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Experimental study of the emission of electronically excited CH*, C2*, OH*, and CO2* during ignition of hydrocarbons behind reflected shock waves

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Abstract. The autoignition of simple hydrocarbons, such as ethane, ethylene, and acetylene, in mixtures with oxygen diluted with Ar behind reflected shock waves in a temperature range of 1150–1800 K and a pressure of ~ 0.1 MPa is studied using the chemiluminescence from electronically excited CH* (λ = 430 nm), C2* (λ = 516.5 nm), OH* (λ = 308 nm), and CO2* (λ = 363 nm). Our experimental results are in good agreement with the published data obtained under similar conditions. Numerical simulations within the framework of a well-tested kinetic mechanism closely reproduce the measured values of the ignition delay times and time profiles of the emission signals. A comparison of the experimental and calculated shapes of the emission signals made it possible to identify key reactions responsible for the chemiluminescence of the indicated emitters.

1. Introduction
Spectroscopic methods for studying the ignition of hydrocarbon fuels are important for monitoring and study of the combustion process [1]. Among them, the emission recording technique of the combustion products possesses considerably higher sensitivity as compared with the absorption methods. In spite of a vast body of information concerning recording of chemiluminescent emission in flames, the problem of interpretation of emission records remains an urgent question. In the current work, we carried out the experimental and computational studies of the emission of electronically excited CH*, C2*, OH*, CO2* components during ignition of a number of hydrocarbons such as ethane, ethylene, and acetylene in mixtures with oxygen diluted with argon. Based on the comparison of time dependences of the intensity of chemiluminescent emission of these particles, we attempted to reveal chemical reactions responsible for this emission.
2. Experimental results and discussion

The experiments were performed on a shock tube (a stainless steel shock tube, 75 mm inner diameter, 1.5 m length of a driver section, 3.2 m length of a driven section). A driver gas was helium. The shock wave was generated by a spontaneous rupture of an aluminum diaphragm of 0.05–0.1 mm in thickness. Pressure was recorded by piezoceramic pressure transducers (lead zirconate titanate) with the diameter of sensitive element of 1 mm, which were mounted flush with the inner wall of the shock tube. Simultaneous chemiluminescent emission of electronically-excited components CH$^*$ ($\lambda = 430 \pm 3$ nm), C$_2^*$ ($\lambda = 516.5 \pm 3$ nm), OH$^*$ ($\lambda = 308\pm4$ nm), and CO$_2^*$ ($\lambda = 363 \pm 10$ nm) was recorded.

The spectral ranges mentioned above were separated with the help of DMR-4 monochromators for CH$^*$, C$_2^*$, OH$^*$, and an interference filter for CO$_2^*$. Photomultipliers FEU-39A were used to record the emission of CH$^*$, C$_2^*$, and OH$^*$ and a photomultiplier FEU-51 was used to record the emission of CO$_2^*$. All experiments were conducted behind reflected shock waves that made it possible to record the emission of electronically-excited components in a quiescent buffer gas. In all experiments the stoichiometric mixtures were used: 0.5% C$_2$H$_4$ + 1.25% O$_2$, 0.5% C$_2$H$_4$ + 1.5% O$_2$ and 0.5% C$_2$H$_6$ + 1.75% O$_2$. A dilution gas was argon. The experiments were carried out for the total mixture density $M$ = 1 x $10^{-5}$ mol/cm$^3$ within the temperature range of 1150–1800 K. The numerical modeling was conducted with the help of CHEMKIN-III software [2] under assumption of constant volume ($V = $ const).

Typical oscillograph records of the emission of all three mixtures under study are presented in figures 1–3. As can be seen from figures 1–3, for all three hydrocarbons the emission profiles demonstrate a more complex character. Such behavior of the emission signal of OH$^*$ for ethane demonstrates a more complex character. Such behavior of the emission signal of OH$^*$ both for ethane and methane was also observed in [3].

To reveal the kinetics of emission signals of the emitters recorded we performed the numerical modeling of the emission profiles for each of them. For this, first, all possible chemical reactions were selected, which according to their energetic characteristics are capable to excite CH$^*$, C$_2^*$, OH$^*$, and CO$_2^*$ within the corresponding wavelength registration ranges. In our kinetic calculations the thermodynamic data borrowed from [5] were used. The final results of selection of such reactions are presented in the table 1 for each of the emitters.

It should be emphasized that particular chemical reactions are capable to generate different emitters in excited states. For example, as can be seen from table 1, reaction C$_2$H + O$_2$ = CH + CO$_2$ can serve as a source of both CH$^*$ and CO$_2^*$. The analysis of possible contributions into the excitation of corresponding particles of each of the reactions presented in table 1 was carried out within the framework of a unique kinetic mechanism [4]. To model chemiluminescence, it was suggested that a fast quasi-stationary concentration of a particular emitter is settled and extinction of its excited state proceeds very fast [6]. In this case, the emission signal from reaction

$$A + B \rightarrow C^* + D$$

can be represented as

$$I_e(C^*) = R_C A_C \times [A][B],$$

(1)

where $I_e(C^*)$ is the emission intensity of C$^*$, $R_C$ is the radiation constant, $A_C$ is a factor that is proportional to the apparatus constant (sensitivity of the detection system) and inversely proportional to the sum of the rates of radiative quenching, collisional quenching, and removal
in reactions. Since the rate of collisional quenching by argon dominates, because of its great excess, the total rate of removal of the electronically excited species can be considered constant, so the emission signal $I_e(C^*)$ is proportional to the product $[A][B]$. This assumption was checked numerically for the mixtures of hydrogen with oxygen where the only possible channel of OH$^*$ formation is the following reaction (see table 1):

$$O + H \rightarrow OH^*.$$  

The profiles of OH$^*$(t) in relative units, calculated by formula (1), completely coincide with the corresponding time profiles of OH$^*$, obtained numerically from the kinetic mechanism borrowed from [4], which was expanded by a set of reactions with participation of OH$^*$ borrowed from [7]. Such interpretation of the analysis of emission signals makes it possible to determine by formula (1) the contribution of each channel in the formation of the emission signals of CH$^*$, C$_2$, OH$^*$, and CO$_2$. 

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**Figure 1.** Experimental time dependences of the emission signals of C$_2^*$, CH$^*$, CO$_2^*$, OH$^*$ for a 0.5% C$_2$H$_2$ + 1.25% O$_2$ mixture in Ar and the corresponding chemiluminescence profiles calculated by the kinetic mechanism borrowed from [4] for $T_5 = 1735$ K and $P_5 = 0.152$ MPa.
Figure 2. Experimental time dependences of the emission signals of $C_2^*$, $CH^*$, $CO_2^*$, $OH^*$ for a 0.5\% $C_2H_4 + 1.5\% O_2$ mixture in Ar and the corresponding chemiluminescence profiles calculated by the kinetic mechanism borrowed from [4] for $T_5 = 1679$ K and $P_5 = 0.132$ MPa.

The kinetic profiles of the emission signals for each of the emitters recorded for ignition of all three hydrocarbons studied, which were calculated with the help of the kinetic scheme borrowed from [4] by formula (1) are shown in figures 1–3. The following conclusions can be made from the comparison of calculated and experimentally observed emission profiles presented in figures 1–3. For emission signal of $C_2^*$ only a single reaction $C + C$ has different kinetics of behavior of $C_2^*$ as compared with the experimentally observed one for all three hydrocarbons. However, this reaction can also give its contribution to the formation of chemiluminescence signal of $C_2^*$ at the stages after the maximum was attained.

For chemiluminescence signal of $CH^*$ only two reactions of atomic and molecular oxygen with $C_2H$ are suitable. The profiles, obtained during the ignition of a $C_2H_2 + O_2$ mixture, are most informative for this. Situation with the choice of reactions for $CO_2^*$ is much more complicated. It should be emphasized that the emission signal of $CO_2^*$ does not decay up to zero. Thus, the first reaction in table 1 for $CO_2^*$ most probably determines this quasi-equilibrium emission at the late stages of burnout of the hydrocarbon mixtures. The reactions $C_2H + O_2$ and $CH + O_2$
Figure 3. Experimental time dependences of the emission signals of $C_2^*$, $CH^*$, $CO_2^*$, $OH^*$ for a 0.5% $C_2H_6 + 1.75% O_2$ mixture in Ar and the corresponding chemiluminescence profiles calculated by the kinetic mechanism borrowed from [4] for $T_5 = 1730$ K and $P_5 = 0.142$ MPa.

describe quite well the emission profile and the position of emission maximum of $CO_2^*$ for all three hydrocarbons. The emission profiles of $OH^*$ (the emission rise up to the maximum and the following decay) are described for all three hydrocarbons by reactions of CH with $O_2$ and $HO_2$.

However, it should be noted that a complex character of the kinetics of emission increase of $OH^*$ up to the moment when the maximum is attained for ethane ignition can be explained by the influence of reaction $HCO + O_2$ (figure 3). In the case of ignition of acetylene and ethylene this reaction does not manifest itself by such a way and it behaves with time similar to reactions $CH + O_2$ and $CH + HO_2$. The analysis conducted shows that various hydrocarbon molecules in mixtures with oxygen make it possible to reveal from the comparison of calculated and experimentally observed emission profiles of $CH^*$, $C_2^*$, $OH^*$, and $CO_2^*$ the additional channels of chemical reactions capable to explain the kinetics of chemiluminescence signals and also to determine their contribution to the electronic excitation of the emitting particles.
### Table 1. Possible reactions of chemiluminescence excitation

| Emitter | Reaction | $\Delta H_{298}$, kcal/mol | Assessed possibility |
|---------|----------|-----------------------------|----------------------|
| C$_2^*$: $\lambda = 516.5$ nm ($E = 56$ kcal/mol) | CH + C = C$_2^*$ + H | $-67.4$ | + |
|         | C + C = C$_2^*$ | $-147$ | + |
|         | CH + CH = C$_2^*$ + H | $-89$ | + |
|         | CH$_2$ + C = C$_2^*$ + H$_2$ | $-55$ | + |
| CH$_2^*$: $\lambda = 429$ nm ($E = 67$ kcal/mol) | C$_2$ + OH = CH$_2^*$ + CO | $-88.3$ | - |
|         | C$_2$H + O = CH$_2^*$ + CO | $-79.6$ | + |
|         | C + C = CH$_2^*$ | $-147$ | - |
|         | C$_2$H + O$_2$ = CH$_2^*$ + CO$_2$ | $-87.7$ | + |
|         | C$_2$ + HO$_2$ = CH$_2^*$ + CO$_2$ | $-151$ | - |
| OH$_2^*$: $\lambda = 308$ nm ($E = 93$ kcal/mol) | O$_2$ + CH = OH$_2^*$ + CO | $-159.5$ | + |
|         | H + HO = OH$_2^*$ | $-101.2$ | + |
|         | CH + HO$_2$ = OH$_2^*$ + HCO | $-126$ | + |
|         | C + HO$_2$ = OH$_2^*$ + CO | $-191.5$ | - |
|         | C$_2$ + HO$_2$ = OH$_2^*$ + C$_2$O | $-119.5$ | - |
| HCO + O$_2$ = OH$_2^*$ + CO$_2$ | $-95.8$ | + |
| CO$_2^*$: $\lambda = 363$ nm ($E = 80$ kcal/mol) | CO + O = CO$_2$ | $-127.8$ | + |
|         | HCO + O$_2$ = OH + CO$_2^*$ | $-95.8$ | - |
|         | C$_2$H + O$_2$ = CH + CO$_2^*$ | $-87.7$ | - |
|         | CH + O$_2$ = H + CO$_2^*$ | $-185.4$ | + |
|         | CH$_2$ + O$_2$ = H$_2$ + CO$_2^*$ | $-170$ | - |
|         | HCO + O = H + CO$_2^*$ | $-114$ | - |
|         | C + HO$_2$ = H + CO$_2^*$ | $-217$ | - |
|         | C$_2$ + HO$_2$ = CH + CO$_2^*$ | $-151$ | - |

Figures 4–6 shows the temperature dependence of the observed ignition delay for the stoichiometric mixtures of acetylene, ethylene, and ethane with oxygen diluted with argon, as determined from the maximum of the chemiluminescence signals and the results of our kinetic calculations by reaction mechanism [4].

For comparison, the data of other authors is also shown, which turned out to be in good agreement with our results. One can see that, in the entire temperature range covered, the time it takes the chemiluminescence signal to reach the maximum emission is practically the same for all the emitters. At the same time, it remains unclear how the maxima of the CH$_2^*$, C$_2^*$, OH$_2^*$, and CO$_2^*$ signals are related to each other for rich and lean mixtures. It is possible that the time profiles of the CH$_2^*$, C$_2^*$, OH$_2^*$, and CO$_2^*$ emissions will differ from each other more significantly, since the chemical reactions that determine the chemiluminescence are sensitive to the fuel-to-oxidizer equivalence ratio and to type of C–C bond in the hydrocarbon. This assumption is indirectly supported by the time profile of the OH$_2^*$ signal, which features a shoulder at a relatively high temperature (figure 3). With decreasing temperature, this shoulder in the OH$_2^*$ time profile for ethane ignition disappears.

Since the rate constants of production of the electronically excited species are unknown, the contributions from the different excitation channels were assessed semi-quantitatively based on the shape, width, and maximum position of each profile. In addition, the enthalpy changes for the
Figure 4. Temperature dependence of the ignition delay time determined from the maximum of the position of the chemiluminescence signal of the indicated emitters for a 0.5% $C_2H_6 + 1.75% O_2 + Ar$ mixture; $[M] \sim 1 \times 10^{-5} \text{ mol/cm}^3$. The black and red symbols represent, respectively, the data of the present work and those from [8]. The results of our kinetic calculations by reaction mechanism [4] are presented by lines.

Figure 5. Temperature dependence of the ignition delay time determined from the maximum of the position of the chemiluminescence signal of the indicated emitters for a 0.5% $C_2H_2 + 1.25% O_2 + Ar$ mixture; $[M] \sim 1 \times 10^{-5} \text{ mol/cm}^3$. The black and red symbols represent the data of the present work and those from [9], respectively. The results of our kinetic calculations by reaction mechanism [4] are presented by lines.
Figure 6. Temperature dependence of the ignition delay time determined from the position of the maximum of the chemiluminescence signal of the indicated emitters for a 0.5% C$_2$H$_4$ + 1.5% O$_2$ + Ar mixture; $\sim 1 \times 10^{-5}$ mol/cm$^3$. The black and red symbols represent the data of the present work and those from [10], respectively. The results of our kinetic calculations by reaction mechanism [4] are presented by lines.

3. Conclusions

- The concurrent monitoring of the emission from the electronically excited molecules and radicals during the ignition of oxygen-hydrocarbon mixtures and comparison with the relevant calculated profiles made it possible to gain insights into the mechanisms of the formation of these excited species.

- Numerical simulations of the time profiles of CH$^*$, C$_2^*$, OH$^*$ and CO$_2^*$ for each experiment enabled to identify the most probable channels of the excitation of these species.

- It was demonstrated that, under certain conditions, OH$^*$ time profiles exhibit a complicated multistage behavior.

- Based on mathematical modeling of the emission time profiles of CH$^*$, C$_2^*$, OH$^*$ and CO$_2^*$ for three different hydrocarbons, ethane, ethylene, and acetylene, differing in the multiplicity of the C–C bond and comparison with experimental measurements over a wide temperature range yielded information on the relative importance of the different channels.

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