Multi-scale Informatics for Low-Temperature Propane Oxidation

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As the power of scientific computing continues to grow, detailed models for complex chemical-transport phenomena play a more significant role in the design process of advanced energy conversion devices (Hwang et al. 2008). As a result, there have been substantial research efforts devoted to the construction and further development of detailed chemical models for conventional and alternative fuels. However, given the enormous range of temperature/pressure/bath-gas conditions of potential interest, kinetic models are often applied at conditions far outside their validation set, resulting in frequent deficiencies in model performance. We have developed a multi-scale approach (Burke et al. 2013) to combustion model formulation that directly incorporates kinetic theory as a means to provide reliable, physics-based extrapolation to engine-relevant conditions. Here, we extend and generalize the multi-scale modeling strategy to treat systems of much greater complexity – involving multi-well reactions and potential for missing reactions, non-statistical product branching ratios, and non-Boltzmann reactant distributions.

The methodology is demonstrated for low-temperature propane oxidation as a representative system for low-temperature fuel oxidation. A multi-scale model is assembled and informed by a wide variety of targets that include ab initio calculations of molecular properties, rate constant measurements of isolated reactions, and complex systems measurements. Optimization variables are chosen to accommodate both “parametric” and “mechanistic” uncertainties. For example, barrier heights of transition states, collisional energy transfer parameters, transition state partition function scaling factors, and other theoretical parameters are included as optimization variables to account for parametric uncertainties in the theoretical treatment; initial temperatures, mixture compositions, absorption cross-sections, and other experimental parameters are included to account for parametric uncertainties in the physical models of the experiments. Additionally, branching ratios among various product channels are included as optimization variables to account for mechanistic uncertainties related to difficulties in modeling sequences of multiple chemically activated steps. RMG software is used to assess potential mechanistic uncertainties due to missing reactions. In this context, multi-scale informatics is employed to 1) extract information from complex systems in the presence of both parametric and mechanistic uncertainties and 2) allow greater utilization of the high information content of ongoing Multiplexed Synchrotron Photoionization Mass Spectrometry (MPIMS) experiments.

1. Introduction

As the power of scientific computing continues to grow, detailed models for complex chemical transport phenomena play a more significant role in the design process of advanced energy conversion devices (e.g. Hwang et al. 2008). As a result, there have been substantial research efforts devoted to the construction and further development of detailed chemical models for conventional and alternative fuels, ranging from hydrogen to green jet fuels. However, given the enormity of temperature/pressure/bath-gas (T/P/M) conditions of potential interest, kinetic models are seldom used for conditions near those of the data available for model development and validation. Examples where kinetic models exhibit significant difficulties in extrapolating to conditions outside of their validation data set are relatively commonplace, particularly for higher pressure conditions of interest to advanced engine technologies – even for relatively simple systems (e.g. Sivaramakrishnan et al. 2007; Burke et al. 2010, 2011). These deficiencies highlight the need for improved techniques for combustion model development, particularly to allow more accurate extrapolation to engine-relevant conditions.
Previous strategies for combustion model development and validation have focused on identifying a set of rate parameters that describe available rate constant and combustion data. Comprehensive modeling, where the set of rate constants is validated against data spanning wide ranges of parameter space and experimental configurations, as described by Westbrook and Dryer (1984), has essentially been integrated into all rigorous model development strategies. Modern mathematical extensions to model optimization largely stem from the early work of Frenklach and coworkers (Frenklach 1984; Frenklach et al. 1992). Using solution mapping techniques that related reaction rate A-factors to global combustion data, Frenklach, Wang, and co-workers optimized models for a variety of fuels (e.g. Smith et al. 1999). They later extended these concepts to allow uncertainty quantification and propagation that included the constraints imposed by combustion targets on reaction rate A-factors (Frenklach et al. 2004; Sheen et al. 2009). More recently, Turányi and co-workers have further extended these approaches to include temperature-dependent parameters from modified Arrhenius expressions in optimization and uncertainty quantification based on direct rate constant measurements and global data (Nagy et al. 2011; Turányi et al. 2012). While the above-mentioned techniques take advantage of the constraints imposed by combustion targets on combinations of rate parameters (and vice versa), their reliability is limited to systems where (1) data is available to sufficiently constrain rate constants over the full range of T/P/M conditions of interest and (2) full uncertainties in the relevant T/P/M dependence of rate constants are considered. Extrapolation to conditions where insufficient data are available to constrain the relevant T/P/M dependence of the underlying rate constants cannot be expected to be reliable in general.

In this regard, direct incorporation of theoretical kinetics calculations into combustion model development appears particularly useful – replacing dependence on rate constant fitting expressions with a physically meaningful kinetic theory. In fact, theory has often been used for extrapolation of limited rate constant experiments by adjusting uncertain theoretical kinetics parameters to reproduce direct rate constant measurements and/or global data controlled by that reaction (e.g. Golden et al. 1998; Huang et al. 2011). Furthermore, the accuracy of theoretical kinetics calculations has progressed to a point that it can provide useful constraints on model parameters in the same way as data from rate constant measurements and global experiments. Theoretical kinetics calculations, most importantly, impose constraints on rate constants at all T/P/M conditions – essentially “filling in the gaps” in the vast T/P/M parameter space and providing reliable, physically based extrapolation to conditions outside the limited experimental data set.

To this end, we have developed a multi-scale informatics approach (Burke et al. 2013) to combustion model formulation that directly incorporates kinetic theory as a means to provide reliable, physics-based extrapolation to engine-relevant conditions. The approach integrates constraints imposed by \textit{ab initio} kinetic theory with experimental data ranging from direct studies of elementary reactions to global studies of chemical mechanisms in a single framework. The ultimate objective of the present modeling strategy is to identify optimized values and quantified uncertainties for a set of theoretical kinetics parameters that describe the overall combustion model, constrained by data spanning fundamental molecular interactions to global combustion phenomena. An essential feature of the present multi-scale approach is that the system is optimized against targets from \textit{ab initio} calculations and experimental data simultaneously – such that theory aids in the interpretation of global data where insufficient direct measurements are available by restricting the solution to be physically meaningful.

Here, we extend and generalize the multi-scale modeling strategy to treat systems of much greater complexity, where both “parametric” and “mechanistic” uncertainties are present. Here, “parametric” uncertainties refer to quantitative uncertainties in the model description due to uncertainties in the model parameters; “mechanistic” uncertainties refer to qualitative uncertainties in the model description due to missing reactions in the starting mechanism or reaction kinetics that defy traditional kinetics assumptions. In this paper, we present an overall modeling strategy capable of addressing complex reaction systems with multi-well reactions, potential missing reactions in starting mechanism, non-statistical product branching ratios, and non-Boltzmann reactant distributions.

The methodology is demonstrated for a subsystem of low-temperature propane oxidation, as a representative system for low-temperature fuel oxidation. In particular, we focus on low-temperature propane oxidation under dilute conditions intended to accentuate R+O\textsubscript{2} and QOOH+O\textsubscript{2} reactions (where R denotes n/i-propyl radicals and QOOH denotes any of the three isomers of hydroperoxyl-propyl radicals). This particular subsystem has been the subject of considerable attention (e.g. DeSain et al. 2001a, 2001b, 2003, 2004; Estupiñán et al. 2005, 2007; Huang et al. 2011; also see references therein) given its suggested role as a prototype for low-temperature oxidation where high-level theory is computationally tractable. In many of these studies (DeSain et al. 2001a, 2001b, 2003, 2004; Estupiñán et al. 2005, 2007; Huang et al. 2011), experimental measurements of time-dependent OH or HO\textsubscript{2} concentrations were used to adjust barrier heights of selected transition states found to be important under the given experimental conditions.
However, a number of factors suggest that the barrier height adjustments may require additional consideration. First, modeling studies (not shown here) indicate that rate constants derived from the most recently adjusted PES (Huang et al. 2011) no longer reproduce time-dependent OH measurements of Huang et al. (2011) when more accurate treatment of pressure dependence for propyl radical decomposition (Miller and Klippenstein 2013) is considered. Second, the results of this study (see Fig. 1) suggest that a number of parameters in addition to barrier heights affect the interpretation of the experimental results. Third, recent high-level ab initio calculations (Goldsmith et al. 2012) of the system with different barrier heights and treatments of entrance channels and torsional modes have become available. Fourth, preliminary results from ongoing MPIMS experiments suggest that previously unidentified channels may be among the major contributors to OH formation. Fifth, we suspect that the system behavior may be affected by non-Boltzmann reactant distributions (e.g. Glowacki et al. 2012) and/or non-statistical product branching ratios following highly energetic transition states. In the present study, we reinterpret the data with a new modeling strategy that is both highly rigorous and adaptive to new information.

Below, we introduce and demonstrate the modeling strategy. First, we discuss its details, procedure, and implementation. Then, we present preliminary results of its implementation for the low-temperature propane oxidation system. Our focus for this preliminary analysis is on optimization against cases where non-Boltzmann reactant distributions and non-statistical branching ratios are not important, though ultimately we are interested to understand to what extent these effects influence system behavior and under what conditions.

2. Methods

The ultimate objective of the present modeling technique is to identify optimized values and quantified uncertainties for a set of theoretical kinetics parameters that describe the overall combustion model in a manner informed by available data from ab initio calculations, rate constant measurements, and global combustion measurements. In order to focus on the physical aspects of the problem, we have implemented only a basic mathematical framework in this initial study, though the general technique can readily be implemented with more powerful mathematical treatments (e.g. Frenklach et al. 2004, Sheen et al. 2009, Turányi et al. 2012, Davis et al. 2011).

We seek the set of uncertain parameters, $X_j$, which minimizes the least-squared error to the set of weighted equations:

$$ F_i(X_j) = Y_{i,j} \pm Z_i $$

where $F_i(X_j)$ is the model prediction for given $X_j$; $Y_{i,j}$ is the target value; and the weighting factor, $Z_i = \sigma_i W_i$, is equal to the uncertainty, $\sigma_i$, times an additional data set weighting factor, $W_i$. Taking advantage of a “surrogate model” of the system (as in solution mapping methods, e.g. Frenklach 1984) in the neighborhood of $\tilde{X}_j$,

$$ F_i(X_j) \approx F_i(\tilde{X}_j) + \sum_j S_{ij}(X_j - \tilde{X}_j) $$

with

$$ S_{ij} = \{dF_i/dX_j\}_{X_j=\tilde{X}_j} $$

Eq. (1) can be expressed as the matrix equation:

$$ \sum_j S_{ij}(X_j - \tilde{X}_j) = Y_i \pm Z_i $$

with $Y_i = Y_{i,j} - F_i(\tilde{X}_j)$. The optimized values and covariance matrix are calculated using a standard weighted least-squares procedure (e.g. as used in the Active Thermochemical Tables of Ruscic et al. 2004). The procedure is initiated starting from the nominal values, $\tilde{X}_j^o$, and repeated in an iterative manner – solving (3) to find $X_j$, recalculating $F_i$ and $S_{ij}$ using the updated $X_j \rightarrow \tilde{X}_j$ values, and repeating – until converged. Prediction uncertainties (as in Fig. 2) were propagated using the covariance matrix. Such an approach approximates all distributions as independent and normal; it also approximates the response surface in the neighborhood of the optimized values as linear. We have intended that uncertainties reflect two standard deviations, though the lack of specification in most studies and difficulty in estimating uncertainties in kinetics experiments make such a designation tentative.
As discussed below, the uncertain parameters, \( X_j \), include theoretical kinetics parameters, rate constant parameters, and experimental conditions (initial/boundary conditions, absorption cross-sections, physical model assumptions, etc.). The targets, \( Y_{lo} \), include molecular properties from \textit{ab initio} calculations, direct rate constant measurements, global combustion measurements, and reported values for the experimental conditions.

The optimization and uncertainty quantification approach discussed above was implemented for the Cl-initiated propane oxidation system. A starting model was created using RMG software by layering various sub-models: H\(_2\)O\(_2\) mechanism from Burke et al. (2013), H\(_2\) mechanism from Burke et al. (2012), R+O\(_2\) and QOOH+O\(_2\) reactions from Goldsmith et al. (2012), propane mechanism from Miller et al. (2013), methyl formate mechanism from Dooley et al. (2010), RMG estimates for additional reactions identified in the reaction search procedure for low-temperature propane oxidation conditions. Reactions involving Cl from DeSain et al. (2001a) were then added to the RMG-generated model. From the starting model, an active model was created from the following components: 1) an active portion of the model described by a set of theoretical parameters; 2) an active portion of the model described by a set of rate parameters; 3) an active portion of the model consisting of the reactions generated with RMG estimates; and 4) a static portion of the model consisting of the remaining reactions.

For each experimental condition, the active model is constructed from the set of active parameters (theoretical parameters, rate parameters, a “missing reactions” parameter, and experimental condition parameters). VARIFLEX is used to calculate rate constants from the theoretical parameters; SENKIN is used to calculate experimental observables from the rate parameters and experimental condition parameters. The active model is automatically produced using a set of scripts that implement the following procedure:

1. The active portion of the model described by a set of theoretical parameters is constructed. VARIFLEX input files for n-propyl+O\(_2\), i-propyl+O\(_2\), and QOOH-1+O\(_2\) reaction systems are constructed based on the set of active parameters. Various important uncertain parameters of the theoretical kinetics calculations are treated as active parameters. These include: barrier heights of each transition state relative to reactants, \( E^a \); a scaling factor for the partition function (by varying lowest five harmonic frequencies) of each transition state, \( Q^a \); scaling factor for the imaginary frequency in the Eckart tunneling correction for each transition state, \( v_{imag} \); a well depth for each well, \( E_a \); a scaling factor for the partition function (by varying lowest five harmonic frequencies) of each well, \( Q_a \); scaling factors for \( AE_d \) and its temperature dependence for each well, \( A_{AE_d} \) and \( n_{AE_d} \); variable reaction coordinate transition state theory (VRC-TST) correction factor to account for uncertainty in the number of states in the entrance transition state, \( f_{VRC-TST} \); and branching ratios discussed below.
   a. Rate constants for the QOOH-1+O\(_2\) reaction system are calculated using a similar treatment to Goldsmith et al. (2012), where QOOH-1 denotes the 3-hydroperoxy-1-propyl radical.
   b. Rate constants for the n-propyl+O\(_2\) reaction system are calculated using a similar treatment to Goldsmith et al. (2012) modified to include a cursory treatment of reaction of QOOH-1 with O\(_2\). A channel is added to the n-propyl+O\(_2\) reaction system to simulate reaction of QOOH-1+O\(_2\). QOOH-1 is assumed to react (with O\(_2\)) with an energy-independent rate equal to \( k_{tot} = k_{QOOH-1+O_2, reaction} \) where \( k_{QOOH-1+O_2, reaction} \) is the total rate constant of QOOH-1+O\(_2\). QOOH-1+O\(_2\) reaction that occurs before energized QOOH-1 is thermalized is given a variable branching ratio between thermal and non-thermal products (to provide an assessment of uncertainties due to non-Boltzmann reactant distributions). Further, the QOOH-1+O\(_2\) reaction that proceeds through TS19 (for QOOH = products, using the nomenclature of Goldsmith et al. 2012) is given a variable branching ratio between OH+2-formyl-ethyl-hydroperoxide and OH+OH+2-formyl-ethoxy (to provide an assessment of uncertainties due to imprecise knowledge of energy redistribution following highly energetic transition states). Reactions and rate constants for the n-propyl+O\(_2\) and QOOH-1+O\(_2\) reaction systems are added to the CHEMKIN model.
   c. Rate constants for the i-propyl+O\(_2\) reaction system are calculated using a similar treatment to Goldsmith et al. (2012). Reactions and rate constants for the i-propyl+O\(_2\) reaction system are added to the CHEMKIN model.

2. The active portion of the model described by a set of rate parameters is constructed. Arrhenius parameters (\( A, n, E_n \)) were treated as active parameters. The reactions and rate constants are added to the CHEMKIN model.

3. The active portion of the model consisting of the reactions generated with RMG estimates is constructed. A binary active parameter describes whether RMG estimated reactions are included or excluded in the CHEMKIN model.

4. The static portion of the model is added to the CHEMKIN model.
Prior to the optimization and uncertainty quantification procedure, a preliminary screening of all experimental data targets is performed to assess the importance of various “mechanistic” uncertainties:

1. If predictions of the experimental observable depend on any of the branching ratios to describe non-Boltzmann or non-statistical effects, those targets are not used to constrain model parameters in the optimization. Though, ultimately, we are interested to understand to what extent these effects influence system behavior and under what conditions.

2. If predictions of the experimental observable depend on the inclusion of RMG estimated reactions, specific reactions responsible are identified and investigated further. Many reactions that were initially identified to influence predictions were later found to have estimated rate constants that appeared unrealistically high. These reactions were removed. (Once these reactions were removed, no other RMG-estimated reactions were identified as important.)

3. If predictions are sensitive to reactions in the static model, those reactions are moved into the active portion of the model.

For the experimental conditions for the global targets, active parameters include initial temperatures, $T_i$; initial pressures, $P_i$; initial mole fractions, $M_{init}$ of $\text{C}_3\text{H}_8$, Cl, O$_2$, and Cl$_2$ or oxalyl chloride (OxCl); and scaling factors for the absorption cross-sections for OH and HO$_2$, $\sigma_{\text{OH}}$ and $\sigma_{\text{HO}_2}$, at the conditions of each experiment.

In this preliminary implementation, optimization targets included: molecular properties from the ab-initio calculations of Goldsmith et al. (2012); selected time-dependent OH concentrations at 10 torr measured by Huang et al. (2011), selected time-dependent OH concentrations at 30 torr measured by Huang et al. (2012), and selected time-dependent HO$_2$ concentrations at ~50 torr measured by DeSain et al. (2001a). Predictions of these targets are minimally affected by non-thermal reactant distributions, non-statistical branching ratios, and RMG-estimated reactions.

5. Results and Discussion

The set of informed theoretical kinetics parameters, rate parameters, and experimental condition variables from the present analysis using the above-mentioned

![Fig. 1. Uncertainty-weighted sensitivity analysis for predictions of OH concentrations in Cl/C$_3$H$_8$/O$_2$/OxCl/He mixtures at 10 Torr and 594 K from Huang et al. (2011).](image1)

![Fig. 2. Time-histories of (a) OH in Cl/C$_3$H$_8$/O$_2$/OxCl/He mixtures at 10 Torr and 594 K and (b) HO$_2$ in Cl/C$_3$H$_8$/O$_2$/Cl$_2$/He mixtures at 60 Torr and 683 K. Black lines denote experimental data from (a) Huang et al. (2011) and (b) DeSain et al. (2001a); long-dashed lines denote confidence intervals.](image2)
targets yield final values and predictions in reasonable consistency with \textit{ab initio} calculations (Goldsmith et al. 2012) and global measurements and experimental conditions (DeSain et al. 2001a, Huang et al. 2011, Huang et al. 2012) used as targets.

Figure 1 shows uncertainty-weighted sensitivity analysis for the OH concentration at the conditions of the 594 K case from Huang et al. (2011). The plot indicates that the greatest contributors to the uncertainty in the model predictions are the barrier heights for TS3 and TS11 (for RO\textsubscript{2} = QOOH, using the nomenclature of Goldsmith et al. 2012), which were the two barrier heights adjusted to match the experimental data in the study of Huang et al. (2011). However, the plot also indicates that additional parameters contribute substantially to the uncertainties in the predictions, viz. imaginary frequencies and partition function scaling factors for TS3 and TS11, the partition function for propylperoxy radicals, and rate constants for Cl+\textit{C}_{3}H\textsubscript{8} = HCl + \textit{n/iC}_{3}H\textsubscript{7}.

Figure 2 shows comparisons of experimental measurements of OH and HO\textsubscript{2} time-histories (DeSain et al. 2001a, Huang et al. 2011) and model predictions using the \textit{a priori} and informed models. The informed model shows significant improvements in reproducing the experimental data compared to the \textit{a priori} model; the informed model also yields predictions with much smaller uncertainties.

6. Conclusions

A multi-scale modeling strategy is presented that is capable of treating highly complex systems, where both “parametric” and “mechanistic” uncertainties are present. In particular, the strategy addresses complex reaction systems with multi-well reactions, potential missing reactions in starting mechanism, non-statistical product branching ratios, and non-Boltzmann reactant distributions. The methodology is demonstrated for a subsystem of low-temperature propane oxidation, as a representative system for low-temperature fuel oxidation. Preliminary implementation for a selected portion of experimental targets yields promising results: predictions using the informed model reproduce experimental data with better agreement and reduced uncertainty compared to the \textit{a priori} model.

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