

Chemical Ionization in Oxidation of *n*-Hexane and Acetone in Reflected Shock Waves

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1 Introduction

The development of detailed kinetic mechanisms for the ignition of *n*-hexane is largely motivated by its use as a component of surrogate fuels.

The kinetic mechanism of the ignition of all five isomers of *n*-hexane was studied in [1]. In [2], the delay time and the composition of the products (CH₄, C₂H₄, and C₃H₆) were measured for the self-ignition of *n*-hexane/O₂/Ar mixtures at temperatures of $T_5 = 1020\text{--}1725$ K and pressures of $P_5 = 1\text{--}7$ bar. The detailed kinetic model (DKM) included 386 reactions involving 61 components. A satisfactory agreement between the results of calculations and experiments has been achieved.

The development and refinement of the DKM of the combustion of various hydrocarbons needs an extensive kinetic database. In this connection, knowledge of the detailed kinetics of the ignition and combustion of ever more complex hydrocarbons, including alkanes, and of the processes of formation of intermediate components, in particular, acetone is required [3–5].

In addition, acetone is used as a marker in the plane laser-induced fluorescence method (PLIF) [6] and as a promising additive to motor fuels [3]. Note also that acetone plays an important role in atmospheric chemistry, since, like other ketones, it is formed in the atmosphere in appreciable amounts during the oxidation of various hydrocarbons [7, 8].

The combustion of hydrocarbons is known to be accompanied by chemical ionization. Significant efforts have been undertaken to establish that the reaction $\text{CH} + \text{O} = \text{CHO}^+ + \text{e}^-$ is the main source of primary ions and free electrons in lean and stoichiometric flames [9, 10], although other reactions can

contribute as well. The rate constant of this reaction was reported to be $k = 2.53 \cdot 10^{11} \text{ cm}^3/(\text{mol}\cdot\text{s})$ in [10, 12].

Our experiments [13, 14] demonstrated that the processes of chemical ionization and chemiluminescence closely correlate with each other. The maxima of the chemiluminescent emission from electronically excited OH* radicals practically coincide with the maxima of the ionization current measured with an electric probe under negative potential. Therefore, chemiionization current, along with OH* chemiluminescent can be used to measure the self-ignition delay time.

The goal of the present work was to experimentally study the kinetics of chemical ionization during the oxidation of mixtures of acetone (CH_3COCH_3) and *n*-hexane ($n\text{-C}_6\text{H}_{14}$) with oxygen diluted with argon behind reflected shock waves and to construct a unified kinetic model of the chemical ionization process based on these experimental measurements and the published results on chemical ionization during the oxidation of methane and acetylene.

2 Experimental

The experimental setup was described in detail elsewhere [15]. 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 light-proof containers. To maintain a nearly constant temperature behind reflected shock wave, the test mixtures were highly diluted with argon. The mixtures were prepared from analytical-grade acetone, analytical-grade *n*-hexane, 99.9% pure oxygen, and 99.998% pure argon.

The gas parameters behind the incident and reflected shock waves were calculated from the initial pressure, the composition of the test mixture, and the velocity of the incident shock wave within the framework of the theory of an ideal flow shock tube [16]. The incident shock wave velocity was measured over two intervals between three pressure sensors. The driver gas was helium.

The emission signals from electronically excited OH* radicals ($\lambda_1 = 308 \pm 3.0 \text{ nm}$) and the absorption signals of CH₃ radicals ($\lambda_2 = 216.5 \pm 2.0 \text{ nm}$) were recorded through optical windows located 11 mm from the endplate of the shock tube. The required wavelengths were selected with DMR-4 two-prism quartz monochromators, converted into electric signals with FEU-39A photomultipliers, which were fed into GW INSTRON GOS-72074 digital oscilloscope.

Signals from two electric probes with a diameter of 0.1 mm, positioned perpendicular to each other at a distance of several millimeters apart in the same measuring section were also recorded. One of them (with an uninsulated surface) measured the total current, while the second (with an isolated one) measured only the displacement current. The same negative electric potential, -9 V, was applied to both probes.

Electric probe technique is a simple and effective method for studying ionization processes. There are a large number of mathematical models of the operation of electrical probes under various conditions [17–19].

The electric probe technique has been developed mainly for stationary plasma [20, 21] and then was extended to measurements behind shock waves [22, 23].

The total current to the electric probe consists of the conduction current of positive ions, negatively charged electrons (if there are no negative ions) and the Maxwell's displacement current:

$$I = Se(j_i - j_e) - \frac{S}{4\pi e} \cdot \frac{\partial^2 \varphi}{\partial t \partial r}, \quad (1)$$

where S is the surface area of the electric probe, e is the charge of electron, j_i is the conduction current density of positive ions, j_e is the conduction current density of electrons, φ is the electric potential at a given time and at a given point in space, t is time, r is the distance from axis of the cylindrical probe in cylindrical coordinates. The last term in this formula describes the displacement current during the non-stationary process of the formation of a charged layer near the probe surface.

Our analysis of the problem of a cylindrical electric probe under a negative potential in a reacting plasma behind reflected shock waves showed that, in such a medium, the probe current is determined not by the electron concentration, but also by the rate of their formation, i.e., chemical ionization rate [22]. In the quasi-neutral region, the concentrations of ions and electrons are almost equal to each other, with the influence of the electric field being negligible. In this region, the concentration of charged particles is given by

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

where $n_e(t)$ is the concentration of free electrons, $W^{(0)}(t)$ is the ionization rate, α_0 is the dissociative recombination coefficient. Determining $W^{(0)}(t)$ from probe measurements and using the known value of the dissociative recombination coefficient α_0 , one can solve equation (2) numerically and obtain the free electron concentration profile $n_e(t)$.

3 Kinetic Simulations

Kinetic simulations of the chemical ionization process were performed using the detailed kinetic mechanism originally developed to describe the process of soot formation [24] and modified in [25]. This mechanism includes an extensive set of gas-phase reactions, which makes it possible to describe the processes of pyrolysis, ignition, and combustion of mixtures of various simplest hydrocarbons, including *n*-hexane, *n*-heptane, and acetone. This mechanism was supplemented by chemical and thermal ionization reactions, presented in [14, 15]. To simulate the oxidation of *n*-hexane and acetone, our mechanism was supplemented with a set of reactions from [26]. This gas-phase reaction mechanism was extended to include a number of ionization reactions for acetylene and methane oxidation [13, 14].

Special attention was paid to the possible processes of formation and consumption of CH_3 , CH_2 , and CH radicals, as well as oxygen atoms O , which participate in the chemical ionization reaction. The modified mechanism of gas-phase reactions consists of 3787 direct and reverse reactions involving 325 different components, with the rate constants for a number of reactions being pressure-dependent. Kinetic simulation demonstrated that, in general, the reactions responsible for ionization produce no significant effect on the oxidation of the initial hydrocarbon. Under the conditions of our experiments on chemical ionization, the formation of soot particles was not observed.

Recently, a new kinetic mechanism of chemical ionization involving experimentally observed intermediates and positive and negative ions was proposed in [31] for describing the behavior of ions in rich premixed methane flames. The AramcoMech 2.0 $\text{C}_0\text{--C}_4$ mechanism for neutral species was extended to include additional reactions of CH_3^+ and C_3H_3^+ , with the thermodynamic properties of the ions being obtained from detailed quantum chemistry simulations.

In [31], special attention was paid to proportion between H_3O^+ and C_3H_3^+ , dominant ions, experimentally observed in lean, stoichiometric, and rich methane–oxygen–argon flames. These new data motivated us to compare the results of kinetic simulations within the framework of our ionization mechanism and the mechanism from [31] (Fig. 2).

4 Results and Discussion

The predictive capabilities of the developed kinetic mechanism were tested by comparing the experimentally measured and calculated self-ignition delay times for various mixtures of acetone and *n*-hexane with oxygen diluted with argon at different temperatures behind the reflected shock wave (Fig. 1), and also by comparing the time dependencies of the concentrations of H, O, and CO, experimentally measured in [27], with the results of our kinetic calculations [15].

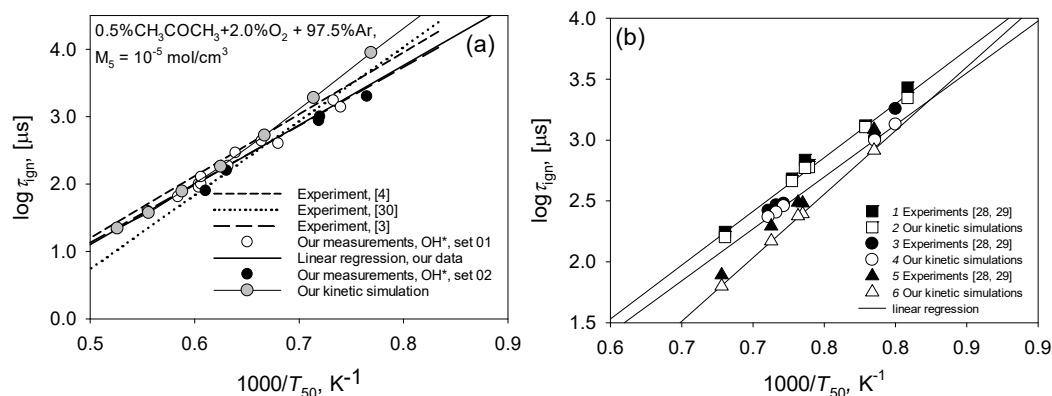


Figure 1. Comparison of experimentally measured and calculated ignition delays for various mixtures of (a) acetone and (b) *n*-hexane with oxygen in argon behind reflected shock waves. For *n*-hexane: (1, 2) 0.42% C₆H₁₄–4.0% O₂–Ar, $p_{50} = 1.76$ –1.93 bar, $\phi = 1$; (3, 4) 0.42% C₆H₁₄–4.0% O₂–Ar, $p_{50} = 3.10$ –3.60 bar, $\phi = 1$; (5, 6) 0.21% C₆H₁₄–4.0% O₂–Ar, $p_{50} = 1.67$ –1.89 bar, $\phi = 0.5$ (closed symbols represent the results of measurements borrowed from [28, 29], whereas the open symbols show the results of simulations within the framework of our kinetic mechanism).

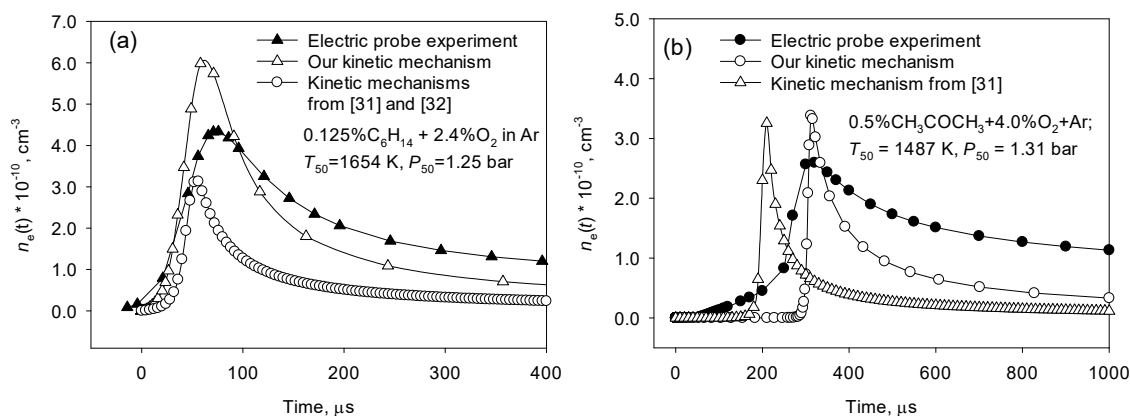


Figure 2. Typical concentration profiles of free electrons obtained from shock-tube experiments as described in [17] and simulated by our detailed kinetic mechanism for (a) *n*-C₆H₁₄–O₂–Ar and (b) CH₃COCH₃–O₂–Ar mixtures. Additional kinetic simulations were carried out using the ionization mechanism developed in [31] and *n*-C₆H₁₄ oxidation mechanism proposed in [32].

Figure 2 shows typical concentration profiles of free electrons obtained from probe measurements [17] and the predictions of our DKM simulations. This figure also displays the results of kinetic

simulations by the ionization mechanism from [31]. As can be seen, the predictions of all the mechanisms tested are in satisfactory agreement with the experimental results.

The reactions $\text{CH} + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{e}^-$ and $\text{CH}^* + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{e}^-$ are expected to produce chemical ionization even in the absence of oxygen. In view of this, in our recent paper [14], we explored the possibility of chemical ionization during the pyrolysis and oxidation of acetylene. The experiments performed in [14] showed that, under the conditions of pyrolysis, the concentration of electrons was below the detection limit. Our kinetic simulations using the mechanism from [31] confirmed this experimental result.

The time dependences of the OH^* chemiluminescence signals are very similar to the time dependences of the total current on the probe; in particular the positions of their maxima practically coincide. This means that until free radicals are formed in the system, no ignition and chemical ionization occur. This is another confirmation of the chemical nature of the observed ionization process.

That the ionization and chemiluminescence signals of electronically excited OH^* radicals exhibit very similar behavior suggests that the electronically excited OH^* radicals and the primary ions CHO^+ have the same precursor. As can be seen from Fig. 3, over the temperature range covered, the process of chemical ionization produces from one to six free electrons per 10^6 carbon atoms. The experiments performed showed that the slope of the temperature dependence of the maximum yield of free electrons practically coincides for methane and *n*-hexane, but is noticeably different from that for acetylene oxidation [14, 15]. In our opinion, this is due to the fact that the chemical ionization rate is determined by the concentration of CH radicals, which is lower in the case of acetylene.

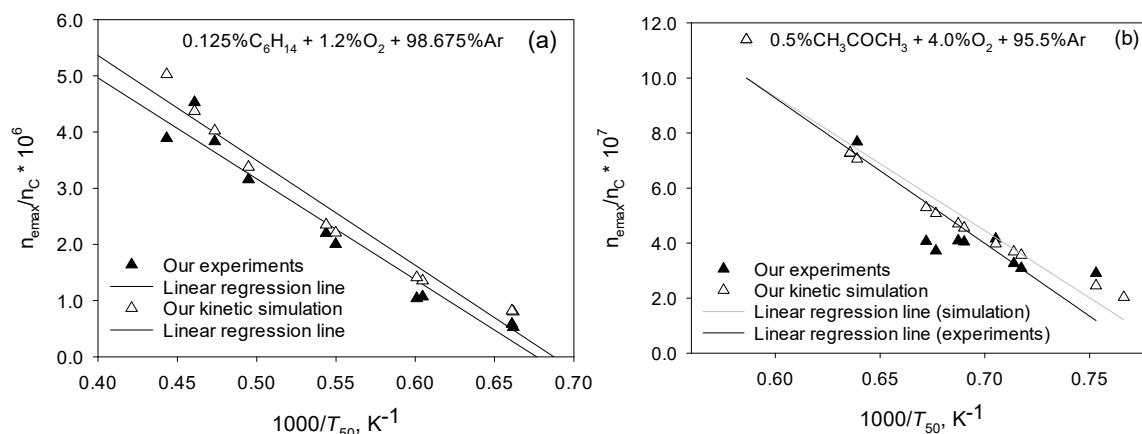


Figure 3. Temperature dependences of the experimentally measured and calculated maximum yield of free electrons per carbon atom in the initial reaction mixture for (a) *n*-hexane and (b) acetone. The closed and opened symbols represent our experimental and simulation results, respectively.

5. Conclusions

New experimental data on chemical ionization during the oxidation of various mixtures of *n*-hexane and acetone with oxygen and argon over a wide temperature range at a pressure of about 1 bar were obtained. A unified detailed kinetic model of the chemical ionization process has been developed, which makes it possible to quantitatively describe the results of experiments on the self-ignition methane, acetylene, *n*-hexane, and acetone mixtures with oxygen. The model makes it possible to improve the kinetic description of the experimental time profiles of the concentration of free electrons for all the hydrocarbons studied at fixed parameters of the detailed kinetic model. The predictive possibilities of the kinetic model were

tested by comparing the simulation results with experimental data on the ignition delays in different mixtures of *n*-hexane, acetone, acetylene, and methane, as well as time profiles of H, O, and CO concentrations measured in reflected shock waves during oxidation of mixtures of acetylene and N₂O in argon. It has been experimentally shown that the process of chemical ionization proceeds only if hydrocarbon and oxygen are present in the reactive mixture. According to our experiments, without oxygen, chemical ionization is not experimentally observed. Given that the peak of chemical ionization current correlates with the chemiluminescence peak, electric probe measurements can be used as a simple and reliable method for measuring the delay time of ignition of hydrocarbon–oxygen mixtures.

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