



Laminar burning velocity of diacetyl + air flames. Further assessment of combustion chemistry of ketene



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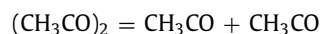
ABSTRACT

Ketene is important intermediate in high-temperature chemistry of several oxygenates, such as acetone, acetic acid, and diacetyl. Ketene reactions appear in the sensitivity spectra of calculated burning velocities of the first two species. To provide independent experimental data for validation of the ketene sub-mechanism, the laminar burning velocities of diacetyl + air flames at 1 atm and initial gas temperatures of 298 K, 318 K, and 338 K were determined for the first time. Measurements were performed using the heat flux method in non-stretched flames, stabilised on a perforated plate burner at adiabatic conditions. Recently developed detailed kinetic mechanism for acetic acid flames with updated ketene sub-mechanism has been extended by reactions of diacetyl and includes revised rate constants for reactions of acetaldehyde and acetyl radical. The model was first compared with available experimental data on ketene pyrolysis and oxidation. Its performance in prediction of C2 species formation was improved by significant reduction of the previously estimated rate constants of ketene reactions with CH₃ and CH₂ radicals. The updated mechanism was then compared with the new measurements for diacetyl and earlier data for acetaldehyde, acetone and acetic acid flames. The model closely reproduces burning velocity of diacetyl + air in lean and rich mixtures while underpredicts in stoichiometric and slightly rich flames. Performance of the model for acetaldehyde + air flames was much improved as compared to the Konnov mechanism version 0.6. Good agreement of the modelling with experimental data for acetone + air flames was also demonstrated. The disparity between predicted burning velocities of acetic acid and recent measurements did not change. The model was further examined using sensitivity analysis for these flames to elucidate common reactions affecting its performance. It was concluded that the mechanism performance in prediction of the burning velocities of acetic acid flames could be improved by revision of reactions between CH₂CO and OH radicals, while keeping its agreement with other flames studied. Remaining uncertainties in the ketene sub-mechanism are outlined.

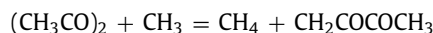
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1. Introduction

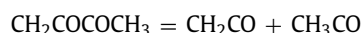
Thermal decomposition of diacetyl (butane-2,3-dione, (CH₃CO)₂), the simplest diketone, has been studied for a long time since 1925. Hurd and Tallyn [1] found that ketene, CH₂CO, is one of the major products of diacetyl pyrolysis with its maximum yield up to 14.5% between 878 and 898 K. The first kinetic studies of the diacetyl pyrolysis [2–4] were interpreted using a free radical mechanism [2] that includes reaction of decomposition



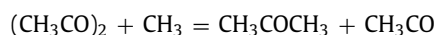
to form two acetyl radicals which rapidly dissociate into CH₃ + CO and subsequent reaction



Radicals CH₂COCOCH₃ were also assumed to decompose rapidly forming ketene



Formation of acetone during thermal decomposition of diacetyl, observed in, e.g., [4] was explained [5] by the radical displacement reaction



The rate constants of diacetyl decomposition and its reactions with methyl were derived in the subsequent studies from the measured product formation rates at moderate temperatures below 690 K [6–9] or maximum up to 776 K [5].

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Decomposition of diacetyl is currently used as a pure source of methyl radicals in shock tube kinetic studies, e.g., [10,11] and therefore pertinent pyrolytic reactions have been revisited experimentally and theoretically in the range of 1200–1800 K [12,13]. Oxidation or flames of diacetyl, however, have never been investigated. Although diacetyl can hardly be considered a fuel or fuel component, the interest is in generation of large concentrations of ketene as a major intermediate similar to combustion of acetone [14] or acetic acid [15]. Hence experimental data on diacetyl combustion can be helpful for independent assessment of the ketene chemistry in flames.

In our recent study of acetic acid + air flames [15] reactions pertinent to acetic acid and ketene have been revised and detailed reaction mechanism was developed. However, the model over-predicted measured burning velocities by about 3 cm/s that exceeded evaluated experimental uncertainty of ± 2 cm/s. The mechanism was also tested comparing with flame structure of the low-pressure flame of acetic acid [16]. Good agreement with the concentration profiles of major products was found, however several minor intermediates were over- or under-predicted by the model. To elucidate reactions responsible for the differences observed, the sensitivity analysis was performed. It was found that the calculated burning velocities are insensitive to the reactions of acetic acid and mostly governed by C1 chemistry typical for all hydrocarbons and by reactions of ketene. Possible modifications of the rate constants were discussed and tested, yet no changes were proposed essentially due to lack of experimental data restraining numerous options and combinations.

The goal of the present study was therefore to determine laminar burning velocities, S_L , of diacetyl + air flames at 1 atm and different initial gas temperatures, and to compare these measurements with the recently developed kinetic model with updated ketene kinetic sub-mechanism [15]. The model is also tested in comparison with the burning velocities of acetaldehyde and acetone, and with available experimental data on ketene pyrolysis and oxidation.

2. Experimental details

The laminar burning velocities were measured using the heat flux method. As a detailed review of the method and its uncertainties was recently published [17], only specific details of the present experiments will be described. Measurements were performed at initial mixture temperatures of 298, 318, and 338 K and ambient pressure for equivalence ratios $\phi = 0.7$ –1.5. The diacetyl was provided by Alfa Aesar and had a purity of 99%. Following a standard procedure [15] two mixing panels of different capacity were used. Initial feasibility experiments at 298 K were performed using Setup II with the smaller evaporator (200 g/h) depicted in [18,19] as this is typically used for heavier fuels with lower laminar burning velocity. It became apparent, however, that the laminar burning velocity of diacetyl were higher than initially anticipated and larger flows were required than achievable with this mixing panel. Further measurements were performed on Setup I equipped with a larger evaporator (1200 g/h) also described earlier [15,17]. Initial temperatures of 298 and 318 K were visited twice to ensure and check data consistency. To avoid fuel condensation a heating tube was connected between the mixing panels and the burner inlet with the temperature set to the same value as the plenum chamber. The measurements of the burning velocity of diacetyl + air flames span over 3 non-consecutive days using two different heat flux setups, yet with the same burner designated “T” by Alekseev et al. [17]. Specific for this burner correction (“flame surface area” [17]) has been implemented. Data analysis included interpolation or extrapolation techniques when determining the laminar burning velocity. Extrapolation is necessary when the

flame cannot be stabilised at unburned gas flows above the laminar burning velocity. The extrapolation range (difference between the laminar burning velocity and highest unburned gas velocity) was below 2.5 cm/s. The total uncertainty of the laminar burning velocity shown as error bars and listed in the Supplemental material includes the error of extrapolation/interpolation.

3. Modelling details

Modelling was performed using CHEMKIN 4 software, release 10112 [20]. Shock tube experiments were simulated using the closed batch reactor module under constant volume and adiabatic conditions. The laminar burning velocity was simulated using the premixed laminar flame speed calculation module with multicomponent transport and thermal diffusion options taken into account. A grid independent solution was ensured by setting the parameters GRAD and CURV to values of 0.03 and 0.02, respectively, resulting in a typical number of grid points above 900.

4. Model development

The original Konnov mechanism version 0.5 was published in 2000 on a dedicated web-site, which also provided information on each rate constant implemented. This web-site (<http://homepages.vub.ac.be/~akonnov/>), however, does not exist anymore. The next version 0.6 was different only in the prompt-NO chemistry retaining all H/C/O reactions, thus the pertinent performance of these two versions was the same as summarised in [21]. These models were mostly validated for combustion of C1–C3 hydrocarbons and nitrogen chemistry in flames. Extension of the mechanism toward carboxylic acids and other oxygenated species was described later [22–24], however no backward compatibility of these updates was verified. Meanwhile new hydrogen sub-mechanism was suggested and validated [25]; its implementation in the model developed for C₃H₆O isomers [23] showed better agreement with the laminar burning velocities of acetone [14].

The paradigm of the detailed kinetic mechanism development assumes that better knowledge of the rate constants implemented in the model should improve its performance. This can be achieved if the model was not adjusted or optimised to accommodate specific measurements. On the other hand, this does not mean that rate constants cannot be derived or modified using comparison of experimental data and modelling, as exemplified in, e.g., [26]. Thus it is believed that recent modifications and extension of the mechanism outlined below does not deteriorate its fundamental predictive capabilities. Since the focus of the present study is on the role of ketene chemistry in flames, the model will be tested against the burning velocities of diacetyl, acetaldehyde and acetone, and with available experimental data on ketene pyrolysis and oxidation.

Major revisions of the kinetic mechanism already implemented include updated hydrogen sub-mechanism [27], further extended by excited species [28], syngas sub-mechanism [29] and reactions of C1 chemistry focusing on CH₂O and CH₃OH combustion [30]. Reactions of C atoms, CH, CH₂, ¹CH₂, HCOH and CH₃ radicals not covered in the previous studies [29, 30] have been re-evaluated [31] simultaneously with updates in the reactions of ketene, ketylenyl radicals and acetic acid [15]. All modifications realised earlier [15,22–24,27–31] are documented in the mechanism file available in the Supplemental material. The model consists of 1236 reactions and 106 species. Reactions introduced and/or revisited in the present study are listed in Table 1 and described below. Rate constants have units of cm³, mol, s and activations energies are in cal/mol.

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