



Measurements of the concentrations of positive and negative ions along premixed fuel-rich flames of methane and oxygen



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ABSTRACT

The positive and negative ions in fuel-rich, pre-mixed flames of $\text{CH}_4 + \text{O}_2 + \text{Ar}$ ($0.4 \leq \text{C/O}$ (atomic basis) ≤ 0.75) burning at 1 atm have been studied mass spectrometrically. The ions in the most oxygen-rich of these non-turbulent flames were found to be similar to those in more fuel-lean flames, previously studied by Goodings et al. In particular, in this flame, ions are produced in only one chemi-ionisation step in the reaction zone, *i.e.* by $\text{CH} + \text{O} \rightarrow \text{CHO}^+ + \text{e}^-$. Subsequently a pool of positive ions is then formed rapidly, mainly by protons being transferred from CHO^+ to intermediates and final products of combustion. Some negative ions were detected in the reaction zone, but none were found in this flame more than 1 mm downstream of the reaction zone, *i.e.* in the burnt gas. These negatively charged species, like the positive ions, reflect the presence of intermediates in and near the reaction zone. In the burnt gas, the dominant positive ion, H_3O^+ , recombines with free electrons, the principal negatively charged species, in $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow$ products. The recombination coefficient was measured to be $2.9 \pm 1.5 \times 10^{-7} \text{ ml ion}^{-1} \text{ s}^{-1}$ at $\sim 2250 \text{ K}$. However, in the richer oxy-methane flames with $\text{C/O} \geq 0.50$, another ion-producing step was found to operate from 1 to at least $\sim 5 \text{ mm}$ downstream of the reaction zone. This new process is deduced to be $\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{e}^-$, and maybe involves electronically excited CH radicals. Certainly, C_3H_3^+ becomes the major positive ion in the more fuel-rich flames. The richest flame studied, with $\text{C/O} = 0.75$, is weakly sooting; in its burnt gas, both positive and negative ions with masses exceeding 170 a.m.u. were formed throughout the first 8 or so mm of the burnt gas. It is likely that the heavy positive ions are produced by proton transfer from a pool of positive ions (with the primary ion being C_3H_3^+) to precursors of soot, including polyaromatic species. Likewise, the pool of massive negative ions reflects these precursors of soot.

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1. Introduction

In the last few years, several attempts [1–14] have been made to model the appearance and disappearance of positively and negatively charged species, usually molecular ions and free electrons, along premixed, flat flames, particularly of methane and oxygen, usually diluted with nitrogen. Of course, this involves modelling the concentration profiles of uncharged radicals, such as CH and free atoms of oxygen, along these flames. As for comparing the results of such computations with actual measurements, there are not many published experimental studies available. In fact, every modeller has to rely on the mass spectrometric investigations of methane/oxygen flames by Goodings and co-workers [15–18]. The first of these important, bench-mark studies [15] was of a flat,

fuel-rich flame of methane with an equivalence ratio (φ , the ratio of the oxygen concentration in the unburnt gas mixture for complete (or stoichiometric) combustion to CO_2 and H_2O to the actual value) of 2. The next papers were devoted to measuring the positive [16] and negative [17] ions along two other flames with $\varphi = 0.216$ (fuel-lean) and 2.15 (fuel-rich). The final one [18] of these four papers was about a methane flame with $\varphi = 0.2$ (fuel-lean). Calcote and Jensen [19] have reported some measurements of positive and negative ions in methane flames. Also, Tanner et al. [20] have made similar studies of one fuel-rich oxy-methane flame (atomic ratio $\text{C/O} = 0.538$) and of another, which used a mixture of CH_4 and C_2H_2 as the fuel. Other measurements have been reported of ionic concentrations along related flames of different fuels, *e.g.* acetylene [21–30], ethylene [24] and propane [31]. Some new experimental work has been published recently on ions in various flames [31–33]. However, the fact that the only systematic mass spectrometric investigations of ions in methane flames appear to be

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Table 1
Properties of pre-mixed oxy-methane flames.

Flame	φ	C/O (atomic basis)	Flow rates of unburnt gases (ml s ⁻¹)				Adiabatic temp. (K)
			CH ₄	O ₂	Ar	Total	
<i>a</i>	1.60	0.40	6.4	8.0	25.6	40.0	2295
<i>b</i>	2.00	0.50	12.0	12.0	16.0	40.0	2299
<i>c</i>	2.46	0.62	19.4	15.8	4.8	40.0	2042
<i>d</i>	3.00	0.75	24.0	16.0	–	40.0	~1950

those of Goodings and co-workers [15–18], who studied only four flames, has prompted us to present some measurements of ion concentrations along the axes of a wider range of fuel-rich, pre-mixed, flames of methane and oxygen, burning at atmospheric pressure. These flames include one, which produces a little soot. These new measurements of ion abundances along non-turbulent flames, enable theoretical models to be tested more fully and stringently, and also areas of doubt resolved.

2. Details of experiments and flames

Details have been given already of the burner [28] and the sampling system [28,34–37] for continuously extracting a sample of the gas from a point along the central axis of a flame, burning at atmospheric pressure, into a mass spectrometer for analysis of the positive and negative ions present in the flame. In brief, the burner was, like that of Goodings et al. [15], a simple quartz tube (i.d. 2.5 mm; o.d. 5.0 mm), so that the premixed gases gave a flame very similar to that on a Bunsen burner, but burning horizontally. In appearance, each flame had a thin, conical, turquoise reaction zone, which extended ~8 mm from the burner's exit. After the luminous reaction zone, the hot gas moved into an extended region (diam. ~10 mm) coloured blue and referred to below as the burnt gas. Such a simple burner is best for sampling close to a flame's reaction zone. The burner was mounted on a moveable carriage, so that the flame could be moved horizontally, whilst burning against the metallic sampling nozzle of the spectrometer. This enabled different points along the flame's axis to be sampled. In fact, the burner-carriage could be moved slowly by a motor, which enabled concentration profiles for each ion to be easily measured. These horizontal flames had an axial velocity in the burnt gas, V , which quickly reached a steady value of ~3.9 m/s, which is low enough for the hot gas to curve upwards after ~15 mm downstream of the tip of the reaction zone. This curving upwards was caused by the buoyancy of the hot gas. Great care was taken to dampen any oscillations in the flows rates of gas to the burner by inserting "capacities and resistances" in the supply lines; this ensured that the reaction zone did not fluctuate in space.

Altogether, four pre-mixed flames burning at atmospheric pressure were studied; details of them are given in Table 1. They are all fuel-rich, ranging from almost stoichiometric (when the atomic ratio C/O=1/4) to a flame, which is just sooting. Argon was used as diluent to avoid ions containing nitrogen, e.g. NO⁺ and NO₂⁻, which can complicate mass spectra, when N₂ is used as the diluent. The temperatures quoted in Table 1 are the adiabatic temperatures computed for equilibrium in flames *a*–*c*. In practice, the temperature on the axis displays an extremely sharp rise just before and through the reaction zone and in the next ~4 mm rises by ~80 K to attain a final, steady temperature of some 50 K below that computed for Table 1. Because flame *d* is weakly sooting, its final temperature has only been estimated. It is clear from the yellow emission of soot that such particles are produced in the reaction zone of flame *d*, which has C/O=0.75. Previously Freeman

[38] discovered that for flames of CH₄+O₂ with no diluent, soot is produced whenever the ratio (C/O) exceeds 0.64. This compares with the theoretical figure of C/O > 1/3 for there being insufficient O₂ to react CH₄ to CO and H₂O. Values of C/O are given in Table 1 for each flame. Unlike the oxy-acetylene flames studied previously [28], these oxy-methane flames do not display a feather [39], whose grey colour indicates the presence of hydrocarbon radicals, such as CH, C₂, C₃, etc. Of course, the turquoise colour of the reaction zones of all hydrocarbon flames derives from radicals such as CH and C₂ [40] being present there. The mechanism of the burning of CH₄ in O₂ is understood [41], but the production of soot in e.g. flame *d* is not. To the naked eye, it looked as if the sooting flame *d* had a thicker reaction zone than the other three.

The structure of these oxy-methane flames is well understood [40–42]. Thus, the majority of the chemistry occurs in the reaction zone, whose thickness is ~0.3 mm. Here the major free radicals H, OH and O are produced, together with radicals like CH_{*i*} (*i* ≤ 3). Free atoms of hydrogen have a high diffusivity and consequently diffuse counter-currently, upstream of the reaction zone into the pre-heating region, to where heat is also conducted against the flow of gas. Reactions such as CH_{*j*}+H→CH_{*j-1*}+H₂, for 1 ≤ *j* ≤ 4, produce H₂, which then enters the reaction zone. In fact, the burnt gas of these fuel-rich flames (even flame *a*) contains appreciable quantities of unburnt H₂. It is notable too that reactions like CH₃+CH₃+M→C₂H₆+M produce C₂-species, particularly in these fuel-rich flames. Here M is any molecule acting as a third-body or chaperon. All this means that methane undergoes pyrolysis in the pre-heating region. One feature of the reaction zone is that chain-branching there, particularly in the oxidation of H₂ [40], generates the flame radicals H, OH and O in amounts larger than those for equilibrium downstream in the flame. Recombination of these three radicals, early in the first few mm of the burnt gas, accounts for the temperature rise there of ~80 K. The temperature on the axis is subsequently expected to remain constant [27–29,42] until air entrained from the laboratory diffuses to the flame's axis [43] after ~12–15 mm downstream of the reaction zone. As seen below, free electrons appear in the reaction zone; they are the species with the largest diffusion coefficient, so they too diffuse into the cooler pre-heating region.

Descriptions have been given previously [28,34–36,44,45] of the sampling system for continuously extracting a sample of the gas from a point along a flame at atmospheric pressure and then forming a beam of either positive or negative ions for mass spectrometric analysis at low pressures below 10⁻⁵ mbar. The aim is to identify the positive and negative ions in a flame and measure their concentrations. Briefly, a small fraction of the gas on the flame's axis continuously enters a vacuum chamber *via* a hole (diam. 0.05–0.22 mm) at the tip of a hollow sampling cone, electroformed from chromium. This sample thus expands supersonically [46] down a conical duct to a low pressure of ~10⁻³ mbar, so in the process there is a change from continuum to molecular flow. If positive ions are being studied, they are accelerated (by an appropriate voltage) into a second chamber (at the lower pressure of less than 10⁻⁵ mbar), but negatively charged species are simultaneously repelled. In the second chamber, the beam of ions of one sign is directed and focussed into a quadrupole mass spectrometer and the current associated with each ion is measured. Negative ions are studied by simply reversing the polarity of the accelerating potentials. Techniques are available [47,48] for converting a current, measured for an ion, into the concentration of that ion in the flame under study. It is worth noting that the gas sampled in this way originates less than 0.5 mm off the flame's axis [49]; this ensures that the observations are unaffected by air-entrainment for approximately the first 12 mm along the burnt gas.

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