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Kinetics of Chemical Ionization in Shock Waves: I. Ionization Kinetics in Hydrocarbon Oxidation

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Abstract—An experimental kinetic study of chemical ionization in shock waves in the oxidation of argon-diluted methane, acetylene, and hexane with oxygen is presented. Time-dependent electron concentrations measured using a microwave interferometer, as well as parameters characterizing the electron concentration profiles, are reported. Comparisons are made between the ionization parameters of different hydrocarbons and between the results of this study and data from other works.

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INTRODUCTION

Ionization observed in hydrocarbon (HC) flames is a classical example of chemical ionization. It is classical in the sense that the chemical ionization phenomenon as such was discovered in HC flames and the great majority of mechanistic studies of chemical ionization have been carried out in these flames. It was found that flame ionization exceeds equilibrium ionization by several orders of magnitude and that the ionization maximum falls into the region of the highest heat evolution rate [1, 2]. Therefore, if there is a high ion concentration in the inner cone of the flame, then chemical reactions yielding charged species occur there. These reactions received the name of chemical ionization.

The present-day concepts of the mechanism of chemical ionization in HC flames are based on the following CHO^+ ion formation and subsequent transformation reactions [3, 4]:

$$CH + O \longrightarrow CHO^+ + e^-, \quad \text{(I)}$$

$$CHO^+ + H_2O \longrightarrow H_3O^+ + CO, \quad \text{(II)}$$

$$H_3O^+ + e^- \longrightarrow H_2O + H. \quad \text{(III)}$$

The CHO^+ ion resulting from reaction (I) enters into a fast proton transfer reaction with water (reaction (II)), which is always in abundance in an HC flame. This is why the flame contains a large amount of H_3O^+. According to thermodynamic data [5], reaction (I) is almost thermoneutral ($\Delta H = 4$ kcal/mol). Thus, reaction (I) is considered to be the most likely primary ion-formation reaction.

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 [6].

However, use of shock wave techniques is impeded by the absence of diagnostic equipment necessary for ionization kinetic studies. The choice of methods applicable to kinetic studies in shock waves is quite limited. Most of these methods make use of the conductivity of the plasma appearing behind the shock wave front. Ionization kinetics under unsteady-state conditions behind reflected shock waves was studied using an original modification of the saturation current method [7, 8]. This technique is very sensitive and makes it possible to measure charged particle concentrations down to ~10^4 cm^{-3}. At the same time, its applicability is limited from above by a concentration of ~10^7 cm^{-3}. Thus, although the end saturation technique is a convenient and highly sensitive means to investigate the early stages of ionization [7–9], unfortunately it does not allow measurements to be made for developed ionization.

Another promising plasma conductivity–based method for studies in shock waves is the electric probe method. Probe theory for quiescent, steady-state, “chemically frozen” plasma has been developed quite well. The probe has been used successfully in the investigation of chemical ionization under steady-state flame conditions [10, 11]. For unsteady-state plasma in which chemical ionization reactions take place, there was no probe theory until studies by Aravin et al. [12] and Vlasov [13]. The probe method devised for flames [10, 11] was used in experimental measurements of the time-dependent ion concentration in shock waves [14]. Very high charged particle concentrations were thus measured, which exceeded the concentrations typical of flames by two orders of magnitude. This was a consequence of the incorrect application of the probe tech-

Mixture compositions and temperatures examined in the study of ionization kinetics

Hydrocarbon	Entry	[HC], %	$[O_2]$, %	T, K	α
CH_4	1	0.20	0.80	2500–3000	2.00
	2	0.50	1.50	1980–3100	1.50
	3	0.50	2.00	2170–3140	2.00
	4	0.75	3.00	2200–2850	2.00
C_2H_2	5	0.26	0.74	1670–2970	1.14
	6	0.27	0.67	1540–2810	0.99
	7	0.28	1.26	1250–2910	1.80
	8	0.27	1.40	2220–3070	2.07
	9	0.51	1.64	1540–2930	1.29
	10	0.52	2.43	1340–2530	1.87
C_6H_{14}	11	0.15	0.80	1630–3250	0.56
	12	0.19	1.92	1820–2800	1.06

nique (which was intended for, and calibrated under, steady-state flame conditions) to the essentially nonstationary process behind the reflected shock wave.

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. There has been a study in which the kinetic simulation of chemical ionization in methane oxidation in shock waves was based on electron concentration profile measurements using a microwave interferometer [15].

Here, we report the results of our experimental kinetic study of chemical ionization using a microwave interferometer. This study was undertaken to continue the investigation reported in [15]. It has augmented the data array available on ionization in methane oxidation and has provided ionization data for acetylene–oxygen and hexane–oxygen mixtures.

EXPERIMENTAL

Measurements were made in argon-diluted hydrocarbon–oxygen mixtures behind reflected shock waves in a shock tube as described in [9]. The thermodynamic parameters of the mixtures behind the reflected shock wave front were derived from incident shock wave velocity data in the one-dimensional shock tube approximation using reference data [16]. The error in the gas temperature and pressure data was no larger than 1.5 and 5%, respectively. The compositions used in the study of ionization kinetics are listed in the table. For each mixture, we specify the measurement temperature range and the oxygen excess factor (α). The gas pressure behind the reflected shock wave was 760 ± 150 Torr in all runs.

We measured the electron concentration as a function of time, $n_e(t)$, using a microwave interferometer with a double-wire line as the probe. Double-wire lines are known to afford a high space resolution of 3–5 mm [17]. The error in the measured electron concentration did not exceed ±30%. A description of the interferometer is presented elsewhere [15, 18].

RESULTS

Figure 1 shows experimental time profiles of the electron concentration for mixtures based on methane (entry 2 in the table), acetylene (entry 5), and hexane (entry 12) at similar temperatures. The electron concentration profiles for these HCs are similar in shape. An increase in the electron concentration begins after some

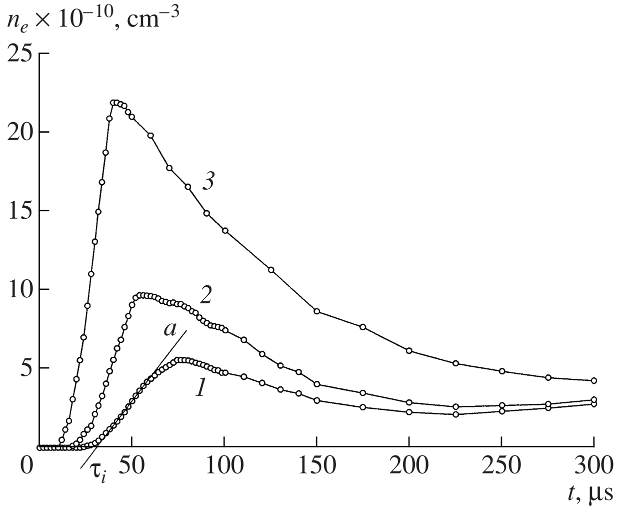

Fig. 1. Time profiles of the electron concentration in hydrocarbon oxidation: (*1*) methane, mixture 2, T = 2525 K; (*2*) acetylene, mixture 5, T = 2540 K; (*3*) hexane, mixture 12, T = 2515 K.

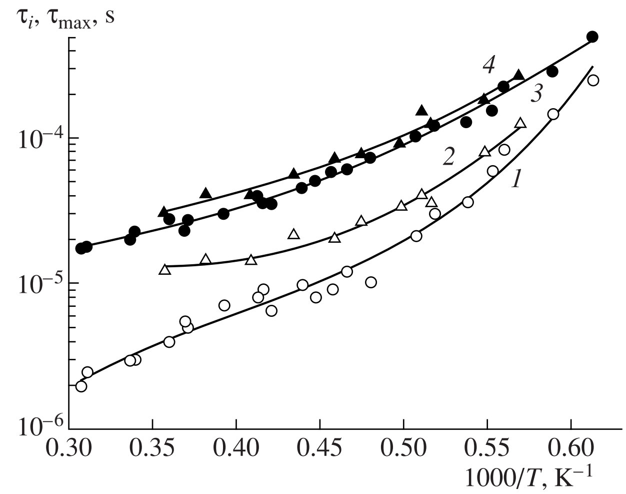

Fig. 2. Temperature dependences of the characteristic times (*1*, *2*) τ_i and (*3*, *4*) τ_{max} for ionization in hexane–oxygen mixtures (*1*, *3*) 11 and (*2*, *4*) 12.

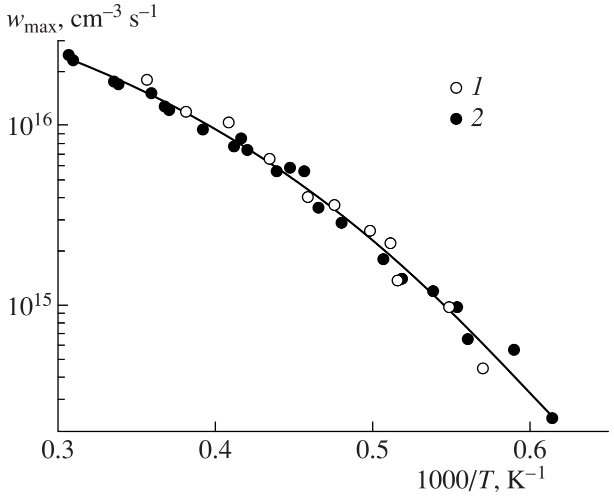

Fig. 3. Temperature dependences of the ionization rate for hexane–oxygen mixtures (*1*) 11 and (*2*) 12.

delay, which is followed by an *S*-shaped ascending portion, after which the electron concentration passes through a maximum and then falls off. The electron concentration does not reach zero, but passes through a minimum and then gradually rises at $t > 200$ μs.

Up to their peak point, such electron concentration profiles are conveniently characterized by the following parameters: the maximum ionization rate (w_{max}) derived from the maximum slope of the electron concentration curve as shown in Fig. 1 (straight line *a*), induction time (τ_i) determined as the intersection point between the line *a* and the time axis, maximum-concentration time (τ_{max}), and maximum electron concentration (n_{max}). For correct comparison of data obtained for different HCs, it is expedient to use, in place of the maximum electron concentration, the maximum electron yield per carbon atom of the HC, $\eta_{max} = n_{max}/xn^0_{C_xH_y}$, where $n^0_{C_xH_y}$ is the initial HC concentration in the mixture behind the reflected shock wave and *x* and *y* are the numbers of carbon and hydrogen atoms in the HC. Below, we will consider the experimental temperature dependences of these parameters.

The following relationships for the ionization profile parameters measured for methane mixtures were obtained by regression analysis:

$$\tau_i = 1.26 \times 10^{-2}(n^0_{CH_4})^{-0.4}\exp(43200/RT), \qquad (1)$$

$$\tau_{max} = 0.48(n^0_{CH_4})^{-0.4}\exp(29900/RT), \qquad (2)$$

$$w_{max} = 1.01 \times 10^{6}(n^0_{CH_4})^{1.5}\exp(-34500/RT), \qquad (3)$$

$$\eta_{max} = 3.38 \times 10^{2}(n^0_{CH_4})^{-0.4}\exp(-17000/RT). \qquad (4)$$

The experimental time profiles of the electron concentration for acetylene oxidation were subjected to regression analysis in the same way as in the case of methane oxidation. We obtained the following expressions relating the electron concentration profile parameters to the initial acetylene concentration and temperature:

$$\tau_i = 3.94 \times 10^{6}(n^0_{C_2H_2})^{-0.8}\exp(19500/RT), \qquad (5)$$

$$\tau_{max} = 2.19 \times 10^{7}(n^0_{C_2H_2})^{-0.8}\exp(15600/RT), \qquad (6)$$

$$w_{max} = 1.05 \times 10^{9}(n^0_{C_2H_2})^{1.65}\exp(-2400/RT), \qquad (7)$$

$$\eta_{max} = 9.33 \times 10^{-5}\exp(-13250/RT). \qquad (8)$$

The ionization kinetics in hexane oxidation was studied only for two mixtures with similar hexane concentrations and different oxygen concentrations (table, entries 11, 12). For this reason, we did not do any analysis to relate the electron concentration profile parameters to the HC concentration in this case. One of the mixtures was rich (entry 11) and the other was stoichiometric (entry 12). By contrast, among the methane and acetylene mixtures, one was stoichiometric (entry 6) and the others were lean. Figures 2–4 plot the electron concentration profile parameters derived from experimental data as a function of temperature for the hexane–oxygen mixtures. In Fig. 4, the electron yield data observed for hexane–oxygen mixtures are compared with the same data obtained for a methane mixture (entry 2) and an acetylene mixture (entry 9). It can be seen in Fig. 2 that the Arrhenius plots of the characteristic times τ_i and τ_{max} and the ionization rate are essentially nonlinear. On passing from rich mixture 11 to stoichiometric mixture 12, the induction period of ionization lengthens several times, while τ_{max} increases by at

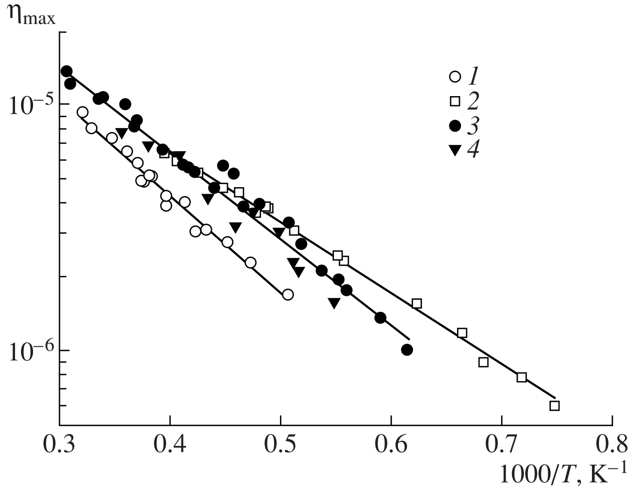

Fig. 4. Temperature dependences of the electron yield for ionization in hydrocarbon–oxygen mixtures: (*1*) methane mixture 2, (*2*) acetylene mixture 9, (*3*) hexane mixture 11, and (*4*) hexane mixture 12.

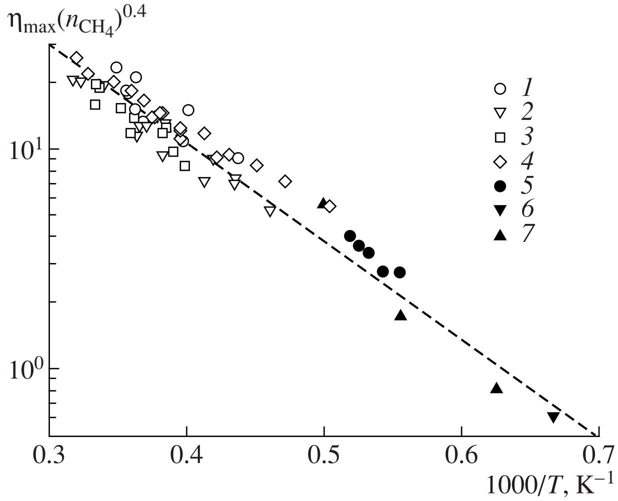

Fig. 5. Temperature dependences of the electron yield for ionization in methane–oxygen mixtures (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4. Data from other studies: (*5*) [14], (*6*) [21], and (*7*) [22]. The dashed line represents the data calculated using relationship (4).

most 25% and the ionization rate (Fig. 3) and the electron yield (Fig. 4) are indifferent to the change in the mixture composition. Note also that, above ~2000 K, the temperature dependences of the electron yield in hexane and acetylene oxidation almost coincide and the electron yield in methane oxidation is much lower (Fig. 4).

DISCUSSION

The induction time, ionization rate, and the maximum electron concentration vary with the HC concentration in the mixture. Therefore, ionization in these experiments is due to the conversion of components of the working mixture and uncontrollable permanent impurities from the atmosphere; the tube walls and oil pumps play no significant role at the initial stage of the process. At later stages, the ionization of impurities likely does come into play. This is indicated by the fact that the secondary rise of the electron concentration is poorly reproducible in replica experiments and, under identical conditions, the $n_e(t)$ spread at $t > 200$ μs exceeds 100%, while the average spread of n_{max} is 15%. Impurities can exert some effect on ionization in shock tubes, and the strength of this effect is unknown a priori. If special measures are not undertaken, the relative content of impurity sodium chloride in the mixtures examined can be as high as ~10^{-5}–10^{-6} [19]. This component is very significant from the standpoint of ionization because Na has a low ionization potential (5.14 eV). Note that the initial mixture contains NaCl not as a vapor, but as a dispersion of single crystals. However, it was reported that they evaporate even in the incident shock wave [20].

Let us compare the data obtained in this study with data from other works. Wortberg [21] studied ionization in a flat methane–air flame (5.1% CH_4/air) at T = 1500 K and atmospheric pressure. Thus, in that study, as in most of our experiments, α was set to be 2, but the diluent was nitrogen rather than argon and the experiments were conducted at a lower temperature. The maximum concentration of charged particles, which was measured by the probe method (Calcote's technique [10]), was found to be 1.7×10^{10} cm^{-3} and, accordingly, the maximum electron yield was $\eta_{max} = 6.9 \times 10^{-8}$. As is clear from Fig. 5, this result is similar to the result obtained using relationship (4). Figure 5 also presents charged-particle yield data obtained by the saturation current method for $CH_4/O_2/N_2$ flames at α = 2 [22].

Ionization profiles for oxidation in argon-diluted methane–air mixtures (α = 2) behind reflected shock waves were studied by probe and microwave methods in [14, 23, 24]. Experimental conditions were chosen so that the sum of the methane and air partial pressures behind the shock wave was 1 atm. The total mixture pressure was ~3.5 atm. Thus, the methane concentration in these experiments was 5–25 times higher than that in our experiments. The gas temperature was lower (1600–2000 K). Nevertheless, the experimental induction periods of ionization obtained in those studies correlate well with our data (Fig. 6). Figure 6 presents only our data and data from [14]. The dashed line corresponds to relationship (1).

Both the induction period of ionization and the maximum electron yield were measured by the probe method in [14]. The values obtained in that study are much larger than those predicted by relationship (4) for the same conditions. However, it was reported in the same work that microwave measurements of the electron concentration under the same conditions lead to

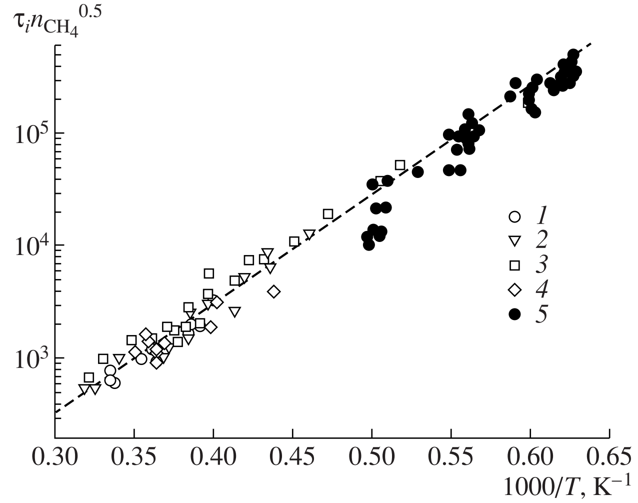

Fig. 6. Temperature dependences of the induction period for ionization in methane–oxygen mixtures (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4. (*5*) Data from [14]. The dashed line represents the data calculated using relationship (1).

electron yields 40–50 times lower. Unfortunately, this claim was not illustrated by particular data. The observed discrepancies were explained under the assumption that the electrons diffuse from the observation region owing to their high diffusion coefficient. Hence, it was inferred that the electron concentration profiles measured by the microwave method do not account correctly for the formation of charged particles, and later the authors relied only on the ion concentrations measured by the probe method. Note, however, that electrons diffuse together with ions, not separately, so ambipolar diffusion takes place. Therefore, the above explanation for the observed discrepancies cannot be regarded as substantiated. A more plausible explanation is that the probe measurements were interpreted incorrectly by the authors (as was mentioned in the introduction). Therefore, there is no reason to cast doubt on the microwave data. If the maximum electron yields reported in those works are divided by 50 (this is the factor by which the electron yields obtained by the microwave method are lower than those obtained by the probe method), the resulting values will be in satisfactory agreement with relationship (4), as is clear from Fig. 5.

Here, it is important to make the following remark concerning the electron concentration measurements under unsteady-state conditions by the probe method. Calcote's technique [10] is widely used in steady-state measurements in flames. It is based on semiempirical considerations and has provided satisfactory results owing to good calibration [11]. It is incorrect to use this technique under conditions that are very different from the calibration conditions (such as in shock waves) without additional testing. Note that, by numerically solving the set of equations describing the operation of the probe under unsteady-state conditions with chemical ionization, it was demonstrated that the probe current is not proportional to the electron concentration in the unperturbed plasma, but is mainly determined by the ionization rate [12, 13]. This deduction was verified by measurements in reflected shock waves. Easy to carry out, probe measurements are a convenient means of investigating ionization processes in shock waves. However, for correct interpretation of the probe signals, it is necessary to use the procedure theoretically substantiated and experimentally tested in [12, 13].

The reliability of the experimental data on ionization kinetics in HC oxidation that were obtained in this study using a microwave interferometer is confirmed by the existence of a correlation with data obtained under other conditions and by other methods [14, 21, 22]. The results of this study are necessary for constructing kinetic models of chemical ionization in hydrocarbon oxidation.

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