

Experimental study of chemiluminescence in UV and VIS range at hydrogen-oxygen mixtures ignition

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Abstract. The nonequilibrium radiation in the spectral range of 210-415 nm at ignition of a 10% stoichiometric hydrogen-oxygen mixture with additives of combustion inhibitors diluted with argon behind shock waves was registered. The detected chemiluminescence is presumably attributed to electronically excited H_2O^* and H_2O_2^* . Instead of the expected quenching of excited radicals and molecules in the ignition zone, with the addition of halogenated hydrocarbons inhibitors, the increase of radiation, particularly in the range of 330-415 nm, was observed. The possible reasons of this phenomenon are discussed.

1 Introduction

It is well known that the zone of ignition of hydrogen-oxygen mixtures is accompanied by the intense UV emission, usually attributed to excited OH^* radicals. At the same time the other electronically excited radicals and molecules (HO_2^* , H_2O^* , H_2O_2^*) can make an important contribution to the observed emission spectra [1-4]. It is assumed that the intensity of overequilibrium emission at ignition is an indicator of the rate of development of the ignition process. Therefore, when studying extremely topical problems of inhibiting the ignition of hydrogen, recording of nonequilibrium UV emission is usually one of the main diagnostic methods. In previous works [5, 6], it was shown that halogenated hydrocarbons are the effective inhibitors of hydrogen ignition and substantially increase the ignition delay times of hydrogen-oxygen mixtures behind shock waves. In a recent paper [7] it was suggested that the one of the possible inhibition mechanisms is the resonance quenching of excited states of active radicals, in particular, the peroxy radical HO_2^* , which plays a key role in chain branching upon ignition of hydrogen-oxygen mixtures $\text{H} + \text{O}_2 \rightarrow \text{HO}_2^* \rightarrow \text{O} + \text{OH}$, $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ [8, 9], in collisions with molecules of inhibitors.

Therefore, the goal of this work is to analyse the effect of halogen-containing combustion inhibitors (CCl_4 , $\text{C}_2\text{F}_4\text{Br}_2$) addition, which effect on hydrogen ignition was previously studied in detail by the authors [5, 6], as well as inert CO_2 addition, on the level of nonequilibrium UV radiation in spectral range from 210 up to 415 nm at ignition of

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stoichiometric hydrogen-oxygen mixture with additives of combustion inhibitors behind shock waves.

2 Experimental

The experiments were carried out in a standard shock tube equipped with modern optical diagnostic methods. The ignition behind the reflected shock wave was detected with the use of piezoelectric pressure sensors, as well as nonequilibrium radiation was detected with a photomultiplier, at 310 ± 5 nm (which corresponds to the electronic transition of the OH* radical). Spectral emission at wavelengths from 210 up to 415 nm was measured with the help of an Acton Research Cooperation SpectraPro 150 diffraction monochromator and photomultiplier Hamamatsu H6780-04 with spectral resolution of ± 4 nm. The spectral resolution is checked using mercury line measurements. The quantum efficiency of the entire setup is calibrated using a tungsten lamp with a known spectral emissivity. The investigated spectral range is characteristic for the emission of electronically excited radicals and molecules HO₂*, H₂O*, H₂O₂* [10, 11]. The parameters of the mixtures studied, as well as the ranges of temperatures and pressures behind the reflected shock waves, are given in the table 1.

Table 1. The experimental mixtures and parameters.

Mixture title	H ₂ , %	O ₂ , %	CO ₂ , %	CCl ₄ , %	C ₂ F ₄ Br ₂ , %	T, K	p, bar
Mixture1	6.7	3.3	--	--	--	1030-1400	4.3-5.8
Mixture2	6.7	3.3	10	--	--	1045-1300	4.3-5.5
Mixture3	6.7	3.3	--	2	--	1180-1400	4.3-4.4
Mixture4	6.7	3.3	--	--	1	1130-1400	5.6-5.8

Examples of characteristic oscillograms are presented in Fig. 1 - pressure profiles (a) and nonequilibrium radiation in the 310 nm (b) and 411 nm (c) regions (for another wavelengths the signal is similar), upon ignition of H₂/O₂ mixtures without an inhibitor and with the addition of 2% CCl₄ at similar temperatures behind shock waves. At the moment of ignition, characterized by a sharp rise in pressure, a peak emission signal appears at all wavelengths.

3 Results

It is clearly seen from the Fig.1 the addition of an inhibitor does substantially increase the ignition delay and, at the same time, reduce the intensity of nonequilibrium emission of the OH* radical at 310 nm. However, in the region of 411 nm, on the contrary, there is a significant increase in nonequilibrium emission.

Similar oscillograms were obtained in all the mixtures studied at different temperatures from 1050 to 1400 K. In additional series of experiments the absorption of intense radiation from a gas discharge lamp DKSSh-150 (having a brightness temperature of about 4000 K in these spectral regions) against a background of the signal was measured. Additional

emission was detected from the source, which indicated a highly super-equilibrium character of the observed emission, with an effective excitation temperature above the brightness temperature of the source.

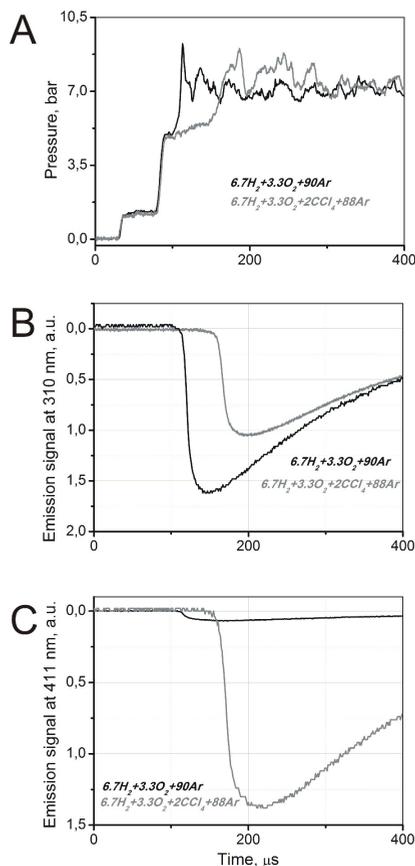


Fig. 1. Characteristic oscillograms of pressure profiles (a), and nonequilibrium radiation at 310 nm (b) and 411 nm (c) regions, at ignition of H_2/O_2 mixtures without an inhibitor ($p_5 = 5.2$ atm, $T_5 = 1215$ K) and with 2% CCl_4 ($p_5 = 5$ atm, $T_5 = 1250$ K).

The spectral dependencies of detected nonequilibrium radiation are shown in Fig. 2. It is seen from this figure that at 310 nm, corresponding to the chemiluminescence signal of the OH^* radical, in the temperature range studied, the presence of additives leads to a slight decrease in the observed amplitude of the signal in 2 - 3 times, while at a wavelength of 210 nm, with the addition of CO_2 , the amplitude of the signal did not change, and with the addition of $C_2F_4Br_2$ and CCl_4 , an increase in the signal of emission was observed almost the tenfold. But the most significant increase in nonequilibrium radiation was observed in a spectral range of 330–415 nm, where all additives, including inert CO_2 , led to an almost 20-fold increase in the radiation intensity.

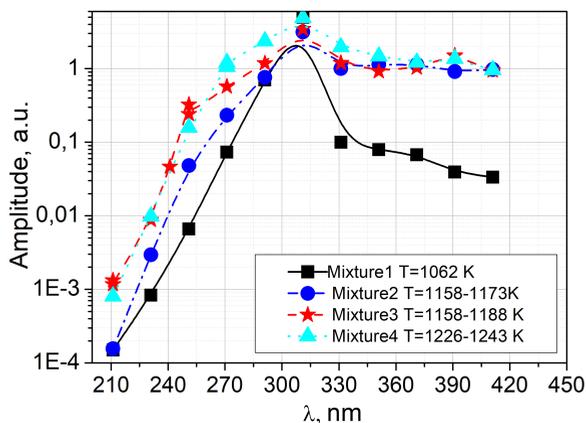


Fig. 2. Nonequilibrium emission spectra detected at ignition of hydrogen-oxygen mixtures.

4 Discussion

To analyse the possible mechanisms of amplification of nonequilibrium UV radiation with the addition of inhibitors to the hydrogen-oxygen mixture, numerical simulation of the kinetics of ignition of the investigated mixtures was carried out using the Chemkin code and kinetic mechanisms proposed in [12] for a hydrogen-oxygen mixture without additives and with the addition of CO_2 , and in a recent paper [5] - for mixtures with CCl_4 additions. Both mechanisms are written in the form of "formal" kinetics, suggesting equilibrium in internal degrees of freedom of molecules. Note that for $\text{C}_2\text{F}_4\text{Br}_2$ no detailed kinetic combustion mechanism has been developed, therefore no numerical simulation has been performed.

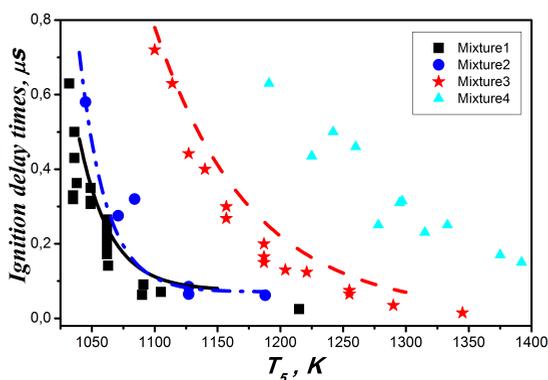


Fig. 3. Temperature dependences of ignition delay times. Points – experimental data, curves – the results of kinetic simulation.

The results of the calculations have shown that the theoretical model describes well the experimentally measured increase in ignition delay times with the addition of inhibitors (see Fig. 3). The addition of the CCl_4 inhibitor leads to a significant decrease in the

maximum concentration of the HO₂ radical (in the ground state) and slightly increases the maximum concentration of hydrogen peroxide H₂O₂. HO₂ is first consumed with addition of inhibitor in the reactions $\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$; $\text{CCl}_3 + \text{HO}_2 \rightarrow \text{COCCl}_2 + \text{Cl} + \text{OH}$ and secondly, it is less formed in the reaction $\text{H} + \text{O}_2(+\text{M}) \rightarrow \text{HO}_2(+\text{M})$ due to consumption of O₂ through the reactions $\text{Cl} + \text{O}_2 = \text{ClO} + \text{O}$; $\text{CCl}_3 + \text{O}_2 = \text{COCl}_2 + \text{ClO}$. Thus, the observed chemiluminescence could hardly be associated with overexcited hydroperoxyl radicals. Hydrogen peroxide and water with addition of inhibitor are formed mainly through reactions $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$; $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}$. The production of OH is in turn connected with atomic hydrogen via $\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$; $\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$, whose formation is promoted by the reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$.

Thus, the observed increase in the intensity of chemiluminescence can be conventionally attributed to an increase in the concentration of electronically excited molecules H₂O₂* or H₂O*, which may indicate a redistribution of the reaction channels, but of course, in any way cannot lead to the observed effect of inhibition.

5 Conclusion

In this study, for the first time, a significant increase in the intensity of nonequilibrium radiation in the range of spectra 210-415 nm at ignition of hydrogen in the presence of inhibiting additions of halogenated hydrocarbons, was experimentally observed. Thus, the assumption of a mechanism for inhibiting the ignition of hydrogen by quenching excited radicals [7] is hardly justified, and the real mechanism of inhibition, as shown in [5, 6], is the capture of the primary radicals by inhibitors.

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