



The opposite influences of flame suppressants on the ignition of combustible mixtures behind shock waves



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ABSTRACT

The experiments were performed to investigate the influence of the flame suppressants CCl_4 , CF_3H , and $\text{C}_2\text{F}_4\text{Br}_2$ on the ignition of hydrogen–oxygen, acetylene–oxygen and methane–oxygen mixtures behind shock waves. The temperature dependencies of the ignition delay times and temperature profiles in the induction zone were measured. The experiments show that CCl_4 and $\text{C}_2\text{F}_4\text{Br}_2$ inhibit the ignition of hydrogen and acetylene and promote the ignition of methane. The influence of CF_3H on the inhibition is much smaller. A qualitative kinetic analysis suggests that at low temperatures typical for hydrogen and acetylene ignition, the flame suppressants participate in only chain termination reactions inhibiting the ignition. For methane ignition at higher temperatures, the pyrolysis of admixture results in the formation of active radicals, which initiate chain reactions of combustion. The results prove that the chemical stability of the suppressants molecules is essential for successive chemical suppression of ignition under given conditions. The strong inhibiting effect of $\text{C}_2\text{F}_4\text{Br}_2$ on ignition of H_2/O_2 mixtures behind shock waves is notable.

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1. Introduction

Various halogenated hydrocarbons are widely used for fire extinguishing. Their efficiency of combustion suppression is commonly attributed to oxygen replacement and the significant endothermicity of their vaporization and pyrolysis, which rapidly reduces the temperature of the heat source, as well as the chemical inhibition of the chain reactions of combustion. Hastie presented the basic chemical inhibition mechanism several decades ago [1]. That classic work, however, also mentioned an opposite, promoting influence of halogenated species on the ignition in particular conditions. A number of recent works have shown that fluorinated hydrocarbons that are normally considered as flame inhibitors may also accelerate ignition [2–5] and may even be combustible themselves [6]. Experimental studies on the ignition of haloalkane-containing mixtures in a wide range of parameters can support the development of a comprehensive model of pyrolysis and oxidation of haloalkanes and their influence of combustion development. This is also a scientific task for the development of modern fire extinguishing systems and the analysis of industrial risks.

Among the most noticeable and severe hazards are hydrogen explosions during emergency situations at nuclear power plants, which have been responsible for several major catastrophes, such as Fukushima. Also notable are methane explosions in coal mines, which result in numerous deaths annually. Another combustible gas is acetylene, which has not produced large-scale disastrous explosions but is widely used in small burners for welding and cutting. Thus, H_2 , CH_4 , and C_2H_2 were investigated as combustible gases in the present work.

In the development of fire extinguishing agents, the attention given to ecological safety has been increasing. Carbon tetrachloride, also known as Halon-104, was used in the beginning of the twentieth century but was later rejected because of its noticeable toxicity. Lately, other, safer halogenoalkanes, particularly fluorocarbon CF_3H (Freon-23) [7] and 1,2-dibromoperfluoroethane $\text{C}_2\text{F}_4\text{Br}_2$ (Freon-114B2) [8], were considered as agents to prevent the explosion and detonation of combustible mixtures and were widely used in fire-extinguishing system. Nowadays, many halogenated compounds are considered toxic, ozone-depleting gases and are thus forbidden [9]. Furthermore, the actual effectiveness of CF_3H as a detonation suppressant is low [10]. Nevertheless, understanding the inhibition and promotion mechanisms of Halon-104 and Freon-114B2 could still be useful for further studies due to their effective influence on the chain reactions of combustion. Therefore, the goal of this work is to experimentally investigate the influence of

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admixtures of CCl_4 , CF_3H , and $\text{C}_2\text{F}_4\text{Br}_2$ on the ignition of stoichiometric mixtures of H_2/O_2 , CH_4/O_2 , and $\text{C}_2\text{H}_2/\text{O}_2$ behind shock waves.

2. Methods

Experiments were carried out behind reflected shock waves in a stainless steel shock tube of a standard design. The tube has an inner diameter of 50 mm, and the lengths of the high- and low-pressure chambers are 1.5 and 3.5 m, respectively. The investigated section has optical windows and is located at a distance of 13 mm from the end plate. The shock tube was equipped with several PCB113B piezoelectric pressure gauges to measure the incident shock wave velocity with an accuracy $\sim 0.5\%$. The specific values of temperature (T_{RSW}) and pressure (P_{RSW}) of shock-heated flow behind reflected shock wave were derived using a common iteration method based on one-dimensional shock tube theory [11]. High-enthalpy admixture pyrolysis may potentially result in significant attenuation of the reflected shock wave and a subsequent decrease of T_{RSW} . A recent investigation, however, has shown that such effects occur at higher temperatures and are thus negligible under the experimental conditions of the present work [12].

The temperature dependence of the ignition delay time (also known as the induction time) is the key feature of the mixtures investigated. OH radicals are the characteristic species for hydrogen and hydrocarbon combustion. During the experiments, an excited OH^* chemiluminescence signal was recorded by a Hamamatsu H9307-03 photomultiplier module equipped with an interference filter (310 ± 5 nm) to determine the ignition delay times. In combustible mixtures, the energy release in ignition is quite abrupt and leads to a dramatic increase in the OH concentration in both ground and excited states. Thus, a rapid rise in OH^* chemiluminescence was considered as the end of induction time. The exact ignition moment was determined as the intersection of the inflectional tangent line of the OH^* radiation plot with the time axis. The increase in pressure was simultaneously recorded by a pressure gauge. Typical experimental signals of pressure and OH^* emission are presented in the upper plots of Fig. 1.

Temperature measurements provide additional integral parameters and are valuable for kinetic mechanism development and verification of numerical models. The temperature was measured during the induction time by applying the generalized line reversal method on CO_2 band at $2.7 \mu\text{m}$. This method is based on the si-

multaneous detection of the emission and absorption of the reactive mixture at the same wavelength. The principal optical scheme of the diagnostic method is described elsewhere [13]. The main advantage of this method is that it requires only a calibrated light source, and it requires no knowledge of either the optical properties of the observable reaction mixture or the spectral sensitivity of the detection system.

The measurements were carried out using two identical optical channels that focus the light from the probe region via a pair of the calcium fluoride windows installed in a horizontal plane of the shock tube, as well as lenses on two IR detectors (Hamamatsu InSn P5968-200) equipped with C4159-04 amplifiers. The first channel registered the emission only, while the second channel was exposed to radiation from the black body calibration source (M335 Lumasense Technologies), which was used as a reference light source of known temperature to detect the combination of absorption and emission of the mixture. The spatial resolution of the detection system was 3 mm, which results in a time resolution of about $10 \mu\text{s}$.

Based on Lambert–Beer’s and Kirchoff’s laws, the expression for the temperature determination is [11]:

$$T(t) = \frac{hc}{\lambda k_B} \left\{ \ln \left[1 + \left(\exp \left(\frac{hc}{\lambda k T_0} \right) - 1 \right) \left(1 - \frac{I_a(t) - I_0}{I_e(t)} \right) \right] \right\}^{-1} \quad (1)$$

where h is Planck’s constant, c is the speed of light, λ is the diagnostic wavelength, k_B is Boltzmann’s constant, T_0 is the temperature of the reference source, and I_a , I_e , and I_0 are the intensities of the emission+absorption signal, the emission signal, and the incoming intensity of radiation of the reference source, respectively.

The accuracy of the method is determined by the relation between the temperature of the reference source and the measured temperature, as well as the signal/noise ratio. The reference source temperature was varied from 1170 to 1375 K, so the main ambiguity was caused by the signal/noise ratio at the two measurement channels. The measurement error increased from an average value of 4.5% for mixtures with methane and ignition temperatures of 1550–1700 K to 9.5% for mixtures with hydrogen at temperatures of 1000–1150 K. The lower plots in Fig. 1 show typical emission signals and emission+absorption signals, as well as the temperature profile obtained from the analysis.

Kinetic modeling was performed using ChemKin software [14] and thermodynamical data [15]. Since in the induction zone the typical rates of chemical reactions are much lower than the characteristic rates of gas dynamic processes behind a reflected shock wave, thus the classic approximation of a constant pressure reactor [11] was applied. Calculations performed with a time-step of $0.5 \mu\text{s}$ provided the time profiles of the concentrations of the investigated species. The ignition delay time was determined using the moment of rapid increase in OH concentration.

3. Test and reference experiments and modeling

Test temperature measurements were carried out in a non-reactive mixture containing 5% CO_2 in argon. Figure 2 presents the obtained dependence of the measured temperature T_{meas} on the calculated temperature behind the reflected shock wave. The two types of dots represent the two possible choices of emission and emission-absorption channels. No dependence on the selected configurations was observed (thus proving that the channels are identical), and the measured values agree quite well with the calculations (the line in Fig. 2).

A typical temperature profile obtained during the induction time in combustible mixtures is presented in Fig. 1. Similarly to the non-reactive mixtures, there is good agreement between the

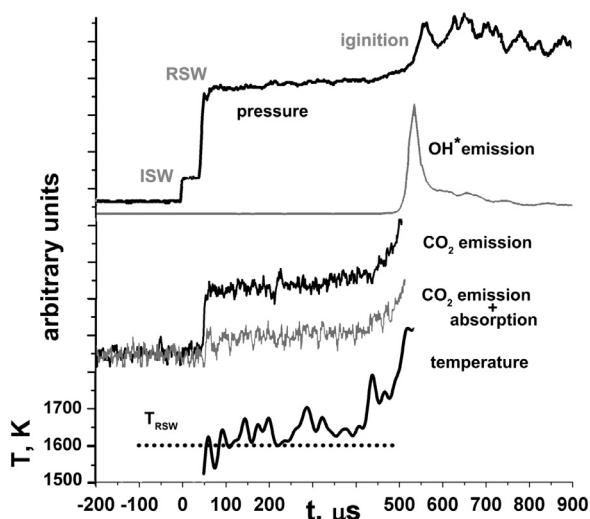


Fig. 1. Typical experimental signals and temperature profile obtained in the mixture $3.3\% \text{CH}_4 + 6.7\% \text{O}_2 + 5\% \text{CO}_2 + \text{Ar}$.

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