The oxidation of methyl formate and methanol: an updated kinetic model.

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In an attempt toward the development of a biodiesel kinetic model, the present study presents an updated kinetic model for the smallest methyl ester, methyl formate, as well as for methanol, one of its main intermediate species. The model is assembled by performing a careful and critical review of elementary rate constants that have been previously measured and/or calculated from first principles. Most sensitive reactions during methanol oxidation and pyrolysis are discussed, and the kinetic parameters used in the present model are validated by comparison against experimental observations. Methanol oxidation was found to be extremely sensitive to HO₂ chemistry (H abstraction reactions on methanol) between 800 and 1300 K in flow reactor and shock tube conditions, while laminar flame speeds are highly sensitive to the hydroxymethyl (CH₂OH) radical decomposition at fuel rich conditions. Methyl formate decomposition reactions, either through concerted elimination reactions or hemolytic bond scission, are discussed. The proposed rate constants were tested against time speciation profiles but could not capture methanol pyrolysis over the entire temperature range. The present study suggests that despite the recent efforts, additional efforts on methyl formate and methanol oxidation kinetics are required.

1 Introduction

Over the last decade, tremendous efforts have been dedicated to kinetic modeling of gasoline, jet fuels, and biodiesel surrogates. Such large kinetic models usually encompass hundreds of species involved in thousands of reactions and are developed based on similarity rules. These rules state that the rate constant is only dependent on the reaction site and its surroundings, and therefore validated rate constants used for small fuels can be propagated to the larger ones (after correction to account for degeneracy). Indeed, investigating the kinetics of every single reaction through ab initio calculations would be both prohibitive and meaningless as combustion properties are mainly sensitive to a small set of reactions. On the other hand, in addition to their small size, small fuels are uniquely sensitive to a limited set of fuel specific reactions over all thermodynamic conditions. Thus, detailed analysis and elementary rate constant calculations are affordable to develop reliable kinetic models.

Methyl formate (C₂H₄O₂) is the smallest methyl ester. Although recent studies [1, 2] have demonstrated that it is not an appropriate biodiesel surrogate because of its specific reactivity, methyl formate oxidation nevertheless deserves specific attention. First, methyl formate radicals (CH₃CO) are generated during the combustion of the larger methyl esters present in biodiesel, whose combustion properties are sensitive to the kinetics of those radicals. Second, as the smallest methyl ester, methyl formate can be studied through high-level quantum chemistry methods and the calculated and validated rate constants used directly or extended to larger fuels using similarity rules. The experimental studies already available on methyl formate pyrolysis and
oxidation have established that methanol is one of the main intermediates. Hence, in order to understand and model the combustion of methyl formate, the development of a comprehensive and validated methanol model is a prerequisite.

Methanol oxidation has been studied in several experimental facilities. There is an abundance of time speciation profiles measured in the Princeton flow reactor by Dryer and co-workers [3, 4]. A large matrix of temperature, pressure, and equivalence ratio has been considered. Dayma et al. [5] have investigated the effect of NO and NO\textsubscript{2} on methanol oxidation in a jet-stirred reactor (JSR). Bowman et al. [6], and more recently Noorani et al. [7], have measured the ignition delays of methyl formate/oxygen/inert mixtures at various temperatures, pressures, and equivalence ratios. The laminar flame speeds of methanol in air have been determined by Egolfopoulos et al. [8], Veloo et al. [9] and more recently Vancoillie et al. [10] for a wide range of initial temperature. Finally, Srinivasan et al. [11] have designed specific experiments in order to determine the rate constant of the H abstraction reaction of OH with methanol. Despite a more recent interest in methyl formate, similar studies have been performed for this fuel. Dooley et al. [2] investigated the oxidation of this methyl ester in a flow reactor and Akih-Kumge and Berghorson [12] published the ignition delays of several methyl formate/oxygen/argon mixtures. Ren et al. [13] monitored methanol and CO formation during the pyrolysis of methyl formate in a shock-tube, whereas Wang et al. [14] and Dooley et al. [2] presented the laminar burning velocities of methyl formate/air mixtures at atmospheric pressure. Recently Kurimoto et al. [15] carried flow reactor experiments of the pyrolysis and oxidation of methyl formate at atmospheric pressure and the exhaust gases were analyzed by using the molecular beam mass spectrometry.

Several kinetic models are also available for these two fuels. As an intermediate species in n-alkane oxidation, various subsets for methanol oxidation have been developed, although few of them were specifically developed for this fuel. Dayma et al. [5] proposed a kinetic model that includes a NO\textsubscript{2} reaction set. This model was validated against speciation profiles in a JSR and used to interpret their experimental observations. Li et al. [16] published an 84-reaction model for methanol that was validated against flow reactor speciation profiles and shock tube ignition delay. Upon this model, Dooley et al. [2] recently published a methyl formate model. The kinetics of methyl formate was established by considering structure-reactivity correlations and was tested against VPFR time speciation profiles, ignition delays, and laminar flame speeds. Besides their publications on biodiesel surrogate modeling, Westbrook et al. [17] proposed a methyl formate kinetic model that has been tested against speciation profiles of low-pressure stabilized flames.

Those models, some of which are pioneer works, were developed based on reactivity-fuel structure considerations in order to reproduce experimental observations. However, recent experimental or theoretical studies focused on reactions involving these two fuels have validated or invalidated some of the assumptions made in these models. These new insights on methanol and methyl formate oxidation suggest that the current models must be revised and updated. Therefore, the aim of this study is to develop a kinetic model for methanol and methyl formate based on reliable thermochemical and kinetic parameters that can be used as a core model for the development of a biodiesel surrogate model. Several essential parameters are discussed in this paper, and the choices made herein are validated through comparison with experimental observations.

2 Thermochemistry and transport database

Thermochemical parameters (heat of formation, entropy and heat capacities) are deeply involved in model predictions as they dictate the heat release rate and affect the kinetics through the calculation of the equilibrium constant and the reverse rate constant. Nevertheless they often receive little attention from model users and developers who focus mainly on the kinetic parameters. In this study, the thermochemistry data of methanol and related species were adopted from the 3rd Millenium database [18]. These data are derived from either experimental measurements or \textit{ab initio} calculations at various levels of theory coupled with experimental validation. The present parameters are in close agreement with the parameters used previously by Li et al. [16], and therefore are not expected to strongly affect the model computations. However, the bond dissociation energy (BDE) associated with the O-H bond in methanol is widely different between the two
The kinetic parameters calculated through the principle of corresponding states agree well with the data adopted by Dooley et al. [19]. However, as the formation of the methoxy radical has been observed to be a minor pathway in methanol oxidation, model performances should not be significantly impacted by this parameter.

The thermochemistry of methyl formate and its radical have been studied by several groups [18-21]. After comparisons of all the available data for methyl formate, the parameters calculated by Goldsmith et al. [19] have been adopted. Those parameters are very close to the calculated average values, and are in close agreement with the data adopted by Dooley et al. [2]. A similar logic was followed for the two radicals CH₃OCHO and CH₃OCO after discarding the outlying data. The entropy and heat capacities calculated by Goldsmith et al. [19] were employed, while BDEs of 100.4 and 98.40 kcal.mol⁻¹ were derived for the CH₃OCHO and CH₃OCO radicals, respectively. Finally, the parameters herein recommended were utilized to update the group additivity values (GAV) contribution in order to estimate the thermochemistry of the minor species involved in the oxidation of methyl formate.

The transport parameters employed in the present study are mainly adopted from the Chemkin transport database [22] and from Westbrook et al. [16]. The transport parameters of methyl formate were calculated through the principle of corresponding states [23]. The updated value of the Lennard-Jones collision diameter is 16% higher than the one used in the Dooley et al. model [2] (4.686 Å against 4.037 Å) while the potential well-depth remains nearly unchanged.

### 3 Methanol pyrolysis and oxidation

The model proposed in this study has been tested and validated against a large set of experimental data. Based on the sensitivity analysis (Table 1) in different thermodynamic conditions, the rate constants of the most sensitive reactions are discussed and the kinetic parameters adopted in the present model rationalized through validation against specific experimental targets.

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**Table 1:** Sensitivity analysis (normalized coefficients) for methanol oxidation performed with the model of this study.

<table>
<thead>
<tr>
<th>Reaction No</th>
<th>Reaction</th>
<th>Ignition delay in shock tube (1258 K and 2.5 atm)</th>
<th>CO₂ formation in JSR (800 K and 10 atm)</th>
<th>Laminar flame speed (φ = 1.00 and 1 atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + O₂ ⇌ O + OH</td>
<td>-0.092 &lt;0.05 1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>HCO (+M) ⇌ H+CO (+M)</td>
<td>&lt;0.05 &lt;0.05 0.600</td>
<td></td>
<td></td>
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<tr>
<td>17</td>
<td>HO₂ + H ⇌ OH + OH</td>
<td>-0.018 &lt;0.05 0.421</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>HO₂ + OH ⇌ H₂O + O₂</td>
<td>0.088 -0.081 -0.307</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>HO₂ + HO₂ ⇌ H₂O₂ + O₂</td>
<td>0.293 -0.612 0.040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>H₂O₂ (+M) ⇌ OH + OH (+M)</td>
<td>-1.000 0.513 0.127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>H₂O₂ + OH ⇌ HO₂ + H₂O</td>
<td>0.024 -0.331 -0.046</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>CO + OH ⇌ CO₂ + H</td>
<td>&lt;0.05 0.386 0.522</td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>HCO + O₂ ⇌ CO + HO₂</td>
<td>0.014 -0.054 -0.200</td>
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</tr>
<tr>
<td>35</td>
<td>HCO + H ⇌ CO + H₂</td>
<td>&lt;0.05 &lt;0.05 -0.334</td>
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</tr>
<tr>
<td>49</td>
<td>CH₂O + OH ⇌ HCO + H₂O</td>
<td>-0.039 -0.461 0.089</td>
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<td></td>
</tr>
<tr>
<td>53</td>
<td>CH₂O + HO₂ ⇌ HCO + H₂O</td>
<td>-0.104 1.000 0.016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>CH₂OH (+M) ⇌ CH₂O + H (+M)</td>
<td>&lt;0.05 &lt;0.05 0.208</td>
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<td></td>
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<tr>
<td>91</td>
<td>CH₂OH (+M) ⇌ CH₂ + OH (+M)</td>
<td>-0.135 &lt;0.05 -0.070</td>
<td></td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>CH₂OH + OH ⇌ CH₂O + H₂O</td>
<td>-0.060 0.383 0.066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101</td>
<td>CH₂OH + HO₂ ⇌ CH₂OH + H₂O₂</td>
<td>-0.836 0.771 0.020</td>
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<td></td>
</tr>
<tr>
<td>102</td>
<td>CH₂OH + HO₂ ⇌ CH₂O + H₂O₂</td>
<td>-0.473 &lt;0.05 0.016</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Models: 104.0 kcal.mol⁻¹ used by Li et al. [16] against 105.2 kcal.mol⁻¹ in the present study. This latter value is in excellent agreement with the recent calculations of Goldsmith et al. [19]. However, as the formation of the methoxy radical has been observed to be a minor pathway in methanol oxidation, model performances should not be significantly impacted by this parameter.
1. Methanol decomposition

Fuel decomposition reactions are endothermic processes that occur only in severe thermodynamic conditions, such as high temperature. In order to investigate methanol decomposition, Srinivasan et al. [11] carried out shock tube experiments of methanol pyrolysis. Using highly diluted mixtures of methanol (isothermal conditions), they monitored the concentration of the OH radical. Those experiments were designed such that the hydroxyl radical concentration is mainly sensitive to the methanol decomposition reactions (R91: CH$_3$OH (+M) ⇌ CH$_3$ + OH (+M) and R92: CH$_3$OH (+M) ⇌ CH$_3$(S) + H$_2$O (+M)), and therefore the results can be used to assess the validity of the rate constants employed for these reactions. Figure 1 shows the experimental OH radical profiles during the pyrolysis of methanol at two different temperatures, as well as the profile computed with the present model and the model of Li et al. [16] The model of Li et al. significantly overestimates the formation of OH at the higher temperature but slightly underestimate it at the lower temperature. The rate constants used by Li et al. were adopted from GRI-Mech 3.0 [24] and were derived from a RKKM analysis of the methanol decomposition subset.

Recently Jasper et al. [25] investigated the CH$_3$ + OH system through *ab initio* calculation at the QCISDT(T)/CBS//B3LYP/6-311G** level of theory. They derived the rate constant of all the methanol decomposition reactions by performing a master equation analysis. In the first modeling attempt, the rate constant calculated by Jasper et al. [25] was used without modification, but resulted in a strong underestimation of OH concentration at the lowest temperature while the model captured the OH profile at the higher temperature in the experimental conditions reported by Srinivasan et al. [11]. Although the use of these new rates gives improved predictions compared to the model of Li et al., the reaction rates have been slightly modified. In the conditions investigated here, the reaction rates of interest are in the fall-off regime. In the master equation analysis, the energy transfer collision is a critical input whose values are usually adjusted to reproduce the experimental observations when they are available. As a consequence, in order to improve the model predictions against the OH profiles, the pressure dependence of these reactions have been modified. The new pressure dependence results in rate constants that are 30% (2600K) and 70% (1600K) higher than the rates initially proposed by Jasper et al., and leads to the model computations displayed in Figure 1. The present model captures the initial formation of OH and its consumption at both temperatures. However, the present rate constants are beyond the uncertainties reported by Jasper et al. and therefore a more detailed analysis of the pressure effect and validation over a larger temperature and pressure range is desired.

2. H abstraction from methanol by the hydroperoxy HO$_2$ radical.

At low and intermediate temperatures, methanol reacts mainly through H abstraction reactions with small radicals and atoms such as OH, HO$_2$ and H. In VPFR [3-4] and JSR [5] conditions, methanol is mainly consumed by reactions with the OH radicals (R98). However, the sensitivity analysis (Table 1) shows that the reactions of methanol with the HO$_2$ radical (R101 and R102) are the most sensitive reactions. While such an observation can be rationalized with the low temperature and high pressure conditions encountered in these
two facilities, the strong sensitivity of the HO$_2$ chemistry, and therefore the reaction 101, around 1300 K in a shock tube is more unusual.

Skodje et al. [26] and Alecu and Truhlar [27] investigated reactions 101 and 102. They calculated the rate constants of each channel at the CCSD(T)/CBS//CASPT2/cc-pVTZ and M08-HX55/maug-cc-pVTZ level of theory respectively. Figure 2 depicts the rate constants proposed by these two groups, as well as the rate used by Li et al. in their methanol kinetic model. The most recent value of Alecu et al. is about three times higher than the one of Skodje et al., but around three times lower than the rate constant adopted by Li et al. The value used by Li et al. was proposed initially by Cathonnet et al. [28], and was chosen to reproduce the flow reactor results. In order to make a decision on the choice of the rate constant of reaction 101, the speciation delays in JSR and VPFR and the ignition delays of methanol/O$_2$/Ar mixtures were considered. The rate constants of Skodje et al. and Alecu et al. result in excellent agreement with the JSR data, but result in over-estimation of ignition delays and failure to capture the methanol consumption in flow reactor (and also required unphysical time shifting). On the other side, the rate constant of Cathonnet et al. captures the flow reactor observations but overestimates the methanol consumption rate in the JSR conditions. To recover an overall good agreement in both JSR and VPFR conditions, the rate constant proposed by Alecu et al. has been modified and a rate of $k_{101}(T) = 5.49 \times 10^5 \times T^{5.24} \times \exp(-5505/T)$ cm$^3$.mol$^{-1}$.s$^{-1}$ has been derived and is reported in Fig. 2. This rate constant is of intermediate value with those of Alecu et al. and Cathonnet et al. Figure 3 shows the performance of the present model and the model of Li et al. against the oxidation of methanol in a JSR at 10 atm. The present model reproduces the methanol consumption and the initial CO and water formation whereas the model of Li et al. predicts a methanol oxidation at slightly lower temperatures. Although not shown here, the present model also shows a good agreement against the flow reactor speciation of Held [4], suggesting that the rate adopted here is an adequate compromise.

3. Decomposition of the hydroxymethyl radical CH$_2$OH

Laminar flame speeds are often used as validation targets for kinetic model validation, since it is an essential combustion property relevant to practical applications. The laminar burning velocities of methanol/air mixtures have been measured by several groups: Egolfopoulos et al. [8]
and Veloo et al. [9] in a counterflow configuration, and Vancoillie et al. [10] using a heat flux burner. Figure 4 presents and compares some of these experimental data. One can observe that both the counterflow and heat flux method provide similar flame speeds for the lean mixtures but diverge on the fuel rich side with differences up to 18% at \( \varphi=1.5 \).

Laminar flame speeds are known to be mainly sensitive to the reactions of the \( \text{H}_2/\text{CO}/\text{O}_2 \) subset. A sensitivity analysis on a stoichiometric methanol/air mixture (Table 1) confirms this common knowledge in the case of methanol. However, the sensitivity analysis also reveals that the laminar flame speed is strongly sensitive to the dehydrogenation of the hydroxymethyl radical (R70: \( \text{CH}_3\text{OH} (+\text{M}) \rightleftharpoons \text{CH}_2\text{O} + \text{H} (+\text{M}) \)), and the sensitivity coefficient of this reaction increases with the equivalence ratio. This reaction has been recently investigated by Yang et al. [29] at the CCSD(T)/CBS//QCISD(T)/aug-cc-pVTZ level coupled to a master equation analysis. The rate constant they calculated is lower than the previous recommendation by Baulch et al. [30], but is in fair agreement with the experimental determinations [6, 31]. As a consequence, this rate constant has been adopted in the present model. This rate is 2 to 4 times higher than the rate constant used by Li et al., who assumed that the reaction is in the low pressure limit and adopted the rate constant determined by Cribb et al. [31] at high temperatures (1900-2700 K) and low pressure (6-20 torr). Computations with the present model and the model of Li et al. are also shown in Fig. 4. Both models surprisingly exhibit a similar behavior: they match the experimental measurements on the lean side, but on the rich side predict flame speeds that are close to the heat flux measurements and thus overestimate the data obtained in the counterflow configuration. The high sensitivity of the laminar flame speeds to this rate constant, combined to the large scattering in the experimental measurements, suggests that new experimental measurements are required to assess the rate of reaction 70.

4 Pyrolysis of methyl formate

Methyl formate pyrolysis and oxidation can be divided in three parts: (i) the initial fuel decomposition reactions, (ii) H abstraction reactions to generate the two methyl formate radicals, and (iii) the decomposition of these radicals. The current section focused on the first group of reactions.

1. Methanol elimination reaction

Fuel decomposition usually proceeds through homolytic bond scission (C–C and C–H). Although such reactions exist for methyl formate, previous studies have demonstrated that the initial methyl formate decomposition is governed by concerted molecular elimination reactions [2, 13]. Experimental observations have shown that the methanol elimination reaction (with CO as a co-product) is the dominant reaction path. The calculations of the potential energy surface [20, 32] of the methyl formate decomposition system have confirmed this reaction as the most favored. Therefore, an accurate rate constant for this reaction is required.

Metcalfe et al. [32] and Peukert et al. [20] have calculated the energetics of the methyl formate system at the CBS-QB3/B3LYP/6-311G(d,p) and CCSD(T)/cc-pv1z//B3LYP/6-311++G(d,p) level of theory, respectively. The rate constants were finally obtained from a master equation analysis. Experiments have been
performed by Ren et al. [13] on methyl formate pyrolysis in a shock tube at ~1.5 atm. They monitored the formation of CO, CH₄, CO₂ and CH₂O by laser absorption and derived the rate constants of each concerted molecular elimination channel.

Figure 5 displays the measurements of Ren et al. for the methanol elimination channel as well as the calculated rate constants of Peukert et al. [20] and Metcalfe et al. [31] and the estimation of Dooley et al. [2] at the high pressure limit and at a pressure of 1.5 atm. First, the calculated high pressure limits of Metcalfe et al. and Peukert et al. are in good agreement with each other (within 25-30%), but are lower than the experimental determinations at the lower temperatures, whereas the estimated high pressure limit of Dooley et al. is in excellent agreement with the experimental data. From Fig. 5 it appears that the methyl formate decomposition reactions are close to the high pressure limit even around atmospheric pressure, which is captured by the pressure dependence proposed by Dooley et al. This was achieved by performing a QRRK analysis of the methyl formate decomposition reactions using a high collisional energy transfer (2.785 × T cm⁻¹). Peukert et al. and Metcalfe et al. used a lower collisional energy transfer (1.557 × T⁻⁰.⁸⁵ and 400 cm⁻¹, respectively), leading to a stronger fall-off effect near atmospheric pressure.

The strong sensitivity of methyl formate pyrolysis to the methanol elimination channel requires an accurate knowledge of the rate constant. The high pressure limit rate constants calculated by Metcalfe et al. have been adopted in this study, and the pre-exponential factor have been scaled by 1.50 to be certain that the high pressure limit is larger than the experimental measurements of Ren et al. Then, similarly to Dooley, a QRRK analysis has been performed (including all the decomposition channels) and a collisional energy

![Figure 5](image_url)

**Figure 5**: Rate constant of the methanol elimination reaction CH₃OCHO (+M) ⇌ CH₃OH + CO (+M). The symbols are experimental determinations by Ren et al. [13] (1.5 atm). The solid and dashed line are the rate constant at the high pressure limit and at P ≈ 1.5 atm respectively. (─) Metcalfe et al. [32], (--) Peukert et al. [20], (--) Dooley et al. [2], and (--) this study.

![Figure 6](image_url)

**Figure 6**: Comparison between experimental and computed CO mole fraction time-history profiles during the pyrolysis of methyl formate (0.1% in argon) at three different temperatures and at ≈1.5 atm. (─) Ren et al. [13], (--) Westbrook et al. [16], (--) Dooley et al. [2], and (--) this study.
transfer of $1.99 \times T^{0.94}$ cm$^{-1}$, which is between the values of Dooley et al. and Peukert et al., was utilized. Those new rate constants (high pressure limit and 1.5 atm) are shown in Fig. 5. The present methodology results in rate constants that are higher than those proposed by Peukert et al. and Metcalfe et al., but are still lower than the experimental determinations and the Dooley et al. estimate below 1400 K.

Figure 6 compares the CO measurements of Ren et al. with the modeled using the present model and the models of Westbrook et al. [17] and Dooley et al. [2]. First, the model of Westbrook computes a faster production of CO than observed experimentally, and overestimates the final CO concentration at the lowest temperatures. The faster CO production by this kinetic model can be attributed to the faster high pressure limit rate constant of the methanol elimination reaction (a factor of two larger than the rate constant used in this study at 1200 K) coupled with the absence of pressure dependence. The model of Dooley et al. captures the initial formation of CO due the methyl formate reaction, but fails to reproduce the contribution of methanol to CO formation at the highest temperature. The present model underestimates the formation of CO at the lowest temperature, as expected from Fig. 5, but captures the first stage (from methyl formate) and second stage (from methanol) of CO formation at the highest temperatures.

2. Methyl formate decomposition

Although the previous section focused on the concerted molecular elimination reactions that control methyl formate pyrolysis, other combustion properties are sensitive to the more traditional fuel decomposition reactions. Through bond breaking, methyl formate can generate four sets of products: CH$_3$ + OCHO, CH$_3$O + HCO, H + CH$_2$OCO, and H + CH$_2$OCHO. Therefore, an adequate description of these processes is required. However, they have so far received little attention. Peukert et al. [20] performed methyl formate pyrolysis shock tube experiments in which the H atom concentration is used as the reactivity marker. Path flux and sensitivity analysis with different kinetic models indicate that H atom is mainly a sub-product of methyl formate fragmentation through the decomposition of the OCHO radical. As a consequence, the experimental data of Peukert et al. can be used to evaluate the rate constant of the reaction CH$_3$OCHO $\Delta$ CH$_3$ + OCHO (R365).

When investigating the rate constant of the methanol elimination reaction, Peukert et al. also considered the methyl formate decomposition reactions. They proposed a rate constant of $4.95 \times 10^{35} \times T^{5.40} \times \exp(-50136/T)$ cm$^3$.mol$^{-1}$.s$^{-1}$ for the high pressure limit of the reaction R365, which is about 6 times higher than the rate constant adopted by Dooley et al. In the present study, the high pressure limit of the reaction R300 has been estimated from the thermochemistry and the reverse rate constant (recombination of two radicals). The rate constant calculated by Klippenstein et al. [33] for the CH$_3$ +CH$_3$ recombination has been adopted and the frequency factor adjusted for the difference in the reduced mass and collision diameter of the
reactants. This methodology results in a high pressure limit that is about two times lower than the calculated rate of Peukert et al., \( k_{65}(T) = 3.23 \times 10^{25} \times T^{-2.52} \times \exp(-47090/T) \) cm³/mol·s⁻¹. Consistent with the concerted elimination reactions, a pressure dependence analysis has been applied.

Figure 7 displays the comparison between the experimental results of Peukert et al. and computations using the model of Dooley et al., the skeletal model of Peukert et al. and the present model. It should be noted that the model of Peukert et al. has been modified in this study to include the decomposition of the methoxy (CH₃O) radical, which significantly affects the computations. The simulation results obtained with the model of Westbrook et al. are not shown here as the model predicts an immediate growth of the H atom pool regardless of the temperature, and therefore strongly overestimates H atom concentration. This behavior is attributed to the absence of pressure fall-off on the fuel decomposition reactions. The model of Dooley et al. overestimates the H atom concentration at higher temperature, but qualitatively capture the formation and consumption of the H atom pool (plateau in Fig. 7 after 800 μs at 1373 and 1371 K), whereas the present model and the model of Peukert et al. show a better quantitative agreement but fail to capture the consumption of H atoms. While the initial formation of H is the consequence of methyl formate decomposition, the sustainability of the H atom concentration results from the H abstraction reactions of methyl formate with H, and especially the reaction producing the CH₂OCO radical. Indeed, H atom concentration is insensitive to the other abstraction reactions as the radicals produced (CH₂OH, CH₃O, HCO, and CH₃OCHO) readily release an H atom. The CH₂OCO radical has two decomposition paths affecting the overall reactivity: a propagation channel (CH₂O + CO) and a termination channel (CH₃ + CO₂). The ratio between these two channels is temperature and pressure dependent, but recent and previous potential energy surface calculations [34, 35] indicate that the termination channel is the preferred channel. However, further constraining experimental data and quantum mechanical calculations are required.

5 Conclusions

A kinetic model for the pyrolysis and oxidation of methyl formate has been presented. The uniqueness of methyl formate reactivity requires the implementation of a validated methanol oxidation submodel. The methanol subset was assembled by carefully reviewing available thermochemical and kinetic parameters. The prescribed parameters have been discussed and rationalized through comparison against experimental measurements in shock tubes, flow reactors, and laminar flames. The methyl formate subset has been added to the methanol model. By considering recent experimental time profiles during methyl formate pyrolysis, rate constants for the methyl formate decomposition reactions (concerted elimination and bond breaking reactions) are proposed, although large uncertainties in the high pressure limits and the pressure fall-off remain to be quantified. The present model demonstrates improved prediction of shock tube, JSR, and flow reactor results. However, the present and other available models do not satisfactorily capture all the experimental targets, especially the H consumption in methyl formate pyrolysis. In a similar study, Kurimoto et al. [15] investigated the pyrolysis and oxidation of methyl formate and found that the current models underestimate the contribution of H abstraction reactions to the methyl formate depletion. Their conclusions and the present ones suggest that a deeper understanding of the methyl formate molecule and radicals is necessary to achieve a predictive methyl formate kinetic model.

Acknowledgements

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References


[18] Elke Goos, Alexander Burcat and Branko Ruscic, Ideal Gas Thermochemical Database with updates from Active Thermochemical Tables
[24] Smith et al., http://www.me.berkeley.edu/gri_mech/
[29] Yang et al., 8th U. S. National Combustion Meeting, Paper 070RK-0163