Ignition and chemical kinetics of acrolein–oxygen–argon mixtures behind reflected shock waves

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HIGHLIGHTS

- Ignition delay-time of acrolein-based mixtures.
- Multi-species emission diagnostics.
- Kinetics modeling with detailed chemistry.

ARTICLE INFO

ABSTRACT

In order to address increasing greenhouse gas emissions, the future fossil fuel shortage and increasingly stringent pollutant emission regulations, a variety of biofuels are being progressively incorporated into conventional transportation fuels. Despite the beneficial impact of biofuels on most regulated pollutants, their combustion induces the increase of a variety of aldehydes that are being considered for specific regulations due to their high toxicity. One of the most hazardous aldehyde compounds is acrolein, C_2H_3CHO. Despite its high toxicity and increased formation during bioalcohol and biodiesel combustion, no experimental data are available for acrolein combustion. In the present study, we have investigated the ignition of acrolein–oxygen–argon mixtures behind reflected shock wave using three simultaneous emission diagnostics monitoring OH^*, CH^* and CO_2^*. Experiments were performed over a range of conditions: $\Phi = 0.5$–2; $T_5 = 1178$–1602 K; and $P_5 = 173$–416 kPa. A tentative detailed reaction model, which includes sub-mechanisms for the three measured excited species, was developed to describe the high-temperature chemical kinetics of acrolein oxidation. Reasonable agreement was found between the model prediction and experimental data.

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1. Introduction

In recent years, biofuels have received growing attention as an alternative to petroleum-based fuels in light of increasing greenhouse gas emissions, supply shortages and stringent regulations on pollutant emissions [1–4]. Depending on the specific biofuel considered, significant reduction in carbon dioxide emission has been reported [3,4]. Despite the positive impact in reducing pollutant emissions, like particulate matter [3,5,6], CO [3,5], and unburnt hydrocarbons [3,5], by incorporating biofuels into conventional fuels, their combustion generates an increase production of a variety of toxic carbonyl compounds, especially aldehydes [2,7–9]. This concern is aggravated by new engine combustion technologies such as homogeneous charge compression ignition and premixed charge compression ignition which involve low-temperature reaction kinetics [8]. Studies [5,6,10] have demonstrated acrolein production is increased up to 1000% for diesel–ethanol and diesel–biodiesel blends [6]. Acrolein or 2-propenal, C_2H_3CHO, is a beta-unsaturated aldehyde with important implications for atmospheric chemistry [11]. High levels of acrolein have been correlated with urban areas having dense automotive traffic as well as rural areas subject to forest fires [12]. In addition to its formation during combustion processes, including burning of fossil fuels [13]; wood; plastic; and tobacco [12], acrolein can be formed in the atmosphere as a result of chemical reactions involving unsaturated hydrocarbons like 1,3-butadiene [14]. Although no conclusive carcinogenic evidence has been found for acrolein, its increased production during the combustion of biofuels is particularly concerning for public heath due to its neurotoxic properties [11]. Acrolein is highly toxic and physiological effects can potentially occur through inhalation or skin exposure for concentrations as low as 0.3 ppm [12].

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Given the expected growing use of biofuels and the physiological implications of acrolein, a better understanding of its chemical kinetics is of importance. While acrolein chemistry is incorporated into a number of chemical reaction models of hydrocarbon fuels, most studies have focused on its reactivity at low temperature in the framework of atmospheric chemistry, see [11]. The objective of the present work is to gain insight into the high-temperature acrolein kinetics independently of the complexity involved in the study of heavy hydrocarbon fuels. To this end, the chemical kinetics of acrolein has been studied behind reflected shock wave by monitoring simultaneously the emission from OH*, CH* and CO_2^*. A tentative detailed reaction mechanism, which includes sub-mechanisms for the three measured excited species, has been developed and analyzed to underline the dominant reaction pathways.

2. Materials and methods

2.1. Mixtures preparation

All gases were of research grade (Air Liquide). A mixture containing 2% by volume of acrolein in argon was used to prepare the blends. Because of the highly toxic and corrosive properties of acrolein, special materials and procedures were employed. Corrosion-resistant regulator and pipe-lines were used. Special care was taken to minimize leaks. Integral gas-mask, protection gloves and laboratory coat were used during mixture preparation and experiment. Homogeneity of the mixtures was obtained by active mixing for one hour. Mixture compositions and experimental conditions are summarized in Table 1.

2.2. Experimental apparatus

The shock-tube used has been described elsewhere [15,16]. It is composed of three parts separated by two diaphragms and is made of stainless steel. The driver section and the driven section are 6.19- and 11.28-m-long, respectively, (i.d. 15.24 cm). The test section is 2.44-m-long (i.d. 7.62 cm). A 2.03-m-long (i.d. 7.62 cm) cookie-cutter is used to transmit the shock wave from the driven to the test section, avoiding perturbation of the incident shock wave. The residual vacuum in the test section is on the order of 1 Pa. The driver gas was nitrogen. The test section of the shock-tube was equipped with diagnostic instruments located close to the end wall: four piezoelectric pressure transducers, mounted flush with the inside wall for shock velocity measurements (uncertainty of 1%), and two quartz optical windows mounted at 13 mm from the tube end, connected to two solarization-resistant multimode optical fibers with a core diameter of 200 µm. One of the optical fiber is linked to a single-photomultiplier (Hamamatsu) equipped with a 306 ± 5 nm band-pass filter for detecting the $\left(A^2\Sigma^+ - X^2\Pi\right)$ transition of excited OH radicals, OH*. The second fiber is linked to a dual-photomultiplier (Thorlabs) equipped with a quartz beam splitter and two band-pass filters centered at 410 ± 5 nm and 430 ± 5 nm for detecting the $\left(A^1B^2 - X^1\Sigma^+\right)$ and $(A^2\Delta - X^2\Pi)$ transitions of CO_2^* and CH* radicals, respectively. Characteristic times of reaction were defined as the time to reach 50% and 100% of the emission peak, $\tau_{50\%}$ and $\tau_{100\%}$ respectively.

Table 1
Mixture compositions and experimental conditions examined in the present study.

N	Φ	X_{ACRO}	X_{O_2}	X_{Ar}	T_5 (K)	P_5 (kPa)
1	0.5	0.0038	0.0266	0.9696	1178–1458	358–381
2	1	0.007	0.0245	0.9685	1168–1539	173–416
3	2	0.011	0.019	0.9698	1179–1602	305–386

The set-ups of the photomultipliers were held constant to obtain normalized peak heights as a function of temperature. Note that the series performed for the stoichiometric mixture was employed to evaluate the sensitivity of the new dual-photomultiplier as well as the emission characteristics of acrolein-based mixtures. These mixtures demonstrated sensibly different emission intensities than mixtures previously studied in our laboratory [15,16]. These aspects resulted in missing parameters as seen in Tables 2–4 which summarize all the results obtained. The thermodynamic conditions behind the reflected shock wave were calculated using the 1D shock theory and the incident shock velocity. Uncertainties on the reflected temperature and pressure are 1%. Uncertainties on the delay-time and the peak height is on the order of 20%. Fig. 1 shows a typical example of OH* emission and pressure signals obtained during the present study.

2.3. Chemical kinetic scheme

The detailed reaction model presently used includes 920 reactions and 115 species. It was developed from the model of Mével et al. [17,18] for $H_2–O_2$ and NO_x chemistry, the Caltech mechanism [19] for hydrocarbon chemistry and the model of Le Cong for NO_x–hydrocarbons interactions [20]. The sub-model for acrolein chemistry was taken from the Jet–Surf model [21] and extended based on an analogy with 1,3-butadiene chemistry. Sub-mechanisms for OH*, CH* and CO_2^* chemistry were respectively taken from Hall et al. [22,23] and Hidaka et al. [24,25]; Devriendt et al. [26] and Smith et al. [27]; and Kopp et al. [28] and Sulzmann et al. [29]. The JetSurf mechanism [21] was also employed for comparison with the present reaction model. Missing thermodynamic properties for acrolein and acrolein radicals, C_2H_3CO, CHCHCHO, CH_2CCHO, were calculated following the methodology outlined in [30]. The model is provided as a supplemental material along with the corresponding thermodynamic properties. The modeling of the experimental results was performed with SENKIN [31] using the constant volume reactor model. Sensitivity and reaction pathway analyses were performed using this code.

The performance of the two reaction mechanisms were quantified using the mean and the maximum errors, respectively defined as

$$E_{mean}^Q = \frac{1}{N}\sum_i^N \left|\frac{\Delta Q}{Q_{expe}}\right|, \tag{1}$$

and

$$E_{max}^Q = max\left|\frac{\Delta Q}{Q_{expe}}\right|. \tag{2}$$

N is the number of data points, $\Delta Q = Q_{model} - Q_{expe}$, with Q_{model} and Q_{expe} are the calculated and experimental characteristic quantities, respectively. The characteristic quantities refer to the delay-times, $\tau_{50\%}$ and $\tau_{100\%}$, and the normalized peak heights. The absolute values are used to avoid positive and negative contributions to the errors canceling out.

3. Results and discussion

3.1. Experimental results

The ignition delay-times based on OH*; CH*; and CO_2^* of acrolein–oxygen–argon mixtures were measured behind reflected shock wave in the ranges: $\Phi = 0.5–2$; $T_5 = 1178–1602$ K; and $P_5 = 173–416$ kPa. Within the experimental uncertainty, the three species monitored yield similar values for the ignition delay-time. Figs. 2–4 display the results obtained for a lean, a stoichiometric and a rich mixture, respectively. For the three monitored emis-