**, 11 (1967).

(160) R. Bleekrode and W. C. Nieuwport, *J. Chem. Phys.*, **43**, 3680 (1965).

(161) R. Bleekrode, *Philips Res. Rep. Suppl.*, No. 7 (1967).

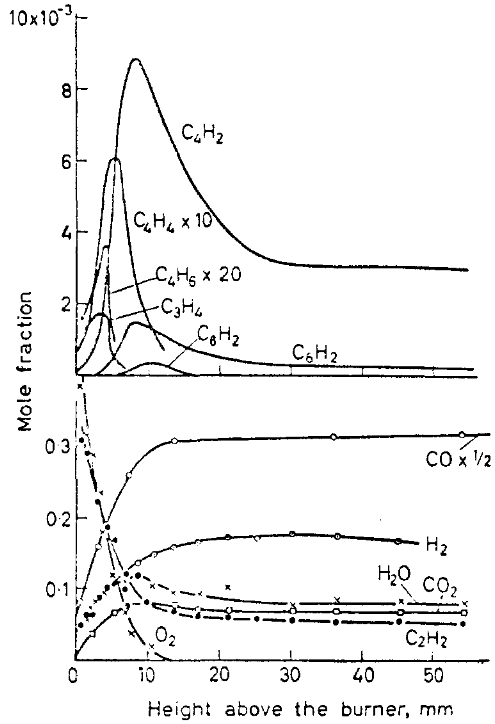


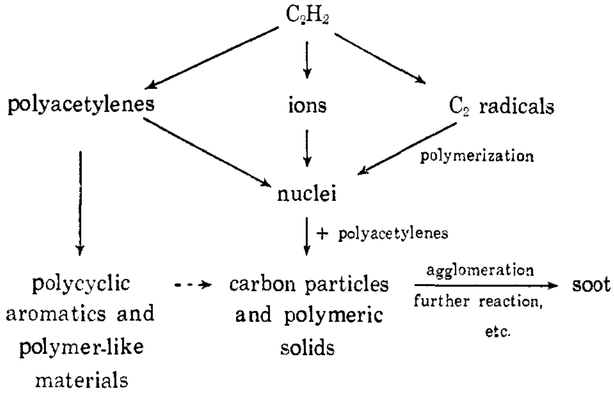
Figure 12. Concentration profiles in a flat C_2H_2–O_2 flame at the visual limit of carbon formation. C/O = 0.95:20 mm burning pressure (after Homann[4]).

Carbon is most readily produced in diffusion flames since on the fuel side of the reaction zone the local C/O ratio is high. Furthermore, the carbon particles are formed in a region of low oxygen concentration and their only consumption reaction is with water to form carbon monoxide and hydrogen. Because of the difficulties of examining the microstructure of diffusion flames, however, the only reported investigations have been limited to spectroscopic examinations[14,162] of flames on a flat-flame burner. The diffusion flame consists of three zones: a yellow carbon-forming luminous zone, an intermediate region which gives hydroxyl emission, and a blue zone on the oxygen side. At the base of the carbon-producing region emission due to C_2 and CH occurs.

In contrast to the relatively few structural studies of diffusion flames, a considerable number of investigations[155,156,163–167] have been made of the structure of carbon-forming premixed flames. In order to obtain a complete understanding of the mechanism, it is necessary to determine the nature and concentration of the intermediate species which result in carbon formation, and also the processes of nucleation and particle growth. Considerable advances[153–157] have been made in this direction by means of molecular-beam sampling and mass spectrometric analysis of low-pressure acetylene flames. A large number of unsaturated hydrocarbon intermediates are produced,[4,156] of which the polyacetylenes (up to the C_{12} species) predominate. Small amounts of benzene, methyl- and vinylacetylene, and similar species are also produced. These species reach their highest concentrations in the reaction zone and subsequently decay to very low concentrations in the burnt gas region. However, in sufficiently rich flames, although the high concentrations of polyhydrocarbons soon decay below their initial levels, they persist in the burnt gas region.[4] Although polyacetylenes form the major part of the unsaturated hydrocarbons in these flames, a variety of aromatic compounds are also present. Homann and Wagner[157] detected a range of polycyclic aromatics of molecular weight 128–550 produced just after the reaction zone, but these polycyclics were no longer present later in the flame. This behavior is paralleled[135] by the C_2 radical which has a relatively high concentration in the reaction zone and then decays to near-equilibrium levels in the burnt gas region.

The exact nature of the nucleation process and the formation of solid material is uncertain, but the basic experimental facts are now fairly well established.[4,168] Various theories of carbon formation have been formulated[168] in which different precursors to the soot particles have been postulated. A number of possible processes are indicated in Scheme I.

Scheme I



Evidence from acetylene decomposition studies and combustion work suggests that the nuclei are formed from unsatuated species[4,168] or from polymers of C_2,[135] and that growth of the carbon particles occurs by decomposition of hydrocarbons on the surface. Nucleation may involve either (or both) a condensation process[169] or positive ions of the type $C_mH_n^+$ serving as nuclei.[170] This latter mechanism is consistent with the finding that the number of nuclei formed increases with the number of positive ions in the flame.[170]

The rate of carbon formation is very dependent[4,168,171] upon a number of factors, such as fuel/oxygen ratio, pressure, etc. However, the nature of the carbon particles formed in flames is, in general, almost independent[168] of the conditions under which they are formed. In the early parts of the flame, a polymer-like material having a high H/C ratio

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(162) W. G. Parker and H. G. Wolfhard, *J. Chem. Soc.*, 2038 (1950).

(163) C. P. Fenimore, G. W. Jones, and G. E. Moore, ref 100. p 242.

(164) R. Long and E. E. Tompkins, *Nature*, **213**, 1011 (1967).

(165) E. E. Tompkins and R. Long, ref 67, p 625.

(166) C. P. Fenimore and G. W. Jones, *Combust. Flame*, **12**, 196 (1968).

(167) K. H. Homann and W. Morgeneyer, *ibid.*, **12**, 284 (1968).

(168) H. B. Palmer and C. F. Cullis, "Chemistry and Physics of Carbon," Vol. 1, Edward Arnold (Publishers) Ltd., London, 1965, Chapter 5.

(169) P. G. Wright, personal communication, 1968.

(170) J. B. Howard, ref 67, p 877.

(171) M. E. Milberg, *J. Phys. Chem.*, **63**, 578 (1959).

Table III

Band Spectra Emitted by Flames

Species	*Transition*	*Name of system*	*Energy levels,[a] kcal mole⁻¹*		*Band head wavelength, Å*
			Upper	*Lower*	
OH	$A^2\Sigma^+ \rightarrow X^2\Pi(1,0)$		101.28	0	2811
	$A^2\Sigma^+ \rightarrow X^2\Pi(2,1)$		109.29	10.19	2875
	$A^2\Sigma^+ \rightarrow X^2\Pi(0,0)$		92.75	0	3064
CH	$C^2\Sigma^+ \rightarrow X^2\Pi(0,0)$		90.88	0	3144
	$B^2\Sigma^- \rightarrow X^2\Pi(0,0)$		73.52	0	3872
	$A^2\Delta \rightarrow X^2\Pi(0,0)$		66.25	0	4312[b]
C_2	$d^1\Sigma_u{}^+ \rightarrow x^1\Sigma_g{}^+(0,0)$	Mulliken	123.58	0	2325 (headless)
	$B^3\Pi_g \rightarrow X^3\Pi_u(0,3)$	Fox–Herzberg	$a + 113.81$	$a + 113.68$	2855[b]
	$B^3\Pi_g \rightarrow X^3\Pi_u(0,4)$		$a + 113.81$	$a + 18.10$	2987[b]
	$c^1\Pi_g \rightarrow b^1\Pi_u(3,1)$	Deslandres–d'Azambuja	112.45	28.16	3398.1
	$c^1\Pi_g \rightarrow b^1\Pi_u(3,2)$		112.45	32.63	3587.6
	$c^1\Pi_g \rightarrow b^1\Pi_u(0,0)$		97.89	23.64	3852.1
	$A^3\Pi_g \rightarrow X^3\Pi_u(1,0)$	Swan	$a + 60.42$	$a + 0$	4737.1
	$A^3\Pi_g \rightarrow X^3\Pi_u(0,0)$		$a + 55.42$	$a + 0$	5165.2
	$A^3\Pi_g \rightarrow X^3\Pi_u(0,1)$		$a + 55.42$	$a + 4.64$	5635.5
CO	$A^1\Pi \rightarrow X^1\Sigma^+(3,4)$	Fourth positive system	197.52	24.09	1647.8
	$A^1\Pi \rightarrow X^1\Sigma^+(0,3)$		185.11	18.19	1712.2
	$A^1\Pi \rightarrow X^1\Sigma^+(1,4)$		189.35	24.09	1729.5
CN	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(1,0)$		79.83	0	3590.4
	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(0,0)$	Violet system	73.73	0	3883.4
	$B^2\Sigma^+ \rightarrow X^2\Sigma^+(0,1)$		73.73	5.83	4216.0[b]
NH	$A^3\Pi \rightarrow X^3\Sigma(0,0)$		85.10	0	3360
	$A^3\Pi \rightarrow X^3\Sigma(1,1)$		93.80	8.92	3371

[a] $a = 1.74$ kcal mole⁻¹. [b] Other heads also.

may be isolated.[164,165] The carbon (or soot-like material) which is first formed[168] in premixed flames has particle diameters of about 40 Å and an empirical formula CH. Particles obtained later have diameters in excess of 100 Å and the approximate composition C_2H. After extended exposure to high temperatures, the composition changes to that characteristic of carbon blacks, namely C_8H. The carbon collected from flames consists[4,168,170] of a network of cross-linked chains of approximately spherical particles. These particles are composed of individual units termed crystallites, which have a hexagonal plane structure similar to graphite. This formation of chainlike aggregates occurs at a rather late stage in the growth of soot particles. Detailed information concerning the properties and crystallographic examinations of carbon have been summarized in recent reviews.[2,4,168]

4. *Studies of Chemiluminescence and Ionization*

The oxidation of acetylene in flames is accompanied by strong radiation and by the formation of ions. It is well established[5,14] that this radiation is mainly due to chemiluminescence arising from the direct formation of species in electronically excited states. This chemiluminescent radiation, which is predominant in the main reaction zone, may be far in excess of that expected from thermal emission. The identities of the major emitting species have long been established, but only recently has any significant progress been made in elucidating their mechanism of formation. The degree of ionization[79] in many flames is also in excess of equilibrium. The nature of the ions has been investigated,[79] but the mechanism of ion formation is not yet fully understood.

The principle band systems found in the emission spectra of acetylene flames are listed in Table III. In acetylene–oxygen flames,[5,14] OH*, CH*, C_2*, and CO* are the major emitters. There is also weak emission from the excited formyl radical CHO*, and a continuum from about 3000 to 4500 Å arising from the reaction

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

In rich acetylene flames, the intensity of OH* decreases and emission due to C_2* and C_3* and a continuum from incandescent carbon particles become of importance. In acetylene–air flames, additional bands due to CN* and NH* are observed, resulting from the reactions of the nitrogen present. These bands become much more important when combustion is supported[14,172,173] by nitrous oxide or nitric oxide.

The excitation of OH to the $A^2\Sigma^+$ state must be predominantly chemiluminescent in origin. Temperature measurements by emission spectroscopy demonstrate[139,140] in many acetylene flames, particularly those burning at low pressures, the nonthermal nature of the excitation. More conclusive evidence is provided by the recent determination[150] of the concentrations of hydroxyl in the $^2\Sigma^+$ and $^2\Pi$ states for low-pressure acetylene–oxygen flames with final temperatures of 1350–1600°K. The measured OH* concentrations exceeded the equilibrium values by a factor greater than 10^6. A number of reactions have been suggested to explain the formation of excited hydroxyl in hydrogen–oxygen systems.[3] Examples include

$$O + H(+M) \longrightarrow OH^*(+M)$$

$$H + OH + OH \longrightarrow H_2O + OH^*$$

The very much greater extent of emission due to OH* in acetylene flames[5] than in hydrogen flames indicates that a

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(172) D. C. Manning, *At. Absorption Newslett.*, **5**, 127 (1966).

(173) G. F. Kirkbright, M. K. Peters, and T. S. West, *Talanta*, **14**, 789 (1967).

different process predominates. The present evidence[14,75,150] suggests that this reaction is

$$CH + O_2 \longrightarrow CO + OH^* \tag{36}$$

A rate constant k_{36} of 6 × 10^{10} cm^3 $mole^{-1}$ sec^{-1} has been reported.[150] Excited hydroxyl, OH*, decays by quenching and radiation processes.

Three excited states of CH* are present in acetylene flames: $C^2\Sigma^+$, $B^2\Sigma^-$, and $A^2\Delta$. A CH($^2\Delta$) concentration of 10^9–10^{10} cm^{-3} has been estimated[160] for a low-pressure acetylene–oxygen flame with a temperature of 2500°K. This exceeds the thermal concentration by a factor of at least 250. In flames at lower temperatures,[150] the factor is considerably greater. Thus, CH* must be formed by means of a chemiluminescent reaction. A number of reactions have been suggested for the production of CH*. These are

$$C_2H + O_2 \longrightarrow CH^* + CO_2 \tag{27}$$

$$C_2H + O \longrightarrow CH^* + CO \tag{38}$$

$$C_2 + OH \longrightarrow CH^* + CO \tag{39}$$

Reactions 27 and 38 were postulated[54] to explain CH* chemiluminescence in shock waves. However, reaction 39 has received wide support[125,150,160] from kinetic and thermochemical analyses and is probably the major contributing reaction. Values for k_{39} of about 10^{12}–10^{13} and 3.6 × 10^{11} cm^3 $mole^{-1}$ sec^{-1} for the formation[150,160] of CH($A^2\Delta$), and of 4.2 × 10^{10} cm^3 $mole^{-1}$ sec^{-1} for the formation[150] of CH($B^2\Sigma^-$), have been reported.

Emission from C_2^*, particularly the Swan bands, $A\,^3\Pi_g \rightarrow X^3\Pi_u$, occurs in all acetylene flames, and is very strong[174] in fuel-rich flames. A $C_2(^3\Pi_g)$ concentration of about 10^{10} cm^{-3} has been estimated[160] for a low-pressure acetylene–oxygen flame at 2500°K. This suggests that the concentration of C_2^* exceeds the thermal concentration by a factor of about 50. An overexcitation factor of about 70 has also been reported[175] for a similar flame. For rich acetylene–oxygen flames[150] at 1400°K, the $C_2(^3\Pi_g)$ concentration is 5 × 10^7 cm^{-3}, more than 10^3 times larger than $[C_2^*]_{thermal}$.

Although it is certain that C_2^* arises from chemiluminescent excitation, the mechanism is obscure. A number of reactions have been postulated[159,168,176,177]

$$CH + CH \longrightarrow C_2^* + H_2 \tag{53}$$

$$C_2H + H \longrightarrow C_2^* + H_2 \tag{54}$$

$$C_2H + O \longrightarrow C_2^* + OH \tag{55}$$

$$C_4H_2 + O_2 \longrightarrow C_2^* + H_2 + 2CO \tag{56}$$

$$C + CH \longrightarrow C_2^* + H \tag{57}$$

Reaction 53 is known[150,160] not to contribute significantly to the excitation of C_2^*, and isotopic tracer experiments eliminate reactions 54 and 55.[177] However, there is little information available concerning the other reactions. An interesting feature of the C_2 chemiluminescence is the intensity alternations that have been observed[160,161] in the rotational fine structure. This is not related to the effect found with homonuclear molecules having nonzero nuclear spins, since C_2 has zero nuclear spin. The observation has led to the suggestion[161] that two nonthermal excitation processes occur, one of which is a selective mechanism, resulting in excess concentrations of the even rotational levels, but as yet this is uncertain.[176]

Vacuum ultraviolet emission has been observed[71,178,179] in acetylene flames, and the emitting species has been identified as CO($A\,^1\Pi$). The essential features of this emission have been described in connection with shock-tube studies in section III.A.3. The species C_2O is almost certainly the precursor to CO* formation, and the likely mechanism is[72]

$$O + C_2H_2 \longrightarrow C_2O + H_2 \tag{33}$$

$$O + C_2O \longrightarrow CO(A^1\Pi) + CO(X^1\Sigma) \tag{34}$$

Some vibrational excitation[73] of C_2O may be necessary.

Weak Vaidya hydrocarbon flame band emission, arising from the excited formyl radical CHO*, also occurs[14] in acetylene flames. A study of the chemiluminescence in a fast-flow system at 300°K suggests[180] that CHO* is formed in the reactions

$$O + C_2H_2 \longrightarrow C_2H_2O^* \longrightarrow CH_2 + CO \tag{17}$$

$$O + CH_2(X^3\Sigma_g^-, \text{vibrationally excited}) \longrightarrow CHO^* + H \tag{18}$$

$$O + C_2H_2O^* \longrightarrow CHO^* + CHO \tag{58}$$

In nitrogen-containing flames, additional emission[172,173,181] is caused by the species CN($A\,^2\Pi$ and $B^2\Sigma^+$) and NH($A\,^3\Pi$). The probable reactions forming the species are[74,182]

$$C_2 + NO \longrightarrow CN^* + CO \tag{59}$$

$$CH + NO \longrightarrow NH^* + CO \tag{60}$$

Ions in flames may arise in two ways: from the thermal ionization of molecular and atomic species, and by chemiionization, where the energy available from a chemical reaction is sufficient to ionize one of the products. The present discussion is concerned solely with the natural chemiionization of unseeded flames, since the extent of thermal ionization is small.[5]

All hydrocarbon flames contain chemiions, but the concentrations of ions and electrons in acetylene flames are higher[79] than for ethylene or ethane flames. Early work was concerned with measurements of electron concentrations, using either electrical conductivity or microwave techniques. Although important information was deduced[79] from such work, a great impetus has been given to the understanding of the mechanism of ionization in flames by the recent use of mass spectrometric techniques.

Mass spectrometric techniques[183–188] have revealed a large variety of positive ions in flames. The nature of the ions is similar for flames burning at atmospheric pressure and at low pressure, and also for shocked gases. The major

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(176) G. Ndaalio and J. M. Deckers, *Can. J. Chem.*, **45**, 2441 (1967).

(177) R. E. Ferguson, *J. Chem. Phys.*, 23, 2085 (1955).

(178) P. H. Kydd and W. I. Foss, General Electric Research and Development Center Report No. 66-C-109, 1966.

(179) P. H. Kydd and W. I. Foss, ref 59, p 1179.

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(181) E. E. Pickett and S. R. Koirtyohann, *Spectrochim. Acta*, **23B**, 235 (1968).

(182) H. Behrens, *Z. Elektrochem.*, **54**, 535 (1950).

(183) H. F. Calcote and J. L. Reuter, *J. Chem. Phys.*, **38**, 310 (1963).

(184) H. F. Calcote, S. C. Kurzius, and W. J. Miller, ref 53, p 605.

(185) P. F. Knewstubb and T. M. Sugden, *Proc. Roy. Soc.*, **A255**, 520 (1960).

(186) K. N. Bascombe, J. A. Green, and T. M. Sugden, *Advan. Mass Spectrom.*, 2, 68 (1963).

(187) J. Deckers and A. van Tiggelen, ref 145, p 254.

(188) J. Poncelet, R. Berendsen, and A. van Tiggelen, ref 145, p 256.

positive ions present in acetylene–oxygen flames are CH_3^+, $C_3H_3^+$, CHO^+, CH_3O^+, CH_5O^+, $C_2H_3O^+$, C_3HO^+, and H_3O^+. In rich flames, $C_3H_3^+$ is the most abundant ion; in near-stoichiometric flames, H_3O^+, and in lean flames, $C_2H_3O^+$.[184] Detailed concentration profiles[183,184] of the major ions through acetylene–oxygen flames have been obtained.

The high energies needed to produce ions necessitates that the species involved in the chemiionization have large enthalpies of formation. This, together with the observation that ionization is largely confined to the main reaction zone of the flame, indicates that the atom and radical species formed in the reaction zone are precursors of positive ions. A large number of reactions have been postulated to account for ion formation. Many of these reactions are discussed[79] in a recent review of ionization in combustion processes. In hydrocarbon flames, and particularly in acetylene flames, the available evidence suggests[80] that the ions CHO^+ and, possibly, under certain circumstances,[188] $C_3H_3^+$ are formed as primary ions by reactions of neutral species, and that the other (secondary) ions are due to ion–molecule reactions.

Two reactions have been proposed[79,189] to explain the formation of the CHO^+ ion.

$$CH + O \longrightarrow CHO^+ + e \qquad (44)$$

$$CH^* + O \longrightarrow CHO^+ + e \qquad (44')$$

The earlier uncertainty in the thermochemistry of these reactions has now been resolved. Recent work has established[190,191] the heat of formation of CHO^+ as 204 kcal $mole^{-1}$, showing that both reactions are thermodynamically feasible. However, reaction 44′ has been shown[150,192] to be unimportant in acetylene–oxygen flames, although it may be of greater significance in other systems.[74] Thus reaction 44 is the likely source of CHO^+. The rate of this reaction is uncertain, although several estimates[184,193,194] have been made by equating the rate of ion formation with ion removal at the maximum ion concentration. At 1 atm, where ion removal is by ion–electron recombination, k_{44} was estimated[193] to be about 8×10^{-13} cm^3 sec^{-1}. In low-pressure (2 Torr) flames with ion removal by ambipolar diffusion,[184] a value of about 3×10^{-13} cm^3 sec^{-1} was obtained. Calculations based on absolute reaction theory suggest[194] a value of 10^{-11} cm^3 sec^{-1}.

The CHO^+ ion once formed undergoes a series of ion–molecule reactions,[79] the more important of which are probably

$$CHO^+ + H_2O \rightleftharpoons CO + H_3O^+ \qquad (46)$$

$$CHO^+ + CH_2O \longrightarrow CO + CH_3O^+ \qquad (61)$$

$$CHO^+ + CH_3OH \longrightarrow CO + CH_5O^+ \qquad (62)$$

$$CHO^+ + C_2H_2O \longrightarrow CO + C_2H_3O^+ \qquad (48)$$

$$RCH^+ + C_2H_2 \longrightarrow R + C_3H_3^+ \qquad (45)$$

e.g.

$$C_2H_3O^+ + C_2H_2 \longrightarrow CH_2O + C_3H_3^+$$

In low-pressure flames, reaction 46 reaches equilibrium,[184] and there is evidence[78] that equilibrium also exists for reaction 45 with $C_2H_3O^+$. Rate constants for reaction 46 have been obtained by a similar procedure as those for reaction 44. At 1 atm, the estimated[186] k_{46} was about 4×10^{-8} cm^3 sec^{-1}, while for low-pressure flames,[79] a value of about 9×10^{-9} cm^3 sec^{-1} was obtained.

Although reaction 45 is undoubtedly one route for $C_3H_3^+$ formation, other evidence[184] suggests that in rich acetylene flames, where it is the most abundant ion, $C_3H_3^+$ is formed as a primary ion (see also section III.A.3). The reaction

$$CH^* + C_2H_2 \longrightarrow C_3H_3^+ + e \qquad (41)$$

was originally proposed,[184] although recent evidence[192] has shown that CH^* is not a precursor of chemiionization in acetylene–oxygen flames. However, the formation of $C_3H_3^+$ may occur[34,52] by reactions such as

$$CH + C_2H_2 \longrightarrow C_3H_3^+ + e \qquad (42)$$

$$CH_2 + C_2H \longrightarrow C_3H_3^+ + e \qquad (43)$$

These reactions are probably only of importance in rich acetylene flames. The $C_3H_3^+$ ion can also participate in ion molecule reactions such as

$$C_3H_3^+ + O_2 \longrightarrow C_2H_3O^+ + CO \qquad (63)$$

$$C_3H_3^+ + O \longrightarrow CHO^+ + C_2H_2 \qquad (64)$$

The overall electrical neutrality in a flame means that negatively charged species must be present at the same concentration as positive ions. Langmuir probe studies[188] and measurements of the mobilities of charged species[195] show that the electron is the most important negatively charged species. However, a large variety of negative ions are also present in acetylene flames,[184,196,197] from the relatively simple OH^-, C_2^-, and C_2H^- up to complex ions CO_2H^-, $C_2OH_3^-$, and $C_5H_3^-$. The total concentration of these ions may approach[196] the positive ion concentration or may be lower[197] by a factor of 10^3, depending on the experimental conditions. In stoichiometric acetylene–oxygen–nitrogen flames at 1 atm,[196] C_2H^- is the most abundant negative ion, followed by $CH_2O_2^-$ and $C_2H_3O^-$; in atmospheric hydrogen–oxygen flames with 2.8% added acetylene,[197] the most abundant negative ion is CO_2H^-, followed by C_2H^- and O_2^-, while in stoichiometric acetylene–oxygen flames at 1 Torr,[184] O^-, OH^-, and C_2^- are most common. A more complete discussion of the relative abundance of ions is given[79] by Miller.

Negative ion profiles have been established[184] for low-pressure acetylene–oxygen flames. In these flames, O^-, OH^-, and C_2^- are the first negative ions formed, although they appear only after the formation of $C_3H_3^+$. C_2^- and, at higher pressures, C_2H^- are probably the primary negative ions,[184,196] although their mechanism of formation is not yet clear. A dissociative attachment reaction of the type

$$A + e \longrightarrow B^- + C$$

is now favored,[79] and various possibilities have been proposed,[79,184] such as

$$C_2H_2O^* + e \longrightarrow C_2^- + H_2O \qquad (65)$$

$$C_2H + e \longrightarrow C_2^- + H \qquad (66)$$

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(189) H. F. Calcote, "Ionization in High-Temperature Gases," Academic Press, New York, N. Y., 1963, p 107.

(190) F. H. Dorman, *J. Chem. Phys.*, **50**, 1042 (1969).

(191) A. G. Harrison, *ibid.*, **50**, 1043 (1969).

(192) E. M. Bulewicz, *Combust. Flame*, **11**, 297 (1967).

(193) J. A. Green and T. M. Sugden, "Proceedings of the Ninth Symposium (International) on Combustion, Cornell University, Ithaca, N. Y., 1962," Academic Press, New York, N. Y., 1963, p 607.

(194) S. C. Kurzius, Thesis, Princeton University, 1964; *Chem. Abstr.*, **66**, 32288*d* (1967).

(195) S. Basu and J. A. Fay, ref 145, p 277.

(196) A. Feugier and A. van Tiggelen, ref 53, p 621.

(197) J. A. Green, "Observations on Negative Ions in Hydrocarbon Flames," 26th AGARD Propulsion and Energetics Panel, Pisa, Italy, 1965.

$$C_2H_2O + e \longrightarrow C_2H^- + OH \qquad (67)$$

Other negative ions may then be formed by ion–molecule reactions such as

$$C_2^- + OH \longrightarrow C_2H + O^- \qquad (68)$$

$$O^- + H_2 \longrightarrow OH^- + H \qquad (69)$$

The high concentrations of ions produced in the reaction zone decay away in the burnt gas region by two processes: recombination and ambipolar diffusion. At high pressures (>*ca.* 30 Torr), recombination is the dominant process,[79] while at lower pressures (<*ca.* 10 Torr) diffusion is more important. The most important ion recombination process is probably

$$H_3O^+ + e \longrightarrow H + (H + OH) \qquad (70)$$

A recombination coefficient α of $2.4 \pm 0.4 \times 10^{-7}$ cm^3 sec^{-1} has been reported.[184]

Ambipolar diffusion arises because of the rapid diffusion of electrons out of the flame zone. The resulting space charge effect causes the positive ions to diffuse at rates greater than those for neutral species. Few ambipolar diffusion coefficients have been determined, although a value for H_3O^+ of 1100 cm^2 sec^{-1} at 2000°K and 40 Torr has been obtained.[184] This reduces to 60 cm^2 sec^{-1} at 298°K and 1 Torr.

5. *Recombination*

At flame temperatures below 2500°K the buildup of the radicals OH, H, and O is so rapid that they may exceed their equilibrium values by large factors. This phenomenon has been termed "overshoot." As a consequence of the slow rates of the third-body recombination reactions leading to equilibrium conditions, these high radical concentrations persist for some distance into the burnt gas regions of the flames.

The chemical steps involved in the near-stoichiometric conditions are well established. They involve[12,13,198,199]

$$H + OH + M \longrightarrow H_2O + M \qquad (71)$$

and the slower reactions

$$H + H + M \longrightarrow H_2 + M \qquad (72)$$

and possibly

$$CO + O + M \longrightarrow CO_2 + M \qquad (73)$$

In lean flames, where molecular oxygen persists in the burnt gas, the following rapid sequence involving hydroperoxyl occurs.

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (74)$$

$$HO_2 + OH(H) \longrightarrow O_2 + H_2O(H_2) \qquad (75)$$

In rich flames, recombination may be catalyzed[200] by acetylene in a similar sequence.

$$H + C_2H_2 \rightleftharpoons C_2H_3 \xrightarrow{H(OH)} C_2H_2 + H_2(H_2O) \qquad (76)$$

D. ACETYLENE SELF-DECOMPOSITION FLAME

Acetylene has the property of decomposing to form solid carbon by means of a reaction which is sufficiently exothermic to support a flame.

$$C_2H_2 \longrightarrow 2C_{(solid)} + H_2 \qquad \Delta H_{298°K} = -54.2 \text{ kcal mole}^{-1}$$

Because of this property and the attendant risks in the commercial handling of acetylene, a number of studies[201–212] have been made of the self-decomposition flame of acetylene.

1. *Conditions Leading to the Formation of Self-Decomposition Flames*

The acetylene self-decomposition flame exhibits the effect of only propagating when the pressure exceeds a certain critical value. At lower pressures, when ignited by a hot wire or similar energy source, it will only exhibit a transient flame phenomenon (or flashing), but a continuous flame is not obtained. Since one of the major combustion products is solid carbon, the acetylene flame is highly radiating, and it has been suggested[213] that this radiation loss accounts for the critical pressure limit observed for this flame.

The first investigation of the effects of pressure, temperature, and various additives on the ignition and propagation of flames in tubes was made[201] as long ago as 1925. Numerous investigations have been made since then, and the data available up to 1964 have been reviewed[202] by Ivanov and Kogarko.

It is usually accepted[202] that flame propagation is not possible at pressures below about 1.4 atm if the initial mixture is at room temperature. However, if sources of energy, such as a spark discharge, are used, which are greatly in excess of the minimum ignition energy requirements, then flame propagation may occur[202] down to 0.65 atm provided a large diameter tube is used. Similarly a hot-wire technique may be employed. Data have also been collected[202] for the minimum diameters (quenching diameters) of tubes that just permit flame propagation. Typical values are 100 mm at 1 atm, and 10 mm at 5 atm for flames in horizontal tubes or burning downwards in vertical tubes. Quenching diameters for flames burning upwards are about one-third of these values.

2. *Properties and Mechanism of Propagation*

Studies of acetylene self-decomposition flames have generally been made[202–207,209–212] using propagating flames in tubes. Stationary flames supported on burners suffer from the disadvantage that the carbon produced from the flame blocks the burner mouth, but one successful investigation[208] using a stationary flame has been reported.

The available data[205,208–211] on burning velocities are

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(198) P. J. Th. Zeegers and C. Th. J. Alkemade, *Combust. Flame*, **9**, 247 (1965).

(199) P. J. Th. Zeegers and C. Th. J. Alkemade, ref 53, p 33.

(200) A. Q. Eschenroeder and J. A. Lordi, ref 193, p 241.

(201) D. Alexejew, *Chem. Zentralbl., Ser. VI*, 7, 125 (1925).

(202) B. A. Ivanov and S. M. Kogarko, *Int. Chem. Eng.*, 4, 670 (1964).

(203) G. W. Jones, R. E. Kennedy, and I. Spolan, *U. S. Bur. Mines, Rep. Invest.*, 3826 (1945).

(204) G. W. Jones, R. E. Kennedy, and I. Spolan, *ibid.*, 4196 (1948).

(205) W. E. Prout and R. C. Anderson, *Fuel*, **33**, 125 (1954).

(206) E. A. Westbrook, K. Hellwig, and R. C. Anderson, ref 94, p 631.

(207) W. E. Hanford and D. L. Fuller, *Ind. Eng. Chem.*, 40, 1171 (1948).

(208) J. D. Chase and F. J. Weinberg, *Proc. Roy. Soc.*, **A275**, 411 (1963).

(209) G. A. M. Cummings, A. R. Hall, and R. A. M. Straker, "Proceedings of the Eighth Symposium (International) on Combustion, California Institute of Technology, Pasadena, Calif., 1960, Williams and Wilkins, Baltimore, Md., 1962, p 503.

(210) B. A. Ivanov and S. M. Kogarko, *Zh. Prikl. Khim. Tekh. Fiz.*, 164 (1964).

(211) B. A. Ivanov and S. M. Kogarko, *Dokl. Akad. Nauk SSSR*, **150**, 1300 (1963).

(212) J. W. Reppe, "Chemie und Technologie der Acetylen-Druck-Reaktionen," Verlag Chemie, Weinheim, 1952.

(213) H. G. Wolfhard, reported in ref 209.

somewhat inconsistent, but it is clear that, despite the high heat of reaction, the velocities are much lower than those usually found for acetylene–oxidant flames and range from about 8 cm sec^{-1} at 2.5 atm to about 15 cm sec^{-1} at 5 atm. Measurements of burning velocities in tubes are complicated by the fact that, unless the tube diameter is sufficiently large, incomplete combustion occurs.[209,210] Furthermore, corrections have to be applied for flame front curvature and gas expansion effects. By the use of large diameter tubes to diminish the extent of incomplete combustion, it has been possible to reduce these errors. Experiments of this type showed[202,210,211] that the burning velocity varied linearly with pressure, ranging typically from about 8 cm sec^{-1} at 2.5 atm to 15 cm sec^{-1} at 5.0 atm. Application of thermal flame theories[112] indicates a reaction order of four. In contrast, Chase and Weinberg,[208] using a flame stabilized on a burner port, obtained data indicating pressure independence and thus a second-order reaction. Obviously the position is somewhat uncertain, but it seems likely that the high radiant heat losses greatly complicate interpretation of the data, particularly of flames propagating in tubes. There is little direct evidence concerning the mechanism of the self-decomposition flame, since examination of the flame structure is experimentally difficult because of carbon formation. The flame spectrum also is not informative[206] since it consists entirely of a continuum. However, the evidence available at present from acetylene pyrolysis studies suggests that the following steps are probably important[68,206]

$$H + C_2H_2 \longrightarrow C_2H + H_2 \qquad E \sim 20 \text{ kcal mole}^{-1}$$

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \qquad E \sim 20 \text{ kcal mole}^{-1}$$

$$\longrightarrow C_4H_3$$

followed by a succession of hydrogen-atom stripping reactions leading to the formation of solid carbon. The reaction scheme is almost certainly further complicated since the acetylene may undergo heterogeneous decomposition on the solid carbon particles.[168]

V. Detonation

Propagating flames of pure acetylene and particularly acetylene–oxidant mixtures readily undergo transition to detonation. The deflagration wave, travelling at a subsonic speed, will under certain circumstances accelerate very rapidly and form a detonation wave moving at a supersonic velocity. The onset of the violent detonation and the conditions which cause it are of obvious relevance to the safe use of acetylene, particularly in large industrial installations. Considerable interest has also centered on the structure and properties of detonation waves.

In early theories of detonation, the detonation wave was considered[214] as a plane one-dimensional shock discontinuity followed by a region of homogeneous chemical reaction, terminating in the Chapman–Jouget (C–J) plane, when reaction was complete. This theory is extremely successful and hence useful in predicting the velocities and pressures of detonation waves. However, recent analyses of detonation waves have demonstrated[215] the dynamic instability of one-dimensional C–J waves. The early theory may thus be regarded as a first-approximation theory.

A. INITIATION OF DETONATION

1. Transition from Deflagration to Detonation

The advent of modern experimental techniques has allowed detailed insights into the processes involved in the transition from propagating flames (deflagration) to detonation. The most quantitive studies of the transition process have employed[216] hydrogen–oxygen detonations. However, data in substantial qualitative agreement with these studies have been obtained[217–219] using acetylene–oxygen mixtures.

Although the precise details of the transition to detonation depend on the experimental conditions, the major aspects of the process[215] are now well established. The compression wave ahead of the flame steepens into a shock wave, causing turbulence and acceleration of the flame. This acceleration in turn reinforces the original shock, and eventually leads to the onset of detonation.

The induction distance between the point of ignition and the establishment of the detonation depends on several factors. It is reduced[218] by increased initial pressure, and also by roughened walls in the tube. Mixtures with high heats of combustion also have short induction distances.[220] Moreover, the induction distance is a function of mixture composition. At pressures of 40 to 100 mm, the minimum distance required (10 to 50 cm) was found[219] for an equimolar mixture, and increased sharply near the limits of detonability. At atmospheric pressure, the minimum distance (2 cm) was observed[220] in a stoichiometric mixture. The data at subatmospheric pressure[219] refer to transmission of detonations through small orifices. A detonation was either quenched, transmitted directly, or transmitted as a flame which underwent the characteristic transition process to re-form a detonation wave.

The transition to detonation has also been studied[221] in cylindrical vessels for equimolar acetylene–oxygen mixtures. True transition to detonation did not occur, although pseudotransitions were observed when the flame interacted with reflected shock waves or when turbulence ahead of the flame was artificially induced. Similar results have been obtained for spherical detonations.[222]

The decomposition flame of acetylene also readily undergoes transition to detonation if a critical initial pressure is exceeded. The value of the critical pressure is dependent on tube diameter and ignition energy. For a tube of 7.6-cm diameter,[223] the value is about 600 Torr, while for a 2.5-cm diameter tube,[224] the critical pressure is about 3.5 atm. The induction distance is a function of both tube diameter and initial pressure. At atmospheric pressure in a wide tube

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(214) H. G. Wagner, "Agardograph 41, Fundamental Data Obtained from Shock Experiments," A. A. Ferri, Ed., Pergamon Press, New York, N. Y., 1961, p 320.

(215) R. A. Strehlow, *Combust. Flame*, 12, 81 (1968).

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(218) R. I. Soloukhin, *AIAA J.*, **1**, 2006 (1963).

(219) B. H. K. Lee, J. H. Lee, and R. Knystautus, *ibid.*, **4**, 365 (1966).

(220) L. E. Bollinger, M. C. Fong, and R. Edse, *Am. Rocket Soc. J.*, **31**, 588 (1961).

(221) J. H. Lee, B. H. K. Lee, and I. Shanfield, ref 53, p 805.

(222) W. G. Struck and H. W. Reichenbach, ref 59, p 677.

(223) R. E. Duff, H. T. Knight, and H. R. Wright, *J. Chem. Phys.*, **22**, 1618 (1954).

(224) S. A. Miller and E. E. Penny, Symposium on Chemical Hazards, Institute of Chemical Engineering, Manchester, 1960, p 87.

(36 cm diameter), an induction distance of 36–44 m has been reported,[225] while at 20 atm the distance[224] is only about 1 m. The detonation wave initially formed after transition process was found to be overdriven,[226] *i.e.*, travelling with an abnormally high velocity.

2. *Direct Initiation of Detonation*

If sufficiently large ignition energies are employed, the direct initiation of detonation is possible. Direct initiation by spark and exploding wire ignition of cylindrical detonations has been investigated.[221,227] in acetylene–oxygen mixtures. For each mixture composition, there existed a critical energy above which direct initiation occurred. The resulting detonations were initially overdriven, but rapidly decayed to constant velocities, corresponding to the C–J values. The minimum critical energies were observed[227] in mixtures containing 30–50% C_2H_2; the energies increased sharply as the composition or pressure limits of detonability were approached. The critical ignition energy is probably related[227] to the thickness of the detonation wave. Essentially the same results have been obtained[222,228] for spherical detonation waves. It also appears[228] that spark power, or rate of energy release, rather than spark energy, is the more meaningful parameter for describing initiation phenomena.

3. *Limits of Detonability*

The very wide composition range of flammability for acetylene–oxidant systems (discussed in section III.A.2) has its counterpart in the wide limits of detonability observed in the same systems. For acetylene–oxygen mixtures at 1 atm, limits of 3–93% C_2H_2 have been reported[229] for a tube of 1.4-cm diameter, while an upper limit of 90% C_2H_2 has been reported[230] for a 10-cm diameter tube. The limits for acetylene–air in a 1.4-cm tube are 4 and 51% C_2H_2.[229] For spherical detonations in glass flasks or rubber balloons, the limits have been found[231,232] to be dependent on the means of initiation of detonation. Initiation by an electric detonator resulted[232] in detonation for acetylene–oxygen mixtures containing 8–76% C_2H_2, and for acetylene–air mixtures containing 8–18% C_2H_2. The limits were widened when more powerful initiation was employed. The composition limits of detonability are obviously dependent on experimental parameters such as vessel geometry, initial pressure, and means of initiation, and under suitable conditions detonation waves are sustained in pure acetylene.

B. MACROSCOPIC DETONATION PARAMETERS

1. *Detonation Velocity*

Of the macroscopic parameters, the detonation velocity has been the most extensively studied. For acetylene–oxygen mixtures, velocities have most frequently been determined[229,230,233–237] for "planar" detonation waves travelling along tubes, the wave progress being recorded by piezoelectric gauges,[230,235] ionization probes,[235] and microwave reflection.[236] The composition dependence of detonation velocity for acetylene–oxygen mixtures initially at atmospheric pressure is displayed in Figure 13. Detonation velocities have been shown[230,235,237] to be dependent on tube diameter, satisfying an expression of the form $D_d = D_\infty - (c/d)$ where D_d and D_∞ are the velocities in tubes of diameters d and ∞, respectively, and c is a constant, dependent on the mixture composition. This velocity deficit in finite tubes is thought[238] to be caused by the formation of a turbulent boundary layer at the tube wall. Early determinations[233,234] of detonation velocity are in error due to this effect, but corrections were applied in later results.

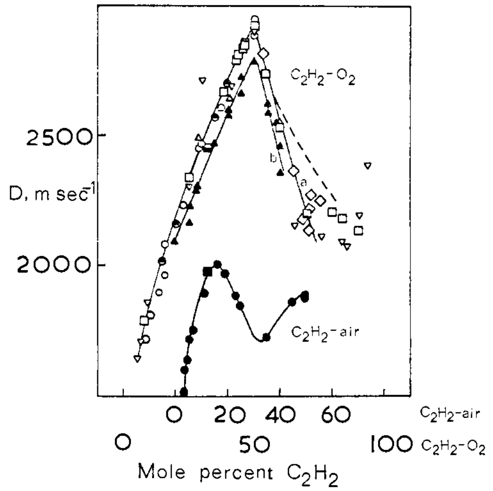

Figure 13. Variation of detonation velocity (D, m sec^{-1}) with composition for acetylene–oxygen and acetylene–air mixtures. Calculated values: (a) initial pressure of 1 atm; —, no solid carbon formed; - - -, solid carbon formed; (b) initial pressure of 100 Torr. Experimental values: ∇, ref 229; □, ref 230; ◇, ref 235; ◓, ref 220; ○, ref 231; △, ref 242; ⬒, ref 239; ▲, ref 221; ●, ref 229; ■, ref 242.

Velocities have also been determined for spherical detonation waves[231,239] of acetylene–oxygen mixtures initially at atmospheric pressure, and for cylindrical waves[221] of mixtures with an initial pressure of 100 Torr. These results are displayed in Figure 13. Also included in Figure 13 are calculated detonation velocities[221,230] at 100 Torr and 1 atm. The calculations were based on the Chapman–Jouget theory of detonation.

The maximum detonation velocity, $D = 2920$ m sec^{-1}, occurs at an equimolar composition. This contrasts with burning velocity, where the maximum is at a near-stoichiometric composition. The discontinuous change in velocity observed[235] in mixtures containing 71% C_2H_2 was thought to be due to the sudden precipitation of solid carbon. The resulting discrepancy between experimental and calculated

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(230) G. B. Kistiakowsky, H. T. Knight, and M. E. Malin, *J. Chem. Phys.*, **20**, 884 (1952).

(231) N. Manson and F. Ferrié, ref 97, p 486.

(232) H. Freiwald and H. W. Koch, ref 193, p 275.

(233) H. le Chatalier, *C. R. Acad. Sci., Paris*, **130**, 1755 (1900).

(234) H. B. Dixon, *Phil. Trans.*, **A184**, 97 (1893).

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(238) J. A. Fay, *Phys. Fluids*, **2**, 283 (1959).

(239) H. Freiwald, *Z. Elektrochem.*, **59**, 910 (1955).

velocities in mixtures with more than 71% C_2H_2 was then explained[235] by the failure to include in the calculations the surface free energy of the extremely fine solid carbon particles (diameters ≤ 100 Å) which are formed in the detonation wave. The sharp increase in velocity reported[229] for mixtures with *ca.* 90% C_2H_2 is probably spurious, and may be a result of the waves in these mixtures being overdriven.

The influence of initial pressure on acetylene–oxygen detonation velocities has been investigated for a range of compositions[220] at 1 and 5 atm, and for an equimolar mixture[240] over the pressure range 2–50 Torr. At an equimolar composition, the results obtained in these two pressure ranges, together with other data[221,235] at 100 Torr and 1 atm, are well represented by the empirical expression $D\,(\text{m sec}^{-1}) = 2582 + 112 \log \{\text{initial pressure (Torr)}\}$.

Detonation velocities of acetylene–oxygen mixtures are also affected[241] by electromagnetic fields. Appreciable velocity deficits (up to 10%) were observed[241] when the $j \times B$ force of the field was directed against the wave propagation.

There are few reports of detonation velocity measurements for the acetylene–air system. The values that are available for "planar" detonations in tubes[229] and for spherical detonations[242] are displayed in Figure 13. The maximum velocity, $D = 2000$ m sec^{-1}, occurs in an equimolar acetylene–oxygen mixture. The sharp rise in velocity in very rich acetylene mixtures[229] is identical with that observed in acetylene–oxygen detonations, and again is probably spurious.

The effect of nitrogen diluent on the velocity of other acetylene–oxygen detonations has also been investigated.[239]

The decomposition of pure acetylene will support detonation, and velocities for such detonations have been reported.[223,243–246] The values obtained are listed in Table IV.

Table IV

Detonation velocity, m sec^{-1}	*Tube diameter, mm*	*Initial pressure, atm*	*Ref*
1870	76	0.8	223
1923	D corrected to infinite diameter	8	243
1935	4	10 to 30	244
1770	8		
1878	40	3 to 6	245
2026	25	6 to 10	246

These reported velocities show considerable scatter. In section III.D.2, similar inconsistencies were noted in the burning velocity data. The anomalous diameter effect observed[244] in very narrow tubes probably arises because measurements were made before the detonation was fully developed. However, the experimental values do indicate that the detonation velocity is independent of initial pressure over a wide pressure range.

Detonations in pure acetylene reveal two peculiarities. The first is the discrepancy between the observed detonation velocities and the calculated value[243] of 2053 m sec^{-1} for an initial pressure of 8 atm. This lack of agreement between theory and experiment, which was also found[235] for detonations in rich acetylene–oxygen mixtures, is probably due to the formation of extremely fine carbon particles. Secondly, acetylene detonation waves have anomalous spin properties.[223] (The phenomenon of spinning detonation is discussed further in section IV.C.) At pressures of 0.8 atm in tubes with diameters of 76 to 40 mm, the detonation waves were spinning,[223] but with spin-pitch to tube-diameter ratios of 3.4 to 4.0. This contrasts with the value of 3.1 found[214] for most gaseous detonations. In narrower tubes, anomalously slow waves were observed,[223] with velocities as low as 1500 m sec^{-1}. These slow waves were nonspinning and had abnormally large thicknesses.

2. *Calculation of Detonation Temperatures and Equilibrium Gas Compositions*

Using the Chapman–Jouget theory and assuming that chemical equilibrium is attained in the detonation wave, values of the temperature and gas composition associated with a detonation wave may be calculated. Such calculations have been performed[230,235,247–249] for a range of acetylene–oxygen mixtures initially at atmospheric pressure, and the results obtained for the detonation temperatures are shown in Figure 14. The maximum theoretical temperature is about 4500°K, occurring at a composition containing 40–45% C_2H_2. The discrepancy between the recent results[248,249] and the earlier calculations[247] results from the use of unreliable thermochemical data in the earlier work.

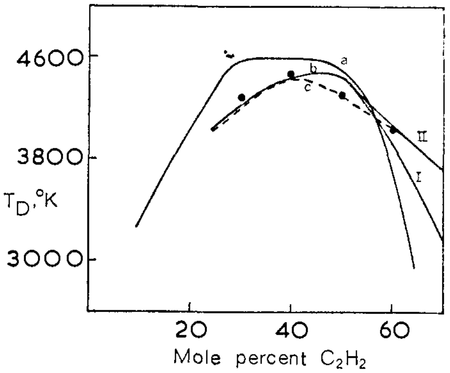

Figure 14. Dependence of detonation temperature (T_D, °K) on composition for acetylene–oxygen mixtures with an initial pressure of 1 atm. Calculated values: (a) ref 247; (b) ref 230 [(I) assuming no solid carbon; (II) assuming formation of solid carbon]; (c) - - -, Soloukhin.[249] Experimental values: ●, ref 249.

Calculations of detonation temperature and equilibrium gas composition have also been performed[250] for stoichio-

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(240) A. L. Bennett and H. W. Wedaa, *J. Chem. Phys.*, 23, 1359 (1955).

(241) J. R. Kelly and T. Y. Toong, ref 59, p 657.

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(250) W. Chinitz, C. L. Eisen, and R. A. Gross, *Am. Rocket Soc. J.*, 29, 573 (1959).

metric acetylene–air mixtures at an initial pressure of 0.001 atm. A temperature of about 2400°K was obtained.

The only report[243] of temperature and composition calculations for acetylene decomposition refer to a mixture of 98.5% acetylene and 1.5% nitrogen initially at a pressure of 8 atm. The computed equilibrium temperature was 3010°K, and the percentage compositions were C_2H_2, 2.1; C, 63.0; H_2, 29.0; H, 5.1; N_2, 0.5.

3. *Experimental Determination of Detonation Temperatures*

For stoichiometric acetylene–oxygen mixtures, measurements of detonation temperatures have been made by a two-line technique,[249] comparing the relative emission intensities of two atomic hydrogen lines (H_β and H_γ) in the Balmer series. Temperatures of more than 5000°K were recorded,[249] but these fell to equilibrium values after about 4 μsec. These values are included in Figure 14. Temperatures have also been determined for detonations of $C_2H_2 + H_2 + 2O_2$ mixtures at initial pressures of 120–180 Torr. Rotational temperatures obtained[251] from the $OH(^2\Sigma^+–^2\Pi)$ absorption spectrum were found to be in good agreement with calculated values.

C. STRUCTURE OF DETONATION WAVES

It has been noted earlier that self-substaining detonations are not steady, one-dimensional waves, but rather have a nonsteady, three-dimensional structure with an amplitude comparable to the wave thickness.[252] The flow behind detonation waves in tubes is turbulent,[253] and instabilities are formed which travel across the detonation front as transverse waves. Instabilities have also been observed[254] in freely expanding spherical detonation waves, although other work suggests[222] the absence of turbulence behind such waves.

The nature of the transverse waves has been extensively explored for acetylene and other systems, particularly by using the elegant smoked-foil technique.[255] The character and spacing of the transverse waves are dependent[255] on tube geometry and the heat capacity ratio of the gas. The waves often exhibit regular spacing, the characteristic size of which is intimately connected[255–257] with the chemistry of the system.

A further manifestation of detonation wave instability is the phenomenon of spinning detonation. The characteristic size of the transverse wave spacing increases as the limits of detonability are approached, until a single spin mode is observed. A discussion of spinning detonation is not included here as the subject has recently been comprehensively reviewed.[258] Spinning detonations have been observed[259,260] in poorly detonating acetylene–oxygen mixtures, and the results have been analyzed[261] in terms of a three-dimensional theoretical model.

Relatively little work has been done on the elucidation of the elementary chemical kinetic processes occurring in the self-sustaining detonation waves of acetylene systems. Attempts have been made,[251,262] particularly by spectroscopic methods, to determine temperatures and concentrations for OH and CH in the detonation. The observed concentrations were in apparent agreement[251] with values calculated from simple detonation theory. But, in view of the present knowledge of the nonsteady structure of self-sustaining detonation waves and the presence of transverse waves, it is unlikely[215] that useful kinetic information can be obtained from such studies.

However, two new techniques[263,264] show promise for the elucidation of chemical structure. A laminar, one-dimensional detonation wave may be produced by passing an ordinary detonation through a convergent–divergent nozzle. Induction zone kinetics of acetylene–oxygen detonations have been investigated[263] by this technique. The temperature variation of the induction time t_i between the shock wave and the onset of chemical reaction was given by the expression log ($[O_2]t_i$) (mole sec $l.^{-1}$) = $-10.0 + (14{,}650/4.58T)$ over the temperature range 1000–1600°K and pressure range 8–40 Torr. This is in fair agreement with shock tube results,[47] suggesting that reaction 22 is the rate-determining step in the induction zone

$$H + O_2 \longrightarrow OH + O \tag{22}$$

of acetylene–oxygen detonations.

The second technique of stabilizing one-dimensional detonation waves downstream of a nozzle,[264] allowing analysis by a variety of methods including probe sampling, has yet to be exploited in the study of acetylene combustion.

The degree of ionization in acetylene–oxygen detonation waves has been investigated[195,248] by direct current probe and microwave reflection techniques. Over a composition range of 20–70% C_2H_2 and pressure range 300–760 Torr, the degree of ionization was found to be consistent with theoretical predictions. Increased ionization in very rich mixtures was thought to be due to the participation of carbon particles in the ionization process; ionized aggregates of 1000–2000 Å radius are probably formed.[248] At lower pressures, enhanced frontal ionization was observed.[248] This was considered to be chemiionization, although it is difficult[256] to resolve nonequilibrium chemical effects from gas-dynamic influences.

VI. Future Developments

In spite of the vast amount of work that has been done on the combustion of acetylene and the considerable progress made in unravelling the complex oxidation kinetics, large areas of uncertainty still remain.

In the low-temperature regime, progress is rendered difficult by the enormous variety of complicated intermediate species that are formed. Studies involving direct sampling from the reacting mixture into a mass spectrometer appear to offer the best hope of elucidating reaction mechanisms. To date, very little progress has been made in determining the kinetic parameters of the elementary reactions.

The situation in the high-temperature oxidation is more promising, since the intermediate species are fewer in number

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Table V

Reaction	*A, cm³ mole⁻¹ sec⁻¹*	*E, cal mole⁻¹*	*Temp, °K*	*Ref*
Initiation				
(a) $C_2H_2 + M \rightarrow C_2H + H + M$	6×10^{14}	80,000	1920–2390	66
(b) $C_2H_2 + O_2 \rightarrow 2CO + 2H$	10^{14}	38,000	1920–2390	66
(c) $C_2H_2 + C_2H_2 \rightarrow C_4H_3 + H$	9.6×10^{13}	44,300	1000–2450	68
Acetylene oxidation				
(d) $O + C_2H_2 \rightarrow CO + CH_2$	$1.43 \pm 0.50 \times 10^{13}$	3150 ± 200	273–729	34
	2.6×10^{13}	3,200	297–398	38
	5×10^{12}	2,500	1000–1700	67
	$1\text{-}2 \times 10^{13}$	. . .	1000–1600	146
(e) $O + C_2H_2 \rightarrow OH + C_2H$	10^{14}	14,000	1920–2390	66
	$3.2 \times 10^{15}T^{-0.6}$	17,000	1000–1700	67
	2×10^{14}	14,000	. . .	34
(f) $OH + C_2H_2 \rightarrow H_2O + C_2H$	1.4×10^{13}	~7,000	1700–2000	151
	6.0×10^{12}	7,000	1000–1700	67
	6×10^{11}	. . .	300	152[a]
(g) $H + C_2H_2 \rightarrow H_2 + C_2H$	2.0×10^{14}	19,000	1000–1700	67
(h) $C_2H + O_2 \rightarrow CO + (H + CO)$	10^{13}	7,000	1000–1700	67
(i) $C_2H + O \rightarrow CH + CO$	5.0×10^{13}	0	1000–1700	67
(j) $CH_2 + O \rightarrow HCO + H$	3.0×10^{13}	0	1000–1700	67
(k) $CH_2 + OH \rightarrow HCO + H_2$	7.0×10^{13}	0	1000–1700	67

[a] This value, when combined with the high-temperature data, suggests an activation energy of *ca.* 1 kcal mole⁻¹ for reaction f.

Table VI

Species of Interest in the Oxidation and Combustion of Acetylene

Species	*Heat of formation, kcal mole⁻¹*	*Ref*	*Species*	*Heat of formation, kcal mole⁻¹*	*Ref*
C	170.89 ± 0.45	7[a]	CO	−26.42 ± 0.04	7
H	52.10 ± 0.001	7	CO_2	−94.054 ± 0.011	7
CH	142 ± 1	7	C_2O	68.5 ± 15	7[f]
CH_2	92–94	*b*	CHO	11 ± 4	*g*
C_2	199 ± 2	7	$(CHO)_2$	−54.8	*h*
C_2H	114 ± 7	7	CH_2CO	−14.5	*i*
C_2H_2	54.19 ± 0.19	7	CHO^+	204 ± 12	190, 191
C_2H_3	49.4 ± 5	*c*	H_3O^+	143 ± 3	*j*, *k*
C_3	189.7 ± 2.3	7	$C_3H_3^+$	265 ± 5 271 ± 2	80 *l*
C_4H_2	102.5	*d*	O^-	24.3 ± 0.5	7
C_4H_3	111.3	*d*	O_2^-	−11.39 ± 0.5	7
O	59.559 ± 0.03	7	OH^-	−34.4 ± 1.0	7
OH	9.432 ± 0.3	7	C_2^-	126 ± 25	7
HO_2	5 ± 2	7			
H_2O	−57.7979	7			
H_2O_2	−32.53 ± 0.04	*e*			

[a] Value for monatomic gas. [b] W. A. Chupka, J. Berkowitz, and K. M. A. Refaey, *J. Chem. Phys.*, **50**, 1938 (1969). [c] Value based on *D* (C_2H_3–H) = 89 ± 5; see footnote *b*. [d] M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962). [e] P. A. Giguère and I. D. Lin, *J. Amer. Chem. Soc.*, **77**, 6477 (1955). [f] Becker and Bayes[72] favor a value of 92 ± 5. [g] Considerable uncertainty in ΔH_f(HCO). Values for *D*(H–CO) of 30, 15, and 18.5 have been reported: R. I. Reed, *Trans. Faraday Soc.*, **52**, 1195 (1956); J. Calvert, *J. Chem. Phys.*, **29**, 954 (1958); R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 4570 (1966). A value of *ca.* 12 has also been suggested: D. M. Golden, quoted by M. J. Yee Quee and J. C. J. Thynne, *Ber. Bunsenges. Phys. Chem.*, **72**, 211 (1968). [h] Calculated value based on the scheme given by Cox: J. D. Cox, *Tetrahedron*, **18**, 1337 (1962). [i] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952. [j] M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **50**, 2028 (1969). [k] A. R. Anway, *ibid.*, **50**, 2012 (1969). [l] K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *J. Amer. Chem. Soc.*, **84**, 3980 (1962). Glass, Kistiakowsky, Michael, and Niki[82] suggest a value of *ca.* 200. For the postulated reactions involving $C_3H_3^+$ to be thermochemically feasible, $\Delta H_f(C_3H_3^+)$ must be considerably lower than 270.

and simpler in structure. Probably the most pressing need here is for information on the reactions of the ethynyl radical, C_2H. In the view of the authors, the most promising areas of approach are flame studies, using the combined techniques of spectroscopy and molecular beam sampling followed by mass spectrometry. Shock tube studies in conjunction with computer modelling of the chemical mechanism also appear to be a useful technique.

Acknowledgments. The authors wish to thank Dr. J. M. Hay and Professor R. G. W. Norrish and the Royal Society for permission to reproduce Figure 1, Dr. K. H. Homann and the Elsevier Publishing Co. for permission to reproduce Figure 11, and Dr. K. H. Homann, The Combustion Institute and Butterworths Publications Ltd., for permission to reproduce Figure 12. They are also grateful to Dr. T. Boddington, Dr. J. Griffiths, and Dr. J. M. Hay for their kind help and useful advice, and to the British Oxygen Co. for the use of their library. One of us (D. B. S.) thanks the Science Research Council for the award of a Senior Research Assistantship.

VII. Appendix

A. RATE CONSTANTS FOR SOME REACTIONS OF INTEREST IN THE OXIDATION AND COMBUSTION OF ACETYLENE

The reported Arrhenius parameters for some of the major reactions occurring in the combustion of acetylene are listed in Table V. In general, these reactions are of importance only in the high-temperature oxidation, where relatively simple intermediates are present. The compilation is limited to reactions of acetylene itself and of hydrocarbon radicals formed from acetylene. Additional reactions of interest are those which also occur in the H_2–O_2–CO system. These reactions are not included here, since they have been discussed in several recent publications.[64,265,266]

For some of the reactions listed in Table V the rate parameters are not well established and should be considered tentative values.

B. HEATS OF FORMATION FOR SPECIES OF INTEREST IN THE OXIDATION AND COMBUSTION OF ACETYLENE

The heats of formation are summarized in Table VI.

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