

APPLICATION OF COMPUTER GENERATION OF REACTION MECHANISMS USING QUANTITATIVE RATE INFORMATION TO HYDROCARBON PYROLYSIS

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ABSTRACT

Novel modifications were made to the core components of the algorithms for rate-based generation of reaction mechanisms¹, including introducing thermodynamic constraints into the estimation of the controlling rate parameters and an alternative approach for determining the species included in the final mechanism. Once implemented, the adapted rate-based building criterion was successfully employed to construct a compact mechanistic model for low-pressure tetradecane pyrolysis. Though thousands of species and reactions were generated, only a small portion of these were deemed necessary and incorporated into the final model. Experimental data were used to determine frequency factors for a subset of the reaction families, while all other kinetic parameters were set based on the literature. The final optimized values for the frequency factors were consistent with literature, and the model was able to accurately fit experimental data from different reaction conditions. With no adjustment to the optimized frequency factors, the mechanistic model for tetradecane pyrolysis was able to accurately predict reactant conversions and product yields for varying reaction conditions. Both relative trends and the actual values were predicted correctly over a wide range of reactant conversions and initial reactant loadings.

I. INTRODUCTION

The advent of tools for computer generation of reaction mechanisms has dramatically reduced the time for the development of complex reaction models and increased the level of detail they may include. One of the challenges in building reaction mechanisms using algorithms for automated model construction, however, is to describe the essential chemistry and enable prediction of experimental data over wide ranges of reaction conditions while maintaining a manageable model size. For example, hydrocarbon pyrolysis is a chemistry in which molecular weight growth reactions may be important, and a mechanism generated automatically would therefore grow to infinite size without the application of external termination criteria. Implementation of a species rank criterion, which restricts those species capable of undergoing reaction based on the order in which they appear in the mechanism, overcame this obstacle¹. However, this criterion is usually not restrictive enough since insignificant species must also be included to capture the important ones.

This limitation motivated development of an alternative strategy for computer generation of reaction mechanisms that includes important reactions based on quantitative evaluation of reactivity¹. This approach exploits the capability to estimate rate constants as the mechanism is generated, allowing it to be solved at any point. The mechanism is built iteratively, as a growing reaction mechanism is alternatively generated and solved. Quantitative evaluation of the formation rates of all species during the mechanism building process determines the next set of species allowed to undergo reaction. The formation rates are compared to a characteristic rate of the current system, and a weighting factor, ϵ , is used to adjust the characteristic rate to allow more or fewer species to be included in the mechanism.

The work that will be described builds upon the previous work¹ but includes several important improvements. The first implementation of the rate-based approach used the disappearance rate of a single reactant to define a characteristic rate in the system to which all of the other rates were compared, and the conversion of this reactant was used as the marker of the completeness of the mechanism. If the reactant quickly equilibrated, the mechanism building process would not advance. In the new implementation, time is used as the independent variable, and the rates of all of the species in the system are used to determine the overall characteristic rate. Secondly, since the mechanism building process requires on-the-fly kinetic information, a lookup capability was implemented to allow experimental rate information to be incorporated. Finally, equilibrium information was obtained through on-the-fly calculation of heat capacity, enthalpy and entropy values. By marking reversible pairs of reactions, the rate constant for the reverse reaction could be calculated from the forward rate constant and the value of the equilibrium constant. This latter capability represents a substantial advance in our ability to generate complex reaction mechanisms via the computer.

II. PROCEDURE

A mechanism for low pressure tetradecane pyrolysis was generated to determine the effectiveness of the adapted rate-based generation algorithm. This reaction system serves as an adequate test for the rate-based generation criterion since thermolysis of a long chain paraffin can lead to thousands of intermediates and stable products. However, only a small fraction of these is actually kinetically significant. Furthermore, experimental information collected in our laboratory² was available to test the ability of the model generated to capture the reactant conversion and product selectivities over a wide range of reaction conditions. Low pressure batch pyrolysis reactions were conducted using initial loadings of tetradecane ranging from 0.01 to 0.045 M for times ranging from 10-150 minutes at temperatures of 420 and 450°C.

The reaction mechanism was built by implementing six reaction families deemed important for gas-phase hydrocarbon pyrolysis at moderate temperatures: bond fission, radical recombination, β -scission, radical addition, disproportionation and hydrogen abstraction (intermolecular and intramolecular through 1,4-, 1,5- and 1,6-hydrogen shift reactions). Estimates of the Arrhenius frequency factors and the parameters of an Evans-Polanyi relationship³, E_0 and α , for each reaction family were obtained from the literature. The model

was constructed using an initial tetradecane concentration of 0.0322 M and a reaction temperature of 420°C. The weighting factor, ϵ , was varied from 1.0 to 5×10^{-5} . The total number of species, the reactive species, the total number of reactions and the number of reactive reactions were tabulated as a function of the weighting factor. Each individual elementary step is specifically tallied; the numbers of reactions reported are not consolidated according to the known reaction path degeneracies nor are reverse and forward pairs lumped as a single reaction.

III. RESULTS

The model characteristics as a function of weighting factor are summarized in Table 1. As the weighting factor decreased, all quantities reported increased. However, the growth in the total number of species was more dramatic than the moderate growth observed for the number of reactive species. Thus, using rate-based building and the weighting factor as a "tuning" parameter, the size of the mechanism solved was easily controlled. The adequacy of the reaction mechanism was assessed by monitoring two key characteristics: whether all of the major products observed experimentally were included and if secondary reactions of olefins were described. For example, at a weighting factor of 1.0, only C_1 - C_7 alkane products were included in the model, while C_7 - C_{13} alkanes were detected experimentally. It was necessary to decrease the weighting factor to 5×10^{-5} before tridecane, the major product observed in the lowest yield, was included in the mechanism as a reactive species.

The mechanism generated employing a weighting factor of 5×10^{-5} was therefore used to capture the experimental behavior. Experimental data from 20 mg pyrolysis reactions of tetradecane conducted at 420°C and 450°C were used to determine controlling rate parameters. There were 27 parameters which could be varied, a frequency factor, an E_0 and an α value for each reaction family. However, only four parameters, $A_{\text{bond fission}}$, $A_{\beta\text{-scission}}$, $A_{\text{H-abstraction by R}}$, and $A_{1,5\text{-hydrogen shift}}$, were fit against the experimental data. All other parameters were set constant at values obtained from the literature. Note that only frequency factors were permitted to vary, while all intrinsic barriers and transfer coefficients were fixed.

A parity plot comparing the fitted model yields to the experimentally observed yields for major and minor products is shown in Figure 1. The model did an excellent job of fitting the experimental data from the pyrolysis reactions over several orders of magnitude. Reactant conversions for both temperatures were fit extremely well, even though no activation energies were used as fitting parameters. Gaseous hydrocarbons and liquid α -olefins were also fit very well.

The predictive capabilities of the model were then assessed by solving for the product yields and conversion at other reactant loadings with no further adjustment to any of the model parameters. A comparison of predicted and experimental yields of undecene as a function of reactant conversion and reactant loading is shown as a representative example of the predictive capability of the model in Figure 2. The model was able to predict accurately the trends in the data and the actual values over a wide range of conversions and reactant loadings. Similar predictive capabilities were observed for gaseous hydrocarbons and other long chain α -olefins.

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Table 1. Summary of model characteristics as a function of the weighting factor used to direct rate-based building.

Weighting factor	Number of total species	Number of reactive species	Number of reactions	Number of reactive reactions
1	1908	103	57116	15605
0.1	2401	107	65866	17633
0.01	3349	120	98286	26116
0.001	4676	130	132450	30436
0.0001	11158	236	319408	63004
0.00005	16269	302	477566	98240

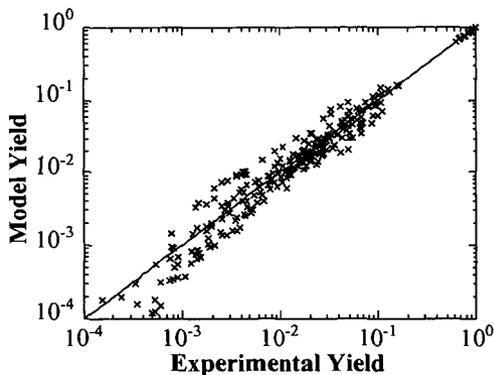


Figure 1. Comparison of fitted model yields and experimentally observed yields for major and minor products of tetradecane pyrolysis.

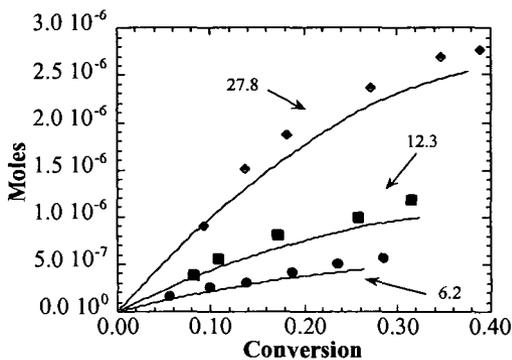


Figure 2. Comparison of the experimental (symbols) and predicted (lines) evolution of undecene for initial tetradecane loadings of 6.2, 12.3 and 27.8 mg.