PRESSURE-DEPENDENT AUTOMATED MECHANISM GENERATION: SYSTEMATIC MODELS FOR DIFFICULT SYSTEMS

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Introduction

Advancement in the design of such important gas-phase processes as hydrocarbon cracking, combustion, and partial oxidation hinges, in part, on the development of correct, detailed chemical kinetic models. But the complexity of the required chemical mechanisms can make them extremely difficult to construct by hand. Modelers turn to software algorithms that build these large mechanisms automatically (e.g. [1], [2]), but the current tools are too limited to treat many difficult systems. We present a new, elementary-step-based mechanism generation algorithm, called "XMG-PDep," which overcomes these limitations with a comprehensive approach to pressure-dependent reactions, and a rational, flux-based criteria for truncating mechanism growth. Applications to the previously intractable methane and high-conversion ethane pyrolysis systems yield predictions which agree well with experimental data, without any parameter adjustment. Important new pathways, not previously considered, but discovered entirely by the new approach, can explain unusual behavior in these systems, and suggest the power of this software tool.

Computational Method: The XMG-PDep Algorithm

XMG-PDep is based upon XMG [3], which developed from NetGen [4]. It employs flux-based termination of the otherwise combinatorial in species and reactions. To do this, the code periodically constructs and integrates the set of differential equations that represent the evolution of the reacting system in time (assuming a well-mixed batch reactor model). It evaluates a characteristic mechanism flux Rchar(t), which is similar to a root-mean-square average of chemical fluxes in the mechanism [5]. XMG-PDep then compares this flux with those to candidate species that have been discovered, but not yet included, in the mechanism. Those species whose fluxes exceed the cutoff flux (equal to a user-specified fraction of Rchar(t)) are included in the mechanism; the rest are not.

XMG-PDep can systematically discover and include arbitrary pressure-dependent reactions, using the algorithm of ref [6]. To allow the most flexibility, XMG-PDep considers any elementary step of the form $A + B \rightarrow C$, $B \rightarrow C$ or $B \rightarrow C + D$ to initiate a partial pressure-dependent network. For each partial network, XMG-PDep uses the QRRK/MSC code CHEMDIS [7] to estimate the k(T,P) values of every net pressure-dependent reaction. It also examines the maximum flux to all non-included portions of the partial pressure-dependent network. If this flux is greater than the cutoff flux, the partial network is "grown" by one isomer, with all its high-pressure-limit elementary steps, and the k(T,P) calculation is repeated. Growth of each partial pressure-dependent network is halted when the flux to non-included portions is less than the cutoff flux. In this way pressure-dependent reactions can be included systematically and rationally. A full description of the integrated algorithm for generating mechanisms is presented in ref. [8].

Finally, XMG-PDep includes a number of other features designed to make it accurate and useful. It employs literature-based libraries of rate constants and thermochemical parameters whenever possible. Its rate rules are subdivided as much as is reasonable to provide the best estimates for high-pressure-limit rates when these are not available from the library. Thermochemical data (when not available from the data library) are taken from a group contribution method [9] and used to ensure thermodynamic reversibility. The code will produce a CHEMKIN mechanism, and a number of analyses of the mechanism (such as the net radical rate of production for each reaction), when finished with generation.

Application to Methane and High-Conversion Ethane Pyrolysis

Methane pyrolysis has been extensively studied for many decades, both for its potential to convert methane to more valuable hydrocarbons, and its importance within larger combustion and pyrolysis mechanisms. But the strange, autocatalytic behavior of methane pyrolysis at extremely low methane conversion has defied mechanistic explanation for at least three decades. The most recent attempt, of Dean in 1990 [10], appeared successful until new thermochemical data for the cyclopentadienyl radical rendered its explanation inadequate.

Applying our tool with the rate rules and thermochemical data described in ref. [8] gives a mechanism which captures the low-conversion autocatalysis, without resort to parameter fitting or adjustment, as shown in Figure 1. The generator suggests that the autocatalytic behavior arises from a number of separate sources, none of which had been considered previously for these conditions. First, cyclopentadienyl radical, produced by the pressure-dependent addition of propargyl radical to acetylene, abstracts a hydrogen from methane to form cyclopentadiene. The cyclopentadiene in turn will dissociate easily to another H atom and cyclopentadienyl radical, causing chain-branching, or a net production of radicals. Second, the reverse disproportionation of methane and allene to form methyl radical and allyl radical plays an important chain-branching role, especially at early times. Finally, as an aggregated group, the set of all reverse disproportionations accounts for about 50% of the chain-branching.

Figure 2 shows a more comprehensive view of the pathways leading to autocatalysis. Many of these pathways are pressure-dependent and could not have been discovered by a tool without this capability. Further validation against other product data, and support for the mechanistic analysis, can be found in ref. [11].

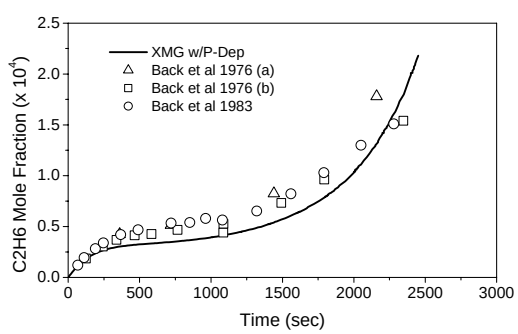

Figure 1. XMG-PDep predicted ethane concentration with time, during static batch pyrolysis of neat methane at 1038 K and 0.58 atm.

The prediction clearly captures the autocatalytic upturn in concentration as reflected in three experimental datasets [12-14].

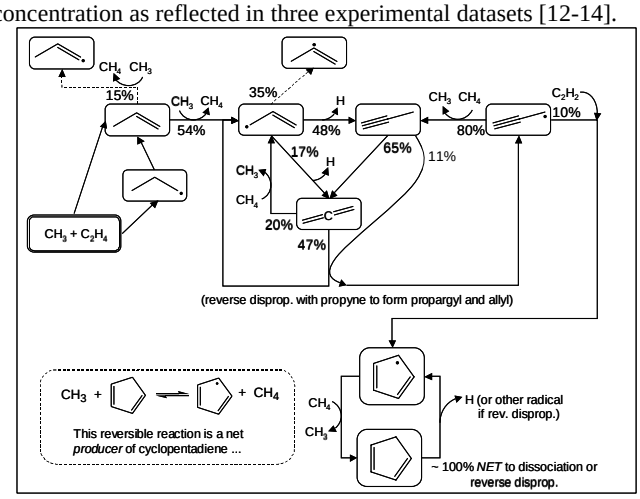

Figure 2. Partial depiction of pathways leading to autocatalysis in low-conversion methane pyrolysis. A number of these pathways are reverse disproportionations; as a whole, the set of all reverse disproportionations provides about 50% of the net radical production. A number of other important pathways (such as the addition of propargyl to acetylene, and the isomerization of allyl radical) are pressure-dependent.

High-Conversion Ethane Pyrolysis. Glasier and Pacey [15] used a laboratory flow reactor to study neat ethane pyrolysis at very high conversion (>98%, 900-1200K, 0.4 atm), in an effort to correlate the concentrations of proposed "soot precursors" with the formation of pyrolytic (deposited) carbon. No existing detailed kinetic mechanism exists for these conditions; the high conversion and large number of pathways make this system extremely difficult to consider by-hand. That fact, coupled with the detailed data available for minor products, makes this experimental work a good but challenging example case for our algorithm. Our generated model's agreement with the data is quite good (as seen in Figures 3 and 4), considering that once again no parameters were adjusted to fit the data, and all steps in the mechanism are "from scratch".

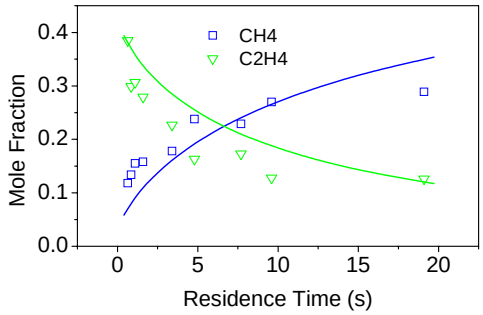

Figure 3. CH_4 and C_2H_4 concentrations with residence time in the Glasier and Pacey flow reactor. Symbols are experimental data points; lines are auto-generated model predictions.

Pathway analysis of the very large mechanism generated for this system suggests that the fates of the minor products, and some major ones, are governed in part by a large and complex set of interconnected reactions. Conventional mechanisms do not capture some of these pathways. Although the Glasier and Pacey system was chosen as a difficult example which would test the limits of strictly elementary-based, gas-phase mechanism generation, the resultant model for these unusual conditions may also prove useful as a base for the understanding of aromatics and soot formation.

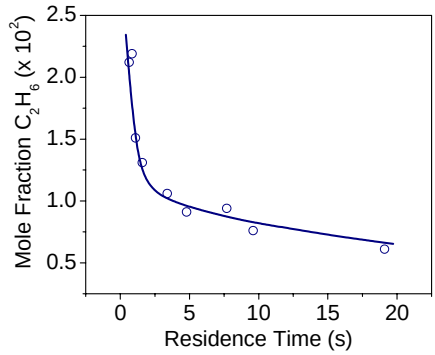

Figure 4. Experimental and predicted ethane concentration with residence time.

Discrepancies in the predictions of H_2 and benzene (not shown here) imply that XMG-PDep is missing whole reaction families for generation, though other explanations (such as globally incorrect rate rules, thermochemistry, or heterogeneous reactions) cannot be ruled out. The lack of good, publicly-available tools for understanding large (>1000 reaction) mechanisms severely hampers the analysis.

Conclusions. The XMG-PDep algorithm for building reaction mechanisms "from scratch", including pressure-dependence, shows promise in helping kineticists understand highly complex systems that could not otherwise be studied easily. The tool suggests new pathways that explain behavior in both of the "demonstration" systems; further work will involve systems of more industrial importance.

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