Emission of OH* and CO₂* during the high-temperature oxidation of acetone in reflected shock waves

A M Tereza¹, V N Smirnov¹, P A Vlasov¹,², V V Shumova³,¹ and A A Garmash²

¹ Semenov Institute of Chemical Physics of the Russian Academy of Sciences, Kosygina 4, Moscow 119991, Russia
² National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe Shosse 31, Moscow 115409, Russia
³ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia

E-mail: atereza@bk.ru

Abstract. Experimental and kinetic modeling study of the ignition of a stoichiometric mixture of acetone with oxygen diluted by argon was carried out behind reflected shock waves within the temperature range of 1350–1810 K for the total mixture concentration \([M] \sim 10^{-5}\) mol/cm³. Emission signals were recorded simultaneously for three different wavelengths: OH* (\(\lambda = 308\) nm) and CO₂* (\(\lambda₁ = 365\) nm; \(\lambda₂ = 451\) nm). It was revealed that the time it takes to reach the maximum of emission of OH* and CO₂* is practically the same over the whole temperature range. At the same time, the emission profiles of CO₂* after the maximum was attained, recorded at \(\lambda₂ = 451\) nm, differ noticeably from the profiles recorded at \(\lambda₁ = 365\) nm. For numerical modeling of the emission profiles of OH* and CO₂*, the corresponding sets of excitation and quenching reactions available in the literature were used. In the course of our numerical simulations we succeeded in good agreement of our own experimental and simulation results on acetone ignition and the results available in the literature for conditions under consideration.

1. Introduction

For development and enhancement of the kinetic mechanisms describing the ignition and combustion of various hydrocarbon fuels a comprehensive kinetic database is required. For such problems, the shock tube experiments provide a way to get the rate coefficients of the elementary reactions, the time profiles of the initial components of combustion mixtures and their products, and, finally, the ignition delay times. Although acetone is not a conventional hydrocarbon fuel, its mixtures with different hydrocarbon fuels are frequently used in industry. Thus, the study of the processes of acetone ignition and combustion is of great importance. In addition, acetone plays an important role in the chemistry of the atmosphere because in common with the other ketones, it is formed in the atmosphere during oxidation of various hydrocarbons [1, 2].

Despite of the experimental studies and numerical modeling of acetone ignition, there are insufficient data in the literature on the kinetic analysis of the emission of various electronically excited components during acetone combustion. Thus, in [3, 4], the experimental studies of
thermal oxidation and pyrolysis of acetone were carried out behind reflected shock waves by recording uv absorption and ir emission of the parent substance and the products. In [3], the authors proposed the simplest kinetic model for description of the basic kinetic parameters of acetone oxidation and thermal decomposition. In [4], the authors considerably extended the kinetic mechanism and were able to describe the observed profiles of the recorded components and to determine a number of rate coefficients of the basic reactions within the framework of the kinetic mechanism proposed. In [5], the authors measured the burning velocity of acetone flame and studied its structure. On the basis of their own measurements of the CH* kinetic mechanism proposed, In [5], the authors measured the burning velocity of acetone flame and to determine a number of rate coefficients of the basic reactions within the framework of the kinetic mechanism and were able to describe the observed profiles of the recorded components acetone oxidation and thermal decomposition. In [4], the authors considerably extended the authors proposed the simplest kinetic model for description of the basic kinetic parameters of recording uv absorption and ir emission of the parent substance and the products. In [3], the thermal oxidation and pyrolysis of acetone were carried out behind reflected shock waves by recording uv absorption and ir emission of the parent substance and the products. In [3], the authors proposed the simplest kinetic model for description of the basic kinetic parameters of acetone oxidation and thermal decomposition. In [4], the authors considerably extended the kinetic mechanism and were able to describe the observed profiles of the recorded components and to determine a number of rate coefficients of the basic reactions within the framework of the kinetic mechanism proposed. In [5], the authors measured the burning velocity of acetone flame and studied its structure. On the basis of their own measurements of the CH* emission behind reflected shock waves and the burning velocity of acetone flame in a constant volume bomb for various mixtures of acetone with oxygen together with the literature data borrowed from [3–5], the authors of [6] developed a comprehensive kinetic model of high-temperature acetone pyrolysis and oxidation.

In [7], the experimental measurements of the ignition delay times were performed for the mixtures of acetone with oxygen in shock waves from the records of pressure and the beginning of CH* emission. Based on the sensitivity analysis, within the framework of the kinetic mechanism proposed, the authors in [7] determined the basic channels and the rate coefficients of some important reactions. In [8], the authors determined the ignition delays of the mixtures of acetone with oxygen by recording the pressure and OH* emission. Using the kinetic mechanism proposed in [6], the authors of [8] succeeded in satisfactory description of their own experimental results. In the later version of the kinetic mechanism [6] presented in [9], the additional sets of reaction were included to describe the emission of CH* and OH*. However, the reactions with participation of CO$_2^*$ are absent in [9]. The importance of kinetic modeling of such emitters as CH*, OH*, CO$_2^*$ is also caused by widespread occurrence of various emission techniques to study and to monitor the processes of ignition and combustion of various hydrocarbon fuels.

The aim of the current work was the simultaneous record of the emission of electronically excited OH* and CO$_2^*$ particles behind reflected shock waves to obtain more comprehensive kinetic data for development of the detailed kinetic mechanism with participation of CO$_2^*$.

2. Experimental results
All experiments were conducted on a shock tube described in [10]. The emission signals of electronically excited OH* ($\lambda = 308 \pm 2.5$ nm) and CO$_2^*$ ($\lambda_1 = 365 \pm 3.5$ nm, $\lambda_2 = 451 \pm 3.5$ nm) were conducted at the same observation cross-section 11 mm apart from the end plate of the shock tube. For OH* the spectral range indicated was separated with the help of a DMR-4 double quartz monochromator. The emission of CO$_2^*$ molecules was recorded with the help of the DMR-4 double quarts monochromators for $\lambda_1 = 365 \pm 3.5$ nm, $\lambda_2 = 451 \pm 3.5$ nm, and with the help of a filter composed of an interference filter and a number of optical glasses UF-2 and SZS-21 3 mm in thickness for $\lambda_3 = 363$ nm. Photomultipliers FEU-39A were used to record the emission of OH* and photomultipliers FEU-51 were used to record the emission of CO$_2^*$.

All experiments were conducted behind reflected shock waves. The gas parameters behind the reflected shock wave ($M_5$, $T_5$, $P_5$) were calculated from the initial pressure, the initial mixture composition, and incident shock wave velocity using the theory of ideal flow in a shock tube [11]. A stoichiometric mixture of 0.5%(CH$_3$)$_2$CO + 2%O$_2$ in argon was investigated. The temperature range of measurements was 1350–1810 K, the total mixture concentration behind the reflected shock wave was $M_5 = (1 \pm 0.2) \times 10^{-5}$ mol/cm$^3$.

Typical oscillograms of the records of OH* and CO$_2^*$ emission are shown in figure 1. As can be seen from figure 1, the maximum of OH* emission practically coincides with the maximums of CO$_2^*$ emission for all three CO$_2^*$ records. In this case, the emission signals of OH* and CO$_2^*$ for $\lambda_1 = 365$ nm are practically symbate. Such coincidence of the signal maximums was observed within the whole temperature range of experimental measurements. Similar results were also observed in [10] for stoichiometric ethane mixtures with argon and in [12] for stoichiometric
Figure 1. Experimental time dependences of the emission signals of OH$^*$ and CO$_2^*$, for a mixture of 0.5%(CH$_3$)$_2$CO + 2%O$_2$ in Ar at $T_5$ = 1350 K and $P_5$ = 0.111 MPa.

ethylene mixtures with argon, when the time profiles of OH$^*$ and CO$_2^*$ emission were compared. One can see from figure 1 that the profiles of OH$^*$ and CO$_2^*$ emission are asymmetric with respect of their maximums and demonstrate slowly decreasing tails up to the amplitude less than 10% from the maximum values of the signal. From the comparison of CO$_2^*$ signals, recorded with the help of the interference filter ($\lambda_3$ = 363 nm) and DMR-4 monochromator ($\lambda_1$ = 365 nm) one can see that the emission signal in the first case has somewhat broader profile with respect to the maximum of CO$_2^*$ emission rather than in the second case. In the case of recording of CO$_2^*$ emission with the help of a DMR-4 monochromator at $\lambda_2$ = 451 nm the profile of signal decay of CO$_2^*$ emission after the maximum demonstrates more slow decay rather than at $\lambda_1$ = 365 nm. Such a difference in the profiles of emission signal decay can be explained by the fact that populations of CO$_2^*$ electronic levels, which correspond to emission at $\lambda_1$ = 365 nm and $\lambda_2$ = 451 nm differ because of different characteristics of excitation and quenching of CO$_2^*$, which correspond to these levels.

3. Discussion
The temperature dependence of the experimentally observed ignition delay times derived from the maximum of emission of OH$^*$ and CO$_2^*$ is presented in figure 2. Because it was revealed
Figure 2. Temperature dependence of the ignition delay time determined from the maximum of the position of the chemiluminescence signal of the indicated emitters for a mixture of $0.5\% (\text{CH}_3)_2\text{CO} + 2\% \text{O}_2 + \text{Ar}$; $[M] \sim 10^{-5}$ mol/cm$^3$. The black and red symbols represent the data of the present work and those from [3], respectively. The results of our kinetic calculations by reaction mechanism borrowed from [9] are presented by lines.

that the maximums of CO$_2^*$ emission for all three systems of records practically coincided, the corresponding values of $\tau_{\text{max}}(\text{CO}_2^*)$ are designated in figure 2 by the same symbol. The data borrowed from [3] are presented in the same figure for the same mixture composition of acetone with argon at $P_5 = 0.5$ MPa. They were derived from the records of the maximum of OH$^*$ emission and from the characteristic time of CO$_2$ yield (the time interval from the moment of arrival of the shock wave at the observation section and the time corresponding to the point of intersection of the tangent to the signal profile at its maximum-slope point with the zero-signal baseline). From the comparison of the experimental results of the current work and the data borrowed from [3] one can see that the 5-fold pressure increase in the reactive mixture results in the approximately 3-fold shortening of the ignition delay time of the mixture investigated.

To describe the experimentally observed profiles of electronically excited OH$^*$ and CO$_2^*$, the kinetic mechanism from [9] was chosen. This mechanism includes the reactions with participation of electronically excited CH$^*$ and OH$^*$ particles and demonstrates good description of various experiments with their participation. However, the reaction with participation of electronically excited CO$_2^*$ molecules are absent in this mechanism. These reactions with CO$_2^*$ are also absent in all other kinetic mechanisms available in the literature. Only in [13, 14] the first attempts
Figure 3. Experimentally measured and calculated time dependences of the emission signals of OH* and CO$_2^*$, for a mixture of 0.5%(CH$_3$)$_2$CO + 2%O$_2$ in Ar, $T_5 = 1469$ K and $P_5 = 0.123$ MPa. Color lines are experimental time histories of the present work, black lines are calculated time histories obtained with the help of the kinetic mechanism borrowed from [9] (see text).

were performed to develop a kinetic mechanism which includes the reactions of formation and consumption of CO$_2^*$ and the first estimates of the rate coefficients of the corresponding reactions are presented. Thus, at the first stage of our research, we used the kinetic mechanism borrowed from [9], which was augmented by the reactions from [13]. Some rate coefficients of the reactions with participation of CO$_2^*$ were adjusted in accord with recommendations presented in [14].

Figure 3 demonstrates the results of calculations in accordance with the procedure described above. One can see that the calculated profile of OH* rather good describes the profile of the experimentally observed OH* emission up to the maximum. At the same time, the calculation describes much worse the rate of descent of OH* emission that was also observed if the kinetic mechanism borrowed from [9] was used to model the experiments on emission profiles of the other hydrocarbons [10, 12, 15]. As it was demonstrated in these works, slowly varying emission of OH* after the maximum and a sharp decay of its amplitude is determined by the reaction H + O $\rightarrow$ OH* and to describe more precisely the decay of emission of OH* after the maximum one should have more accurate kinetic data concerning the rate coefficients of excitation or quenching of OH*.

In contrast to OH* description, the calculated profile of CO$_2^*$ at the initial stage of emission describes much worse the experimental signal of CO$_2^*$ emission. This is expressed in the earlier
appearance of CO$_2^*$ in calculations as compared with the experimental observations. In the course of description of CO$_2$ profiles at the higher temperatures (see figure 3), it was revealed that the calculated profiles of CO$_2^*$ demonstrate not only the higher rate of increase of CO$_2$ emission, but also have the shape of the profile of CO$_2^*$ emission, which differs from the experimentally observed one. This circumstance can be explained by the fact that several channels of CO$_2^*$ formation are considered in the mechanism [13, 14]. Competition between these channels determines both the rate of formation and the shape of profiles of CO$_2^*$ emission:

\[
\begin{align*}
    \text{CO} + \text{O} + \text{M} &= \text{CO}_2^* + \text{M}, \\
    \text{CH}_3\text{CHCO} + \text{OH} &= \text{C}_2\text{H}_5 + \text{CO}_2^*, \\
    \text{HCO} + \text{O} &= \text{CO}_2^* + \text{H}, \\
    \text{H} + \text{H} + \text{CO}_2 &= \text{H}_2 + \text{CO}_2^*, \\
    \text{CH}_2 + \text{O}_2 &= \text{CO}_2^* + \text{H} + \text{H}. 
\end{align*}
\]

Comprehensive analysis of these reactions was conducted in [12]. In this work, in studies of the ignition of the mixtures of ethylene with oxygen in shock waves it was demonstrated that the signal of emission of CO$_2^*$ can be modeled quite well with the help of two channels of excitation of CO$_2^*$, namely, channel (1) and channel (6):

\[
\text{CH} + \text{O}_2 \Rightarrow \text{CO}_2^* + \text{H},
\]

which can replace excitation channels (2)–(5). Exactly channels (1) and (6) at the second stage of the numerical modeling were included in the kinetic mechanism borrowed from [9]. The rate coefficients for reactions (1) and (6) were borrowed from [12] and had the following values:

\[
k_1 = 2.5 \times 10^{10} \, \text{cm}^6/\text{mol}^2/\text{s} \quad \text{and} \quad k_6 = 1.8 \times 10^{11} \, \text{cm}^3/\text{mol}/\text{s}. \]

The results of calculations are presented in figure 3. One can see that the numerical description of both the experimentally observed profiles of CO$_2^*$ emission and the time it takes to reach the maximum of emission of CO$_2^*$ shows a great improvement if reactions (1) and (6) were included in the kinetic mechanism. In order to improve the description of the profiles of OH$^*$ and CO$_2^*$ after their maximums it is necessary to conduct a comprehensive analysis of the channels and the corresponding rate coefficients of the formation and consumption of atoms and radicals, which in turn form the excited particles in the corresponding reactions. However, since a particular kinetic mechanism borrowed from [9] was used in the current work, such a procedure was not performed. At the same time, the replacement of reaction (2)–(5) by reaction (6) demonstrates no effect when the profiles of CO$_2^*$ emission are calculated. This can be explained by the fact that for this particular kinetic mechanism [9], in the course of simulation of the profiles of CO$_2$ emission, reactions (2)–(5) and reaction (6) form the CO$_2^*$ maximum by a symbate manner. The same fact was also revealed in [16] in the course of analysis of various channels of excitation of CO$_2$.

Comparison of the calculated ignition delay times $\tau$, determined in the current work and in [3], is depicted in figure 2. The values of $\tau$ were calculated with the use of the final kinetic mechanism [9] with reactions (1) and (6). One can see that the ignition delay times, determined from the maximum of emission of OH$^*$, CO$_2^*$ and from the characteristic time of CO$_2$ yield practically coincide in our calculations and the kinetic mechanism describes quite well their experimentally observed temperature dependencies.

### 4. Conclusions

As a result of the work carried out it was revealed that during the self-ignition of the stoichiometric mixture of acetone with oxygen behind reflected shock waves.

(i) The records of CO$_2$ emission are differed by their shapes for $\lambda_1 = 365$ nm and $\lambda_2 = 451$ nm.
(ii) The time it takes to reach the maximum of emission of OH$^*$ and CO$_2^*$ coincides within the whole temperature range studied and for CO$_2^*$ it is independent on the wavelength at which the emission of CO$_2^*$ was recorded.

(iii) The numerical modeling of the profiles of CO$_2^*$ emission carried out with the use of the kinetic mechanism borrowed from [9] supplemented by the reactions with participation of CO$_2^*$, made it possible to describe quite well the initial stages of the time profiles of CO$_2^*$ up to the time it takes to reach the maximum of emission of CO$_2^*$.

(iv) The numerical modeling carried out demonstrates a good agreement of the temperature dependences of the ignition delay times obtained in the current work and presented in the literature.

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