Estimating uncertainties in the derivation of phenomenological rate constants from theory

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Global uncertainty analysis [1-3], which considers the uncertainty in the mechanistic parameters of a model in combination with the sensitivity of the predicted outputs to their values, is proving to be a valuable tool for developing and improving chemical mechanisms for combustion. The coupling of such analysis with theoretical kinetics allows for focused improvement of the mechanism [2,3]. Such uncertainty studies require estimates for the uncertainty of the input parameters (e.g., rate coefficients, Arrhenius terms, thermodynamic parameters) that make up the chemical mechanism. Traditionally, these parameters and uncertainties were obtained from experiments and in many cases evaluation studies were able to provide quantified information on not only the recommended value of a parameter, but also its range of feasible values or uncertainty factor. This has mainly been true for parameters derived from detailed kinetic experiments. However, with the improving accuracy of theory, more and more parameters are now being obtained from theoretical predictions. Unfortunately, theoretical kineticists rarely provide any indication of the uncertainty in their predictions. In this study, global uncertainty and sensitivity analysis is used to predict the propagation of uncertainties in fundamental theoretical parameters through to uncertainties in the predicted temperature and pressure dependent phenomenological rate coefficients. Predictions are obtained from *ab initio* transition state theory based master equation calculations. The fundamental parameters for these rate predictions include barrier heights, well depths, vibrational frequencies, collision frequency, and energy transfer parameters. A random sampling high-dimensional model representation (HDMR) approach [1] is used to first determine the predicted distributions of the phenomenological rate coefficients. Sensitivity analysis then identifies the main parameters which contribute to variance in the predicted distributions. Here the approach will be demonstrated for a study of the oxidation of the propyl radical, employing the parameters derived in recent theoretical studies.

[1] T. Ziehn, A.S. Tomlin, *Environmental Modelling and Software*, 2009, 24, 775-785.
[2] R.T. Skodje, A.S. Tomlin, S.J. Klippenstein, M.J. Davis, *Journal of Physical Chemistry*, 2010, 114(32), 8286-301.
[3] S.J. Klippenstein, L.B. Harding, M.J. Davis, A.S. Tomlin, R.T. Skodje, *Proceedings of the Combustion Institute*, 2011, 33, 351-357.