Electric probe measurements of chemical ionization behind reflected shock waves

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Abstract. Chemical ionization is the process of formation of charged particles as a result of energy release during the formation of chemical bonds in chemical reactions between neutral components. Chemical ionization is most often observed in the processes of hydrocarbon combustion. Measurements of ionization current in internal combustion engines are of great practical interest. Most experiments on chemical ionization were carried out in flames with obvious limitations: the composition of the mixture cannot be changed in an arbitrarily wide range of concentrations of fuel and oxidant, to investigate the pyrolysis processes, to arbitrarily change the temperature and pressure, it is impossible to dispose of the transfer processes and gradients of temperature and reactive components. Experiments in shock tubes in the reflected shock waves are free of all of the above disadvantages. In the present work, electric currents to the electrically insulated and uninsulated cylindrical probes were recorded, to which a negative (~9V) or positive (+9V) potentials were applied. In these experiments, the displacement and the total currents were recorded respectively. In the same experiments, the signals of chemiluminescent emission of electronically excited OH* radicals (λ = 308 nm) were simultaneously recorded. The main goal of the present work was to measure experimentally (1) the displacement currents on positive and negative probes, (2) the total and displacement currents on a negative cylindrical probe during acetylene pyrolysis and oxidation, and (3) to confirm correlation of the displacement currents and the signals of chemiluminescent emission of electronically excited OH* radicals.

1. Introduction

In a typical hydrocarbon–air flame, depending on particular conditions, the concentration of charged particles (positive and negative ions and free electrons) can reach the values of 10⁸–10¹² cm⁻³. At present, the mechanism of their formation is well known [1]. This is the mechanism of chemical ionization. Possible influence of the processes of thermal ionization of impurities and contribution of electronically excited particles do not exert a significant impact on the process of chemical ionization [2]. The process of chemical ionization with the following charge transfer and recombination of ions and free electrons can explain the high concentrations of charged particles even in lean and cold flames and variety of ions experimentally observed in lean, stoichiometric and rich flames. Chemical ionization is a process of formation of charged particles due to the energy release accompanied the
formation of a new chemical bond as a result of collisions of reactive neutral particles [3]. It is generally admitted that the primary positive ions and free electrons are formed in the reaction [1] \( \text{CH} + \text{O} = \text{CHO}^+ + \text{e}^- \) followed by a fast charge transfer reaction \( \text{CHO}^+ + \text{H}_2\text{O} = \text{H}_2\text{O}^+ + \text{CO} \). Positive ions \( \text{H}_2\text{O}^+ \) dominate in lean, stoichiometric and even slightly rich hydrocarbon–oxygen mixtures. In more rich mixtures, \( \text{C}_3\text{H}_5^- \) ions dominate [4, 5]. The origin of \( \text{C}_3\text{H}_5^- \) ions is still a question of discussion: they can be formed in the fast reactions of charge transfer or in the reactions of chemical ionization.

The most probable reactions of formation of \( \text{C}_3\text{H}_5^- \) as the primary ions are the following ones [6]: \( \text{CH} + \text{C}_2\text{H}_2 = \text{C}_3\text{H}_5^- + \text{e}^- \) and \( \text{CH}_2^* + \text{C}_2\text{H}_2 = \text{C}_3\text{H}_5^- + \text{e}^- \). These additional reactions of chemical ionization can proceed even in the absence of oxygen. To check such possibility it is expedient to carry out experiments on ionization measurement during acetylene pyrolysis. In this case one can expect the maximal concentration of \( \text{C}_3\text{H}_5^- \) molecules during the pyrolysis process.

The electric probe method for plasma diagnostic is a simple and efficient way to obtain information on the local plasma parameters. Usually, theoretical treatment of the experimentally measured probe currents deals with the conduction currents of positive and negative ions and free electrons. For stationary low-temperature plasma with a relatively slow source of thermal ionization, this is fully justified. However, in the case when charged particles are formed in fast reactions of chemical ionization, a particular contribution into the total current can be provided by the displacement current, which is caused by variation with time of the electric field strength near the probe surface as a result of formation of a double electric layer.

To record displacement currents in our experiments the surface of a probe was covered by a thin layer of insulator. A similar probe without this layer will record the total current (the sum of the conduction currents and the displacement current) in the same experiment and in the same measurement cross-section. Comparison of these currents (the total and displacement currents) make it possible to determine the contribution of the displacement current into the total current on an electric probe.

One can expect that the displacement currents on electrically insulated probes will be insensitive to the ionization processes with participation of various impurities on the surface of an electric probe and they will be sensitive only on the chemical ionization processes in the reactive mixture, which result in the formation of a double electric layer near the probe surface.

The main goal of the present work was the experimental study of (1) the displacement currents on a cylindrical electric probe under positive (+9 V) and negative (−9 V) electric potential, (2) the displacement currents and the total currents on an electric probe under negative potential (−9 V) during the pyrolysis of an acetylene–Ar mixture and oxidation of an acetylene–oxygen–Ar mixture and (3) to confirm correlation of the displacement currents and signals of chemiluminescent emission of electronically excited OH* radicals under conditions behind reflected shock waves.

2. Experimental

A stainless steel shock tube, with an inner diameter of 75 mm, driver section length of 1.5 m, and driven section length of 3.2 m, was used [7]. The low-pressure section was evacuated with two 2-
NVR-5D forepumps to a residual pressure of \( 10^{-2} \) Torr and with an NVDS-100 oil diffusion pump to \( 10^{-3} \) Torr. The residual pressure was monitored with a VIT-2 ionization-thermocouple vacuum gage. The high-pressure section was evacuated with a 2-NVR-5D forepump through a liquid-nitrogen trap to a residual pressure of 0.1 Torr. Air leakage into the driven section did not exceed \( 10^{-4} \) Torr/min. Before each experiment, the low-pressure section was purged twice with argon used for preparation of the mixtures, with intermediate pumping to \( 10^{-1} \) Torr.

The test mixtures were prepared manometrically and stored in light-proof containers. The components were acetylene (reagent grade), methane (reagent grade), hydrogen (reagent grade), and oxygen (99.0% pure). The diluent gas was argon (99.998%). In preparing the acetylene-containing mixtures, additional purification and chromatographic purity-control procedures were performed [8]. The test mixtures were highly diluted with argon. In quantitative measurements of ionization processes under typical shock-tube conditions, the level of possible impurities is very important. In [9], it was
demonstrated that, in experiments with “pure” argon, the main contaminants are 40% H$_2$O, 50% N$_2$, 5% CO$_2$, and 5% hydrocarbons (mostly CH$_4$). The oxygen concentration was below the sensitivity limit of the mass spectrometer. It was demonstrated in [9] that the Fe concentration is negligibly small, and only NaCl is to be taken into account. The NaCl concentration in the shock tube was estimated as 4 · 10$^{10}$ to 5 · 10$^{11}$ cm$^{-3}$.

The parameters of the gas behind the incident and reflected shock waves were calculated from the initial pressure, mixture composition, and incident shock wave velocity using the theory of ideal flow in a shock tube [10]. The velocity of the incident shock wave was measured over two measuring distances with three pressure sensors. The distances were 528 and 281 mm, respectively. The pressure transducers, with a sensing element 1 mm in diameter, were made from piezoceramics (lead zirconate titanate).

The driver gas was helium. Since the diaphragms ruptured at a nearly the same driver-gas pressure, the temperature behind the incident or reflected shock wave could be additionally adjusted by diluting helium driver gas with air: the lower the temperature to be achieved behind the shock wave, the higher the percentage of air should be added.

The emission of electronically excited OH* radicals ($\lambda = 308$ nm) was also monitored. In our experiments, the total electric probe current and the displacement current were simultaneously recorded in the same cross section of the shock tube behind reflected shock waves. No mutual influence of these signals was observed. In a separate set of experiments, two electric probes (0.01-cm-diameter stainless steel wire and 0.012-cm-diameter vanish-insulated copper wire with an insulation thickness of 0.001 cm) were used, which were installed crosswise and perpendicular to the shock tube axis in the measurement section at a distance of 1.5 cm from the endplate. The electrically insulated probe measured only the displacement current. A voltage of −9 V or +9 V was applied to both probes.

3. Electric probe method
The electric probe method is a simple and efficient way to obtain information on the local parameters of plasmas. For collision-free plasma, wherein the mean free paths of electrons and ions considerably exceed the characteristic size of the electric probe, the theory of electric probes is well developed, enabling to obtain reliable information on the properties of such plasmas by measuring the electric current flowing through the probe [11]. The situation becomes more complicated in the case of collisional plasma, wherein the mean free paths of the charged particles become commensurate with or even smaller than the characteristic size of the electric probe [11].

There are many mathematical models of electric probe operation under various conditions [11–13]. The electric probe method was developed mainly for stationary plasmas [14, 15] and later was extended to the conditions realized behind reflected shock waves [16, 17]. The total current recorded by the electric probe consists of the conduction currents of positively charged ions, negatively charged free electrons (in the absence of negative ions) and the displacement current:

$$I = Se(j_i - j_e) - \frac{S}{4\pi e} \cdot \frac{\partial^2 \phi}{\partial t \partial r}$$

where $I$ is the total current, $S$ is the electric probe surface area, $e$ is the electron charge, $j_i$ and $j_e$ are the density of conduction currents of positive ions and free electrons, $\phi$ is the electric potential for a particular time and at a given point in space, $t$ is time and $r$ is the distance from the axis of a cylindrical probe in cylindrical coordinates. The last term in this relationship is the displacement current which is caused by the non-stationary process of formation of a double electric layer near the probe surface.

Our analysis of the mathematical model of cylindrical probe operation under conditions realized behind reflected shock waves demonstrated that the rate of appearance of free electrons and primary positive ions $W(t)$ is the major parameter which influences the total current [17]. The results show that
the electric current passing through the probe under the specified conditions depends mainly on $W(t)$, whereas variation of a recombination coefficient $\alpha$ over a relatively wide range exerts only minor effect on the current. The total current is nearly proportional to the rate of formation of positive ions in the gas phase. Thus, based on the results of our numerical simulations, it is possible to derive the expression relating the ionization rate and the total electric current for a particular electric potential applied to the probe. From this relationship one can derive the rate of chemical ionization $W(t)$ from the experimentally measured total electric currents. Then, one can derive the time dependence of the concentration of free electrons in a quasi-neutral zone. The concentrations of positive ions and free electrons in a quasi-neutral zone of the plasma investigated are described by the following nonlinear equation:

$$\frac{dn_e(t)}{dt} = W^{(0)}(t) - \alpha_0 n_e^2(t)$$

where $n_e(t)$ is the concentration of free electrons, $W^{(0)}(t)$ is the rate of chemical ionization derived from the total current and $\alpha_0$ is the coefficient of dissociative recombination. This equation can be easily integrated numerically if $W^{(0)}(t)$ is derived from the total current and $\alpha_0$ is known and to determine $n_e(t)$.

4. Results and discussion

In the first set of experiments we tried to estimate the role of formation of C$_3$H$_3^+$ ions as the primary ions. For this we carried out experiments on the intensity of chemical ionization during C$_2$H$_2$ pyrolysis and oxidation [18]. In the case of acetylene pyrolysis the reaction CH + C$_2$H$_2$ = C$_3$H$_3^+$ + e$^-$ should dominate. In the case of acetylene oxidation a traditional reaction of chemical ionization dominates: CH + O = CHO$^-$ + e$^-$. As showed our experiments, at low temperatures in the case of acetylene pyrolysis the concentration of electrons is below the probe detection limit (figure 1a).

![Figure 1](image_url)

Figure 1. The experimentally measured profiles of the pressure, the intensity of chemiluminescent emission of OH$^*$ radicals and the total and displacement currents for acetylene pyrolysis (the upper row) and oxidation (the bottom row) for three different pairs of temperatures.
Figure 1 demonstrates that in the case of acetylene oxidation clearly expressed maximums of the total and displacement currents of chemical ionization are observed at times of several tens of microseconds. The total currents exceed the displacement currents but its contribution into the total current is rather large. The time of peak achievement of the displacement current is somewhat shorter than that of the total current. The displacement currents rapidly drop up to zero after the peak achievement. This is evidence of termination of chemical ionization processes. The total currents drop more slowly after the peak achievement due to diffusion and mobility processes of charged particles. At high temperatures, the total currents demonstrate certain growth most probably due to the influence of thermal ionization of various impurities in the gas phase and on the probe surface. Good agreement is observed between the peak achievements of the signals of OH* chemiluminescent emission and the total and displacement currents. Thus the times of maximum achievement of the displacement currents can be used to determine the ignition delay times, which are usually derived from the chemiluminescent emission of OH* radicals.

Very different behavior of the probe currents is observed in the case of acetylene pyrolysis. Probe currents are not observed at the low temperature (figure 1a) that is evidence of very low intensity of possible chemical ionization processes under these conditions. Ionization signals appear at the higher temperatures (figures 1b and 1c) but the maximum typical of chemical ionization during acetylene oxidation are not observed. At the highest temperature (figure 1c) the characteristic maximum of the displacement current appears, which however considerably smaller than the displacement current during acetylene oxidation at similar temperature (figure 1f). At the same time, behavior of the total current is not regular most probably because of the influence of thermal ionization processes on the conductive probe surface.

The chemiluminescent emission of OH* radicals is not observed because oxygen is absent in the reactive mixture. This means that the level of oxygen as impurity in the shock tube before an experiment is rather low and does not influence the ionization process.

![Diagram](image-url)
Figure 2. The experimentally measured profiles of the displacement currents on the probes with electrically insulated surface under (1) positive +9 V and (2) negative potential −9 V, (3) the signals of chemiluminescent emission of electronically excited OH* radicals and (4) the pressure for a 0.5%C₂H₂ – 2.5%O₂ – 97.0%Ar mixture behind reflected shock waves.

In the second set of experiments the influence of the sign of potential applied to the electrically insulated electric probe was investigated (figure 2). Figure 2 demonstrates the different values of the displacement currents on the identical electric probes under positive (+9 V) and negative (−9 V) potential. In the former case, the currents are higher. The times of peak achievement by the displacement currents are also different and their difference increases with temperature decrease. At the same time, as can be seen from figure 2d, the maximum of chemiluminescent emission of OH* radicals is much closer to the maximum of the displacement current on the probe under negative potential. This maximum of the displacement current on the probe under positive potential is attained at a shorter time. Thus, one can conclude from these experiments that good correlation is observed between the times of peak achievement on the signals of emission of OH* radicals and the displacement currents on the electric probes under negative potentials.

5. Conclusions
Our experiments on the pyrolysis and oxidation of various acetylene–Ar and acetylene–oxygen–Ar mixtures demonstrate that the displacement currents on the electric probes under negative potentials for conditions realized behind reflected shock waves are subjected to the influence of surface ionization processes of various impurities on the insulated probe surface in a lesser extent than the total currents. The displacement currents on the electric probes under positive and negative potentials demonstrate noticeably different behavior. Good correlation is observed between the maximums of displacement currents on an insulated electric probe under negative potential and the maximum of intensity of chemiluminescent emission of OH* radicals.

Our experiments indicate that the process of chemical ionization proceeds intensively only in the presence of oxygen in a reactive mixture and the primary charged particles are formed in the reaction \( \text{CH} + \text{O} = \text{CHO}^+ + \text{e}^- \). In principle, during acetylene pyrolysis the other reaction of chemical ionization is possible \( \text{CH} + \text{C}_2\text{H}_2 = \text{C}_3\text{H}_3^+ + \text{e}^- \). However, the peak on the displacement current, which can be attributed to this reaction, is observed only at the highest temperature being investigated.

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