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The effects of applying electric fields on the mass spectrometric sampling of positive and negative ions from a flame at atmospheric pressure

Allan N. Hayhurst *, John M. Goodings [1], Stephen G. Taylor

Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, England, United Kingdom

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ABSTRACT

Flames are plasmas, because they contain free electrons and both positive and negative ions. The concentrations of ions in a flat flame, burning at 1 bar, have been measured by continuously sampling the hot (2400 K) gas into a mass spectrometer at low pressure. The voltage, $\Delta\phi$, between the metallic burner and the plate holding the metallic sampling nozzle was varied; also, the flame was seeded with an alkali metal and doped with much larger quantities (mole fraction $\leqslant$1.7%) of chlorine. Currents of ions such as K^{+} and Cl^{-} were measured with the mass spectrometer for different $\Delta\phi$ and indicated that the sampling nozzle repels free electrons, when it is at a negative potential with respect to the burner ($\Delta\phi < 0$); consequently the nozzle is then covered by a cathodic sheath of positive ions. Likewise, when $\Delta\phi \gg 0$, the inlet orifice is covered by charged species from the plasma, forming an anodic sheath, from which some electrons reach the nozzle; also some positive and negative ions follow them and so leave the sample. Because the sampled gas is accelerated to a Mach number of unity on entering the inlet orifice, some ions have enough momentum to pass through both a sheath and the entrance hole into the mass spectrometer. The measurements enabled the non-uniform, electric potential between the burner and the plate housing the sampling nozzle to be sketched. The thicknesses of the sheaths were also measured; a cathodic sheath of positive ions is much thicker than an anodic plasma sheath. Also, for $\Delta\phi$ between zero and ~+30 V, the sheath around the inlet orifice is at its thinnest and the current detected for positive ions a maximum. This is when quantitative measurements of concentrations should be made for positive or negative ions. This study reveals the importance of the electron concentration, the diameter of the inlet orifice, the presence of a halogen, and $\Delta\phi$, for determining the thicknesses of these sheaths, which do affect the sampling of ions. With chlorine in the flame, the equilibrium: $H + C1^{-} = e^{-} + HC1$ is sufficiently fast to be maintained, whilst the sampled gas passes through the inlet orifice. This equilibrium usually freezes at some point during the sample's subsequent, supersonic expansion into the first vacuum chamber; freezing temperatures were deduced. Also the additional cooling of a sample by heat transfer to the sampling nozzle was estimated. It can be difficult to measure accurately the concentration of a negative ion in a flame, because negative ions, unlike positive ones, are often lost during sampling by participating with free electrons in such a chemical equilibrium, which shifts while the sample is cooled.

1. Introduction

The study of ions in flames has a long history [1,2], whereas, the use of mass spectrometers to identify the positive and negative ions present, dates from around 1957 [3,4]. The general topic of ionisation in flames has been reviewed many times [1,5–8], and one important aspect of the subject has been the direct and continuous sampling of a flame into a mass spectrometer to investigate the ions present [9,10]. Such an application of mass spectrometry has proved very successful at identifying the positive and negative ions, particularly in hydrocarbon flames [*e.g.*, [7,11–15]]. In spite of these and other successes, the technique has often been questioned, because of the many problems of continuously sampling a flame, often burning at atmospheric pressure, into a mass spectrometer for analysis. These problems include the flame's flow field possibly being disturbed [16,17], changes of composition consequent upon a sample being cooled on entering the first vacuum

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* Corresponding author. Fax: +44 1223 334796.
E-mail address: anh1000@cam.ac.uk (A.N. Hayhurst).

[1] Current address: Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario M3J 1P3, Canada.

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Nomenclature

A	area through which a flame sample moves
e	electric charge on an electron
$[H]$	concentration of free hydrogen atoms in a flame
I	an ion current measured by the mass spectrometer
K_6	equilibrium constant of reaction (VI)
k_9	rate constant of forward step of reaction (IX)
k_B	Boltzmann constant
L	characteristic distance
M	Mach number of gas sampled from a flame
M_W	mean relative molecular mass of a gaseous sample
m_e	mass of an electron
m_i	mass of a charged species i
n_e	concentration of free electrons
R	gas constant
Re_e	electric Reynolds number
r	distance away from axis of sampling system from which ions are detected
r_p	radius of sampling cone's inlet orifice
T	temperature of a flame sample
V	velocity of a gaseous sample from a flame
γ	ratio of the principal specific heats of a gas
ΔH_9^0	standard enthalpy change of reaction (IX) at 298 K.
$\Delta\phi$	potential difference between "nozzle" and burner; nozzle is positive if $\Delta\phi > 0$
δ	thickness of the sheath from which positive ions are removed during sampling
δ_i	thickness of an ion sheath
λ_D	Debye length in a flame plasma
μ	viscosity of flame gas
μ_i	mobility of the ith ion
ρ	density of a sample flowing from a gaseous flame
τ_9	time constant for reaction (IX) to attain equilibrium
ϕ	electric potential

chamber of the mass spectrometer [18–21], chemical reactions catalysed by the material of the sampling nozzle and finally the effects of natural (or applied) electric fields [22–26] on the motion of ions from a flame into the sampling system. The latest design of a mass spectrometer [27] for studying ions in a flat flame at atmospheric pressure has succeeded in solving or minimising most of these problems. However, some difficulties do remain. This paper deals with one of them, *viz*, how best to sample negative ions, bearing in mind that to date few quantitative studies of negative ions in flames have been reported. This contrasts with positive ions, of which there have been many fully quantitative investigations [9,28], especially to measure the rate constants and enthalpy changes for a wide variety of their reactions [20,21,29–39]. Only singly charged ions are normally found in a flame.

One well characterised, fuel-rich, flat flame of $H_2 + O_2 + N_2$, with a temperature of 2400 K, was burnt here on a Mèker burner. Without any additives to such a flame, there is very little natural ionisation [40]. The few charged species present are mainly H_3O^+ ions and free electrons. These appear to be mainly produced by the overall reaction [41]:

$$H + H + OH \rightarrow H_3O^+ + e^- \tag{I}$$

occurring in the burned gas, *i.e.* that region downstream of the flame's slightly luminous reaction zone. These burned gases, being the products of combustion, in this case consist of H_2O, N_2 and excess H_2. In addition, there are minor (<1 mol%) amounts of the usual free radicals, O, H and OH, found in almost every flame. It will be seen below that very small amounts of an alkali metal (mole fraction $\approx 10^{-8}$), such as potassium, were added to the unburned gas mixture supplied to the burner. In the burned gas, potassium is typical of all the alkali metals in that it exists [42] as free atoms, as revealed by their blue resonance emission, and also molecules of its hydroxide, KOH. In addition, free atoms of potassium undergo thermal ionisation [31,42,43] in times of ~1 ms or so, *via*:

$$K + M \rightarrow K^+ + e^- + M, \tag{II}$$

where M is any molecule in the burned gas. Ions of potassium are also produced [37] by either proton transfer in:

$$KOH + H_3O^+ \rightarrow K^+ + 2H_2O \tag{III}$$

or by electron transfer in:

$$K + H_3O^+ \rightarrow K^+ \cdot H_2O + H, \tag{IV}$$

followed by the rapid equilibrium [21]:

$$K^+ + H_2O = K^+ \cdot H_2O. \tag{V}$$

In the work described below, negative ions were created by also adding chlorine (*i.e.* a typical halogen) to the flame's unburned gas supplies. The result is that chlorine exists in the burned gas as either free atoms or molecules of hydrogen chloride. In fact, these two species have their concentrations coupled by the reaction:

$$H + HCl = H_2 + Cl; \quad \Delta H_6^0 = -4\ \text{kJ/mol} \tag{VI}$$

being rapidly equilibrated in such a fuel-rich flame of H_2 [44,45]. Here ΔH_6^0 is the reaction's standard change in enthalpy at 298 K. One further consequence of adding chlorine to a flame is that in the presence of an alkali metal, such as potassium, molecules of the stable salt are formed [44,46] in:

$$K + HCl = KCl + H, \tag{VII}$$

which is also rapid enough to be at equilibrium in the flame's burned gas. This means that its time constant is less than ~40 μs. As for the level of ionisation in such a flame with small traces (mole fraction $\sim 10^{-8}$) of potassium present and perhaps up to ~1 mol% of chlorine, an additional way of generating ions is:

$$K + Cl \rightarrow K^+ + Cl^-, \tag{VIII}$$

which has been shown to operate in these flames [35,45,47]. In addition, the concentrations of $C1^-$ ions and free electrons are coupled by the reaction:

$$H + Cl^- = HCl + e^-; \quad \Delta H_9^0 = -78\ \text{kJ/mol} \tag{IX}$$

being rapidly equilibrated [45,47]. That reactions (VI) and (IX) are at equilibrium results in:

$$\frac{[Cl^-]}{[e^-]} = \frac{[Cl]_T}{[H]K_9\left\{1 + \frac{K_6[H]}{[H_2]}\right\}}, \tag{1}$$

where $[Cl]_T = [HCl] + [Cl]$; also K_6 denotes the equilibrium constant of reaction (VI), *etc.* This seemingly complex scheme of reactions is of course simplified by several reactions being at equilibrium; this is typical of the chemistry proceeding in flames and is a consequence of their high temperatures [44]. One more, rapidly established equilibrium, which might have been specified above, is:

$$KOH + H = K + H_2O. \tag{X}$$

The above reactions provide the background, against which the observations below can be considered.