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Computer-Aided Construction of Chemical Kinetic Models

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I. Program Scope

The combustion chemistry of even simple fuels can be extremely complex, involving hundreds or thousands of kinetically significant species. 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 kinetic model in the first place. Because these large models contain so many numerical parameters (e.g. rate coefficients, thermochemistry) one never has sufficient data to uniquely determine them all experimentally. Instead one must work in “predictive” mode, using theoretical rather than experimental values for many of the numbers in the model, and as appropriate refining the most sensitive numbers through experiments. Predictive chemical kinetics is exactly what is needed for computer-aided design of combustion systems based on proposed alternative fuels, particularly for early assessment of the value and viability of proposed new fuels before those fuels are commercially available. This project was aimed at making accurate predictive chemical kinetics practical; this is a challenging goal which requires a range of science advances. The project spanned a wide range from quantum chemical calculations on individual molecules and elementary-step reactions, through the development of improved rate/thermo calculation procedures, the creation of algorithms and software for constructing and solving kinetic simulations, the invention of methods for model-reduction while maintaining error control, and finally comparisons with experiment. Many of the parameters in the models were derived from quantum chemistry calculations, and the models were compared with experimental data measured in our lab or in collaboration with others.

II. Accomplishments

A. Methodology for Computer-Aided Kinetic Modeling

1. Automated Reaction Mechanism Generation

The main focus of this research project was the development of advanced methods for automatically constructing combustion simulations for any user-specified fuel and reaction conditions. [2,9,18,27,32,35,57,60] During the course of the project we created the Reaction Mechanism Generator (RMG) software package and then took it through several versions (now in version 4). The latest publicly-released version and associated manuals are available at http://rmg.sourceforge.net/. This software package takes the initial composition and reaction conditions as input from the user, and from them creates the reaction mechanism including all the intermediates, products, and byproducts. The software estimates the values of the thermochemistry and other molecular properties of all the molecules in the reaction network, and also estimates all the rate coefficients.

A unique and important feature of RMG is that it automatically computes the pressure-dependence of the rate coefficients (due to chemical activation or fall-off), so accurate models can be generated at any pressure;[3,9,52] this is particularly important for connecting low-pressure laboratory flame experiments with high-pressure combustion in engines. The methodology for doing these automated pressure-dependence calculations was developed by this project.[3,9,18,52] We have made most of the thermochemistry and rate calculation tools used by RMG, including pressure-dependence calculations, accessible separately through the CANTHERM package and a website (http://rmg.mit.edu), for the convenience of researchers who are focused on individual reactions rather than large reaction networks.

An important feature of RMG is that the chemistry specifics are kept separate from the source code, so that for example rate parameters for a particular type of reaction can easily be edited by the users without needing to have any knowledge of how RMG works inside, nor any need to recompile the software package. This encourages the community to contribute the best available rate coefficients, and so cumulatively continuously improves the quality of the RMG models. It also makes it relatively easy to add additional elements and reaction types. When RMG was first created, it could only handle hydrocarbon chemistry, but during the course of this project, that capability has been expanded significantly. It can now also accurately predict a huge range of combustion, pyrolysis, and partial oxidation chemistry of CHO compounds,[48,64,vii,ix] a significant range of organosulfur chemistry,[x] and some organonitrogen chemistry. Markus Kraft's group at Cambridge University has independently added silicon chemistry important in chemical vapor deposition for electronic device manufacture. You can see most of the rate coefficients etc. via our database viewer at http://rmg.mit.edu.

During this project, with some complementary support from a DOE center, we also have added the capability to include solvent effects [i,24,45], e.g. to understand liquid-phase reactions leading to fuel injector and lubricant failures in advanced engines. In the long run, the capability to predict condensed phase chemistry is likely to be even more valuable than the ability to predict gas phase chemistry, but more work is needed to improve the accuracy of these predictions.

We are continuously improving the methodology used to compute the thermochemistry and rate parameters; at the time this project began we were using Density-Functional Theory (e.g. B3LYP) to compute reaction barriers, but now we are routinely using CCSD(T)-F12a, which is dramatically more accurate. This project also developed improved methods for computing the thermochemistry of fused cyclic molecules [57] and for handling the coupling between hindered rotors.[47]

Another unusual feature of RMG is that it is open-source. This has encouraged many other researchers to use the software, and some to contribute to the software; overall it has dramatically increased its deployment and impact. At present, about twenty different university, national lab, and industrial research groups are using RMG to build kinetic models. Although most of the RMG software was written at MIT supported by this project, the software includes contributions from researchers at Northeastern University, Belgium, England, and France.

2. Numerical Methods including Automated Error-Controlled Model Reduction

Fuel chemistry is quite complicated, and so the automated reaction mechanism generation software creates very complicated kinetic models. These models can be challenging to solve numerically, particularly when the reactions are happening in a complex geometry and flow (velocity) field. During this project, we have made many advances in the methodology for dealing with this problem.

One line of research where we made an important advance was to apply sparse linear algebra techniques to reduce the memory requirements of stiff ODE solvers. Our key innovation, leveraged by industrial funding, was to reformulate the differential equations, adding an extra variable and equation, in a clever way that makes the Jacobian highly sparse.[ii,2] Combining this with automatic differentiation and automatic sparsity detection led to a solver which required two orders of magnitude less memory and one of order of magnitude less CPU time [20] than the conventional solvers LSODE, VODE and DASSL. Our published method has since been independently implemented in commercial kinetics software such as CHEMKIN-PRO, and other research groups (e.g. Reitz, Maas, Flowers) have further developed this theme.

Another related line of research where this project led the way was the invention of the Adaptive Chemistry technique for solving reacting flow simulations.[11,15,16] In this method, different reduced chemistry models are employed at different spatial locations and at different times during the simulation; for example a very simple chemical kinetic model can be used behind the flame front, since most of the chemical species have been destroyed by passing through the flame, but a quite complicated chemistry model is needed just upstream of the flame front. After we first proposed this idea, several research groups developed it. My group focused on error control, to ensure that the reduced models used were always sufficiently detailed, and in some cases we were able to guarantee that the Adaptive Chemistry solution matched the full-model solution within an error tolerance.[26,31] We also invented a method guaranteed to give the smallest-possible chemical kinetic model subject to the user-specified error tolerance.[2,12,16,30,37] However imposing rigorous error control and finding the guaranteed-smallest-possible model increases the computational cost; as a consequence so far most users have decided to take the risk of omitting error control in order to speed the calculations. This field has advanced significantly since we invented this concept, and the best practical Adaptive Chemistry implementation available at present was invented by Rolf Reitz's group building on KIVA and a fast model-reduction method invented by C.K. Law, demonstrated by a group at ExxonMobil, and is now distributed in the commercial FORTE software package by Reaction Design.

The most popular method for solving reacting flow simulations is to use operator splitting to numerically separate the chemistry from the flow equations. Most solvers use "Strang Splitting" [iii], which has several advantages over alternative approaches. However, Strang Splitting suffers from "splitting error", so that even when the calculation converges to the steady-state solution, the numerical solution can be significantly different from the true solution of the original partial differential equations. We developed splitting schemes which avoid this error [15], and recently published a paper with Strang demonstrating operator splitting schemes we invented where the splitting error exponentially vanishes as the calculation converges to steady-state.[iv]

Of course, one option is to just solve the equations by brute force on big computers. Pursuing this line of research, during this project with support from NASA and a DOE center we wrote the first efficient stiff ODE solver for GPU's, demonstrating efficient accurate solutions for quite large systems (>10,000 coupled stiff ODE's), and also demonstrating a method for solving the reacting flow equations using GPU's.[v,vi]

During the time period of this project we made significant advances in four of the main numerical/computer approaches for solving combustion simulations (sparse Jacobians, Adaptive Chemistry and model reduction, operator splitting, and use of GPU's), and most of these spawned a multitude of follow-up research by others; at least two of the new methods were later commercialized and widely distributed.

3. Rate and Thermochemistry Calculations

During the course of this project we computed a large number of reaction rate coefficients and the thermochemical parameters for many molecules.[1,2,4,6-9,13,17-19,21,23,29,34,38,42-44,46,47,49,50,54,56,62] From these quantum chemical calculations, we derived a large number of thermochemical group values, and also several rate-estimation rules for new reaction families.[4,6-8,13,21,29,47] We also developed a group-additivity method for computing reaction rates based on quantum calculations of transition states.[4,7] We studied too many functional groups and reactions to list here (for full details see the cited papers), but some of the highlights are that we heavily studied the reactions of peroxy radicals and hydroperoxyalkyl radicals [13,21,47,49-50,54], reactions of cyclopentadienyl species leading to aromatic rings [18,42,43,46], reactions of phenyl and vinyl radicals (both computationally and experimentally) [23,34,38,40,44,55,56], and we elucidated the thermochemistry of highly substituted carbons and of ketenyl groups [6,8]. In the course of our study of peroxyl radicals, we discovered a significant error in conventional methods for handling internal rotors, with big effects on many reaction rates.[47]

A portion of this project involved experimental work, measuring the reactions of vinyl radicals with themselves and with alkenes.[34,38,40,44] In most cases the calculations and experiments are in good agreement with each other and with our prior expectations. However, in the course of that work and associated quantum chemistry calculations we discovered a reaction family (radical addition to terminal alkenes) where the rate coefficient does not follow the normal Evans-Polanyi correlation, but instead the rate increases as the exothermicity decreases; this unusual phenomenon was independently discovered for a different addition reaction in calculations by Radom.

Towards the end of the project, we investigated advanced methods for improving the accuracy of the rate calculations. We had excellent success with the Ring Polymer Molecular Dynamics (RPMD) rate-calculation method developed by Manolopoulos. We created an efficient open-source software package for RPMD calculations called RPMDRate, and tested the accuracy of RPMD on several different types of systems.[58,59,61,63,xii,xi] For some of these systems the exact quantum mechanical rate is known for comparison. The RPMD results are always within a factor of 3 of the exact solution, and are quite accurate (~30%) at combustion-relevant temperatures. The main disadvantage of RPMD is that a full-dimensional PES is needed, implying a lot of quantum chemistry calculations and CPU time. A major advantage of RPMD is that the results are insensitive to the choice of dividing surface, this is very helpful for situations where the transition state is floppy or poorly localized.

B. Applications of the Newly-Developed Methods to Interesting Systems

The first system where our computer-aided modeling approach made a big contribution was the pyrolysis of methane.[18] That system sounds very simple, but the kinetics are very tricky, with autocatalysis and run-away beginning after a long induction time, when the key species cyclopentadiene is formed via a rather complicated route.

As the computer capabilities and our software improved, we were able to tackle larger molecules. The second big success was the RMG-constructed model for hexane pyrolysis, which was found to be in excellent agreement with experimental results measured in a flow reactor in Belgium.[27] Since that time RMG has been repeatedly used to model flow pyrolysis experiments (relevant to the industrial steam-cracking process and to fuel cracking upstream of a flame front).

Another important demonstration was automated construction of detailed models for the doped-diffusion-flame experiments of McEnally and Pfefferle, predicting the effects of doping hexadienes into a methane flame.[24] Towards the end of this grant period, we collaborated with the Brezinsky group to understand how alkene oxidation chemistry depends on the position of the double bond [64], an issue relevant to biodiesel combustion.

The numerical methods developed in this project have been applied to many systems, and have proven particularly helpful in modeling HCCI and similar engines, to understand the limits on operability.[20,36] Some of the numerical methods invented in this project have proven so useful that they have been incorporated into commercial simulation software, and are being used in industry to develop advanced engines and new fuels.

The software and methods developed during this project have been applied (with separate funding) to other systems, notably the pyrolysis and combustion synthetic jet fuel JP-10 [48,xiii,xiv] and diisopropyl ketone combustion [ix]. The most exacting test of the predictive modeling technique to date has been the development of the detailed model for the combustion chemistry of isobutanol and comparison of the model predictions with a dozen different experiments, most measured by the Combustion EFRC. In the most impressive case, dozens of species profiles in a set of premixed isobutanol flames were predicted prior to the experimental data being analyzed.[vii]

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