



Investigation of ethane pyrolysis and oxidation at high pressures using global optimization based on shock tube data

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Abstract

Tranter et al. conducted a series of experiments of ethane oxidation and pyrolysis covering a wide range of temperature (800 K–1500 K) and pressure (40 bar–1000 bar) in a high pressure shock tube. The reaction products were measured using gas chromatography. The results of these experiments were re-evaluated by optimizing selected rate parameters of the NUIG C5 v49 combustion mechanism updated with a previously optimized H₂/CO combustion mechanism. The rate parameters of 14 reactions were selected based on sensitivity analysis and preliminary uncertainty estimations for optimization. Arrhenius parameters (A , n , E) of the selected reaction steps were optimized using not only the experimental data of Tranter et al., but also the results of direct measurements and theoretical determinations related to these reactions. The obtained mechanism with the optimized rate parameters described the experiments of Tranter et al. much better than the original mechanism. New rate coefficient expressions were obtained for the 14 reactions with temperature dependent uncertainties, recommended for the temperature and pressure ranges above.

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1. Introduction

The pyrolysis and oxidation of ethane have been investigated by numerous research groups using various experimental techniques. The available

measurements cover a wide range of temperature (600–2000 K), but have been carried out mostly below 10 bar pressures.

Tranter et al. [1–3] published several studies in which the pyrolysis and oxidation of ethane was investigated using a high-pressure shock tube. Experiments were carried out in the temperature range of 829–1491 K and pressure range of 5–1000 bar, using pure ethane diluted with argon for the

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Table 1
Summary of the experimental conditions of the ethane pyrolysis experiments of Tranter et al. used in the present work [2,3].

p / bar	Pyrolysis experiments	
	T / K	Measured species
340	996–1400	C_2H_6 , C_2H_4 , C_2H_2
613	1040–1401	C_2H_6 , C_2H_4 , C_2H_2
1000	1186–1425	C_2H_6 , C_2H_4 , C_2H_2 , CH_4

pyrolysis experiments, and stoichiometric and fuel rich ($\varphi=5$, not used in the present work) ethane–oxygen mixtures diluted with argon for the oxidation experiments. In the experiments, the concentrations of the stable products were measured behind the reflected shock wave using gas chromatography. The measured species were C_2H_6 , C_2H_4 , C_2H_2 , CH_4 , CH_2O , CO , CO_2 and O_2 . The experimental conditions of the data utilized in the present work are summarized in Tables 1 and 2.

Simulations of the experiments were performed by Tranter et al. using the GRI 3.0 mechanism [4] and the mechanism of Miller et al. [5] (which was referred to as the Miller 2001 mechanism). Neither mechanism could reproduce their experimental data at all conditions. Some modifications were made [3] to the Miller 2001 mechanism in order to create a model that is able to provide an overall good description of the experimental data, however, this aim was not fully achieved. So far, a good overall reproduction has not been provided for the data of Tranter et al., and no clear mechanistic implications on the combustion of ethane, or recommendations for rate coefficient values were derived.

We have applied our recently developed optimization methodology [6] to create a mechanism that can provide a good description of these experimental data and extract as much information as possible on the rate coefficients of the important reactions of high pressure ethane combustion.

2. Selection of a mechanism for optimization

Our optimization methodology requires a starting mechanism that can qualitatively describe the experimental data that we wish to use as optimization targets. The NUIG C5 v49 hydrocarbon combustion mechanism [7] was developed for the combustion of hydrocarbons and validated against experiments carried out in a wide range of conditions. The NUIG C5 mechanism has recently been modified using theoretical calculations of rate coefficients, the validating experiments were extended towards oxygenate combustion, and the improved mechanism was published as the Aramco Mech 1.3 [8]. The Aramco Mech 1.3 contains extensive usage of the PLOG formalism for describing the pressure dependence of rate coefficients, which provides

an interpolation formula between rate coefficients expressed at given pressures. Unfortunately, many pressure dependent reactions, including potentially important ones, do not contain 1000 bar within their interpolation range in the Aramco Mech 1.3. Although extrapolation could be possible at relatively short ranges, the upper limit for provided rate coefficients is as low as 10 atm for some reactions. For this reason the NUIG C5 mechanism was preferred over the Aramco Mech 1.3.

We have updated the NUIG C5 mechanism with our recently optimized hydrogen and syngas combustion mechanism [9]. All C_4 and C_5 species, and their reactions were removed from the mechanism. The removal of the C_4 and C_5 molecules had less than 1% effect on all simulated concentration values. This modified version of the NUIG C5 mechanism was used as a basis of our further investigations. The original and the modified versions of the NUIG C5 mechanism and figures showing the effect of the removal of the certain species are present in the Supplemental Material.

3. Selection of reactions for optimization

The authors of articles [1–3] indicated that the oxidation experiments at 5 and 15 bar ($\varphi=1$), and at 50 bar ($\varphi=5$) were considered the least dependable, and therefore these were omitted from our optimization. The rate coefficients with the largest influence on the considered simulation results at the experimental conditions of Tranter et al. were identified using local sensitivity analysis [10] of Arrhenius parameters A of each reaction of the updated NUIG C5 mechanism, including the A factors of both the low and high pressure limit rate coefficients for pressure dependent reactions. The results of the sensitivity analysis are presented as a Supplemental Material. 14 reaction steps were identified that could be determined with relatively low posterior uncertainty (lower than one order of magnitude) in certain temperature ranges based on the experimental results of Tranter et al. These elementary reactions are listed in Table 3. These reaction steps include four pressure dependent reactions and in each case the high pressure limit rate coefficients could be optimized. Apart from the 14 selected reactions, certain further reactions belonging to the hydrogen/syngas combustion system are also important for ethane combustion. The rate parameters of these reactions have already been optimized in our previous work [9]. The rate coefficients of these reactions were not modified here since the previous optimization was based on large amount of experimental data covering wide ranges of temperature (800–2500 K) and pressure (0.5–50 bar), where these reactions were very important. Although the amount of experimental data related to high pressures used for the H_2/CO combustion mechanism optimization was limited, sensitivity

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