Shock Tube and Modeling Study of Chemical Ionization in the Oxidation of Acetylene and Methane Mixtures

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1 Introduction

The electrical nature of flames had been realized long time ago. The phenomenon of chemical ionization in flames, that is, the formation of ions via chemical reactions between electrically neutral particles, was discovered in the late 1940s [1]. The high level of ions of non-thermal origin was experimentally observed in the reaction zone of flames and it was concluded that this was an evidence of chemical ionization. It has become clear that a hydrocarbon fuel was needed for chemical ionization, and the shock tube experiments had additionally shown that oxygen had to be present [2]. It is also practically assured that HCO^+ is the major primary ion formed in the reaction $CH + O = CHO^+$ $+ e^{-}$. Ionization kinetics has been extensively studied in flames. At the same time, there is an obvious lack of kinetic data obtained in shock tubes under conditions such that there are no problems arising from complicated gas dynamics, transfer limitations, or temperature gradients. These data are needed to establish systematic correlations between combustion and ionization, which are expected to be of great practical significance [3]. The microwave probing of plasma is the most promising method for investigating ionization in shock waves. Obvious advantages of this method over the others are that it does not cause any significant perturbations in the plasma being examined and allows the free electron concentration to be measured with a high spatiotemporal resolution. Another promising plasma conductivity-based diagnostic technique for studies in shock waves is the electric probe method [4].

In [5], an intriguing similarity between ionization, soot formation, and even prompt NO was emphasized. This connection between these three processes is seen to originate from their parallel dependences on the extent of free unburned carbon. An exciting similarity can also be recognized between chemilumenescence and chemi-ionization processes observed in hydrocarbon-oxygen flames [6]. In particular, there are some experimental evidences that electronically excited OH* radicals and primary CHO⁺ ions have the same precursor [6]: CH + O₂ = OH* + CO and CH + O = CHO⁺ + e⁻.

The aim of the present work was to carry out the experimental measurements of the concentration of free electrons by a microwave interferometer and by the electric probe method, as

well as the emission of the electronically excited OH* radicals during acetylene and methane oxidation behind reflected shock waves and to examine the predictive validity of a novel kinetic model of chemical ionization process, based on our gas-phase reaction mechanism of the formation of soot particles [7].

2 Experimental

The experimental setup was described in detail elsewhere [8, 9]. The experiments were performed in a stainless steel shock tube (inner diameter, 75 mm; driver section length, 1.5 m; driven section length, 3.2 m). The test mixtures were prepared manometrically and stored in lightproof containers. The components were acetylene (reagent grade), methane (reagent grade), and oxygen (99.0%). The diluent gas was argon (99.998%). In preparing the acetylene-containing mixtures, additional purification and chromatographic purity-control procedures were performed [7]. To maintain a nearly constant temperature behind reflected shock wave, the test mixtures were highly diluted with argon: $(0.002-0.0075)CH_4+(0.008-0.03)O_2+Ar and (0.0028-0.0052)C_2H_2+(0.0126-0.024)O_2+Ar.$



Figure 1a. Schematic diagram of the microwave imterferometer: (1) klystron generator, (2) active modulator (G5-6A generator), (3) ferrite valve, (4) waveguide directional coupler, (5) calibrated attenuator, (6) phase inverter, (7) shock tube cross-section, (8) phase-path length compensator, (9) two-probe waveguide section, (10) Lecher-line wavemeter, (11) narrow-band amplifier, (12) double-beam oscilloscope.

Figure 1b. Schematic diagram of the probing system with the Lecher line: (1) Lecher line, (2) Teflon measuring section of the shock tube, (3) flat conical waveguide junction, (4) waveguide.

The concentrations of free electrons $n_e(t)$ and the effective collision frequency of electrons and diluent gas v_{eff} were determined by a microwave interferometer (Fig. 1a) operated at a wavelength of $\lambda = 1.6$ cm. The measuring arm of the interferometer contains the Lecher line (Fig. 1b), which provides good (of the order of several millimeters) spatial resolution and a clearly defined relation between the plasma and microwave parameters. The Lecher line was also used as an electric probe [4]. The Lecher line consists of two 0.3-mm-diameter stainless steel wires connected with the help of flat conical plates to waveguides separated by 4.5 mm and stretched perpendicular to the direction of propagation of the shock wave in the observation section. The latter was made of Teflon in the form of a hollow cylinder (wall thickness ~15 mm, 115 mm in length, the inner diameter coincided with the shock tube one). The uncertainty of the maximum concentration of free electrons measured by the microwave interferometer did not exceed $\pm 20\%$, the uncertainty in the determination of the collision frequency was 50—100%.

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In separate sets of experiments the emission of electronically excited OH* radicals ($\lambda = 308$ nm) and the electric probe signals were measured (Fig. 2). Two electric probes (0.012-cm-diameter stainless steel wires) were used, which were installed crosswise in the measuring section of the shock tube 1.5 cm apart from the end-plate. One of these wires was electrically insulated to measure the displacement current. A voltage of -9 V was applied to both probes.



Figure 2. The oscilloscope records of the signals of pressure transducer (yellow curves), emission of electronically excited OH* radicals (green curves), electric probe ($r_p = 0.006$ cm, $\varphi_p = -9$ V) measurements of the displacement current (pink curves) and the total current (cyan curves) are shown in the upper row for different conditions behind reflected shock wave (see below). The next row demonstrates the ionization rates derived from the total electric probe currents and the parameters of non-linear approximation of these ionizations rates for the same parameters behind reflected shock waves. The bottom row shows the concentration of free electrons derived from these ionization rates (red triangles) and obtained from the detailed kinetic modeling (open blue triangles) for a mixture of $0.005C_2H_2 + 0.025O_2 + 0.975Ar$ for different temperatures and pressures behind reflected shock waves: (a) $T_{50} = 1515$ K, $P_{50} = 1.20$ bar, (b) $T_{50} = 1965$ K, $P_{50} = 1.33$ bar, and (c) $T_{50} = 2080$ K, $P_{50} = 1.45$ bar.

The theoretical treatment of the electric probe records is presented in detail in [4]. We applied exactly the same procedure as described in [4] to derive the time profiles of the concentration of free electrons from the electric probe records (Fig. 2). As can be seen from Fig. 2, the records of emission of electronically excited OH* radicals and electric probe current demonstrate very similar behavior. This can testify in favor of the assumption that electronically excited OH* radicals and primary CHO⁺ ions have the same precursor [6].

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3 Kinetic model

Kinetic modeling was performed using the reaction mechanism of the formation of soot particles developed in [9] with all modifications made in [7]. The kinetic model of soot formation is based on the mechanism of gas-phase reactions that describes the pyrolysis and oxidation of the initial hydrocarbon, in particular acetylene and methane, and the formation and growth of PAH molecules through different pathways up to coronene. This gas phase reaction mechanism was extended to include a number of ionization reactions in acetylene and methane oxidation presented in Table 1.

Table 1. Ionization reactions in acetylene and methane oxidation with the rate coefficients expressed in moles, cm³, s, kJ/mole

	Reaction	А	E	n	Reference
1	$CH + O = CHO^+ + e^-$	2.530E+11	7.060	0.00	[5]
2	$\mathrm{CHO}^{+} + \mathrm{H}_{2}\mathrm{O} = \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{CO}$	9.030E+15	0.000	0.00	[10]
3	$\mathrm{H}_{3}\mathrm{O}^{+}+\mathrm{e}^{-}=\mathrm{H}_{2}\mathrm{O}+\mathrm{H}$	4.577E+22	0.000	-1.60	[10]
4	NaCl + M = Na + Cl + M	5.000E+14	334.9	0.00	[10]
5	$Na + M = Na^+ + e^- + M$	1.870E+15	494.0	0.50	[10]
6	$NaCl + M = Na^{+} + Cl^{-} + M$	4.940E+22	561.0	-2.00	[10]
7	$H_3O^+ + Na = Na^+ + H_2O + H$	6.620E+15	0.000	0.00	[10]

Special attention was directed towards the possible processes of formation and consumption of CH_3 , CH_2 and CH radicals and atomic oxygen O, which are required for the occurrence of the chemical ionization reaction (1). The modified gas-phase reaction mechanism was comprised of 3559 direct and reverse reactions between 309 different species, with the rate coefficients of some important reactions being pressure-dependent. Soot particles were not formed under the conditions considered. It should be noted that the reactions responsible for ionization did not exert any significant effect on the parameters of the main combustion process. This was ascertained by relevant calculations.

4 Results and discussion

Experimentally measured and calculated time dependences of the concentration of free electrons, formed during acetylene and methane oxidation behind reflected shock waves are presented in Figs. 3a and 3b for various $C_2H_2/O_2/Ar$ and $CH_4/O_2/Ar$ mixtures and for different temperatures. In all experiments the pressure behind the reflected shock wave was close to 1 bar. In the case of acetylene oxidation a very good agreement is observed between the calculated time dependences of concentration of free electrons and the measured ones by the microwave interferometer and derived from the electric probe measurements (Fig. 3a). In the case of methane oxidation this agreement is satisfactory (Fig. 3b).

The calculated concentration profiles of the main charged species such as CHO^+ , H_3O^+ , and Na^+ positive ions and free electrons $n_e(t)$, the ionization rate $W_{ionization}(t)$ and the concentration of free electrons experimentally measured by the microwave interferometer are presented in Fig. 4a. Initially, CHO^+ ions are formed, but because of rapid ion charge exchange the H_3O^+ ions are formed whose concentration sufficiently exceeds the concentration of CHO^+ ions. The contribution of the Na+ ions, formed from NaCl (a possible contaminant in shock tube experiments), becomes apparent at longer times, when the chemical ionization rate tends to zero. At the maximum, the electron concentration practically coincides with the concentration of H_3O^+ ions, which further decreases due to consumption of CH radicals and mainly because of recombination reaction (reaction 3 in Table 1). As this takes place, the concentration of Na⁺ ions gradually increases. The sum of H_3O^+ and Na⁺ concentrations is equal to the concentration of free electrons, which time dependence practically coincides with the experimentally increases.

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The calculated concentration profiles of some neutral species important for chemical ionization process (reaction 1 in Table 1) such as O_2 , O, CH_4 , CH_3 , CH_2 , and CH and the time dependence of ionization rate $W_{\text{ionization}}(t)$, which is a product of the rate coefficient of reaction (1) and the concentrations of O and CH radicals are demonstrated in Fig. 4b. The concentrations of CH_3 , CH_2 , and CH radicals successively reach their maximum values. The maximum of the ionization rate is reached soon after the maximum of the concentration of CH radicals.



Figure 3. Experimentally measured by a microwave interferometer and by an electric probe and calculated concentrations of free electrons for various $C_2H_2/O_2/Ar$ and $CH_4/O_2/Ar$ mixtures: (a) $0.0052C_2H_2 + 0.0243O_2 + 0.9705Ar$ (triangles), $T_{50} = 2057$ K, $P_{50} = 1$ bar, $0.0028C_2H_2 + 0.0126O_2 + 0.9846Ar$ (squares), $T_{50} = 2061$ K, $P_{50} = 1$ bar, (b) $0.0075CH_4 + 0.03O_2 + 0.9625Ar$ (triangles), $0.005CH_4 + 0.02O_2 + 0.975Ar$ (inverted triangles), $0.002CH_4 + 0.008O_2 + 0.99Ar$ (squares), $T_{50} = 2750$ K, $P_{50} = 1$ bar. Black symbols represent the results of measurements by a microwave interferometer, blue triangles represent the results derived from the electric probe measurements, green and red symbols represent the results of detailed kinetic modeling.



Figure 4. Experimentally measured by a microwave interferometer and calculated (a) time histories of the concentration of free electrons and calculated concentration profiles of charged species, ionization rate and (b) some neutral species important for ionization processes for a mixture of $0.005CH_4 + 0.02O_2 + 0.975Ar$, $T_{50} = 2739$ K, $P_{50} = 1$ bar.

At the initial stage of the ionization process, free electrons and positive ions are formed mainly in reaction (1) (reaction 1 in Table 1). The primary CHO^+ ions react rapidly with water molecules (reaction 2 in Table 1). This yields H_3O^+ ions, which are the most abundant at the initial stage of the process. The electron concentration maximum almost coincides in time with, and is approximately equal in magnitude to, the H_3O^+ concentration peak. The maximum electron concentration time nearly coincides with the completion of the chemical conversion of the initial hydrocarbon (acetylene and methane). After passing the maximum, the electron concentration falls to some minimum value due to

recombination process and then begins to increase owing to the continuing ionization of sodium atoms.

5 Conclusions

The results of the numerical calculations of chemical ionization in acetylene and methane oxidation provide a qualitative and for particular conditions even quantitative description for the time variation of the electron concentration. They confirm the existing assumption that the primary ionization event in hydrocarbon combustion is the associative ionization reaction (1). The calculated dependences of the parameters of the electron concentration profile on temperature and on the initial acetylene and methane concentration in the mixture are close to the corresponding experimental dependences.

The secondary increase in the electron concentration is independent of ionization associated with acetylene or methane oxidation, because it begins after these hydrocarbons are completely burnt. It can be stated that the chemical ionization wave, which is characterized by an electron concentration peak, is followed by an impurity ionization wave, which is most likely due to the thermal ionization of sodium.

Since there are some discrepancies between the experimental and calculated characteristics of ionization, the kinetic model of hydrocarbon combustion needs further refinement. Therefore, kinetic studies of combustion-induced ionization are a helpful extra source of information about hydrocarbon combustion and thus contribute to the fundamental knowledge of this process.

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