Postprint: Study on the Chemical Kinetic Mechanism of Ethane Ignition

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Abstract

This study measured the ignition delay times of ethane at various pressures, temperatures, and equivalence ratios using a shock tube, and conducted numerical simulations and chemical kinetic analysis of the premixed gas ignition process using CHEMKIN software with the GRI-Mech 3.0 mechanism. The results indicate that the GRI-Mech 3.0 mechanism cannot accurately predict the ignition delay times of ethane. Sensitivity analysis of the ignition process revealed that reactions exert significant influence on ignition delay times, and the reaction rate constants were modified. The modified mechanism substantially improves the prediction of ethane ignition delay times while maintaining accurate predictions of laminar burning velocities.

Full Text

Study on the Chemical Kinetic Mechanisms of Ethane Ignition

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Abstract

Ignition delay times of ethane were measured behind reflected shock waves under different pressures, temperatures, and equivalence ratios. Simulations and chemical kinetic analysis of the ignition process were carried out using the CHEMKIN software package with the GRI-Mech 3.0 mechanism. The results indicate that GRI-Mech 3.0 cannot accurately predict ethane ignition delay times. Sensitivity analysis of the ignition process revealed that reactions $C_2H_5+O_2=C_2H_4+HO_2$ and $C_2H_4+H+M=C_2H_5+M$ have significant influence on ignition delay times, and their rate constants were modified accordingly. The optimized mechanism provides improved prediction of ethane ignition delay times while maintaining accurate prediction of laminar flame speeds.

Keywords: ethane; ignition delay time; GRI-Mech 3.0 mechanism; chemical kinetics; sensitivity analysis

Introduction

The world faces the dual challenges of non-renewable fossil fuel depletion and increasing pressure to control pollutant and greenhouse gas emissions. Improving fossil fuel combustion efficiency while seeking clean alternative fuels represents a global research priority. Fundamental combustion studies of low-carbon fuels play a crucial role in addressing these challenges, including research on ethane combustion and chemical reaction kinetics. First, ethane is the second most important component in natural gas after methane, and natural gas is one of the most successful alternative fuels currently in use. Second, ethane exists widely as an intermediate species in hydrocarbon oxidation processes, and kinetic mechanisms for larger hydrocarbon fuels are often constructed based on those of low-carbon hydrocarbons. Therefore, detailed and accurate investigation of ethane chemical kinetics is essential for understanding ethane combustion and oxidation processes and for developing kinetic mechanisms for larger molecular fuels.

Ignition delay time is a fundamental parameter describing fuel ignition characteristics, serving as critical data for combustion chamber design and optimization in practical combustion devices and as necessary data for constructing fuel kinetic models. Numerous experimental measurements and studies of ethane ignition delay times have been conducted internationally. In 1970, Bowman [1] first measured ethane ignition delay times behind shock waves at pressures of 0.2-0.8 MPa. Cooke et al. [2] measured ignition delay times at high temperatures (1400-2200 K) in 1975. Hidaka et al. [3,4] studied ethane pyrolysis and oxidation mechanisms using shock tubes and measured intermediate species concentrations. Shim et al. [5] and Lamoureux et al. [6] also measured ethane ignition delay times in shock tubes. Tranter et al. [7] investigated ethane pyrolysis and oxidation at ultra-high pressures (34 MPa and 61.3 MPa) and found that existing mechanisms could adequately predict ignition delay times under these conditions. de Vries et al. [8] measured ethane ignition delay times and compared them with previous results, finding variations among correlations from different researchers. Although ethane ignition delay times have been extensively measured and its pyrolysis and oxidation mechanisms have been studied in detail, experimental data are primarily concentrated at pressures of 0.02-1.0 MPa and equivalence ratios of 0.5-2.0. More comprehensive experimental data across wider operating conditions would facilitate further development of ethane ignition chemical kinetic mechanisms.

This study employs a shock tube and CHEMKIN software to investigate ethane ignition delay times under various temperatures and pressures. The influence of initial mixture parameters (temperature, initial pressure, and fuel concentration) on ignition delay times is examined, with particular focus on the validation and improvement of the GRI-Mech 3.0 kinetic mechanism for ethane. The fundamental experimental data obtained not only enrich the database for ethane combustion but also promote the development of ethane chemical kinetic models.

1.1 Experimental Apparatus and Methods

Ignition delay time measurements were conducted using a shock tube experimental platform. The shock tube body, constructed of stainless steel pipes, was divided into high-pressure and low-pressure sections (5.3 m and 2.0 m long, respectively) by a PVC diaphragm. The shock tube was evacuated to below 1×10^{-3} kPa before experiments. Three pressure sensors (PCB113B26) were installed at different positions from the end wall to measure incident shock wave velocities, from which reflected shock temperature and pressure were calculated using one-dimensional ideal normal shock equations. Test gas mixtures were prepared in a stainless steel mixing tank and mixed for over 24 hours, with the tank evacuated to below 1×10^{-3} kPa before gas preparation. Ignition was diagnosed using a pressure sensor (PCB113B03) and a photomultiplier tube (PMT) located at the end wall of the low-pressure section. A narrow-bandpass filter was placed before the PMT to detect CH* chemiluminescence at 430 nm. Detailed descriptions of the experimental apparatus can be found in reference [9].

Table 1 Compositions of the test mixtures

The ethane used in experiments had a purity of 99.9%, O_2 purity of 99.995%, and Ar and He purity of 99.999%. Experimental conditions included equivalence ratios of 0.5, 1.0, and 2.0; ignition pressures of p=0.12-2.0 MPa; and mole fractions of mixture components as shown in Table 1.

Figure 1 [Figure 1: see original paper] shows the definition of ignition delay time used in this study. Ignition delay time is defined as the time interval between the arrival of the incident shock at the end wall and the intersection point of the tangent line at the maximum slope of the CH* signal curve with the baseline. First, pressure data and the timing of pressure rise were obtained from four pressure sensors (PCB, B26) located at the wall and end wall, which triggered three time-interval counters (FLUKE PM6690) mounted on the wall. The incident shock velocity was then determined through linear interpolation of the three measured time intervals. The CH* signal was detected by a photomultiplier tube located at the end wall.

1.2 Calculation Methods and Chemical Kinetic Mechanism

Numerical simulations and kinetic analysis of ethane autoignition characteristics were performed using the SENKIN module of the CHEMKIN chemical kinetics software. The GRI-Mech 3.0 mechanism [10] was employed in this study. Based on our experimental data and the computational results of DeSain et al. [11], sensitivity analysis was conducted on the GRI-Mech 3.0 mechanism, and modifications were made to improve its predictive capability for both ethane ignition delay times and laminar flame speeds.

2.1 Validation of Experimental Ignition Delay Times

Figure 2 [Figure 2: see original paper] compares the experimental results from de Vries et al. [8] with those from the present study at two conditions: p=0.11 MPa, ϕ=0.5, Xethane=0.25% and p=0.2 MPa, ϕ=1, Xethane=2%. The results show excellent agreement between our experimental data and those of de Vries et al., demonstrating good repeatability of our measurements and providing a reliable reference for validating ethane chemical kinetic mechanisms.

2.2 Comparison of Experimental and Calculated Ignition Delay Times

Figure 3 [Figure 3: see original paper] presents a comparison between measured and calculated ethane ignition delay times. Symbols represent shock tube experimental data, dashed lines represent calculations using the GRI-Mech 3.0 mechanism, and solid lines represent calculations using the modified GRI-Mech 3.0 mechanism. The results show that at constant equivalence ratio and fuel concentration, higher initial pressure leads to shorter ignition delay times. Similarly, at constant initial pressure and equivalence ratio, higher fuel concentration results in shorter ignition delay times, indicating that increased initial pressure and fuel concentration promote ethane ignition. The calculated ignition delay times reveal that the GRI-Mech 3.0 mechanism significantly overpredicts ethane ignition delay times at equivalence ratios of 0.5 and 1.0, with differences reaching up to one order of magnitude under certain conditions. Therefore, modifications to the GRI-Mech 3.0 mechanism were implemented, and the modified mechanism provides substantially improved predictions of ignition delay times under these conditions. However, at an equivalence ratio of 2.0, both the original and modified mechanisms show unsatisfactory predictive performance, warranting further investigation. The following section details the mechanism modification process through chemical kinetic analysis.

2.3 Chemical Kinetic Analysis

To determine the influence of elementary reactions on ignition delay times, sensitivity analysis was performed for ethane ignition. According to the definition by Petersen et al. [12], the sensitivity coefficient for ignition delay time is given by:

$$S_i = \frac{\partial \ln \tau}{\partial \ln k_i}$$

where τ is the ignition delay time and k_i is the rate coefficient of the i-th elementary reaction. Reactions with positive sensitivity coefficients produce stable products or radicals, reducing overall reactivity and increasing ignition delay time, while reactions with negative sensitivity coefficients generate more active radicals or increase radical concentrations, enhancing overall reactivity and decreasing ignition delay time.

Since the original mechanism shows large prediction deviations at low pressure, sensitivity analysis was primarily conducted under these conditions. **Figure 4** [Figure 4: see original paper] shows the sensitivity coefficients for ignition delay times using the GRI-Mech 3.0 mechanism at T=1250 K and ϕ=0.5. Similar to other hydrocarbon fuels, reaction R8 ($H+O_2=O+OH$) is the most sensitive reaction promoting ignition under high-temperature conditions. Among the 11 reactions with the largest sensitivity coefficients, six are related to ethane fuel molecules:

- R74: $C_2H_4+H(+M)=C_2H_5(+M)$
- R78: $C_2H_6+H=C_2H_5+H_2$
- R112: $C_2H_4+OH=C_2H_3+H_2O$
- R158: $2CH_3(+M)=C_2H_6(+M)$
- R175: $C_2H_5+O_2=C_2H_4+HO_2$
- R294: $C_2H_3+O_2=CH_2CHO+O$

The remaining reactions involve small species that have been extensively validated for fuels such as hydrogen and methane. Therefore, modifications to the GRI-Mech 3.0 mechanism in this study focused on these six ethane-related reactions.

Zhang et al. [13] found through reaction pathway analysis that most ethane is consumed by dehydrogenation reactions forming ethyl radicals. The generated ethyl radicals undergo further dehydrogenation, with some reacting with oxygen atoms to form ethylene and HO_2 radicals. DeSain et al. [11] proposed theoretical calculations for the rate constant of the $C_2H_5+O_2$ reaction in 2003, which includes multiple reaction channels. Since this study focuses primarily on high-temperature regions where the dominant channel is the direct dehydrogenation reaction $C_2H_5+O_2=C_2H_4+HO_2$, considering only this channel in GRI-Mech 3.0 is reasonable. However, the rate constant for reaction R175 in GRI-Mech 3.0 differs significantly from DeSain' s theoretical value. Substituting DeSain' s theoretical rate constant for the direct dehydrogenation reaction noticeably reduces predicted ignition delay times, though the predictions remain higher than experimental values under certain conditions.

Additionally, most ethyl radicals undergo unimolecular decomposition to form ethylene and H radicals, thereby increasing H radical concentrations in the system. In fact, the chain-branching reaction R74 can significantly promote ethane ignition. Considering that the original mechanism overpredicts ethane ignition delay times, the high-pressure and low-pressure limits of the R74 rate constant were both doubled. The modified mechanism then provides relatively good predictions of ignition delay time variations. The experimental and simulation work in this study provides important reference and basis for high-precision calculations of the R74 rate constant.

To further validate the modified mechanism's prediction of ethane laminar flame speeds, **Figure 5** [Figure 5: see original paper] compares calculated laminar flame speeds from GRI-Mech 3.0 and the modified mechanism. The results show that the modified mechanism differs only slightly from the original mechanism in predicting ethane laminar flame speeds. According to experimental data from Hassan et al. [14] and Jomaas et al. [15], GRI-Mech 3.0 accurately predicts ethane laminar flame speeds. Therefore, the modified mechanism maintains the original mechanism' s accurate prediction of laminar flame speeds while improving the prediction of ethane ignition delay times.

3 Conclusions

This study measured and analyzed ethane ignition delay times under various temperatures, pressures, equivalence ratios, and fuel concentrations using a shock tube and CHEMKIN chemical kinetics software. The main conclusions are:

1. Ignition delay times of ethane were obtained under different conditions. Within the experimental range of this study, increased pressure and equivalence ratio significantly promote ignition. The logarithm of ignition delay time shows a good linear relationship with the reciprocal of temperature.
2. Comparison between experimental and calculated ignition delay times reveals that the GRI-Mech 3.0 mechanism overpredicts ethane ignition delay times.
3. Through sensitivity analysis, the most influential elementary reactions affecting ethane ignition delay times in the GRI-Mech 3.0 mechanism were identified, and their rate constants were optimized. The modified mechanism provides improved prediction of experimental ignition delay times while maintaining accurate prediction of laminar flame speeds.

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