Evaluation of the influence of thermodynamic data for propane and propene ignition delay times.

León L.[1], Goos E.[2], Klauer C.[1], Seidel L.[1], Mauss F.[1] and Zeuch T.[3]

[1]Chair of Thermodynamics / Thermal Process Engineering – Brandenburg University of Technology Cottbus, Siemens Halske Ring 8 / 03046 Cottbus, Germany

[2]Institute of Combustion Technology, DLR German Aerospace Center,Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

[3]Institut für Physikalische Chemie – Georg-August-Universität Göttingen, Tammannstrasse 6, 37077 Göttingen, Germany

1 Abstract

The influence of thermodynamic data on auto ignition chemistry for propane and propene has been investigated. Thermodynamic data with high sensitivity on simulation results have been evaluated thoroughly. It was found that a small change in the heat of formation of C_3H_6 has high impact on calculated ignition delay times for propene and propane / oxygen mixtures. The new thermodynamic data was calculated through statistical methods from quantum chemical results of the benchmarked quantum chemical method G3B3. This resulted in a very small decrease of the standard heat of formation at 298 K of C_3H_6 from 20.574 kJ/mol to 19.973 kJ/mol, which resulted in a 36% increase in the calculated ignition delay times. Additionally the calculated heat of formation of C_3H_5 was 33.6 kJ/mol higher than in the previously used data set. This major change of the heat of formation of allyl results in a 91% increase in calculated ignition delay time for propene as fuel at 1440 K. Allyl (C_3H_5) shows to be a sensitive specie to the change of the thermodynamic data on the ignition delay times. The differences established through the comparison of these quantities shows a positive influence on the prediction of the propene and propane ignition delay times.

2 Introduction

The motivation of this work is to improve the propane (C_3H_8) and propene (C_3H_6) chemistry from our standard reaction mechanism [1] by evaluating the influence of the thermodynamic data, especially the enthalpy of formation at 298 K, on the simulation of ignition delay time experiments. Species enthalpy sensitivities towards ignitions delay time were calculated. We found that the heat of formation of species propane (C_3H_8), propene (C_3H_6), ethene (C_2H_4), ethane (C_2H_2) are sensitive for the simulation of propane ignition delay times; for the propene case: propene, allyl (C_3H_5) and ethene were identified as sensitive species.

Shock tube experiments with propane as fuel have been studied for a temperature range from 1050 K to 2200 K, equivalence ratios from 0.1 to 2.0 and pressures between 0.5 and 30 bar [2-5]. Recently ignition delay time of propane mixtures were measured by Mann et al. (2013) [6]. The ignition delay times measurements in shock tubes with propene as fuel available in the literature are from Zhang et al. (2010) [7], Qin et al. (2001) [8] and Burcat et al. (1971) [9], with an experimental range from 1271 K to 1900 K, 1 bar to 5 bar and equivalence ratio from 0.5 to 2.0.

The quality of available thermochemical data of C_3H_6 and C_3H_5 are critically analyzed and accompanied by quantum chemical calculations using state of the art techniques. Based on the analysis of C_3H_6 and C_3H_5 thermochemistry and using a comprehensive kinetic model, the effect of replacing this thermochemical data in the model regarding to ignition delay time predictions will be discussed.

3 Methods

(a) Thermochemistry:

Molecular properties such as vibrational frequencies, rotational constants as well as energies were calculated with the benchmarked quantum chemical composite method G3B3 and the atomisation approach. They are used for calculation of partition functions with statistical methods [10], which results in calculation of thermodynamic temperature dependent functions of enthalpy, entropy, Gibbs free energy and heat capacities. The resulting thermochemical data is fitted in the NASA polynomial format for easy use in modeling software and is available in Goos, Burcat, Ruscic "Extended Third Millennium Thermodynamic Database for Combustion and Air-Pollution Use with updates from Active Thermochemical Tables" [11].

(b) Kinetic Model:

The current version of the base chemistry [1], which goes back to the work of Hoyermann et. al (2004) [12], was used to perform all calculations. In the original work by Hoyermann et al. (2004) the relation among C1-C3 species chemistry was analyzed by acetylene and propene burner stabilized flames experiments; flame speeds and ignition delay times for C1-C4 fuels were also validated. Recently the mechanism has been extended accounting now for the high-temperature oxidation of butene species (but-1-ene C_4H_8-1, but-2-ene C_4H_8-2 and isobutene I-C_4H_8) and the thermochemical data of most of the species with 4 carbon atoms were updated, using the thermodynamic data of the database of Goos et al. [11]. The mechanism used for the simulations in the present study consists of 163 species and 1009 reversible reactions with additional 94 forward reactions. All calculations were performed with the adiabatic constant volume reactor of the current version of the DARS software package [13]. For the calculations fresh gas composition, pressure and temperature are used as input.

(c) Sensitivity Analysis:

The sensitivity analysis of enthalpy towards ignition delay times were performed to determine which species of the thermochemical data had the largest influence on the simulation results. The sensitivity analysis was performed by incrementing the value of the 6th and 13th term of the seven term NASA polynomials of the thermochemical data of each species by 1 kJ. A complete ignition delay time computation for every perturbation was made. Sensitivity in the present study is defined as $S_{i,j}$:

$$S_{i,j} = \frac{H_{fuel}}{\tau_{ref}} \left(\frac{\partial \tau_i}{\partial \bar{h}_{T,j}} \right)$$

Where: τ_i is the ignition delay time calculated with the updated thermochemical data of the specie j, $h_{T,j}$ is the enthalpy of specie j at temperature T. τ_{ref} is the ignition delay time calculated with the original thermochemical data and H_{fuel} is the enthalpy of the starting composition of the fuel at 298 K. The sensitivity results are shown in the next section in figure 2.a and 2.b.

4 Results and Discussions

In this section results of sensitive reactions for fuel oxidation and sensitive species to the change of the thermochemical data are presented and discussed. Ignition delay times of propane and propene as fuels are shown together with the influence on the change of thermodynamic data for sensitive species.

Thermochemical data of propene (C_3H_6):

The updated thermochemical data is calculated from our G3B3 [14] quantum chemical results and uses the atomisation approach for calculation of the according energies. Thereof a heat of formation of 19.97 kJ/mol is obtained for propene at 298.15 K. Considering the uncertainty of less than ±2 kcal/mol of this value, the result agrees well with the 4.88 kcal/mol from the API 44 tables [15].

Thermochemical data of Allyl (C_3H_5):

Using our G3B3 quantum chemical results of allyl, the calculation of updated thermochemical data of allyl results in a heat of formation of 167.78 kJ/mol or 40.103±2. kcal/mol at 298.15 K.

Considering the accuracy of the calculations and the experiments, the aforementioned used value is in agreement with the standard enthalpy of formation at 298.15 K of 39.1 kcal/mol, which can be obtained from Wu and Kern´s shock tube study of allene pyrolysis [16]. Additionally, and more important, our calculation result was confirmed by a recent recommendation of the heat of formation of allyl at 298 K of 168.6±1.8 kJ/mol [17] with lower uncertainty, which was obtained with high-accuracy extrapolated ab initio thermochemistry data (HEAT) approach.

In comparison to the replaced thermochemical data of allyl, used for e.g. by Appel, Bockhorn and Frenklach, [18] the used standard heat of formation at 298.15 K is 33.6 kJ/mol higher.

Propane and Propene ignition delay time and sensitivity results.

The mechanism was validated against a shock tube experiment from Burcat et al. (1971) [9] for propane and against a shock tube experiment performed by Qin et al. (2001) [8] for propene as fuel. Maximum pressure rise was the criteria for choosing the propene ignition delay time and maximum formation of CO_2 was the criteria for the propane ignition delay time as described in the experimental conditions of the original sources [9],[8]. Figure 1.a shows results for propene / oxygen mixture ignition delay times, where the simulation results are on average 66.7% lower than the experimental data. Figure 1.b shows the results for propane ignition delay time where the values of the simulation results are approximately 48% lower than the experimental data. This is opposite to the otherwise very good predictability of the employed reaction mechanism.

The consumption of propene is dominated by abstraction of hydrogen in allylic position producing resonance stabilized allyl radical C_3H_5 (CH_2=CH-CH_2^*) and C_3H_5-T (CH_2=C^*-CH_3); a further important oxidation pathway is the addition of O to the propene molecule producing C_2H_4 (CH_2=CH_2) and methyl. In figure 2.a, sensitivity analysis of enthalpy towards ignition delay time for propene as fuel for 1440 K, 1540 K and 1660 K are shown where C_3H_6, C_3H_5 and C_2H_4 are the most sensitive species under these experimental conditions.

In the case of propane, fuel consumption is dominated by abstraction of hydrogen in allylic position producing *i*-C_3H_7 and *n*-C_3H_7, removal of methyl group from fuel molecule leads to the production of C_2H_5 (H_2C^*-CH_3). I-C_3H_7 can produce C_3H_6 (CH_2=CH-CH_3) by abstraction of hydrogen and *n*-C_3H_7 (CH_3-CH_2-CH_2^*) can produce C_2H_4 (CH_2=CH_2) by removal of methyl group. Figure 2.b shows the sensitivity analysis of enthalpy towards ignition delay time for propane as fuel for 1380K, 1460K and 1540K where most sensitive species are C_3H_8, C_3H_6, C_3H_4, C_2H_5, C_2H_4 and C_2H_2.

Species sensitivity analysis of entropy towards ignition delay times was also performed. HCCO and but-2-ene (C_4H_8-2) were the sensitive species obtained from these calculations. The sensitivity of but-2-ene (C_4H_8-2) can be explained due to the fact that in the 2-butene sub-mechanism the addition of H (R396) $H+C_4H_8-2=CH_3+C_3H_6$, and OH (R397) $OH+C_4H_8-2=CH_3O+C_3H_6$ are very sensitive pathways that lead to the formation of C_3H_6 molecule.

Figure 3 shows a comparison from the simulation results using the original thermodynamic data, e.g. used by Appel, Bockhorn and Frenklach [18], updates of the thermochemical data of the C_3H_5 molecule and updates of the thermochemical data of the C_3H_6 molecule which improves the prediction of the ignition delay time. Red line is the simulation result using both updated thermodynamic data, where a good agreement with respect to the experimental data can be observed. Similar results are observed for propane ignition delay time as it can be seen in figure 4. The use of the updated thermochemical data leads to a slightly improvement of the modelling predictions of ignition delay times for propane-oxygen mixture. Similar behavior is present in validations done under other experimental conditions as can be observed in figures 5.a and 5.b.

Simulations of premixed laminar flame speed using the updated thermodynamic data from this study were performed. No significant influence in the prediction of this property was observed for propene- and for propane-air mixtures at 1bar and 298 K in an equivalence ratio range from 0.2 to 2.0.

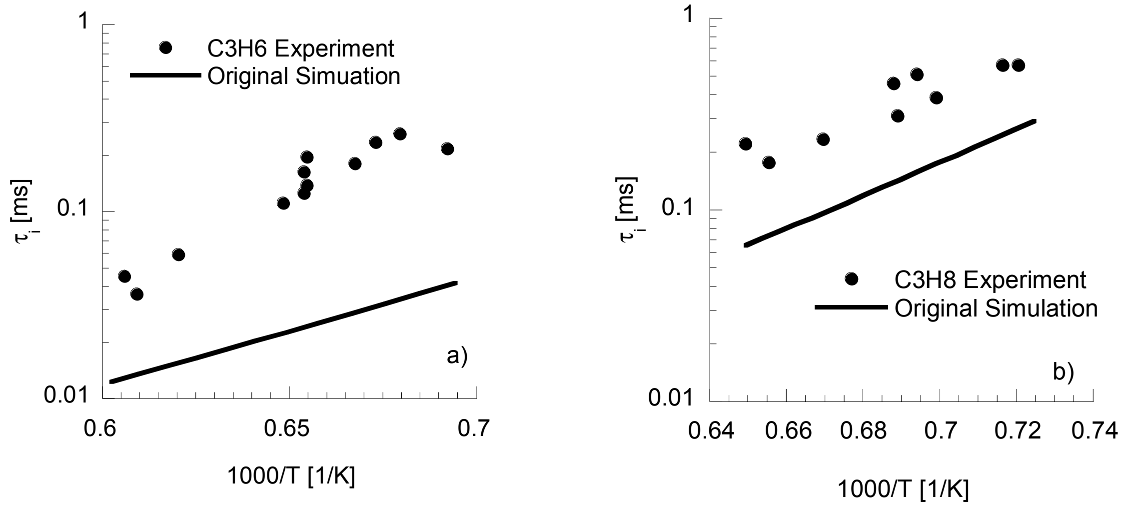

Figure 1: a) Ignition delay time of 1.6 % C_3H_6 / 7.2% O_2 mixture in Ar in a shock tube, 4 bar and a temperature range of 1440-1660 K. Symbols [8] represent experimental data. b) Ignition delay time of 0.84% C_3H_8 / 2.1% O_2 mixture in Ar in a shock tube, 7.5 bar and a temperature range of 1380-1540 K. Symbols [9] represent experimental data. Black lines are simulation results.

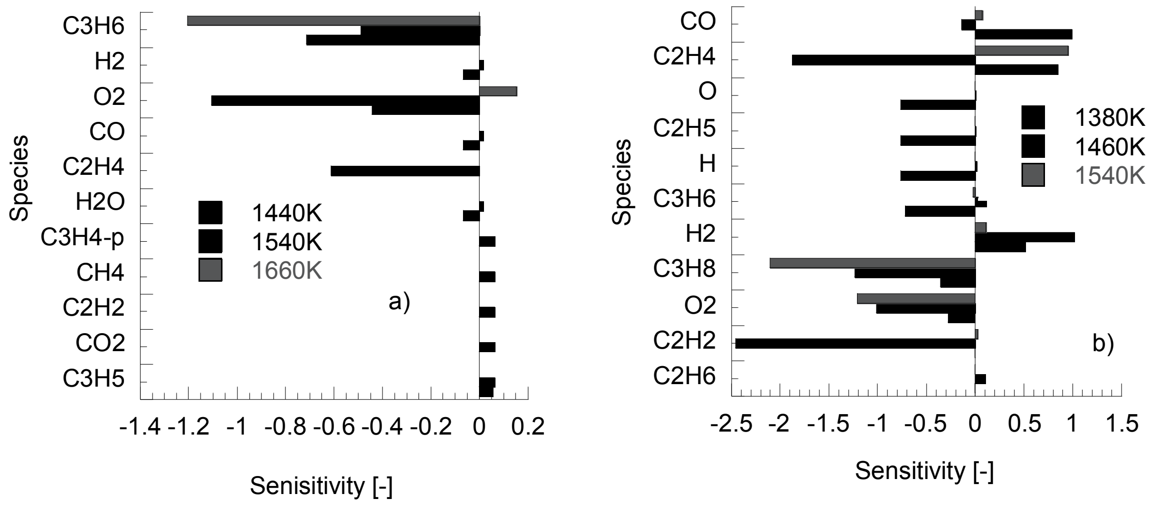

Figure 2: a) Sensitivity analysis of enthalpy towards ignition delay time for propene as fuel for 1440 K, 1540 K and 1660 K. b) Sensitivity analysis of enthalpy towards ignition delay time for propane as fuel for 1380 K, 1460 K and 1540 K.

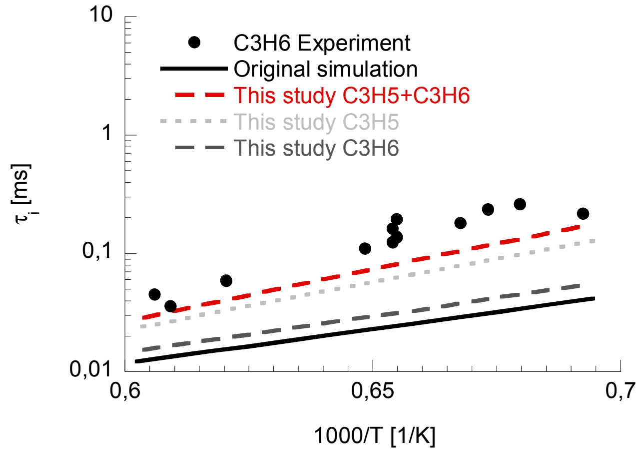

Figure 3: Ignition delay time of 1.6% C_3H_6/ 7.2% O_2 mixture in Ar in a shock tube, 4bar and a temperature range of 1440-1660 K. Symbols [8] represent experimental data. Black line is original simulation result, light grey dotted line: updated C_3H_5 thermodynamic data, dark grey dashed line: updated C_3H_6 thermodynamic data, red dashed line: updated C_3H_6 and C_3H_5 thermodynamic data.

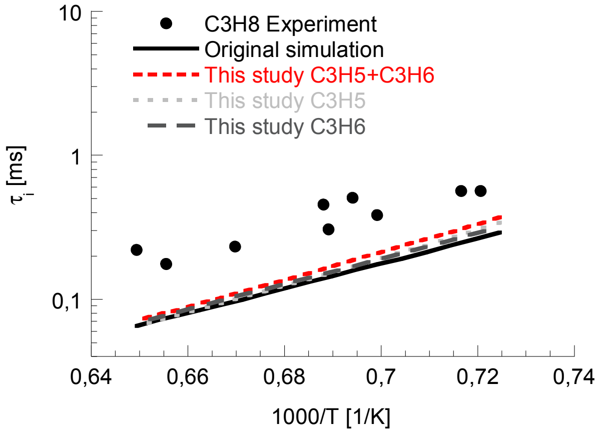

Figure 4: Ignition delay time of 0.84% C_3H_8/ 2.1% O_2 mixture in Ar in a shock tube, 7.5 bar and a temperature range of 1380-1540 K. Symbols [9] represent experimental data Black line is original simulation result, light grey dotted line: updated C_3H_5 thermodynamic data, dark grey dashed line: updated C_3H_6 thermodynamic data, red dashed line: updated C_3H_6 and C_3H_5 thermodynamic data.

Conclusions

In this study it was found that C_3H_6 and C_3H_5 molecules are very sensitive species for the change of the thermodynamic data (enthalpy of formation) toward ignition delay times for propane and propene-oxygen mixtures. Updated thermochemical data, obtained from reliable quantum chemical results, was implemented in our reaction mechanism and a better agreement for the prediction of ignition delay times under different experimental conditions was observed. Due to the different sensitivities the updated thermochemistry data influences only minor the prediction of laminar flame speeds for propene and propane oxygen mixtures.

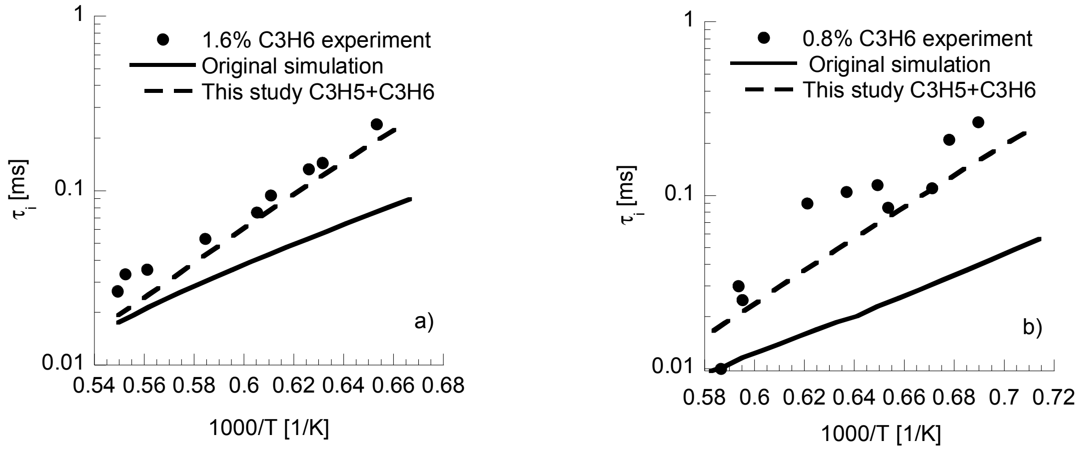

Figure 5: a) Ignition delay time of 1.6 % C_3H_6/ 7.2% O_2 mixture in Ar (Φ=1) in a shock tube, 1 bar and a temperature range of 1500-1820 K. b) Ignition delay time of 0.8 % C_3H_6/ 7.2% O_2 mixture in Ar (Φ=2) in a shock tube, 4 bar and a temperature range of 1440-1720 K. Symbols [8] represent experimental data. Black line: simulation result using original thermodynamic data, dashed line: using updated C_3H_6 and C_3H_5 thermodynamic data.

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