Kinetic Influence of Small Additives of Fe(CO)₅ on the Ignition of H₂–O₂–Ar Mixtures behind Reflected Shock Waves

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1 Introduction

The study of the self-ignition of hydrogen–air mixtures is of fundamental and practical importance, directly related to the issues of hydrogen explosion safety and the development of new economically viable and environmentally friendly engines and power plants. For practical applications, it is of particular interest to promote or inhibit the process of self-ignition with small additives. It should be borne in mind that nonhomogeneous chemical reactions in the gas phase [1–3] can produce a significant effect on the self-ignition of H_2 – O_2 mixtures. The shock-tube technique makes it possible to eliminate many side factors, being currently the most convenient tool for conducting such studies.

Of great interest is to investigate the effect of small additives of various metal carbonyls on the ignition and combustion of hydrogen–air mixtures behind reflected shock waves. It is known that, on the one hand, iron pentacarbonyl (IPC) promotes the processes of ignition and flame propagation in combustible mixtures, on the other, it was demonstrated to produce an inhibitory effect [4, 5]. A separate problem in experimental studies of the combustion of hydrogen–air mixtures containing gaseous IPC is to examine the condensation of iron atoms and other fragments of $Fe(CO)_5$ decomposition and the influence of this process on the ignition mechanism. It was shown [6] that the pyrolysis of 100 ppm $Fe(CO)_5$ –Ar mixtures at temperatures above 1000 K does not yield any condensation products. Based on the experimental results obtained, the authors of [6] concluded that, with increasing temperature and decreasing concentration of Fe(CO)₅ in the mixture, the intensity of the process of condensation of iron atoms and other fragments.

Detailed kinetic mechanisms (DKMs) of the high-temperature decomposition of IPC have been proposed in [4, 5, 7, 8, 9]. While in [8], a detailed kinetic mechanism including gas-phase reactions of Fe(CO)₅ and its decomposition fragments was developed, in [9] a kinetic model of the condensation of iron atoms and various fragments of Fe(CO)₅ decomposition with the formation of condensed particles was proposed and analyzed in detail. However, the published DKMs cannot explain the kinetic effects of IPC additives on the self-ignition of hydrogen–air mixtures [4]. It should be noted that, except for [10], the self-ignition of H₂–O₂–Ar mixtures containing additives of metal carbonyls in shock waves has not

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been investigated. Based on this, the aim of the present work was to obtain experimental data on the selfignition of H_2 - O_2 -Ar mixtures behind reflected shock waves in the presence of small additives of IPC and to perform numerical simulations in the framework of known kinetic mechanisms.

2 Experimental

The experiments were carried out behind reflected shock waves on a shock tube equipped with pressure sensors and spectroscopic means for recording the absorption and emission of the components under study. The characteristics of the setup are described in detail in [10]. Mixtures of 3% H₂ + 3% O₂ in argon with additions of 100, 300, and 600 ppm Fe(CO)₅ were investigated. The influence of Fe(CO)₅ was studied over a temperature range from 930 to 1515 K. In all experiments, the total concentration of the mixture was approximately constant, $[M_{50}] \approx 10^{-5}$ mol/cm³. The kinetics of the self-ignition process was studied by recording OH* emission at a wavelength of $\lambda = 308 \pm 4$ nm and OH absorption at one of the rotational-vibrational-electronic lines ($\lambda = 306.770$ nm) of the A² $\Sigma^+ \rightarrow X^2\Pi$ transition. The light source for recording the OH absorption signal was a bismuth-filled microwave electrodeless ball lamp excited by a PPBL-3B high-frequency generator. The required wavelengths were selected with DMR-4 double-prism monochromators. The light signals were converted into electric signals using FEU-39A photomultiplier tubes. In separate experiments, IR emission from the water formed was recorded at a wavelength of $\lambda = 1.8 \,\mu\text{m}$.



Figure 1. Oscilloscopic recordings of various signals for the self-ignition of 3% H₂–3% O₂–Ar mixtures (**a**) with 100 *ppm* Fe(CO)₅ and (**b**) without additives. (**a**) $T_{50} = 1116$ K, $P_{50} = 0.907$ atm; (**b**) $T_{50} = 1110$ K, $P_{50} = 0.908$ atm. In panel (**a**): yellow beam, pressure; purple and green, OH* emission at different sensitivities; blue, the ground-state OH absorption. In panel (**b**): yellow beam, pressure; green, OH* emission; violet, the absorption of ground-state OH; blue, the emission of vibrational overtones of the H₂O molecule

Figure 1 shows typical time profiles of the pressure behind the shock wave front, emission of electronically excited OH* radicals, the absorption of OH radicals, and the emission of thermally excited water molecules for similar experiments with mixtures doped (a) and undoped (b) with Fe(CO)₅. Comparison of the signals shows the following. The ignition delay time in the absence of the additive is approximately ~1.5-fold shorter. Note also that the absorption profile of the radical OH changes dramatically in the presence of Fe(CO)₅. While without Fe(CO)₅, the hydroxyl concentration increases, passes through a weakly pronounced maximum and then remains at a quasistationary level, in the presence

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of $Fe(CO)_5$, the OH absorption signal passes through a sharp maximum and then decays to nearly zero. In all experiments, it was found that the maximum concentration of OH in the ignition of hydrogen–oxygen mixtures in the presence of a $Fe(CO)_5$ additive is lower than that without the additive.

3 Kinetic simulation

The DKM for describing the ignition of hydrogen-oxygen mixtures with $Fe(CO)_5$ additives was based on the DKM from Ref. [10]. It was supplemented by the reactions involving $Fe(CO)_5$ from [8] and the initial stages of condensation from [9] with the corresponding thermodynamic data from [8, 9, 11]. All calculations were performed using the CHEMKIN III code [12] under constant volume conditions, V =const.

4 Results and discussion

Since the self-ignition delay time τ for the test mixtures was carried out using various techniques, it was defined as the time interval between the arrival of the reflected shock wave and the characteristic features of the corresponding signals. For the recorded pressure and water emission signals, such features were the moments of the beginning of their growth, for the OH absorption signal, the instant of maximum growth of the OH output, and for the OH* emission, the time it takes to reach the maximum emission intensity. Figure 2 displays the temperature dependences of the ignition delay time for a 3% H_2 -3% O_2 -Ar mixture containing various concentrations of $Fe(CO)_5$ additive. As can be seen in Fig. 2, the inhibitory effect grows with the concentration of Fe(CO)₅ additive. At 100 ppm Fe(CO)₅, the value of τ is essentially the same as for the corresponding undoped mixture, whereas at 300 ppm and 600 ppm, the values of τ are substantially lower, by a factor of three. At the same time, it can be noted that, with increasing temperature, the inhibitory effect of small Fe(CO)₅ additives decreases. Thus, based on Fig. 2, it can be argued that the greatest inhibitory effect occurs at relatively low temperatures, T < 1400 K. Comparison Figs. 2b and 2c shows that the value of τ is almost the same for 300 and 600 ppm Fe(CO)₅ additives. This may be due to the fact that, with increasing concentration of $Fe(CO)_5$ in H₂-O2 mixtures, the fraction condensed iron atoms increases, leading to an increase in the temperature of mixtures during the induction period of ignition.

To gain insights into the kinetic mechanism of the influence of small $Fe(CO)_5$ additives, we performed numerical simulations using the developed DKM. The value of τ corresponding to the OH* luminescence maximum was calculated numerically, since the experimental determination of this characteristic of the self-ignition is straightforward and reliable over the entire temperature range covered. However, as can be seen from Fig. 2, the first direct attempt to describe the observed temperature dependences did not succeed, although the proposed DKM correctly reproduced the general tendency of the influence of small additives of $Fe(CO)_5$. To refine the DKM, a sensitivity analysis of the most important reactions influencing the OH absorption OH* emission profiles was carried out, which showed that it was necessary to modify the rate constants for the reactions

 $Fe + O_2 = FeO + O,$ $FeO + O_2 = FeO_2 + O,$

 $Fe + O_2 + M = FeO_2 + M.$

The values of the rate constants for these reactions were set be equal to those experimentally measured in [7]. Next, it was necessary to increase the value of the reaction rate constant for the reaction $F_{1}O_{1} + M_{2} + F_{2}O_{2} + M_{3}$

 $FeO_2 + H + M = FeOOH + M$

and to reduce the reaction rate constant for

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$FeOH + H = FeO + H_2$.



These modifications provided a better description of the temperature dependence of τ in Fig. 2.

Figure 2. Temperature dependencies of the ignition delay time for 3%H₂-3%O₂-Ar mixtures containing (**a**) 100, (**b**) 300, and (**c**) 600 ppm Fe(CO)₅ (triangles) and without Fe(CO)₅ (0 ppm, circles). The circles represent the results for a reference mixture containing no Fe(CO)₅. The lines represent the results of simulations: (1) without Fe(CO)₅ and (2, 3) with Fe(CO)₅ using the (2) initial and (3) modified mechanisms (see the text)

5 Conclusions

Thus, it has been established that small additives of $Fe(CO)_5$ inhibits the process of ignition of H_2-O_2-Ar mixtures. With increasing temperature and $Fe(CO)_5$ concentration in the H_2-O_2-Ar mixture, the inhibitory effect of $Fe(CO)_5$ additives decreases. The DKM developed in this work made it possible to satisfactorily describe the observed effect of inhibition and to identify the main reactions that determine its kinetics.

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