Emission of CH* and C₂* during the high-temperature oxidation of propane in reflected shock waves

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Abstract. The autoignition of a stoichiometric propane–oxygen mixture diluted with argon was studied behind reflected shock waves in the temperature range of 1230–1700 K at the total concentration of \([M]_{50} \sim 10^{-5}\) mol/cm³. Emission signals from electronically excited CH* (at \(\lambda = 429\) nm) and C₂* (at \(\lambda = 516\) nm) radicals were recorded. It was found that the CH* and C₂* emission time profiles reached their maxima almost simultaneously over the entire temperature range covered. The temperature dependence of the ignition delay time measured from the time of reaching the maximum by the CH* emission signal was simulated within the framework of several published data kinetic mechanisms. It was found that, at temperatures below 1400 K, all the kinetic models tested predict ignition delay times severalfold longer than that experimentally observed. Using a sensitivity analysis to the reaction rate constants in the induction period, the main reactions that affect the ignition delay time were identified.

1. Introduction
Propane is a simple hydrocarbon fuel; it is of considerable interest for the processes of ignition, combustion and detonation. In addition, as one of the simplest hydrocarbons, propane is widely used as a model fuel for studying the kinetics of the ignition of various hydrocarbons and for constructing detailed kinetic mechanisms [1–6]. Measurements of the ignition delay time of propane make it possible to identify the main chemical channels that determine the rate of oxidation of propane during the induction period. Although the ignition delay time for propane–oxygen–dilutant mixtures has been extensively measured, the discrepancy between the reported experimental data and the results of numerical simulations within the framework of detailed kinetic mechanisms [1,2,4,6,7] remains poorly understood. The availability of a large number of detailed kinetic mechanisms, leading to different numerical simulation results, and a wide scatter in the experimental data significantly complicate the understanding of the kinetics of ignition of hydrocarbon fuels in various technological processes. In this regard, spectrophotometric measurements in combination with numerical simulations of the signal profiles constitute an efficient approach [8,9].
Recording the chemiluminescence signals during the ignition of hydrocarbons in shock tubes is a reliable source of new kinetic information, since it allows experimenting with highly dilute gas mixtures, thereby avoiding the influence of many physicochemical factors [6].

Only a few detailed kinetic mechanisms presented in the literature include reactions involving electronically excited species, largely CH* and OH* [9]. Simulations performed in work [9] demonstrated that CH* and OH* emission signals differ significantly for different kinetic mechanisms and poorly reproduce experimentally measured signals. This motivates obtaining additional kinetic information on the emission of electronically excited species and refining reaction blocks involving these species.

In the present work, we carried out experiments on recording the emission of CH* and C2* and the overall radiation in the visible region of the spectrum (IE) during the ignition of a propane–oxygen mixture behind shock waves. The aim of the work was to analyze the concentration profiles of the indicated emitters, compare the obtained experimental results with the published data, and carry out a numerical simulation of the available experimental data using published kinetic mechanisms involving electronically excited species.

2. Experimental results and discussion

The experiments were carried out on a shock tube facility described in detail elsewhere [9]. The emissions from electronically excited CH* (at $\lambda = 429 \pm 3.5$ nm) and C2* (at $\lambda = 516 \pm 3.5$ nm) radicals were recorded in one section at a distance of 11 mm from the end face of the shock tube. The indicated spectral ranges were isolated with DMR-4 two-prism quartz monochromators (LOMO, Russia). The photodetectors were FEU-39A photomultipliers. In a number of experiments, the integrated emission (IE) from the combustion products was recorded with a D-256 photodiode (400–950 nm). The gas parameters behind the reflected shock wave (total density $M_5$, temperature $T_5$, and pressure $P_5$) were calculated from the composition and initial pressure of the test mixture and the velocity of the incident shock wave within the ideal-flow shock tube theory [10].

A 1 vol % C3H8–5 vol % O2–Ar stoichiometric mixture was investigated. Temperature behind the reflected shock wave was varied within 1230–1700 K, whereas the total concentration of the mixture was maintained nearly constant $M_{50} = (1.05\pm0.07) \times 10^{-5}$ mol/cm$^3$, which corresponds to a pressure range of 0.97–1.37 bar.

Typical oscillograms of the CH* and C2* emission signals and IE are displayed in figure 1. As can be seen, the times it takes for the CH* and C2* emission signals to reach the maximum are nearly identical, being close to the time point of the intermediate maximum of the IE. In addition, the time profiles of the emission signals are very similar. This coincidence of the maxima and signal profiles was observed throughout the temperature range of the measurements. Analogous results were also observed when comparing the profiles when recording the CH* and C2* signals when measuring the emission of the corresponding radiators in stoichiometric ethane mixtures [9] and ethylene [11] in argon.

Figure 1 shows that the CH* and C2* emission time profiles are nearly symmetric with respect to their maxima and decay practically to zero. The IE exhibits a completely different behavior. It appears much earlier than CH* and C2*, passes through an intermediate maximum, decreases approximately twofold, and then begins again to increase. The earlier appearance of the IE may be due to an early appearance of other radiators, in particular, electronically excited CO2*, which emit well in the visible spectral region [11]. The rise of the IE signal in later stages can be contributed by a variety of propane combustion products, notably water.

Figure 2 shows the temperature dependence of the ignition delay time defined as the time $\tau_{\text{max}}$ it takes for the CH*, C2*, IE signals to reach the maximum. Since it was found that the emission maximum for all three recording systems occurred practically at the same, the corresponding values of $\tau_{\text{max}}$ (CH*, C2*, IE) are represented in figure 2 by one type of symbols.
Figure 1. The CH* and C2* emission signals during the ignition of a 1 vol % C3H8–5 vol % O2–Ar mixture at T5 = 1462 K and P5 = 0.132 MPa.

Figure 2 also displays the data from [1] for a propane–oxygen–argon of similar composition at a pressure of 0.9 bar, obtained from the registration of the onset of OH* luminescence and the data from [5] for a 1.27 vol % C3H8–6.17 vol % O2–Ar mixture at a pressure of 1.2 bar. In [5], the ignition delay was defined as the point of time corresponding to the maximum rate of CH* emission rise as recorded from the side of the shock tube end face.

As can be seen in figure 2, at temperatures above 1400 K, the ignition delay times measured in the present work and in [1, 5] agree to within a factor of 2. At temperatures below 1400 K, various physicochemical processes determined by the design of the shock tube can influence the ignition of propane–oxygen–dilutant mixtures [2–4, 7].

The recorded CH* emission profiles were simulated using the detailed kinetic mechanisms from papers [11–14]. These mechanisms include sets of reactions describing the formation and consumption of the electronically excited CH* and OH* radicals. With varying degrees of success, the mechanisms [11–14] describe not only the temperature dependence of the ignition delay time, but also the luminescence profiles for a number of the simplest hydrocarbons, such as methane, ethane, ethylene, acetylene, acetone. All the calculations were performed using the CHEMKIN III package [15] under the constant volume condition, V = const. The temperature dependences of the ignition delay time for the experimental conditions of this work simulated within the framework of the kinetic mechanisms from works [11–14] are displayed in figure 2. It can be seen that, at T > 1400 K, the experimental results are well reproduced by all the kinetic mechanisms. At the same time, the kinetic mechanism [12] gives τ values approximately 2 times lower in the entire temperature range than those predicted by the mechanisms from papers [11, 13, 14]. These three mechanisms yield practically the same values of τ.

The results of a sensitivity analysis aimed at identifying the reactions most important for the induction period was performed for the kinetic behavior of OH (figure 3). Two kinetic
Figure 2. The ignition delay time found from the chemiluminescence signal of the indicated emitters for a C$_3$H$_8$–O$_2$–Ar stoichiometric mixture as a function of the reversed temperature. The open triangles represent the current work data; closed circles, [5]; and yellow rhombs, [1]. The results of our kinetic calculations by reaction mechanisms [11–14] are shown by lines.

Mechanisms, from papers [11] and [12], were compared. The sensitivity to the leading reactions at a time of 0.5τ for each of the kinetic mechanisms, [11] and [12], was calculated in accordance with the values of τ they predict. As can be seen in figure 3, the same reaction determine the kinetic behavior of OH radical in the induction period, one of the major radicals involved in chain-branched reactions. At the same time, the contributions from the different reactions are different. In the [12] mechanism, the effects of the reactions leading to n-propyl (n-C$_3$H$_7$) and isopropyl (iso-C$_3$H$_7$) radicals

\[ C_3H_8 + H \rightarrow n-C_3H_7 + H_2, \]
\[ C_3H_8 + H \rightarrow iso-C_3H_7 + H_2 \]

differs approximately twofold in favor of the first reaction, while according to the [11] mechanism, the influence of these two channels is the same. At the same time, a positive effect of the reactions

\[ HCO + O_2 \rightarrow CO + HO_2, \]
\[ CH_3 + O_2 \rightarrow CH_2O + OH \]

on the increase in the OH concentration in the [12] mechanism is the same, while according to the [11] mechanism, the second reaction in this pair dominates. Note that, in the [12] and [11] mechanisms, the rate constant for the decomposition of the propane molecule into an ethyl and methyl radical differs approximately twofold in comparison with the dominant chain-branching reaction

\[ H + O_2 \rightarrow O + OH. \]
Figure 3. Local sensitivities of the basic pathways of formation and consumption of OH radicals at a time of 0.5\(\tau\) for a C_3H_8–O_2–Ar mixture under the conditions specified in the caption to figure 1. The line represents the numerical calculations produced by kinetic mechanisms from [12] (a) and [11] (b).
Figure 4. The OH* chemiluminescence intensity profiles [1] for a 2 vol % C\textsubscript{3}H\textsubscript{8}–10 vol % O\textsubscript{2}–Ar mixture. The experimental data are shown by solid black line; the simulation results are represented by the red dashed line (mechanism [11]); violet dash-dot line [14], blue dot-dot line [13], and green dash-dot-dot line [12]. The conditions behind the reflected shock wave: $T_{50} = 1430$ K, $P_{50} = 0.97$ bar. All profiles are normalized.

The same is true for the chain-termination reaction of recombination of two methyl radicals. Changes in these relationships and in the rate constants can also alter the temperature dependence of the ignition delay time. However, given that the simulation and experimental results differ from each other within a factor of 2, this is inadvisable, especially since the kinetic mechanisms are adapted to wider ranges of fuel-to-oxidizer equivalence ratios $\phi$, pressures, and concentrations.

Figure 4 shows the OH* emission signal recorded in [1] for a less dilute stoichiometric mixture, 2 vol % C\textsubscript{3}H\textsubscript{8}–10 vol % O\textsubscript{2}–Ar. It can be seen that the times of reaching the maximum for the OH* emission signal as calculated by the [11,14] schemes practically coincide with the experimentally observed value. Close to them are the values of $\tau_{\text{max}}(\text{OH}^*)$ calculated by the [13] mechanism. At the same time, $\tau_{\text{max}}(\text{OH}^*)$ predicted by the [12] mechanism is approximately three times shorter that the experimentally observed. Note that the shape of none of the calculated OH* profiles coincides with the experimentally OH* observed profiles. At the same time, for simpler hydrocarbons, the OH* profiles calculated by the mechanisms from [11–14] are well described in the initial stage until the maximum in the OH* emission signal is reached and satisfactorily reproduced for the descending part of the luminescence signal [8, 9, 11].

Figure 5 compares the CH* and C\textsubscript{2}* emission signals recorded in the highest-temperature experiment of the present work. As can be seen, the maxima of the CH* and C\textsubscript{2}* signals are reached practically at the same time. It is also seen that none of the kinetic mechanisms [11–14] we tested satisfactorily describes the measured CH* profile. In all calculations, the half-width is much narrower than recorded in the experiment. Note also that the simulations within the
Figure 5. Chemiluminescence intensity profiles CH* and C2* measured during the ignition of the 1 vol % C3H8–5 vol % O2–Ar mixture behind a reflected shock wave at T50 = 1694 K and P50 = 1.56 bar. The solid lines represent the measured CH* and C2* emission signals, whereas the broken curves are simulated CH* signals [11–14].

framework of all four kinetic mechanisms [11–14] give an approximately identical half-width of the CH* emission signal.

The fact that none of the OH* (see figure 4) and CH* (see figure 5) emission signals can be satisfactorily described within the framework of the kinetic mechanisms from [11–14] is indicative of a poor performance of these mechanisms in predicting the kinetic behavior of various key species, such as C, H, O, C2, CH, CH2, HCO, C2H. It is the reactions involving these species that yield electronically excited emitters in the zone of ignition of hydrocarbons [9]. At the same time, the concentrations of these species are so low that most of them produce no influence on the calculated ignition delay time for propane.

3. Conclusions
Thus, by the example of study of the ignition of C3H8–O2–Ar stoichiometric mixtures in reflected shock waves, we made certain as follows:

- At temperatures above 1400 K, the ignition delay time measured by recording the emission of CH* and C2* are in close agreement with the data reported by other authors and are satisfactorily described by the published kinetic mechanisms including reactions involving electronically excited emitters.
- The times it takes for the CH* and C2* emission signals to reach the maximum turned out to be practically identical over the entire temperature range covered.
• None of the kinetic mechanisms tested make it possible to satisfactorily describe the CH* and OH* time profiles.

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