

ACCURATE REACTION NETWORKS FOR ALTERNATIVE FUELS: BUTANOL ISOMERS

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Summary

A detailed pressure-dependent reaction mechanism for normal-, sec- and tert-butanol is presented. These mechanisms were generated using the open-source software program, Reaction Mechanism Generation (RMG), and were validated against pyrolysis experiments performed in a bench-scale set-up at the Laboratory of Chemical Technology of Ghent University and butanol-doped methane diffusion flame experiments previously reported by McEnally and Pfefferle. Using butanol as a prototype, the reaction pathways of primary, secondary, and tertiary alcohols will be discussed.

Keywords

Deployable software and databases for reaction engineering; Reaction Path Analysis

Introduction

Meeting the world's energy demands for the twenty-first century and beyond will require the development of alternative, renewable fuel sources. Validating an alternative fuel source or fuel additive inherently comes from *a posteriori* knowledge: run a series of experiments whose results will assist in determining whether additional experiments should be conducted. Unfortunately, this knowledge is acquired at the expense of the fuel.

Shifting from *a posteriori* to *a priori* knowledge would improve the efficiency of the validation process, in particular by limiting the amount of resources necessary to conduct experiments. *A priori* knowledge requires extracting as much useful information out of the already available, yet limited data. For example, if one possessed validated pyrolysis mechanisms for normal-, sec- and tert-butanol (the smallest hydrocarbon system that contains a primary, secondary, and tertiary alcohol), one should then have many of the necessary tools to predict the pyrolysis of larger alcohols, regardless of the molecule's complexity.

One of the emerging fuel additives is bio-butanol. Although much effort has been placed on understanding the reaction pathways of n-butanol, recent emphasis has been placed on exploring the possibilities of sec- and tert-butanol as either a fuel additive or alternative; sec-butanol is produced primarily as a precursor to methyl ethyl ketone while tert-butanol is an industrial solvent produced for paint removal or the production of highly-branched ethers, e.g. methyl tert-butyl ether (MTBE).

There have only been a handful of studies published on the pyrolysis or combustion of sec- and/or tert-butanol. Barnard studied the pyrolysis of tert-butanol¹ over the

temperature range 487 – 620 °C. Butanol flame studies, including diffusion flames of the four butanol isomers², butanol-doped methane diffusion flames³, and low-pressure, premixed butanol flames⁴, have been reported though none of the studies reported a detailed kinetic mechanism. Recently, a detailed kinetic mechanism for the oxidation of all four butanol isomers was published⁵, validating the mechanism against shock-tube ignition delay times; the fuel's maximum concentration was 1 mol. %.

In this work we describe the construction of detailed, pressure-dependent mechanisms for normal, sec- and tert-butanol by the automated reaction mechanism generator, RMG, and compare its predictions against both pyrolysis and combustion experiments.

Automated Mechanism Generation

The Reaction Mechanism Generator (RMG) software package is an automated, rate-based kinetic model generator that constructs pressure-dependent reaction mechanisms for isothermal, isobaric batch systems^{6,7}. The user must supply: the system temperature and pressure; the initial species concentrations; and a termination goal. The user may also input a list of preferred species' thermochemistries and a list of preferred reaction rate coefficients. The output files of a RMG simulation include species concentration profiles and a reaction mechanism, in the form of a CHEMKIN file.

For a given iteration, the RMG software has two species classifications: (1) "core species," or the species RMG

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predicts will be significant in the reaction mechanism, and (2) “edge species,” or all other species generated in the mechanism. Utilizing a list of extensible reaction family templates, RMG generates all possible reactions for the “core” species present in the mechanism. For each species generated, its rate of formation is computed. The largest of these rates is then compared to the “minimum rate of formation,” R_{\min} , derived using a user-defined tolerance. If the rate of formation is greater than R_{\min} , the species is labeled a “core” species and the mechanism enlarging algorithm is continued; if not, it remains an “edge” species. The software continues this process until the user-specified time of reaction or species conversion is reached.

To perform the rate analysis and to predict species concentrations as a function of time, the software requires reaction rate coefficients and thermodynamic parameters for all reactions and species generated in the model, respectively. When a new species is generated, RMG initially checks for any user supplied thermochemical parameters; this allows the user to override any thermochemical value RMG would implement in a mechanism with their personal preference. If no user-defined data is found, RMG next checks against the community’s recommended data set, as defined by the Process Informatics Model (PrIme) project. If this search is also unsuccessful, RMG will estimate the species’ thermochemistry using Benson’s group-additivity approach. A similar hierarchy is employed for estimating reaction rate coefficients.

The PrIme project is a community-collaborative initiative that collects, stores, and validates data with the ultimate goal of processing and assembling the data into kinetic models⁸. Two components of the PrIme project are the data depository, which houses the community’s raw data, and the data library, which stores evaluated data. The data library is the data set alluded to previously; RMG mines this data set for thermochemical data after any user-specified inputs but before estimation routines.

Contributions

A detailed, pressure-dependent reaction mechanism for both sec- and tert-butanol will be presented. The mechanisms were validated against experimental data, including pyrolysis experiments performed in a bench-scale set-up at the Laboratory of Chemical Technology of Ghent University⁹ and butanol-doped methane diffusion flames previously reported by McEnally and Pfefferle³. The pyrolysis experiments are modeled using the CHEMKIN plug flow module; the measured temperature and pressure profiles are supplied. The reactor model used to emulate the doped methane flame is the same reactor model constructed and utilized by Sharma *et al.*¹⁰ in their work on constructing reaction mechanisms for three hexadiene isomers. The solver uses the method of lines to solve the species conservation equations arising in the

diffusion flame; the temperature and velocity profiles of the doped flame are assumed to be the same as those of the undoped flame. The resulting program is able to solve the mass conservation equation of ~100 species with ~1000 reactions at each spatial position in a few hours. Rate of production and sensitivity analysis are used to identify the most important pathways to the main products and soot-precursors.

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References

1. Barnard, J. A., Pyrolysis of tert-butanol. *Transactions of the Faraday Society* **1959**, 55, 947-951.
2. Smith, S. R.; Gordon, A. S.; Hunt, M. H., Diffusion flames. III. The diffusion flames of the butanols. *Journal of Physical Chemistry* **1957**, 61, 553-8.
3. McEnally, C. S.; Pfefferle, L. D., Fuel decomposition and hydrocarbon growth processes for oxygenated hydrocarbons: butyl alcohols. *Proceedings of the Combustion Institute* **2005**, 30, (Pt. 1), 1363-1370.
4. Yang, B.; Osswald, P.; Li, Y.; Wang, J.; Wei, L.; Tian, Z.; Qi, F.; Kohse-Hoinghaus, K., Identification of combustion intermediates in isomeric fuel-rich premixed butanol-oxygen flames at low pressure. *Combustion and Flame* **2007**, 148, (4), 198-209.
5. Moss, J. T.; Berkowitz, A. M.; Oehlschlaeger, M. A.; Biet, J.; Warth, V.; Glaude, P.-A.; Battin-Leclerc, F., An Experimental and Kinetic Modeling Study of the Oxidation of the Four Isomers of Butanol. *Journal of Physical Chemistry A* **2008**, 112, (43), 10843-10855.
6. Van Geem, K. M.; Reyniers, M.-F.; Marin, G. B.; Song, J.; Green, W. H.; Matheu, D. M., Automatic reaction network generation using RMG for steam cracking of n-hexane. *AIChE Journal* **2006**, 52, (2), 718-730.
7. Green, W. H. *RMG - Reaction Mechanism Generator* <http://rmg.sourceforge.net/>, 3.1; 2009.
8. Frenklach, M., PrIme: Process Informatics Model <http://www.primekinetics.org/>. **2006-2009**.
9. Chen, Q.; Froment, G. F., Thermal-Cracking of Substituted Aromatic-Hydrocarbons. 1. Kinetic-Study of the Thermal-Cracking of i-Propylbenzene. *Journal of Analytical and Applied Pyrolysis* **1991**, 21, (1-2), 27-50.
10. Sharma, S.; Harper, M. R.; Green, W. H., Modeling of 1,3-hexadiene, 2,4-hexadiene and 1,4-hexadiene doped methane flames: Flame modeling, Benzene and Styrene formation. *Combustion and Flame* **2009**.