A kinetic model for methyl formate oxidation is generated using our open-source Reaction Mechanism Generator (RMG) software, supplemented with high level quantum calculations and transition state theory (TST). New rate coefficients are calculated for the decomposition pathways of methyl formate, methoxy-formyl (CH$_3$OC′O), and formyloxy-methyl (C′H$_2$OCHO), and hydrogen abstractions from methyl formate by H and methyl radicals. We compare the predictions to experimental data including previously unpublished shock tube ignition delays over a wide range of $T$ and $P$, as well as atmospheric-pressure laminar burning velocities and low-pressure flame species profiles from the literature. Using RMG we investigate the effect of changing the small molecule (C$_0$–C$_1$) “seed mechanism” and show that predictions of all the experiments are sensitive to these reactions. Until the small molecule chemistry is resolved it is impossible to have a conclusive mechanism for the fuel molecule oxidation.

1 Introduction

Methyl esters are an important class of biofuel; the smallest methyl ester is methyl formate (MF), CH$_3$OCH=O. This is a useful species to study because the reaction mechanism will be an important subset of any larger alkyl ester mechanism, and the reaction pathways of other alkyl esters will be similar. Training automatic kinetic model building software to predict methyl formate combustion will improve the software’s ability to predictively model other esters. Methyl formate oxidation has recently been the subject of many experimental [1–3], computational [4,5], and modeling [1,2] investigations.

2 Kinetic Model Generation

The open-source software Reaction Mechanism Generator (RMG) was used to build a kinetic model for methyl formate oxidation. The species predicted by this model were the basis of a library of thermochemical data calculated ab initio. The reaction rate coefficients of some important methyl formate reactions were also calculated (section 2.2). With this data, RMG was used to construct kinetic models built on three different seed mechanisms from the literature. The thermochemistry, methyl formate reaction rate coefficients, transport parameters, and all other settings were consis-
tent across models. The three resulting kinetic models were used to simulate dilute shock tube ignition delays ($\phi=0.5, 1, 2$), atmospheric pressure laminar burning velocities ($0.7<\phi<1.6$), and a low pressure (22 torr) $\phi=1$ flame.

2.1 Reaction Mechanism Generator (RMG)

Reaction Mechanism Generator (RMG), an open-source tool for building kinetic models, is available at [6]. RMG uses reaction family templates to generate all possible reactions that a species can undergo in the presence of the other species in the model. The thermochemistry of each species and rate coefficient of each reaction is either taken from a library of stored values or estimated using a group additivity scheme organized in a hierarchical database such that the group value used is the most specific matching group with data available. The kinetic model is expanded by identifying the ‘edge’ species with the highest rate of creation (flux) according to the existing model at the conditions of interest, adding it to the model core, and finding all its possible reactions. This is repeated until the flux to all non-included (edge) species falls below a user-defined threshold (relative to the characteristic flux of the included core species). The principles are further described in [7].

The current study motivated many improvements to RMG so was performed on many versions of the software, culminating in version 3.2.3. Some key features of this version that were used in building these models include:

- Pressure-dependent reaction networks are calculated using the reservoir state method[8] to predict important fall-off and chemically-activated reaction rate coefficients[9].

- Thermochemistry of cyclic species, for which Benson group additivity estimates are often inadequate, are calculated using on-the-fly semi-empirical PM3 calculations in Gaussian03[10]. For cyclic radicals, PM3 calculations are performed for the saturated parent molecule and hydrogen bond increments[11] are applied. For more details see [12].

- Multiple reaction systems are simulated during the generation of the model, so that the model is valid at a wide range of temperatures, pressures, and concentrations.

- When the rate estimation rules would otherwise predict a kinetic barrier $E_a$ that is less than $\Delta H_{298K}$ for an endothermic reaction, it is raised to equal $\Delta H_{298K}$. When the estimation rules provide an Evans-Polanyi relationship ($E_a = E_0 + \alpha \Delta H_{298K}$) that predicts a negative barrier due to a large negative $\Delta H_{298K}$, then the barrier is set equal to 0.

- “Reaction Libraries” of trusted high-pressure rate coefficients takes precedence over RMG’s rule-based estimates when considering new reactions to expand the kinetic model.

- “Seed Mechanisms” of trusted reactions are added to the core of the model before model building begins. These take precedence over Reaction Libraries and RMG’s estimated reactions if duplicates are found. In this study several different seed mechanisms are compared.
2.2 Ab initio thermochemistry and kinetics calculations

To find thermochemistry for each of 194 species that appeared in a previous RMG-generated kinetic model of MF oxidation, we performed our own RQCISD(T)/CBS//B3LYP/6-311++G(d,p) calculations using the methodology of Goldsmith et al.\textsuperscript{13}. All DFT and CBS-QB3 calculations were done using Gaussian03\textsuperscript{10}. All MP2 and QCISD(T) calculations were done using MOLPRO\textsuperscript{14}.

Similar calculations were performed on the transition states of decomposition reactions of methyl formate, methoxy-formyl (CH\textsubscript{3}OC ‘O), and formyloxy-methyl (C’H\textsubscript{2}OCHO), and of hydrogen abstractions from methyl formate by H and methyl radicals. For the C\textsubscript{2}H\textsubscript{4}O\textsubscript{2} and C\textsubscript{2}H\textsubscript{3}O\textsubscript{2} decomposition reactions, the same high-level RQCISD(T) calculations as for the thermochemistry were performed. For H-abstraction reactions, the CBS-QB3 electronic energy was used. Hindered rotor calculations were treated in the same manner as \textsuperscript{13}. The high-pressure limit for each reaction rate coefficient (Table 1) was computed using transition state theory \textsuperscript{15}.

Table 1: High-pressure rate coefficients common to all models. \(k = A(T / 1 K)^n \exp(-E_a/RT)\). See text for calculation details.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(A \text{ (cm}^3\text{, mol, s)})</th>
<th>(n)</th>
<th>(E_a \text{ (kcal/mol)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular decomposition ( QCISD(T) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}OCHO (\rightleftharpoons) CO + CH\textsubscript{3}OH</td>
<td>(6.49 \times 10^4)</td>
<td>2.62</td>
<td>64.4</td>
</tr>
<tr>
<td>CH\textsubscript{3}OCHO (\rightleftharpoons) CO\textsubscript{2} + CH\textsubscript{4}</td>
<td>(6.88 \times 10^6)</td>
<td>2.01</td>
<td>134</td>
</tr>
<tr>
<td>CH\textsubscript{2}OC ‘O (\rightleftharpoons) CO\textsubscript{2} + C’H\textsubscript{3}</td>
<td>(2.34 \times 10^9)</td>
<td>1.09</td>
<td>14.3</td>
</tr>
<tr>
<td>CO + CH\textsubscript{3}O ‘ (\rightleftharpoons) CH\textsubscript{3}OC ‘O</td>
<td>(1.97 \times 10^9)</td>
<td>1.27</td>
<td>5.81</td>
</tr>
<tr>
<td>HC’O + CH\textsubscript{2}O (\rightleftharpoons) C’H\textsubscript{2}OCHO</td>
<td>(5.03 \times 10^3)</td>
<td>2.48</td>
<td>9.32</td>
</tr>
<tr>
<td>H-abstraction ( CBS-QB3 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H ‘ + CH\textsubscript{3}OCHO (\rightleftharpoons) H\textsubscript{2} + CH\textsubscript{3}OC ‘O</td>
<td>(2.28 \times 10^5)</td>
<td>2.5</td>
<td>6.56</td>
</tr>
<tr>
<td>H ‘ + CH\textsubscript{2}OCHO (\rightleftharpoons) H\textsubscript{2} + C’H\textsubscript{2}OCHO</td>
<td>(1.16 \times 10^5)</td>
<td>2.55</td>
<td>7.62</td>
</tr>
<tr>
<td>C’H\textsubscript{3} + CH\textsubscript{3}OCHO (\rightleftharpoons) CH\textsubscript{4} + CH\textsubscript{2}OC ‘O</td>
<td>(6.34)</td>
<td>2.82</td>
<td>6.81</td>
</tr>
<tr>
<td>C’H\textsubscript{3} + CH\textsubscript{4}OCHO (\rightleftharpoons) CH\textsubscript{4} + C’H\textsubscript{2}OCHO</td>
<td>(0.257)</td>
<td>3.96</td>
<td>8.02</td>
</tr>
<tr>
<td>Radical-Radical recombination (estimated)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH\textsubscript{3}O ‘ + HC’O (\rightleftharpoons) CH\textsubscript{3}OCHO</td>
<td>(1.8 \times 10^{13})</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>C’H\textsubscript{3} + O ‘CHO (\rightleftharpoons) CH\textsubscript{3}OCHO</td>
<td>(1.8 \times 10^{13})</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

2.3 Seed mechanisms

Table 2

Three different seed mechanisms are used in this study, which are referred to as GRI, Glarborg, and Dooley. The number of species and reactions for each seed mechanism is shown in Table 2.

**GRI** The GRI seed mechanism is constructed from the GRI-Mech 3.0 methane oxidation mechanism \textsuperscript{16}. All species and reactions involving nitrogen-containing compounds and the lumped C\textsubscript{3}H\textsubscript{7} species, which RMG models as two distinct species, were removed.

**Glarborg** The Glarborg seed mechanism contains all C\textsubscript{0} – C\textsubscript{1} reactions from the Glarborg group’s Master Mechanism, most recently reported by Lopez et al. \textsuperscript{17}. All species and reactions involving nitrogen-containing compounds were removed.
**Dooley** The Dooley seed mechanism contains all \( C_0 - C_1 \) reactions from the Dryer group’s methyl formate oxidation mechanism by Dooley *et al.*[2]. It also includes most of the \( C_2 - C_3 \) species (their reactions are estimated by RMG).

### 2.4 RMG model generation

Thermochemical data were taken from (in order of preference): the RQCISD(T)//B3LYP database described in section 2.2; GRI-Mech 3.0; semi-empirical PM3 calculations (for cyclic species only) with hydrogen bond increment corrections (HBI) for radicals; estimates based on Benson’s group additivity method with HBI for radicals. Transport parameters were taken from GRI-Mech 3.0 where available, and estimated by RMG otherwise. Reaction rate coefficients were taken from (in order of preference): the specified seed mechanism (different for each model; see section 2.3) with the assumption that pressure-dependence has already been accounted for; the *ab initio* rates shown in Table 1; the Glarborg Master mechanism [17]; estimates based on RMG’s reaction family kinetics estimation rules. With the exception of those from the seed mechanisms, all rate coefficients are assumed to be reported in the high-pressure limit and Master Equation calculations are performed to correct for fall-off and chemical activation. The Master Equation calculations are performed on a Gauss-Chebyshev grid of 8 temperatures (290–3500 K) and 5 pressures (0.02–100 bar) and Chebyshev polynomials of order 6 in \( T \) and 4 in \( P \) are fitted to the results for use in CHEMKIN. All the species reported in the low pressure flame experiments[3] were added to the model core with zero concentration (this ensures the species appear in the final model, even if their rate of creation is predicted to be low). Species with more than 6 oxygen atoms were forbidden. Thirty two reaction systems were simulated, formed by the product of 4 temperatures (600, 1000, 1500, 2000 K) \( \times \) 4 pressures (0.03, 1, 3, 10 bar) \( \times \) 2 \( MF:O_2:Ar \) molar ratios (1:2:97 and 1:2:1; both \( \phi = 1 \)). The 32 reaction systems were each simulated for 0.5 seconds under isothermal isobaric batch conditions with the edge fluxes (to determine what next to include in the core) evaluated at every time-step of the stiff ODE solver. The termination criterion was 0.05 although not all reaction systems ran to completion. The final models were generated with a release candidate of RMG version 3.2.3 (precise version hash: 62d1a55f). Model generation took 11–14 hours per mechanism on a single 2.66 GHz Intel Xeon processor, although most of the \(~6000\) PM3 calculations for cyclic species had already been performed (existing results are re-used). The sizes of the models are summarized in Table 2.

**Table 2:** *Kinetic model sizes.* The ‘model core’ is the final model used for the CHEMKIN simulations; the ‘model edge’ includes all candidates considered for inclusion in the core in the next RMG expansion step.

<table>
<thead>
<tr>
<th>Seed mechanism</th>
<th>Species</th>
<th>Model seed reactions</th>
<th>Species</th>
<th>Model core reactions</th>
<th>Species</th>
<th>Model edge reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRI</td>
<td>33</td>
<td>199</td>
<td>123</td>
<td>7289</td>
<td>9620</td>
<td>11990</td>
</tr>
<tr>
<td>Glarborg</td>
<td>26</td>
<td>148</td>
<td>113</td>
<td>6607</td>
<td>7579</td>
<td>9644</td>
</tr>
<tr>
<td>Dooley</td>
<td>121</td>
<td>157</td>
<td>174</td>
<td>8147</td>
<td>15633</td>
<td>18476</td>
</tr>
</tbody>
</table>
3 Experiments: Shock tube ignition delays

The shock tube study was performed in 3 different shock tubes. The first is a pyrex tube (50 mm i.d.) with a low pressure section 9 m long and a metallic high pressure section 2 m long. The second is a stainless steel shock tube with a 2 m long high pressure section (114 mm i.d.) and 5.15 m long low pressure section (52.5 mm i.d.). The third shock tube is also stainless steel, with a 1 m driver section and a 2.5 m driven section, both 38.4 mm i.d. The pyrex tube was used for the low pressure studies and the stainless steel tubes for the high pressure studies. The last section of each tube is equipped with 4 pressure transducers (equally spaced by 150 mm) mounted flush with the inner surface of the tube, the last one being 10–15 mm before the shock tube end wall. At the same plane as the last pressure transducer, a fused silica window (9 mm optical diameter and 6 mm thickness) is mounted across a Jobin–Yvon monochromator, M25, equipped with a UV-sensitive photomultiplier, R928. The monochromator was set to 306 nm which is characteristic of OH* emission. The shock wave velocity is deduced from the pressure jump monitored by the pressure transducers. The temperature and pressure behind the incident (P_2, T_2) and reflected (P_5, T_5) shock waves are deduced using the classical procedure [18]. Each shock tube and associated tubing are connected with 2 primary vacuum pumps, which allows the whole experimental setup to be vacuumed below 1 Pa before every run. The high pressure gas is He (purity > 99.995%). The MF was distributed by Fluka with a purity better than 99%. Liquid MF was degassed several times then vaporized under vacuum conditions. To avoid condensation, the partial pressure of MF in mixtures was below the saturated vapor pressure of MF at room temperature. The purities of O_2 and Ar, are 99.999 mol%. All gasses are distributed by Air Liquide. MF / Oxygen / Argon and MF / Argon mixtures were prepared in a mixing tank using the partial pressure method. The mixtures were mixed for one to two hours to ensure homogeneity. The ignition delay time is defined as the time between the passage of the reflected shock wave and 50% of the maximum OH* emission signal at 306 nm. The error (ΔT/T) in the temperature is estimated to be less than 1% while that of the pressure ΔP/P is 1.3%. The estimated error Δτ/τ in the auto-ignition delay times varies between 2% and 14% and is the highest at high T. The experimental conditions behind the reflected shock were in the range 151 < P_5 < 1446 kPa and 1268 < T_5 < 1812 K. In total 109 experiments were performed at 99 mol% Ar and equivalence ratios of \( \phi = 0.5, 1, \) and 2.

4 Simulations

4.1 Shock tube ignition delays.

Shock tube simulations are zero-dimensional and begin at the reflected shock temperature and pressure (T_5 and P_5) corresponding to each of the 109 experiments. Constant volume and adiabatic conditions are assumed. The boundary layer effect, which will cause a gradual rise in T_5 and hence a shortening of observed ignition delay times [19], has not been modeled. The simulations were performed with CHEMKIN Pro (v2011.03). The ignition delay time was defined as the temperature inflection point (maximum in \( dT/dt \)) for all simulations.
4.2 Laminar Flames

Laminar burning velocities of MF in synthetic air at 1 atm were calculated using the freely propagating flame solver PREMIX from CHEMKIN Pro (v2011.03). A 2 cm domain was simulated and CURV and GRAD limits of 0.1 were met with 150–250 grid points. Thermal diffusion was considered, with a mixture-averaged transport model and an unburned gas temperature of 298 K. The \( \phi = 1.0 \) low pressure flame of \([3]\) was modeled in PREMIX from CHEMKIN (v2011.03). The experimental temperature profile was supplied, thermal diffusion was considered, and a mixture-averaged transport model was employed. CURV and GRAD limits of 0.3 and 0.1, respectively, were met with > 100 grid points for all three kinetic models. The predicted mole fraction profiles were not shifted to account for probe effects.

5 Results
5.1 Shock tube ignition delays

The ignition delay times have been measured over a wide range of temperature and pressure. As usual, the auto-ignition delay times decreased exponentially with increasing temperature \( T_s \). The relationship \( \tau_{scaled} = \tau_{measured} \cdot (P_s)^{\alpha} \) can be used to scale the ignition delay times according to the pressure of the reflected shock. The correlation between \( \log(\tau_{scaled}) \) and \( (1000/T) \) is maximized for the experimental data when \( \alpha = 0.69 \), with a correlation coefficient exceeding 0.982 for all three equivalence ratios tested. The scaling with \( \alpha = 0.69 \) was applied uniformly to all the experiments and simulations in Figure 1.

![Shock tube ignition delays with equivalence ratios \( \phi=0.5, 1.0, \) and 2.0 (left to right), with 99% Ar and \( 1.5 < P_s < 15 \) atm, scaled by \( (P_s)^{0.69} \).](image)

Figure 1: Shock tube ignition delays with equivalence ratios \( \phi=0.5, 1.0, \) and 2.0 (left to right), with 99% Ar and \( 1.5 < P_s < 15 \) atm, scaled by \( (P_s)^{0.69} \).

Overall the agreement between the experimental data and the simulations is good, especially with the stoichiometric equivalence ratio (\( \phi = 1 \)) at which RMG generated the models. At \( \phi = 1 \) (middle plot) the model with the Glarborg seed is the slowest to ignite (on average \( \tau \) is 35% higher than the experiment). Similarly Dooley is 15% too slow, but GRI 8% too fast. At lean conditions (\( \phi = 0.5 \), left plot) all three models are too fast, under-predicting \( \tau \) by between 31 (Dooley) and 45% (Glarborg). Now the model with the Glarborg seed is the fastest, and the Dooley the slowest. At fuel-rich conditions (\( \phi = 2 \)) all three models are now too slow, over-predicting \( \tau \) by between 35
(GRI) and 82% (Glarborg). As the changes due to a different seed mechanism are the same order of magnitude as the discrepancies between model and experiment, it is difficult to use ignition delays to validate or invalidate the methyl formate sub-mechanism.

5.2 Laminar Burning Velocities

Figure 2 shows the calculated laminar burning velocities of methyl formate in synthetic air at 1 atm from fuel lean ($\phi = 0.7$) to rich ($\phi = 1.6$) conditions. The experimental data come from Dooley et al.[2], and simulations using the kinetic model from that study are also shown. All of the RMG-generated kinetic models significantly over-predict the burning velocities; we are investigating the cause of this. The difference between seed mechanisms is apparent from the figure. The model with the Glarborg has the highest maximum burning velocity (45 cm/s), occurring at the lowest equivalence ratio ($\phi = 1$). The model with the Dooley seed is closest to the experimental data, which peak at $\phi = 1.2$, 36 cm/s.

![Laminar burning velocities of methyl formate in synthetic air at 1 atm with $T_{\text{inlet}} = 298$ K. Experimental data ($T_{\text{inlet}} = 295 \pm 2$ K) and Dooley (2010) model are from [2].](image)

5.3 Low Pressure Flames

The effect of the differing seed mechanisms is shown in Figure 3, where the experimental and predicted mole fraction profiles for two minor species in methyl formate oxidation are presented. Of the three kinetic models studied, only that built on the Glarborg seed mechanism predicts the maximum $\text{C}_2\text{H}_4$ mole fraction within a factor of two of the measurements reported in [3]; none of the models predict the $\text{C}_2\text{H}_2$ mole fraction profile (not presented) well.

6 Concluding Remarks

Three mechanisms for methyl formate oxidation are constructed using the open-source software Reaction Mechanism Generator (RMG); each was generated from a different $\text{C}_0$--$\text{C}_1$ seed mechanism. The difference in base chemistry is evident when comparing the models’ predictions for ignition delays, laminar burning velocities, and speciation data against one another. The noticeable difference in combustion properties demonstrates that it is difficult to make conclusions about any fuel combustion model’s predictive ability until the $\text{C}_0$--$\text{C}_1$ chemistry is resolved.
Figure 3: The predicted (lines) and experimental [3] (shapes) mole fraction profiles for CH$_3$ (left) and C$_2$H$_4$ (right) in the $\phi = 1.0$ low-pressure methyl formate flame.

Acknowledgements

We would like to thank Stephen Dooley for several very helpful conversations.

7 References