

# Assessing the impact of accuracy of *ab initio* calculations in describing chemically activated systems

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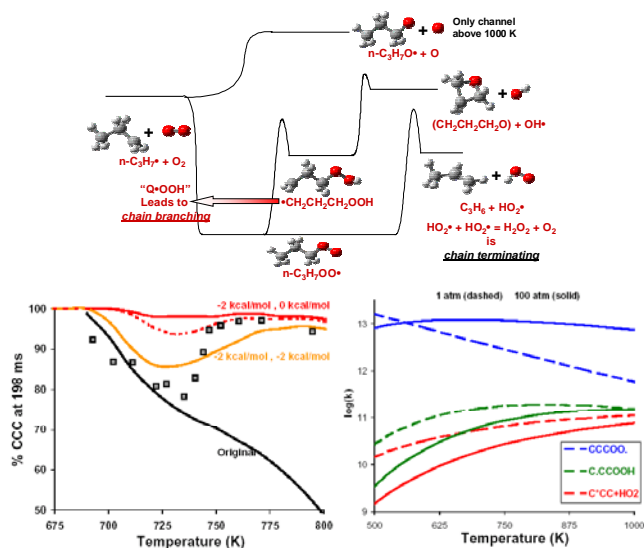
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**Abstract.** Chemically activated systems play an important role in combustion and atmospheric chemistry. The overall reaction paths exhibit complex pressure and temperature dependence because each intermediate involves a coupled system of competing multi-step isomerization, deactivation and dissociation paths. A number of estimation techniques exist for deriving the required thermo and elementary kinetic input parameters for rate estimation. The availability of high-level *ab-initio* methods promises to remove the inaccuracies associated with older empirical methods. The objective of this study is to evaluate the importance of the various thermochemical parameters entering the rate calculation. We describe and illustrate a computational framework to quantify the functional relationship between the thermochemical properties and the macroscopic observables through appropriate response surface methods. The approach is demonstrated by analyzing the impact of thermochemical properties in estimating autoignition delays in propane oxidation.

## The complexities of combustion

Important initial products from oxidation reactions of saturated and unsaturated hydrocarbons are the corresponding radicals. The subsequent elementary reactions of the radicals with molecular oxygen are complex and difficult to study experimentally. These reactions represent the principal pathways of the radical conversion in many hydrocarbon oxidation and combustion processes. Low temperature oxidation of hydrocarbons (600K-700K) is critically important in their use as fuels in internal combustion engines. A distinguishing feature of the low temperature chemistry of many molecules is the "negative temperature coefficient", NTC [20]. At very low temperatures, as the temperature is raised the ignition delay of a fuel is decreased. However, for many fuels, at a certain temperature the ignition delay reverses its course and becomes longer as the temperature is raised. At some higher temperature the ignition delay decreases again. A simplified reaction potential energy diagram is illustrated in **Figure 1** for the addition of oxygen to the propyl radical [1,6]. The key species for modeling the NTC of propane are the propylperoxy radicals and their isomers.

The relative rate of isomerization of the peroxy radicals and the concerted HO<sub>2</sub> elimination are key to properly capturing the NTC behavior. •CCCOOH readily promotes chain branching and therefore accelerates the chemistry at low temperatures. In the NTC range however, the concerted HO<sub>2</sub> elimination pathway from CCCOO• radicals becomes faster, which reduces the concentration of •CCCOOH, and hence reduces chain branching. Therefore, the NTC is the manifestation of the subtle balance between the chain branching and chain termination. The accurate prediction of the relative values of the barriers for the isomerization and HO<sub>2</sub> becomes very critical. The importance of the concerted elimination step has also been recently verified computationally for



**Figure 1.** C<sub>3</sub>H<sub>7</sub> + O<sub>2</sub> potential energy diagram and model predictions

the ethyl + O<sub>2</sub> system [21,23]. **Figure 1** also demonstrates the critical sensitivity of the predictions in terms of the kinetic parameters. In [1] a detailed propane mechanism with 216 species and 3078 reactions was developed to reproduce numerous experimental conditions. Several sensitivity studies were also performed to demonstrate, among others, (a) the effect of adjustments in E<sub>A</sub> for the CCCOO• = C•CC + HO<sub>2</sub> reaction (lower left **Figure 1**), and (b) the pressure effects on the reactions of the n-

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propyl radical with O<sub>2</sub> (lower right, **Figure 1**). For internal combustion engine applications, experiencing wide pressure variations, accurate pressure dependence is critical.

### Automated Mechanism Generation and Chemically Activated Reactions

Existing kinetic model construction algorithms are based on a series of rules that describe known elementary reaction steps. Numerous structural algorithms that identify and manage reactant and product species exist in the literature [10,13,24]. Rates are often expressed in a modified Arrhenius form ( $k = AT^n e^{-E/RT}$ ) on the basis of experimental data, quantum chemical calculations, or Evans-Polanyi correlations. For combustion chemistry applications, *chemically activated reactions* play an important role [15]. Such reactions involve highly energized nonthermalized species that undergo rapid internal isomerization or dissociation before collisional stabilization. The energized nonthermal intermediates are sufficiently short-lived that these reactions appear to be direct elementary reactions between the thermalized species, but the chemical changes between reactants and products reflect the multi-step nature of the process. In the propyl example of **Figure 1** the entrance species, propyl and oxygen, form a highly energized CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OO•\* adduct which can be subsequently collisionally stabilized and form the peroxy radical (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OO•) or react according to any of the remaining steps. However, when building the apparent mechanism only stabilized adducts and molecular species are accounted for. Because each energized intermediate adduct involves a coupled system of competing multi-step isomerization and deactivation pathways, the overall rate constants for the apparent reactions exhibit complex pressure and temperature dependencies. For a computer algorithm to construct accurate kinetic models, these chemically activated processes should be included in the construction process. The apparent rate constants can be evaluated by calculating the rate constants of the individual processes based by many different ways, such as the Rice-Ramsberg-Kassel (RRK) or Rice-Ramsberg-Kassel-Marcus (RRKM) theory [15,27]. An efficient Quantum RRK (QRRK) is described in [7,8] and an implementation (CHEMACT) of it is described in [9] in conjunction with the application of modified strong collision theory for the treatment of deactivation. An improved 3-frequency QRRK was recently proposed [3,4,5]. The required inputs include: high-pressure rate constants ( $A^\infty, E^\infty$ ) for all elementary reactions,  $\Delta_f H_{298}$ ,  $S_{298}$ ,  $C_p(T)$  for all species and collision parameters for the system. It should be noted that we propose a general computational framework, which does not depend on the specific rate estimation methodology. Our choices are based primarily on the demonstrated computational efficiency of the combined use of QRRK/MSM. The more involved Master Equation analysis can be readily incorporated.

### The impact of thermochemical quantities on macroscopic observables

A number of straightforward approximate techniques exist for deriving input parameters required for kinetic model construction without any electronic structure calculations, [2]. However, the availability of high fidelity *ab-initio* methods promises to remove the inaccuracies associated with the various empirical methods [26]. A recent comprehensive study [23] demonstrated the feasibility of deriving all the necessary input from first principles calculations without the need for any parameter adjustments. However, significant uncertainties remain in the estimation of the fundamental thermochemical properties given that the required accuracy of calculation is not always achievable. The impact of, even slight, variability in kinetic parameters has been shown to be significant. It was recently shown [18] that variations in activation energy estimates within the expected accuracy of quantum chemical calculations can lead to significant variations in terms of the model predictions. The impact of high pressure-rate constants on the autoignition delay of propane was discussed in [1], whereas in [17] the effect of a single reaction (CO + OH → CO<sub>2</sub> + H) in predicting CO<sub>2</sub> emissions in a supercharged engine was analyzed and deemed significant. These calculations emphasize the impact of variability in fundamental thermochemical properties on the prediction of macroscopic responses and clearly demonstrate that slight errors in critical reaction steps significantly impact the overall predictions of a complicated calculation.

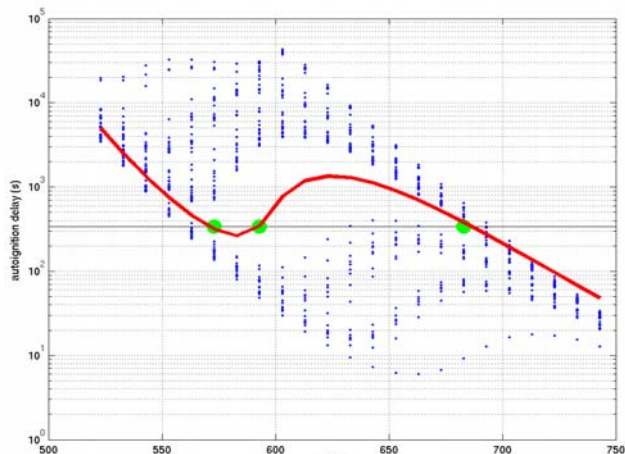
Even though accurate quantum chemical calculations are beginning to resolve some discrepancies, they remain quite expensive, scaling as a high power of the number of electrons in the system and their effective application in a specific system remains an art. Furthermore, forward propagation of estimates of thermochemical properties across highly complicated potential energy diagrams is not a trivial task. As a result, from a mechanism analysis point of view, a number of critical questions have to be addressed:

- What is the expected range of variability of a macroscopic kinetic observable given an expected uncertainty range in thermochemistry?
- Which thermochemistry parameters most critically impact specific apparent reaction rates?
- Which microscopic parameters most critically affect a macroscopic observable of interest?

### Propagating errors in thermochemical property estimation

In order to address these issues we propose to treat the thermochemical properties, which are the input to the rate calculations algorithms such as CHEMACT [4,5], as *uncertain parameters*. *Ab-initio* and density functional calculations and empirical methods will be used for estimating thermochemical properties of reactants,

products and transition states in chemically activated systems. Reasonable bounds on these estimates can be identified based on the method used for their calculation [22]. In order to quantify the functional relationship between the thermochemical properties and the macroscopic observables the definition of a response surface is proposed. For our studies we choose as the macroscopic property of interest a measure of the autoignition delay, and more specifically we will be monitoring fuel conversion after certain reaction time. More details about the system will be discussed latter. For the purpose of developing the input/output relationship we employ the *Stochastic Response Surface Method*, SRSM, [16] integrated with CHEMACT. SRSM uses computationally efficient instantiations of the input variables responsible for the variability. Based primarily on the *Deterministic Equivalent Modeling Method* [19,25], SRSM expresses random outputs in terms of the polynomial chaos expansion [12] of Hermite polynomials and the implementation utilizes an efficient collocation scheme combined with regression to determine the coefficients of the expansion. This polynomial form possesses several useful properties including straightforward determination of the statistics of the output distribution. Although other response surface methods [11] are similar in spirit, SRSM offers the advantage that the probability density functions of the output metrics better approximate the actual distribution



**Figure 3:** Effect of  $(A^\infty, E^\infty)$  variability on autoignition delay

of the output parameters. Evaluating the SRSM expansion consists of the following steps: (1) input uncertainties are expressed in terms of a set of standard random variables (srvs); (2) a functional form is assumed for selected groups or output metrics; and (3) the parameters of the functional approximation are determined. For example an uncertain model output  $U$  can be expressed as first- or second-order Hermite polynomial approximation ( $U_1$  and  $U_2$ ) as shown in Eqn (1).

$$U_1 = \alpha_{0,1} + \sum_{i=1}^n \alpha_{i,1} \xi_i$$

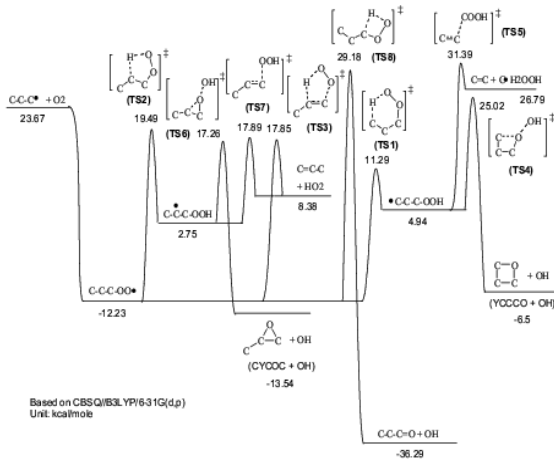
$$U_2 = \alpha_{0,2} + \sum_{i=1}^n \alpha_{i,2} \xi_i + \sum_{i=1}^n \alpha_{ii,2} (\xi_i^2 - 1) + \sum_{i=1}^{n-1} \sum_{j>i}^n \alpha_{ij,2} \xi_i \xi_j \quad (1)$$

where  $n$  is the number of srvs used to represent the uncertainty in the model inputs and the coefficients to be estimated are  $\alpha$ 's. The parameter  $m$  denotes the order of the polynomial expansion. Higher-order polynomial approximations are developed accordingly. The determination of the coefficients is done using an extension to collocation methods based on a combination of regression and an improved sampling scheme. The integrated SRSM/CHEMACT framework permits, through the analysis of a minimal number of calculations, the development of quantitative models that identify (i) critical pathways within a given potential energy surface, and (ii) critical thermochemical data that impact model predictions. As discussed earlier the critical thermochemical parameters include any of the following: high-pressure rate constants  $(A^\infty, E^\infty)$  (effective barrier heights and A-factors) for all channels, transition state geometry,  $\Delta_f H_{298}$ ,  $S_{298}$ ,  $C_p(T)$ , activation barriers, well depths, vibrational frequencies, frequency and collision parameters for all isomers. The basic elements of the calculation are as follows:

- Generation of estimates of the “nominal” values for all the required CHEMACT inputs
- Appropriate estimates of the “errors” are selected for the parameters estimated in (i) and the expected distribution of the thermochemical parameters is postulated. In absence of any specific bias we can assume that the parameters follow a uniform distribution within pre-specified bounds. This distribution will be subsequently sampled to generate the instances required by SRSM. The samples points are selected based on the collocation scheme defined by SRSM
- For a given set of parameter values, sampled according to the distribution in (ii), apparent chemical reactions rates, in the form of modified Arrhenius expression, are estimated using CHEMACT including pressure dependence corrections. Detailed reaction mechanisms are assembled in the form of CHEMkin files
- Reactive flow simulations are performed using the aforementioned detailed kinetic mechanism
- Macroscopic observables are recorded as output of the simulations in step (v)
- Steps (iii-vi) are repeated according to the requirements of SRSM until the necessary number of simulations has been performed. These usually scale as power of, where  $n$  is the number of uncertain thermochemical parameters estimated in (i)

- The SRSM coefficients are estimated and the model relating the macroscopic observable estimated in (vi) – autoignition delay for example – and the thermochemical properties estimated in (i) is generated.

Unlike previous approaches that determine rate constant estimates that match experimental observations the proposed approach estimates a physically meaningful range of values for the kinetic parameters. This is critical information because parameter values outside this range will signify fundamental limitations of the reaction scheme that should not be overwritten by adjusting kinetic parameters. These limitations are pointing to incomplete kinetic networks missing important reaction species and steps that need to be included in the description of the chemistry. The approach represents a novel idea since traditional local and global sensitivity analysis connects, at best, a macroscopic observable and apparent rates.



Reaction	$A^\infty$	$n^\infty$	$E^\infty$
CCC•+O2=CCCQ•	2.94E+10	-0.44	0
CCCQ•=CC•CQ	2.10E+07	1.29	31
CCCQ•=C•CCQ	5.79E+06	1.39	21
CCCQ•=C*CC+HO2	1.89E+07	1.51	28
CCCQ•=CCCHO+OH	1.14E+09	1.15	41
CCCQ•=CCCO•+O	2.98E+15	-0.09	62
CC•CQ=CCY(CCO)+OH	8.54E+08	0.85	15
CC•CQ=C*CC+HO2	6.74E+09	0.67	15
C•CCQ=CY(CCCO)+OH	1.26E+10	0.37	20
C•CCQ=C2H4+CH2OOH	1.06E+12	0.57	27

**Figure 4:** Potential energy diagram and nominal high pressure rate constants,  $[E^\infty]=\text{kcal/mol}$

### Oxygen addition to propyl radicals

Propane oxidation will be used to demonstrate the proposed integrated framework. First one needs to notice that even for a small hydrocarbon molecule, such as propane, a detailed kinetic mechanism (216 species, 3078 reactions) [1] is required to accurately predict the experimentally observed "negative temperature

coefficient" behavior. The proposed framework is applied using reasonable expected ranges of  $(A^\infty, E^\infty)$ . These are

assumed to be within the following ranges around appropriately selected nominal values:

$$\left\{ \begin{array}{l} A_i^\infty = [0.3 * A_{i,\text{nominal}}^\infty, 3.0 * A_{i,\text{nominal}}^\infty] \\ E_i^\infty = E_{i,\text{nominal}}^\infty \pm 3\text{kcal/mol} \end{array} \right\}$$

The effect of the expected variability can be substantial as shown in **Figure 3**. The NTC behavior is totally distorted under many combinations of  $(A^\infty, E^\infty)$  values, within the reasonably

postulated ranges of variability. The solid line denotes the nominal parameter value model predictions of conversion, using the values from **Figure 4**, whereas the various points correspond to the estimated ignition delay if we assume "errors" in the nominal high-pressure rate parameters  $(A^\infty, E^\infty)$  sampled uniformly from the ranges

just defined. Focusing on autoignition delay (approximated in this study as the % fuel conversion after 198 ms or reaction time [134]) as the macroscopic observable, the first oxygen addition to propyl radical is analyzed since it involves the most critical steps of isomerization and HO<sub>2</sub> concerted elimination described earlier, **Figure 1**. The detailed potential energy diagram for this step (oxygen addition to propyl radical) assembled in [1] is shown in **Figure 4** along with high pressure modified Arrhenius parameters. These along with the thermodynamic parameters of the key species were calculated using *ab initio* and density functional techniques.

The obtained SRSM model of the autoignition delay was able to correctly identify the critical dependence of the delay on the isomerization and HO<sub>2</sub> elimination steps in the NTC regime [580K - 650K]. For illustration purposes we summarize the linear SRSM coefficients of the fuel (propane) conversion after 198 ms of reaction time,

$$X_{\text{CCC}}^{t=198\text{ms}} = \alpha_0 + \alpha_1 A_1^\infty + \sum_{i=2}^{10} (\alpha_i A_i^\infty + \varepsilon_i E_i^\infty), \text{ in Table 1.}$$

The analysis is performed at three temperatures (573K, 593K, and 683K), which are selected because they correspond to the same macroscopic observable (autoignition delay ~350s, **Figure 4**) although the underlying chemistry is very different. At 573K low temperature chemistry dominates, at 593K we have entered the NTC regime, while at 683K high temperature chemistry takes over. From the results shown in **Table 1**, the following important observations can be made:

- The isomerization reaction (Rxn 3) and the direct HO<sub>2</sub> elimination reaction (Rxn 4) are the dominant contributors to low temperature chemistry since their coefficients are an order of magnitude larger than the remaining.

**Table 1.** Linear SRSM coefficients

Rxn #	Parameter	Description	T=573K	T=593K	T=683K
1	A	CCC.+O2=CCCQ.	-116.92	-204.20	31.17
2	A	CCCQ.=CC.CQ	21.36	50.91	0.81
	E		-143.78	-292.36	-2.95
3	A	CCCQ.=C.CCQ	<b>-376.02</b>	<b>-348.21</b>	<b>1.35</b>
	E		<b>1460.46</b>	<b>1250.47</b>	<b>5.74</b>
4	A	CCCQ.=C*CC+HO2	<b>2878.25</b>	<b>3863.99</b>	<b>52.20</b>
	E		<b>-2045.07</b>	<b>-8630.83</b>	<b>-110.12</b>
5	A	CCCQ.=CCCHO+OH	-0.09	1.25	0.17
	E		-1.94	-8.82	-0.11
6	A	CCCQ.=CCCO.+O	-0.03	0.47	-0.02
	E		-3.77	0.93	-0.61
7	A	CC.CQ=CCY(CCO)+OH	-17.63	-88.73	0.08
	E		38.06	184.63	2.94
8	A	CC.CQ=C*CC+HO2	-11.29	-63.20	0.60
	E		22.95	128.51	1.70
9	A	C.CCQ=CY(CCCO)+OH	0.55	3.44	0.28
	E		-0.51	-5.15	-0.01
10	A	C.CCQ=C2H4+CH2OOH	1.73	7.73	-0.64
	E		-2.27	-9.21	-3.39

2. Based on the relative coefficient values of these reactions steps (Rxn 3 and 4), the  $CCCQ \bullet = C \bullet CCQ$  isomerization is critical for the low temperature, whereas the  $HO_2$  elimination more important at the NTC regime.

3. At high temperatures, most of the reactions become irrelevant and their accuracy/variability has a very minor effect in the macroscopic response of the system.

4. Observations (1) and (2) are very consistent with the current working hypothesis regarding the nature of NTC, according to which the  $HO_2$  radicals are acting against chain branching, **Figure 1**. Furthermore, these results illustrate the need for accurate description of low temperature kinetics since high temperature phenomena can be described with very simplified chemical kinetics mechanisms and would completely miss the important pathways giving rise to low temperature autoignition which is critical for all internal combustion applications.

5. The results of this analysis provide feedback and directions in order to improve the *ab initio* estimates of key parameters. For example, if one wanted to improve low temperature ignition prediction, then the high-pressure estimates of Rxn 3 and 4 should be considered. Given that for Rxn 3 and 4 the SRSM coefficients are 3-4 orders of magnitude larger than the corresponding coefficients of Rxn 9 one can safely assume that Rxn 9 is reasonably well characterized. If on the other hand one was interested in high temperature oxidation only, then even the high-pressure parameters of Rxn 3 and 4 could be considered accurate.

This example illustrates the power of the method since we unraveled, in a systematic way, the highly non-linear dependencies of the macroscopic observable to fundamental parameters such as high-pressure rate constants whose calculation depends on high-level theory *ab initio* calculations. Given that the most difficult challenge in automated mechanism generation remains the accurate estimation of high-pressure rate constants

[14] the proposed framework provides direct feedback, in an iterative way, to automated mechanism generation schemes. One begins with low level and the uncertainty analysis determines for which parameters the available estimates are adequate or improved, i.e., higher level, estimates are needed.

## Conclusions

We have proposed a systematic methodology for quantifying the impact of uncertainty in the thermophysical parameters entering the complex calculation of fundamental kinetic parameters. The proposed methodology allows the identification of the expected ranges of variability of reaction rates when fundamental properties are only known approximately. The framework integrates uncertainty propagation models (SRSM), the chemical activation formalism, automated mechanism generation schemes and reaction simulations and makes use of a reasonable number of model calculations for deriving approximate correlations between macroscopic observables, such as autoignition delay, and microscopic parameters, such as high-pressure rate parameters.

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