

COMPUTER-AIDED CONSTRUCTION OF COMBUSTION CHEMISTRY MODELS

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Introduction

The combustion, oxidation and pyrolysis chemistry of even simple light hydrocarbons can be extremely complex, involving hundreds or thousands of kinetically significant species. Even relatively minor species can play an important role in the formation of undesirable emissions and byproducts. Recently, a number of researchers [1-8] have recognized that the most reasonable way to deal with this complexity is to use a computer not only to numerically solve the kinetic model, but also to construct the model in the first place. We are developing the methods needed to make this feasible, particularly focusing on the need for reliable computer estimates of the pressure-dependent rate constants, rate constants of the reactions with large stereoelectronic effects, and methods for handling situations where the reaction conditions change significantly with time or with spatial position.

We previously devised [8] the first general algorithm for constructing kinetic models appropriate to particular reaction conditions, by numerically testing whether particular species are significant under those conditions. This algorithm can very rapidly and reliably construct rather complex kinetic schemes, testing hundreds of thousands for reactions to find the smaller set which is actually important. It is much less prone to inadvertently omitting an important reaction than other model construction techniques. It has the advantage of clarifying the relationship between the reaction conditions and the kinetic model required. Unfortunately, the existing algorithm is explicitly designed for perfectly mixed, isothermal, isobaric simulations. Relaxing these restrictions raises a number of issues.

Results and Discussion:

A priori rates for combustion reactions

The key issue in constructing any kinetic model, of course, is how to reliably estimate the rate constants required. Many of the important rates for light alkane combustion are known experimentally, though usually over a restricted range of temperatures and pressures (e.g. at room temperature, atmospheric or sub-atmospheric pressure). The highly non-linear combustion process typically involves hundreds of kinetically significant reactive intermediates and even more reactions; it seems unlikely that all the rate constants needed to describe these systems will ever be measured experimentally. What is needed are reliable methods for estimating these reaction rates *a priori*.

Although transition state theory (TST) was proposed more than 60 years ago, and the debate about its microcanonical quantum version known as RRKM has sparked a tremendous amount of effort since the 1960's, this theory was still controversial into the 1990's. It was only over the last decade that conclusive experiments and the elucidation of the connection between TST and quantum scattering decisively established that TST/RRKM is the correct way to calculate most reaction rates. [9-11] Recent advances in computer power and quantum chemistry algorithms have now made it possible to calculate single points on molecular potential energy surfaces (PES's) with something close to "chemical accuracy" of 1-2 kcal/mol. In addition, current DFT technology allows one to calculate rather extensive portions of the PES for even fairly large molecules, albeit with somewhat lower accuracy. [12,13] Several research groups have combined modern quantum chemistry and TST techniques to make *a priori* rate predictions; recent results look very promising. [9,14,15] We have found that in many cases the largest error in *ab initio* rate estimates comes from errors in the calculated barrier height, so one should use high levels of theory for calculating it, but apparently lower levels of theory suffice for estimating the entropic Arrhenius "A" factor (which may be T-dependent). This allows rather accurate rate extrapolations to different temperatures. With some care, complexities such as tunneling, isotope effects, and the large amplitude motions in floppy transition states (TS's) can be modeled accurately *a priori*. [9,14].

Typically rate estimates are made for whole reaction families rather than for individual reactions, an extremely important simplification. The idea is that reaction rates are determined by the functional groups directly involved; the rest of the molecule is more or less a spectator. For example, one would expect that the reactivity of octyl amine and hexyl amine would be very

similar. Usually there are insufficient data to directly verify whether the reaction family idea is valid; but for functional group ideas to work at all it must be at least approximately correct. (For a rare experimental verification see ref. 16).

The Hammond postulate indicates that within a reaction family, the reaction barrier and TS properties should shift with the heat of reaction. These shifts are typically modeled by assuming that the rates follow the simple Arrhenius formula $k(T) = A \exp(-E_a/RT)$, and making linear interpolations between reactions with experimentally determined E_a 's (these interpolations are called "Evans-Polanyi", "LFER", or "Semenov" relations). It is known that the true relationship cannot be linear. Denisov has recently proposed a type of parabolic interpolation. [17] Unfortunately, the experimental data required to make either of these interpolations are often unavailable for the systems of greatest current interest, including many of the reactions important in combustion.

Quantum-chemistry based TST calculations could provide the missing data, but the most accurate quantum techniques are so computationally demanding that only single-point (i.e. fixed geometry) energy calculations are feasible. Much cheaper methods are needed to map out the PES and to determine the vibrational frequencies, etc. required for a TST rate calculations. The method of choice is DFT, which is computationally inexpensive but still fairly accurate in most cases. Unfortunately, current DFT functionals are not reliably enough to be really useful for quantitative kinetics. Current DFT functionals are particularly poor for free-radical oxidations, since they seriously underpredict the strength of peroxidic O-H bonds. [15] We recently developed a method for systematically improving DFT functionals, using as input the results of high-accuracy quantum chemistry calculations. [18] Our approach is based on the fact that the DFT functional determines the electron density as well as the energy; so high-accuracy electron densities provide a strong and very useful constraint on trial functionals.

Many of the components required to make accurate predictions of the chemical kinetics of technologically important processes like combustion already exist. Development and validation of reliable, systematic, quantum/TST-based rate estimation methods would allow us to finally make quantitative predictions about these important chemical processes.

Estimation of pressure-dependent rate constants

For many reactions, pressure-dependent fall-off and chemical-activation effects are very significant. In many cases of importance in combustion chemistry, the initial complex is formed very highly excited, and chemically-activated channels dominate over the thermal pathways. We are currently automating the process of computing pressure-dependent rate constants, so that the computer can do this "on-the-fly" as it constructs the kinetic model. We have devised a general algorithm which constructs every chemically-activated and stabilization reaction pathway, and so can construct and solve the equations which describe the pressure dependence. The required $k(E)$'s and $\rho(E)$'s can be obtained from the high-pressure limit $k(T)$'s and the group-additivity heat capacities by the inverse Laplace transform technique [19] and the "3-frequency" technique [20] respectively. The pressure dependence can be estimated in many different ways ranging from simple approximations to full-blown time-dependent master equations; we will explore the tradeoffs between accuracy and computational speed.

At least initially, we will use the exponential-down model for energy transfer, and the corresponding Troe $\beta_k[M]$ approximation.[21] For chemically-activated reactions of large molecules, there are a very large number of possible reaction pathways, and some pruning will be necessary. This can be done by setting a criterion for kinetic significance which suppresses the most minor channels. Once one has constructed the pressure-dependence model, it can be solved for a range of pressure and for different initial energy distributions of the activated complex (corresponding to different entrance channels and temperatures). We will test this new tool by computing the pressure dependence of a large number of reactions; in addition to validating the method we expect to find some surprises.

Adaptive complex chemistry for reacting flows

In combustion, the overall rate of reaction is usually controlled as much by mixing as by any rate constant. Conventional reacting-flow simulation techniques can only be used if the chemistry model is very small, since they typically attempt to solve for the concentration of every chemical species in the model at every spatial position at every time point in the simulation. Since the computer can rapidly construct kinetic models adapted to each reaction condition, it should be possible to construct an "adaptive chemistry" reacting flow simulation, where different truncated kinetic models are used at different spatial positions and times. This could dramatically reduce the number of equations which must be solved in the simulation. As a first step towards developing such a simulation, we have been examining how one could in practice develop truncated kinetic schemes known to be reliable over a specific range of reaction conditions. We

will also devise methods for dealing with boundaries between finite elements with different kinetic schemes (involving different numbers of species). For the numerical solution, we will draw heavily on numerical methods for solving differential-algebraic equations with discrete control variables recently developed at MIT. [22] Initially, we will construct the reacting flow simulations by hand, for very simple geometries. Once we demonstrate that the "adaptive chemistry" approach provides a significant advantage over current approaches, we can begin to incorporate the technology developed by others for adaptive gridding [23] that would be required for reacting flows through complex geometries.

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