FORMATION OF SMALL AND LARGE IONS IN RICH AND SOOTING ETHYLENE AND ACETYLENE PREMIXED FLAMES

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ABSTRACT

The objective of this work is to determine the mechanisms of formation of both small |12 - ≃ 300 u| and large ions |several thousands u| in sooting C_2H_4 and C_2H_2 flames. These ions are formed in two independent ionization zones, the small ions by chemionization and the large ions by the direct thermoionization of "young" soot particles in the primary soot formation zone.

1. INTRODUCTION

Very few results have been published on the ion composition of rich and sooting flames (1). WERSBORG et al (2) have recently shown that the positive charge carriers in the primary soot formation zone of premixed acetylene flames (P = 20 torrs), are large ions ranging between 1,000 and 8,000 u and maximum concentration as high as 10^{12} ions-cm^{-3}. These authors have not however measured the absolute concentration of the small ions (below 300 u). It was further concluded that the large ions were likely formed by a charge transfer process from small ions like $H3O^+$ or $C_3H_3^+$ to large hydrocarbon molecules and "young" soot particles, and that the direct thermoionization of these species was playing only a minor role (3).

The object of the present study was to determine the nature and absolute concentration of both small ions and larger positive charged species in rich and sooting ethylene and acetylene flames.

2. EXPERIMENTAL

Since the formation of the large ions and soot particles is largely dependent on the flame conditions (pressure, equivalence ratio, cold gas velocity, temperature and diluent gas concentration), all the measurements have been performed on premixed flames stabilized on the same water cooled flat burner.

The concentration of the charged species is obtained by means of a cylindrical Langmuir probe. The current delivered to the probe is converted in absolute ion concentration (N_1^+ and N_2^+) using the relation of CLEMENTS and SMY (4).

A multistage molecular beam sampling mass spectrometer is used to detect both small and large positive charged species in two mass ranges 12 - ≃ 300 u and ≃ 300 - ≃ 7,000 u (5). The generation rate of the small chemi-ions in non sooting flames is measured by the current saturation method (6).

The volume concentration of the soot particles X_p and their temperature T_p is measured by an optical method (7). The flame temperature is also measured by the sodium line reversal method.

The ethylene and acetylene flames are studied at various equivalence ratios ($1 < \lambda < 3.5$), cold gas velocities ($29 < Vo < 37$ cm.s^{-1}) and pressures ($25 < P < 54$ torrs).

3. RESULTS

In stoichiometric and slightly rich flames, the positive current delivered to the cylindrical probe peaks at the upper edge of the blue-green reaction zone: when λ increases, the intensity I_1^+ of this maximum decreases. When the flame becomes sooty, a second peak of maximum intensity I_2^+ appears, located at the beginning of the soot formation zone, which intensity increases with λ (Figure 1). Figure 2 represents the variation of the maximum intensities N^+, and N_2^+ for ethylene and acetylene flames.

Saturation currents are reached up to the onset of soot formation. When the flame becomes sooty, the current increases continuously with the applied voltage (Figure 3).

From the electrostatic probe and saturation current measurements, it appears that ions are produced by two distinct mechanisms in sooting flames: the chemionization one in the oxidation zone and a second one in the large sooting zone.

The mass spectrometric experiments show that the mass distribution within the two ionization zones are different. The first maximum is related to the small ions, which are found usually in lean and stoichiometric flames (8). Increasing λ beyond 1.2 decreases their concentration in agreement with the electrostatic probe results. In rich and sooting flames, $C_3H_3^+$ is the main ion, all oxygenated ions having disappeared, but no shift toward high mass numbers has been observed when λ increases (Figure 4). The treatment of the mass spectrometric ion signal in the second zone leads to an average ion mass (300-5000u) which increases rapidly conversely with the amount of soot. The large ion diameters are in the range 6 to 22 Å, assuming that they are charged spherical carbon particles of equal density $\rho = 1.8$ g.cm^{-3}. This shows, as WERSBORG et al. (2) , that the main fraction of the positive charges in sooting flames is carried by large molecules and "young" soot particles (Figure 2). The concentration of these large ions ranges between 10^8 and 10^{10} ion.cm^{-3} for the different conditions studied.

4. DISCUSSION

The generation rate U^+ of the chemi-ions calculated from the saturation current decreases continuously from $\lambda = 1.2$ up to the onset of soot formation by roughly two orders of magnitude as the total concentration of the small ions measured by the electrostatic probe or by mass spectrometry (Figure 4). This indicates that their concentration decay is only due to the decrease of U^+, and not to a charge or proton transfer from the chemi-ions to heavy hydrocarbons and "young" soot particles. The absence of a displacement toward high mass numbers in the small ion-mass spectrum is also in favour of this argument.

The most likely hypothesis to explain the formation of large ions is the direct thermoionic charging of heavy hydrocarbon molecules and "young" soot particles. To verify this hypothesis, the heavy ion concentration N_2^+ has been compared with the number N_{th}^+ of the charged particles in equilibrium with the neutrals N at the temperature T using the SAHA's equation. N is calculated from the soot volume concentration X_p, assuming that the charged and neutral particles have the same size, which is a valuable assumption in the earlier flame region. The ionization potential is calculated for spherical carbon particles (9). Table 1 shows that there is a good agreement between N_2^+ and N_{th}^+: this strongly supports the mechanism of direct ionization of heavy hydrocarbon and "young" soot particles by thermoionization, ruling out the indirect charge transfer process, in contrast with the reverse hypothesis (3).

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TABLE 1

Height above the burner (cm)		1	1.5	2	2.5	3	3.5	4
C_2H_4 $\lambda = 3$ $v_o = 37$ cm.s^{-1}	N_2^+			0.2	0.95	2.0	2.2	2.1
P = 45 torr $(Xp)_{max} = 9.1.10^8$ $cm^3.cm^{-3}$	$N^+_{thermal}$ $10^9.cm^{-3}$			1	1.8	1.4	1.0	0.8
C_2H_2 $\lambda = 3$ $v_o = 29$ cm.s^{-1}	N_2^+	1.2	13.5	9.0	5.0	3.3		
P = 45 torr $(Xp)_{max} = 2,5.10^{-8}$ $cm^3.cm^{-3}$	$N^+_{thermal}$ $10^9.cm^{-3}$	1.1	7.0	5.0	3.4	2.0		

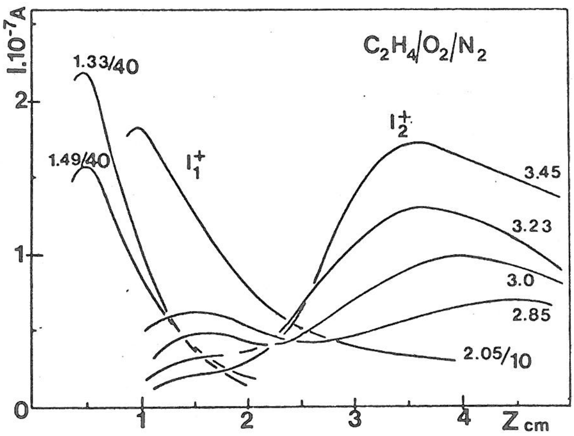

Figure 1: Cylindrical probe intensities I_1^+ and I_2^+ for different fuel equivalence ratios λ

(V_o = 27.4 cm.s^{-1} - P = 45 torrs - N_2/O_2 = 0.6

λ = 1.33 and 1.49 Intensity divided by 40} non sooting flames

λ = 2.05 and 1.49 Intensity divided by 10}

λ = 2.85-3.0-3.23-3.45} sooting flames

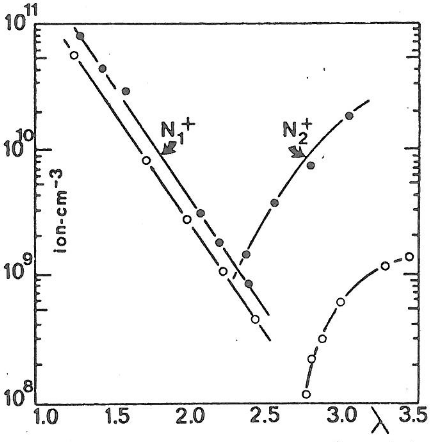

Figure 2: Maximum ion concentrations N_1^+ and N_2^+ versus the fuel equivalence ratio λ (v_o = 27.4 cm s^{-1} - P = 45 torrs- N_2/O_2 = 0.6).

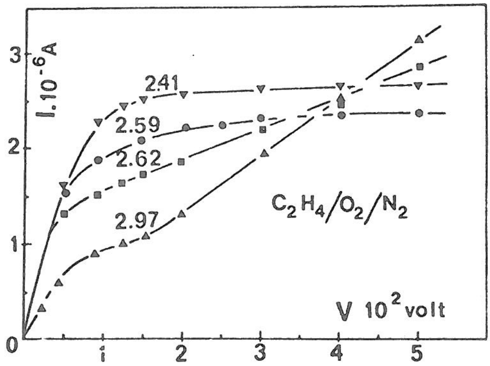

Fig. 3: Saturation current (v_o = 25.5 cm.s^{-1}- P = 45 Torr - N_2/O_2 = 0.6). The yellow zone of the soot emission appears for 2.59 < λ < 2.62

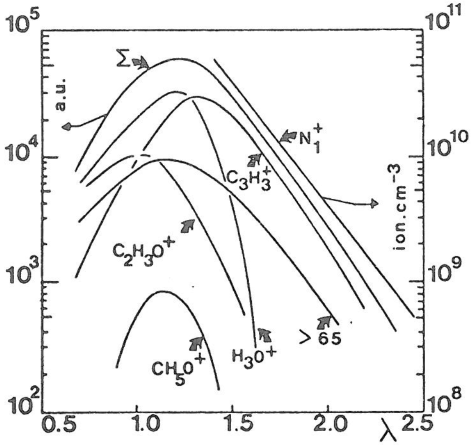

Fig.4: Small ion concentration in non sooting ethylene flames (v_o = 27.4 cm.s^{-1} - P = 45 torrs - N_2/O_2 = 0.6).

Σ = total ion intensity measured with the mass-spectrometer

> 65 = ions above 65 u

N_1^+ ion concentration from the Langmuir probe.