COMPUTATIONAL CHEMISTRY AND REACTION ENGINEERING SOFTWARE INTEGRATION

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ABSTRACT

The management of chemical information has become more important as the complexity of the chemical applications grow. Reaction engineering is hampered by the abundance of incomplete reaction mechanisms that have been compiled.

The motivation behind this work is to provide users with a simple unified interface to manipulate existing chemical data, and to create estimates to unknown chemical properties. The OpenChem Workbench is a software program that will assist computational chemists, and reaction engineers in their pursuit of building a mechanism out of reaction rate expressions.

The necessary data structure to store and retrieve reaction kinetics data was encoded. The OpenChem Workbench framework is now a freely available application, which can be downloaded for application or development purposes from sourceforge.net.

Modularity of component plugins assist in the creation of tasks specifically tailored to the needs of the user, whether they are industrial, academic, or just an interested software developer. Existing modules are tailored for the creation and manipulation of the data structures.

Analysis of the benzene mechanism was studied to demonstrate the ability of the OpenChem Workbench as a modeling tool. The validity of reaction rate expressions was analyzed, and the resulting concentrations were compared to experimental. It was found that the mechanisms studied do not describe the combustion of benzene compounds well.

The OpenChem Workbench demonstrated an ability to make several reaction engineering tasks easy. The OpenChem Workbench can be found through sourceforge at http://sourceforge.net/projects/openchemwb/

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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CHAPTER 1
INTRODUCTION

Chemical study has developed such a large amount of data that powerful tools are required just to organize this ever-expanding body of information. Chemical engineering has a specific need for computational tools that will create, organize, store, and apply thermodynamic and kinetic information under a single interface toward the analysis and improvement of reaction engineering.

The difficulties incurred by a non-uniform data formats and awkward user interfaces have become an irritation to the chemical modeler. The OpenChem Workbench program ameliorates some of these problems by giving a user the ability to manipulate thermodynamic and kinetic parameters, and to apply kinetic rate data to some idealized chemical reactor models. In addition, when thermodynamic or kinetic data are unsatisfactory or nonexistent, the program is capable of using theoretical methods to estimate thermodynamics.

All of the tools necessary to perform these calculations exist outside the OpenChem Workbench, but a lack of integration has weakened the potential use of each component. Difficulties occur due to a required familiarity with several unrelated components, before application of chemical information can produce results. In order to unify the interface, several problems unique to chemical information must be addressed.

The OpenChem Workbench program must handle the problem that thermodynamic data are frequently reevaluated, causing an abundance of values for the same property. Additionally, the program must handle when the opposite is true, a lack of thermodynamic properties for chemical species. In the OpenChem Workbench program, thermodynamic property display has shown that discrepancies such as incorrect temperature limits or unrealistic or discontinuous data fits can be detected and corrected.

A third problem is the complexity of reaction engineering. Chemical reaction processes are described by a network of elementary reactions organized into reaction mechanisms. A reaction mechanism that describes a specific chemical system often includes on the order of hundreds to thousands of individual elementary reactions, and changing the value of one node in this network of reaction rates has consequences upon the calculated concentration of a variety of chemical species within the reaction network. Mechanisms are frequently born out of a combination of semi-empirical fitting to concentration data and calculated elementary reaction rate constants, which typically apply to a narrow region of pressure and temperature. Modification or refactoring of a mechanism frequently occurs via computational modeling. The OpenChem workbench project provides an interface for the advanced tasks of organization of mechanistic data from multiple sources and applications of that data in idealized chemical reactors.

The Workbench design team is made up of academic as well as industrial partnerships. Contributions to the project were made by:

Adapco
Blue Star Technologies
Exxon Mobil
DuPont
Gaussian
Wesleyan University
Mitsubishi
NIST
NREL
Reaction Design
University of Delaware

CHAPTER 2

CHEMINFORMATICS

Chemical informatics helps chemists investigate new problems and organize and analyze scientific data to develop novel compounds, materials, and processes through the application of information technology"[1]. A system using cheminformatics must enable the user to take raw data about molecules and reacting systems, and transfer it to useful application. To do this, a system implementing cheminformatics must have a interface for the management and presentation of multiple, complex data.

This project is focused on Reaction Engineering Cheminformatics. Where Cheminformatics is the transfer of raw chemical information to useful chemical knowledge. Reaction Engineering Cheminformatics takes data regarding molecules and reacting systems, and transfers it to useful application.

An example for the need for a cheminformatics software package is apparent when reviewing the existing tools used by reaction engineers. Software tools such as Chemkin and Gaussian began as packages with source code that were freely distributed between interested users. After a time, the license owners began discouraging users from continuing to use the distributed versions. Consequently they created a large, slightly disgruntled user base, and a lot of information already available in their preferred format. The chemical input to these two programs are small and simple, and do not make any directed effort to uniquely identify chemical compounds.

In comparison to this, the OpenChem Workbench has always been intended as Open Source Software. There are different kinds of Open Source software licenses[2], each modifying the severity of restrictions placed on code integrated with it.

The most severe is the Gnu General Public Licensing agreement, which states basically that all source code and distributions are to remain free, and anyone that derives code from, or uses this code, must not make any profit from it, and must make their code also freely available.

A less stringent licensing agreement is the Lesser General Public Licensing (LGPL) agreement. This document states does not force derived and implementing code to also be freely available, but it does indicate that distributions should also make the open source part of the code available.

2.1 Problems of implementation

There are three core tasks of cheminformatics implementation, user interface, data storage, and algorithm implementation. Implementing a cheminformatics package requires the ability to store accurate data, and a user interface to accurately convey the data to a user.

The storage of data can be implemented through a relational database, or through flat data files. The benefits of using a relational database are that data is less likely to become corrupted, and there is a rapid searching capability with the methods implemented by whatever database management system (DBMS) chosen. There are several DBMS programs available, such as PostGreSQL, MySQL, mSQL, and Microsoft Access.

Proposed solutions to user interface issues have been abundantly researched and discussed[3,4,5,6]. Following the rules established in user interface design allows experienced computer users to get accustomed to the functionality of the workbench without having to get accustomed to the interface.

The third problem of cheminformatic software integration is the implementation of the myriad cheminformatic algorithms and components that have been developed during the past 20-30 years. One method of working around this problem is using the proprietary method libraries developed by companies such as MDL Information Systems, Inc.[7], Daylight Chemical Information Systems, Inc.[8], or Advanced Chemistry Development[9]. Derived programs must pay for the ability to use the proprietary function libraries.

A recent development in making freely available algorithms is in the Chemical Development Kit[10] (CDK) package, which gives free, open-source Java software that implements many cheminformatic algorithms. This software package uses a different object modeling strategy that does not include the persistence, or the storage and retrieval, of thermodynamic chemical data, as well as not providing a user interface for the manipulation of the data structure described in section 2.2. Although the CDK data structure is not sufficient for the OpenChem Workbench, some of modules available from the CDK are usable. For example, the Workbench currently uses the two-dimensional viewer component and chemical isomorphism algorithms found in the CDK.

The philosophy of the CDK developers is that "Sharing of ideas and results within communities is probably the most central paradigm in science. By publishing his results a scientist allows his colleagues to verify and build upon his results, thereby advancing the particular field as a whole [If I have seen further it is by standing on the shoulders of giants. - Isaac Newton]." This is the reason for their choice of the open-source code and LGPL. *A freely available tool greatly increases the usefulness of a chemical information* package.

2.2 Object Modeling

Object modeling is important to the programming of the OpenChem Workbench because we wish to save and retrieve data that group themselves as abstract chemical concepts.

The OpenChem Workbench is written as object-oriented software. Object Oriented Programming (OOP) is a way of thinking abstractly about a problem using real-world concepts, rather than computed concepts.

Four benefits of Object Oriented code include Abstraction, Encapsulation, Inheritance, and Polymorphism. Abstraction is the discarding of detailed information unnecessary to the understanding of the Object. Encapsulation is the separation of interface and implementation. Inheritance is the action of reusing features of one object in another. Polymorphism is the behavior invoked by an object that is most appropriate for that object.

The object model of the OpenChem Workbench include the following user objects shown in figure 2.1. Further description of these entities is included in the gossary.

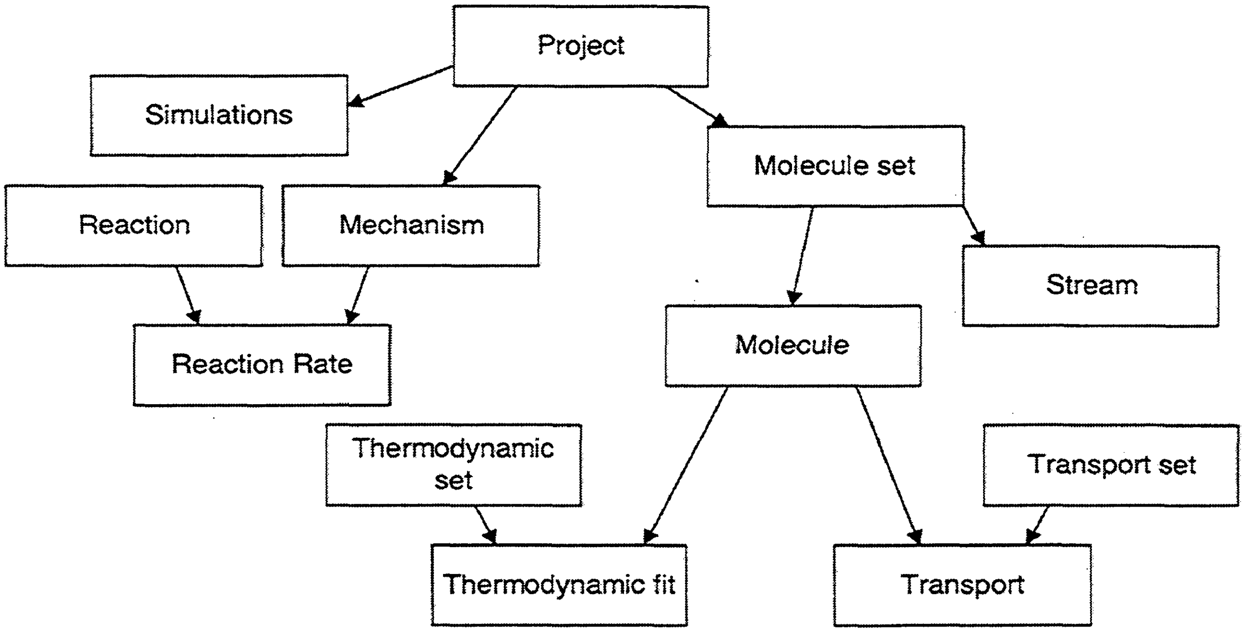


Figure 2.1: Object model. The Object model for the OpenChem Workbench, illustrating the relationships between conceptual entities.

The implementation of each conceptual entity uses the paradigms of abstraction, encapsulation, inheritance, and polymorphism. An object is created first with an entity implemented by creating a base class for abstraction purposes. An entity class inherits the properties of this base class, and implements the methods. Then a façade that is distributed to client applications implements the ideas of encapsulation and polymorphism. This is explained in further detail in section 2.4.

The fundamental entity of the OpenChem Workbench is the molecule.

Molecule

For a molecule, the UML class diagram is in figure 2.2. In UML, the arrow with the triangle head means "is inherited from", and the open backed arrow head means "contains within this object". The complex properties of a molecule extend the MoleculeProperty class because they typically have a reference and comment associated with them. The MoleculeProperty class provides an abstract implementation of retrieval methods for references and comments common to these complex properties.

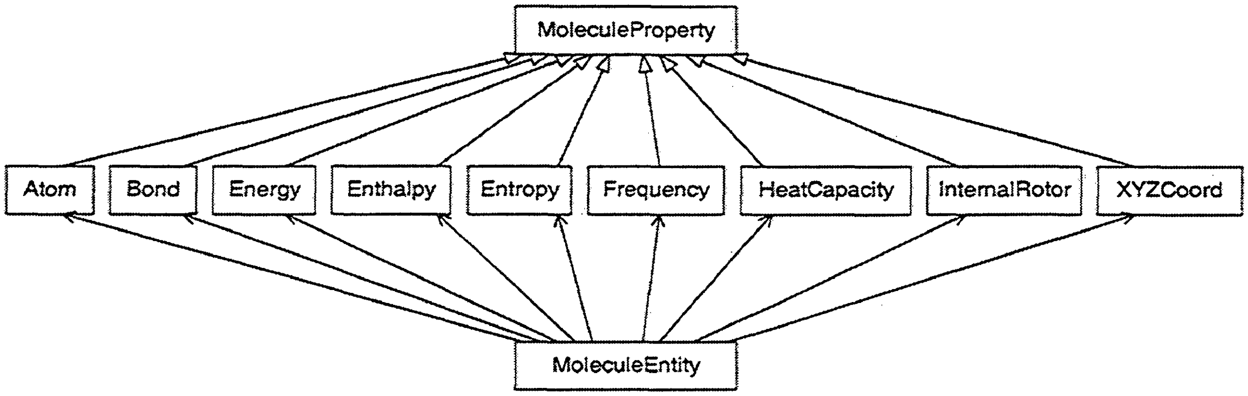


Figure 2.2: Class Diagram for Molecule Entity.

The molecule entity contains multiple instances of the 9 other objects implementing the Molecule property interface. None of these 9 objects alone are unique, so they cannot distinguish one molecule from another. To distinguish them, we define Fundamental Properties elaborated further in section 2.3. There are no default values for any fundamental properties, and the Workbench will allow molecules to be saved with incomplete molecule specification. Although the MoleculeEntity could have simply had several MoleculeProperty objects as properties, it was decided that an explicit declaration of properties contained by the molecule would be useful for maintenance and further development.

Molecule Sets

Molecule sets are simply collections of molecules. The Molecule sets are used to create common input streams, and to define what species to calculate for equilibrium calculations. A Molecule set is used to organize groups of molecules considered important to a user.

Stream

Molecule stream is a subset of a molecule set with a given composition, specified flow rate, pressure, and temperature. These are used as input composition to idealized reactor models.

Transport

Transport data can also be multi-valued, so multiple transport objects can be associated with a single molecule. The transport object contains: accentricity (ω), Lennard-Jones Well Depth (ε/K), Lennard-Jones collision diameter (σ), dipole moment (μ), polarizability (α_0), and rotational relaxation collision number (Zrot). The transport object is used in the calculation of transport properties such as diffusion coefficients and heat transfer coefficients.

Transport Set

A Transport Set is a collection of transport data, with one representative set of data per molecule. A molecule can only be represented once within a single transport set. A transport set is used to define a collection of transport properties used for a set of molecules in an idealized reactor simulation.

Thermodynamic Fit

Another property of a molecule is a thermodynamic fit, called a ThermFit in the OCW source code. Thermodynamic fits are derived from reference enthalpy, entropy and heat capacity as a function of temperature.

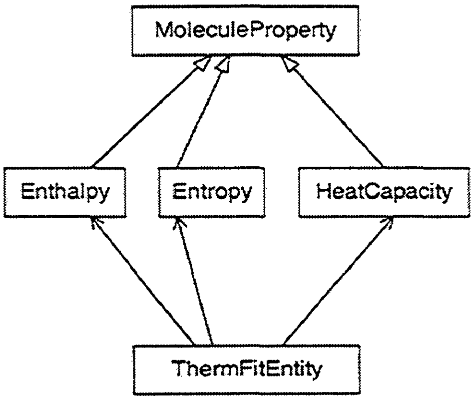


Figure 2.3: Class Diagram for ThermFit Entity

The ThermFit entity can contain zero instances of these three objects, because the fit parameter may not have knowledge of the source data. The ThermFit also contains an instance of several ThermFitParam objects, which contain coefficients for a polynomial fit in temperature. The polynomial format follows the following equations:

$$Cp/R = a_{-2}T^{-2} + a_{-1}T^{-1} + a_0 + a_1T + a_2T^2 + a_3T^3 + a_4T^4$$

$$\Delta_fH/R = -a_{-2}T^{-1} + a_{-1}\ln(T) + a_0T + a_1T^2/2 + a_2T^3 /3 + a_3T^4 /4 + a_4T^5 /5 + H_{ref}$$

$$\Delta_fS/R = -a_{-2}T^{-2} /2 - a_{-1}T^{-1} + a_0\ln(T) + a_1T + a2T^2 /2 + a_3T^3 /3 + a_4T^4 /4 + S_{ref}$$

In the OCW, the thermodynamics can be fit to three subsets of this polynomial. The first is as stated, named the New NASA polynomial format[11]. The second is an older version of the NASA polynomial[12], in which a_{-2} and a_{-1} is zero. The third is the Shomate equation[13], which sets a_{-1} and a_4 are zero.

Thermodynamic Set

A Thermodynamic Set is a collection of thermodynamic fits data, with one representative set of data per molecule. A molecule can only be represented once within a single thermodynamic set. The thermodynamic set defines a set of thermodynamic properties to be used for a given set of molecules in a idealized reactor simulation.

Reaction

Reactions in the OCW are described as reactants, products, and stoichiometric coefficients. The simplicity of a Reaction is partly a consequence of the complexity of the molecule specification. The Reaction is used for determining which rates to compare between mechanisms.

Reaction Rate

Reaction Rate parameters in OCW can take four forms: modified Arrhenius, Lindemann, Troe, or SRI. A single reaction can have multiple Reaction Rates associated with it. The reaction rate is used to represent a reaction in an idealized reactor modeling.

Mechanism

The mechanism consists of a collection of reaction rates, combined with a reference to an existing thermodynamic set. The Thermodynamic Set enables the reverse reaction rate to be calculated using microscopic reversability. The mechanism does not restrict the reaction to be represented by a single rate, allowing duplicate reaction rates to be in the same mechanism. The mechanism is used to determine which collection of rates to use in an idealized reactor simulation.

Project

The project is simply an OpenChem Workbench tool for organizing the user's data. The project contains molecule sets, streams, mechanisms, and chemical kinetic runs run in the OpenChem Workbench environment.

2.3 Object Identity

Determining an object's unique identity is of major importance when we implement a cheminformatics package. This is important because when an object is uniquely described in the database comparisons can be made between similar data, data can be consolidated, and data can be linked. The uniqueness criteria must be stringent enough to discern between two chemically distinct species. The most difficult object to identify uniquely is the molecule, because of the complexity of molecular species.

Discerning between similar molecules has been the subject of much investigation. Attempts to uniquely identify a molecule by naming have resulted in a myriad of misinterpretations, corruptions, and popular extensions[14]. Consequently, any method that translates a molecule name to the corresponding structure must also include the unwritten rules that have developed in popular use of the method.

For example, the IUPAC[15] convention has become a popular method of enumerating chemical structure. As a result of its popularity, mistakes have occurred, and consequently small groups of data do not follow the original specification. If the associated data is valuable, then adoption of the poorly formulated IUPAC name can become popularized.

Another attempt at discerning between molecule structures is achieved through a SMILES[16] string. This method incorporates a few rules in the building of a formula that describes the structure of a molecule. Again this has the same disadvantage as the IUPAC name, of being easily corrupted due to its complexity.

The OpenChem Workbench does not use these structured strings to uniquely identify a molecule. The uniqueness of the molecule is determined from explicit declaration of the atomic elements in a molecule, combined with connectivity information and the fundamental properties charge, spin, radical, and natural abundance. The identification of molecules without bond connectivity information is left up to the resources of the user. The OpenChem Workbench will make a judgement on similarity of thermodynamic quantities, and will default to the closest molecule match within the database.

The only other object that must be matched within the OpenChem Workbench database are reactions. The Reaction identity is determined by the molecules it has as reactants and products.

Once we have determined the identity of the object, a reliable method for exchanging this object is needed.

2.4 Data structures and XML

The importance of exchanging data between users is an incredibly useful feature. If the information is easy to exchange, then the usefulness of the application grows. Data in outdated or unused data formats is almost useless. Consequently, there has been an effort to define a golden data structure that will not need to be modified for data storage. This is very useful because the programmers who read from and write to this data structure will not need to modify their code when the format has changed.

Currently employed standards, such as the NASA polynomial format for thermodynamics, serve the scientific and engineering communities well.

An example of NASA thermodynamic data formatting is:

```
HE              L 5/66HE  1   0   0   0G   300.000  5000.000 1000.000    01
 2.50104422E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-7.45686320E+02 9.08589239E-01 2.50104422E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-7.45686320E+02 9.08589239E-01                   4
AR              L 5/66AR  1   0   0   0G   300.000  5000.000 1000.000    01
 2.50104422E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-7.45686320E+02 4.36103012E+00 2.50104422E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-7.45686320E+02 4.36103012E+00                   4
N2              J 9/65N   2   0   0   0G   300.000  5000.000 1651.000    01
 2.99595345E+00 1.23650803E-03-3.70307884E-07 5.05346607E-11-2.62980289E-15    2
-9.13275934E+02 5.68044098E+00 3.26021756E+00 5.91317648E-04 2.24046943E-07    3
-1.95572836E-10 3.61873219E-14-9.99926012E+02 4.27471787E+00                   4
```

The NASA formatting provides a simple description of the thermodynamic quantities of a molecule, combined with its atomic composition. But there is no information about the connectivity of a molecule to specify its unique identity. More modern computational technologies allow of a richer description of the data.

Data exchange is typically done with XML[17] (extensible markup language) format. XML provides more flexible and adaptable information identification. XML is a 'metalanguage', a language for describing other languages, which lets you design your own customized markup languages for different types of documents.

The data description for molecules and reactions were created, and included the contributions of many of the industrial partners. This was done so that the information contained in the document would meet any needs they could foresee. This data interchange format information is described on the ReactionXML[18] website.

2.5 Distributed Architecture

Distributed architecture is important for the isolation of duties performed by code. The 3-tier distributed architecture is useful because it separates out the code written to save an object, the code written to store data on the server side, and the code written to display data on a user's machine. So the other two tiers are insulated by changes to code on the third tier. If we decided to switch our storage and retrieval of data from a database to a file based storage, then the job would be easier because all of the storage code is isolated on the server side. The design of the distributed architecture was taken from Reese[19]. The method of implementing distributed object persistence is outlined in figure 2.4.

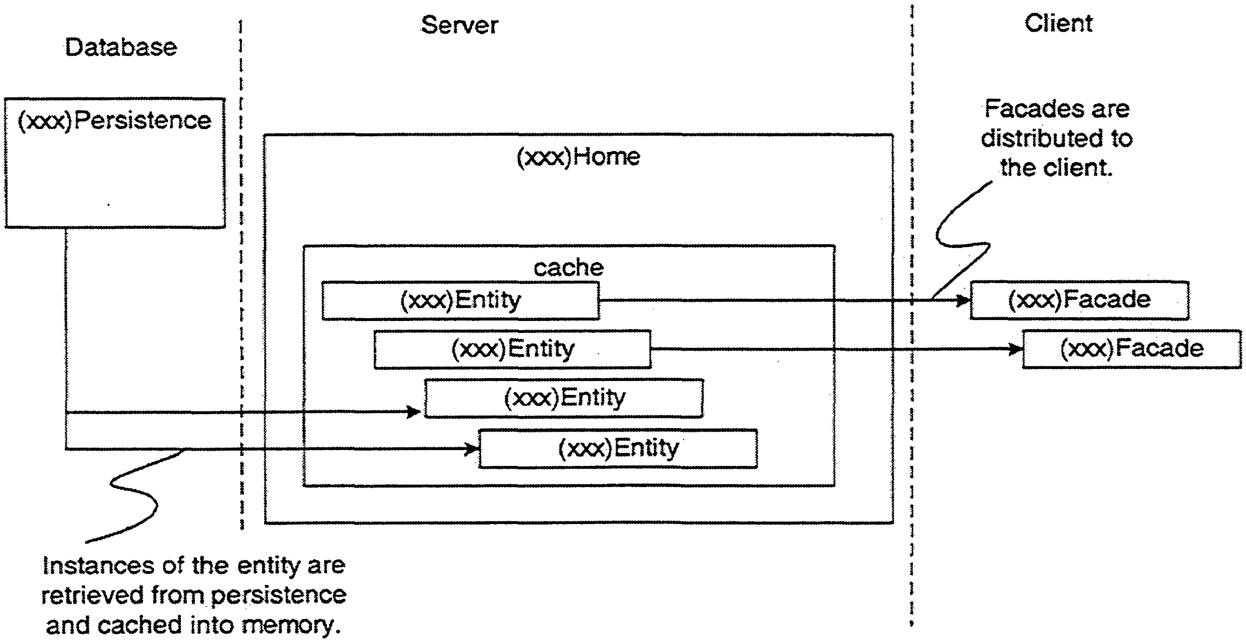


Figure 2.4: The Format of Retrieving Objects from the Database. The (xxx) is generic, it can stand for molecules, reactions, mechanisms, etc.

Every entity outlined in section 2.2 has been designed to separate the implement the transfer of data to and from temporary memory to permanent memory. This is achieved through the memento design pattern[19]. The memento design pattern captures an object's state without the implementation. Design patterns are useful concepts for the implementation of code.

The factory pattern[19] is implemented on the server side, but is called a Home, which provides method for retrieving an entity. Factory patterns are the objects that create instances of other objects. The Home retrieves an instance of the entity from the database, and caches it into memory. Subsequent requests for the object return the cached copy in memory.

The Facade captures the state of the entity object cached in the Home's memory, and allows the same data to be displayed on multiple clients. This is the data stored on the client side in temporary memory.

This distributed architecture allows the entity persistence to be separated from the modules that display the data manipulation tools.

2.6 Data display modularization

Modularity of code is important, because we want the ability to customize an application to the needs of interested partners. If we want an application to implement the thermodynamic modules of workbench only, then that is possible because all of the thermodynamic modules have a degree of independence. This does not mean the duplication of code. Common utilities utilized by code are kept in the core OpenChem Workbench distribution.

Application modularity is achieved by having all modules of the Workbench extend the OCWModule class. Examples of modules are given in Chapter 3. A module in this context is a isolated set of code that can be added to the workbench to extend the functionality of data modification or application interaction. The available modules are stored in the client configuration file, and made available through the client menu and client toolbar. Once a module is activated, the module is appended to the current tasks, and the client frame prompts the module for the desired display.

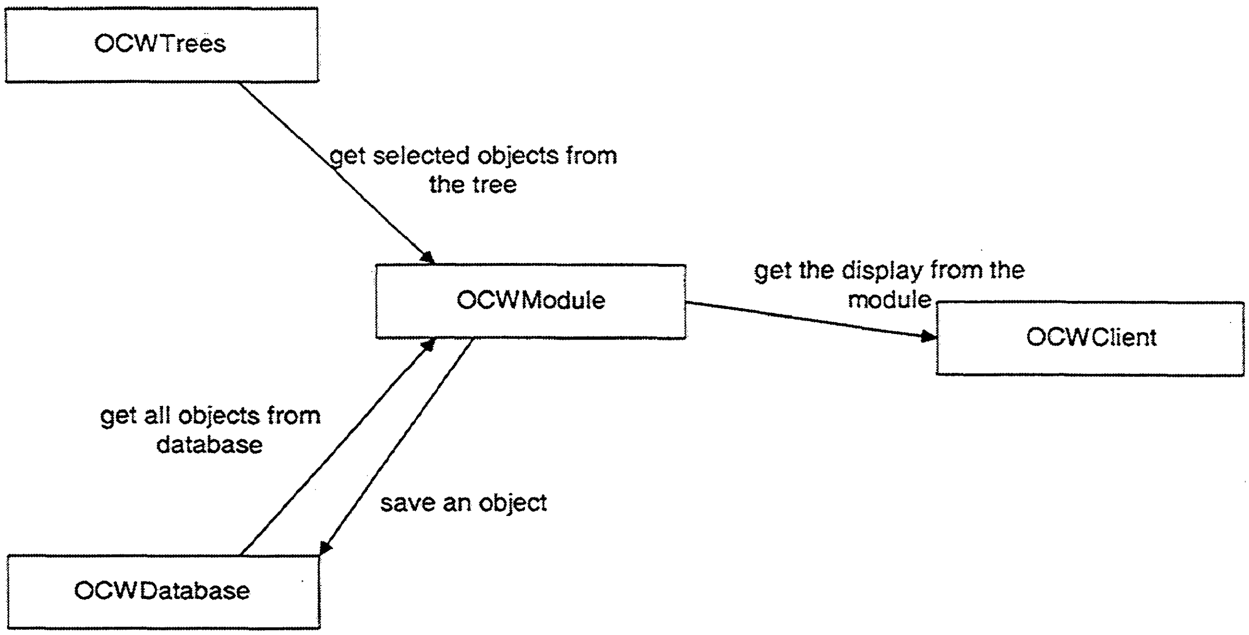


Figure 2.5: Summary of Classes Interacting with a Module.

A module will retrieve data from the database from the OCWDatabase class, but will retrieve user-selected data through the trees.

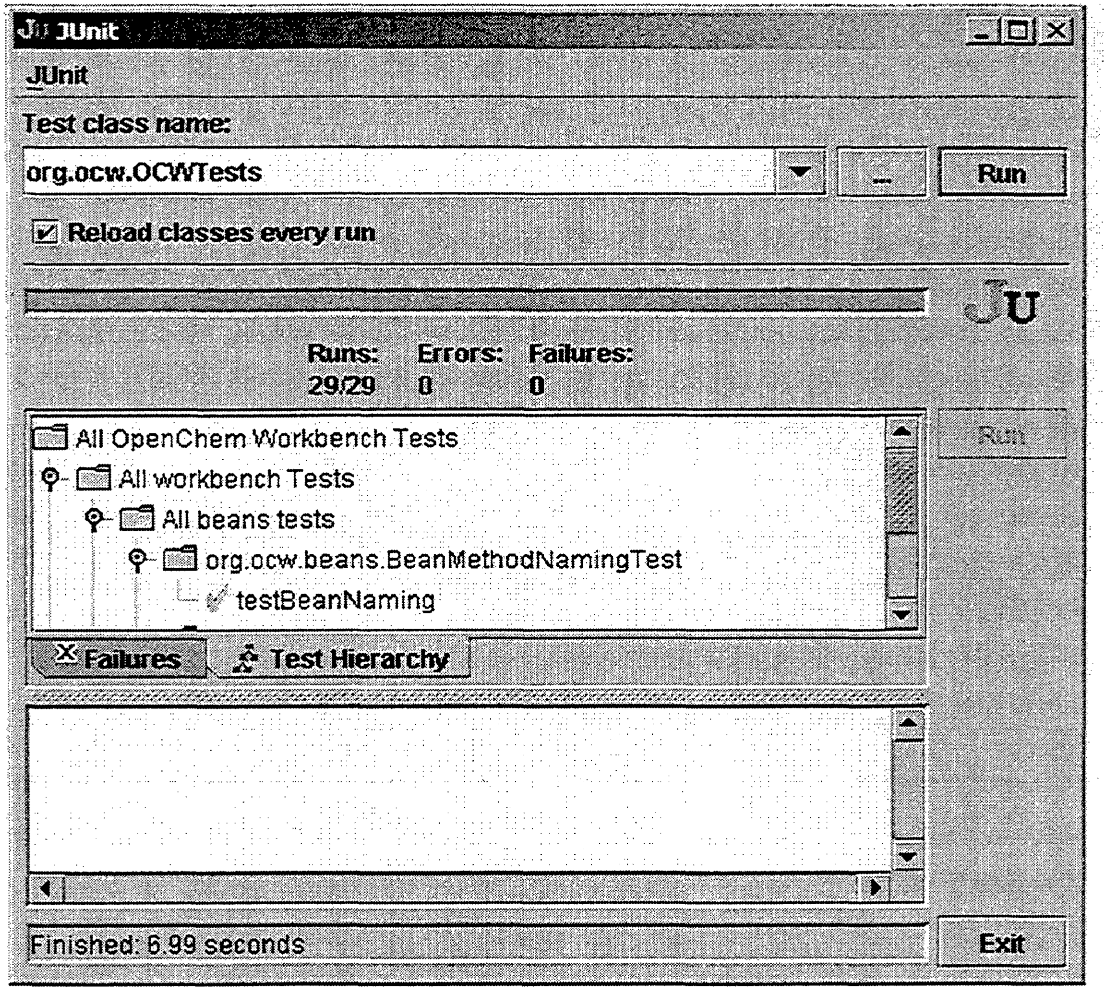
The data is displayed as trees because users are comfortable with organizing data in trees, and the drag & drop paradigm provides a simple interface for data organization tasks.

Any module has access to the static trees displayed in the client through the OCWTrees class, and has access to the objects available to the database from the OCWDatabase class. OCWTrees have static methods to retrieve any selected object in any of its currently displayed trees. OCWDatabase has methods for retrieving any group of objects from the database, often with methods for restricting searches, such as restricting a molecule search to molecules that is represented within a thermodynamic set. OCWDatabase also has methods for saving objects to the database. Consequently any module has ability to modify any data, and has a standardized data object access through the tree.

2.7 Testing

The quality of programming code is greatly enhanced by the existence of testing. There exist several testing techniques used in the measurement of the ability of code. One such technique is a publicly available testing utility named JUnit, a unit testing code that specifies a format for the structure of the unit tests.

When a programmer changes one piece of code, the programmer needs to know if that change has corrupted the existing structure in ways unforeseen. JUnit will run every possible test in the testing suite.



Test class name: org.ocw.OCWTests

☑ Reload classes every run

Runs:	Errors:	Failures:
29/29	0	0

All OpenChem Workbench Tests
  All workbench Tests
    All beans tests
      org.ocw.beans.BeanMethodNamingTest
        ✓ testBeanNaming

Finished: 6.99 seconds

Figure 2.6: JUnit testing suite. The JUnit

For integrated testing, there are several people dedicated to testing the OpenChem Workbench, trying to use the workbench for real world application. When errors occur, the integration testers fill out a report describing the error, and submit it to a web-based bug tracker. Information about bugs and feature requests can be found at the same website: http://gems.mines.edu/cgi-bin/ccrewb?user=guest;addsignature=1.

CHAPTER 3
MODULE SUMMARY

The modules implemented within the workbench are functional collections of code that perform a specific set of use case tasks. A use case defines the set of actions performed by a user, and the corresponding responses made by the application, including any foreseeable errors that may result from the action.

Many of the modules that have been implemented for the workbench are simple persistent object manipulation modules. These modules implement methods for modifying properties of the data objects outlined in the previous chapter.

The following modules were left to myself for initial design and implementation. After an initial design following established design rules[3,4,5,6], many other feature requests resulted and were implemented.

3.1 Molecule Builder

To specify a molecule's structure the molecule builder is often the simplest solution. A large portion of the molecule builder was designed by myself, but since this was a collaborative effort, I cannot take credit for the entire module. Other method of specifying the structure would be to find it on the NIST Webbook, find a MDL mol file of the species, import a Gaussian output file, or to find the molecule in the XML format described in section 2.4. The Molecule Builder user interface has simple methods for specifying atoms, bonds, and the following molecule properties: formula, specifier, alternate names, IUPAC name, CAS registry number, molecular weight, linear, charge, cis/trans, electronic state, spin multiplicity, radical, chirality, transition state, symmetry, natural abundance, and number of rotors.

Building a molecule from atomic constituents involves deciding which three dimensional shapes would best represent the shape of atoms in a molecule. The wire frame shapes were chosen to represent sp^3, sp^2, and sp hybridization, single, double, triple bonds, and a five-fold and six fold symmetric bond center. The available atom shapes are combined with each other so that the dihedral between bonding sites are correct. For example, ethane and propadiene would both have their hydrogen atoms in a staggered[20] formation.

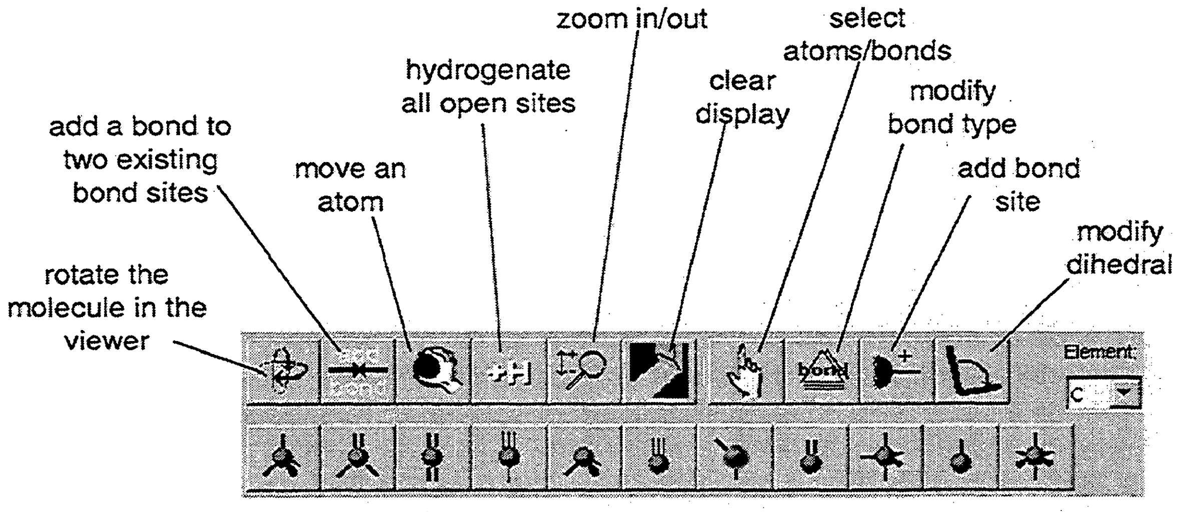


Figure 3.1: **Available Tools for the Molecule Builder.** The available tools for the molecule builder explained.

Figure 3.4 shows the available tools for creating and manipulating a three dimensional structure of atoms in a molecule.

The three dimensional shapes were chosen to be composed of triangles, which would be used to create the orientation of subsequent connecting atoms. The three dimensional shapes are created in the classes extending the TriangleBlock class. The class structure is given in figure 3.6.

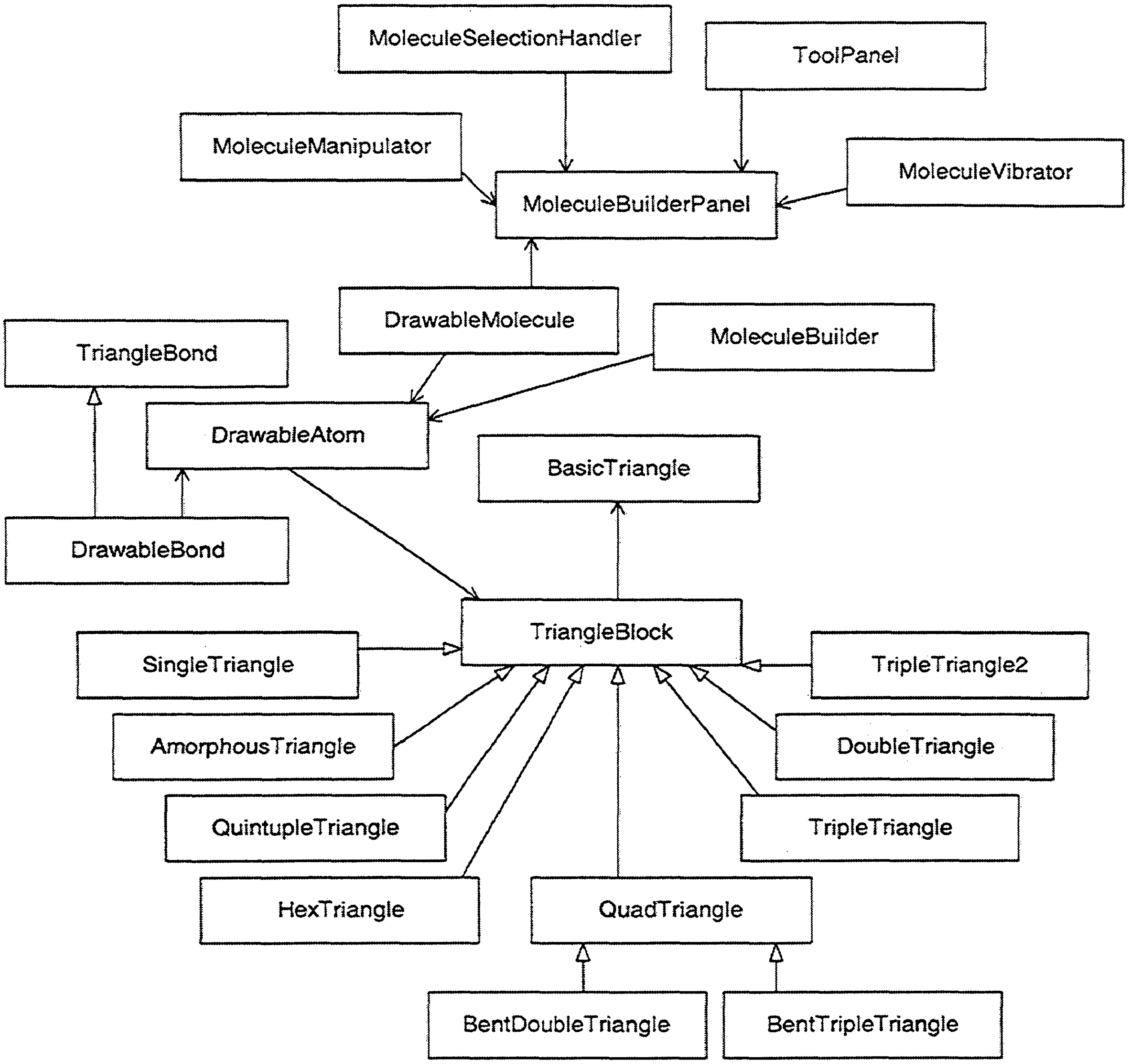


Figure 3.2: Class Structure Molecule Builder. The class structure of the classes in the molecule builder module.

Figure 3.2 shows a UML diagram of the classes used to create the wire frame for a molecule and draw and manipulate the wire frame as a classic picture of a molecule.

3.1.1 Dihedral bonding

The Builder automatically sets dihedral angles according to the shape of the bond sites chosen to represent a molecule.

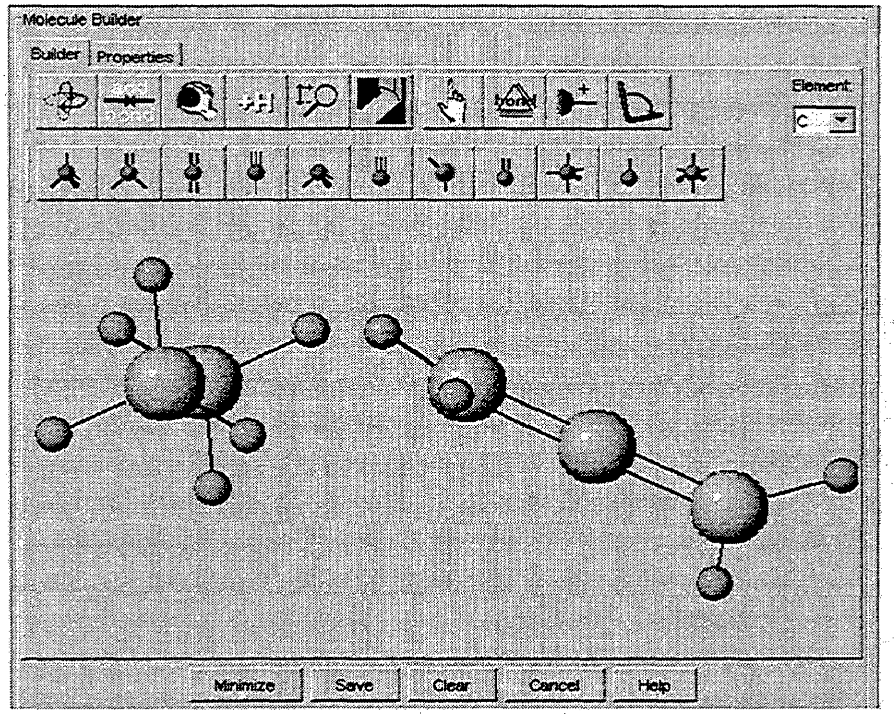


Figure 3.3: **Molecule Builder**. The molecule structure is edited here.

The correct dihedral is achieved by using reference points to align additional atomic hybridization shapes. Since the dihedral angle requires a reference point, and the bond requires a two-point vector, the basic unit of a bonding site consists of three points. This triangular unit was based on the right triangle connecting one vertex to the opposite plane on a tetrahedron.

3.1.2 Available bond hybridization

The types of objects available for building atoms are given in figure 3.8. This figure displays the wire frame structure of atomic objects as a series of triangles.

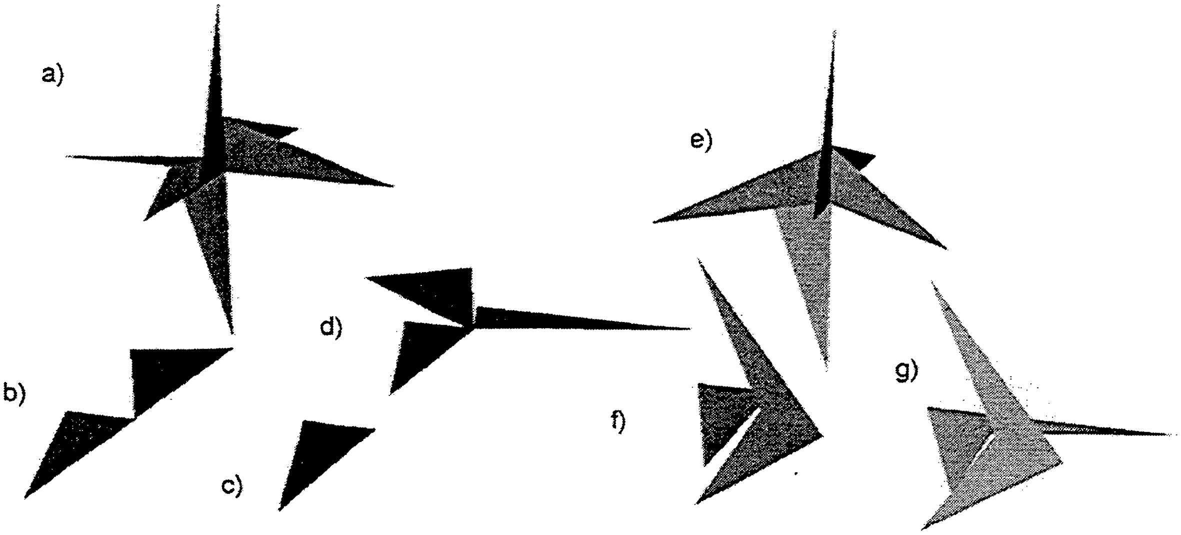


Figure 3.4: Atomic Shapes. Possible 3 dimensional shape skeletons for atoms, a) the six-fold bonding center b) the sp hybridization atom c) a single bonding site which contains the unit triangle d) the sp2 hybridization atom e) the five fold bonding center f)sp3 with one filled orbital g) the sp3 hybridization atom

3.1.3 Clean up command

If the molecule builder in unable to create a molecular structure, the clean up functionality can often provide a quick way to approximate a molecules preferred structure. The Clean up command will minimize the following function:

$$f = \sum_{i=1}^{n}\sum_{j=i}^{n}(d_{ij} - R_{ij})^2 + \sum_{i=1}^{m}(a_i - A_i)^2 + \sum_{i=1}^{p}\begin{vmatrix} x_i & y_i & z_i & 1 \\ x_{i+1} & y_{i+1} & z_{i+1} & 1 \\ x_{i+2} & y_{i+2} & z_{i+2} & 1 \\ x_{i+3} & y_{i+3} & z_{i+3} & 1 \end{vmatrix}^2 \qquad 3.1$$

Where n is the total number of atoms, d_{ij} is the distance between atoms i and j, R_{ij} is the preferred distance between the atoms i and j, m is the total number of angles formed by three atoms connected by a bond, a_i is the direction cosine between the three atoms, A_i is the preferred direction cosine between the atoms, p is the number of planar atoms in a molecule, and x_i y_i z_i are the positions of the planar atoms within a molecule. The minimum of this function will give an approximation to the preferred structure of this molecule.

The minimization algorithm, SOLVOPT version 1.2 (June, 1997), was written by Alexei Kuntsevich and Franz Kappel at the University of Graz, Austria. The function SOLVOPT performs a modified version of Shor's r-algorithm in order to find a local minimum respective maximum of a nonlinear function defined on the n-dimensional Euclidean space or a solution of a nonlinear constrained problem:

min { f(x): g(x) (<)= 0, g(x) in R(m), x in R(n) }

3.1.4 Shortcut keys

The following shortcut keys have been implemented in the molecule builder for the advanced user. Shortcut keys[3] allow someone familiar with an interface to move quickly between functional tools.

S- activate bond/atom selection mode.
B- modify the order of a selected bond.
I- display the atom indices.
R- activate default spin mode. (or space)
C- clear the atoms in this molecule.
Z- activate the zoom mode.
D- activate the dihedral modification mode.
H- hydrogenate the molecule.
A- activate the add bond mode.
N- create a bond site for the selected atom.

3.2 Gaussian Post Processor

The information available from calculations made in the Gaussian software package is diverse and can be highly accurate. For that reason, the inclusion of a Gaussian post processor in the OpenChem Workbench was an important task.

Designed to model molecular systems, Gaussian performs its computations starting from the basic laws of quantum mechanics. Gaussian is useful for studying molecules and reactions of interest, including both stable species and compounds which are difficult or impossible to observe experimentally, such as transition states.

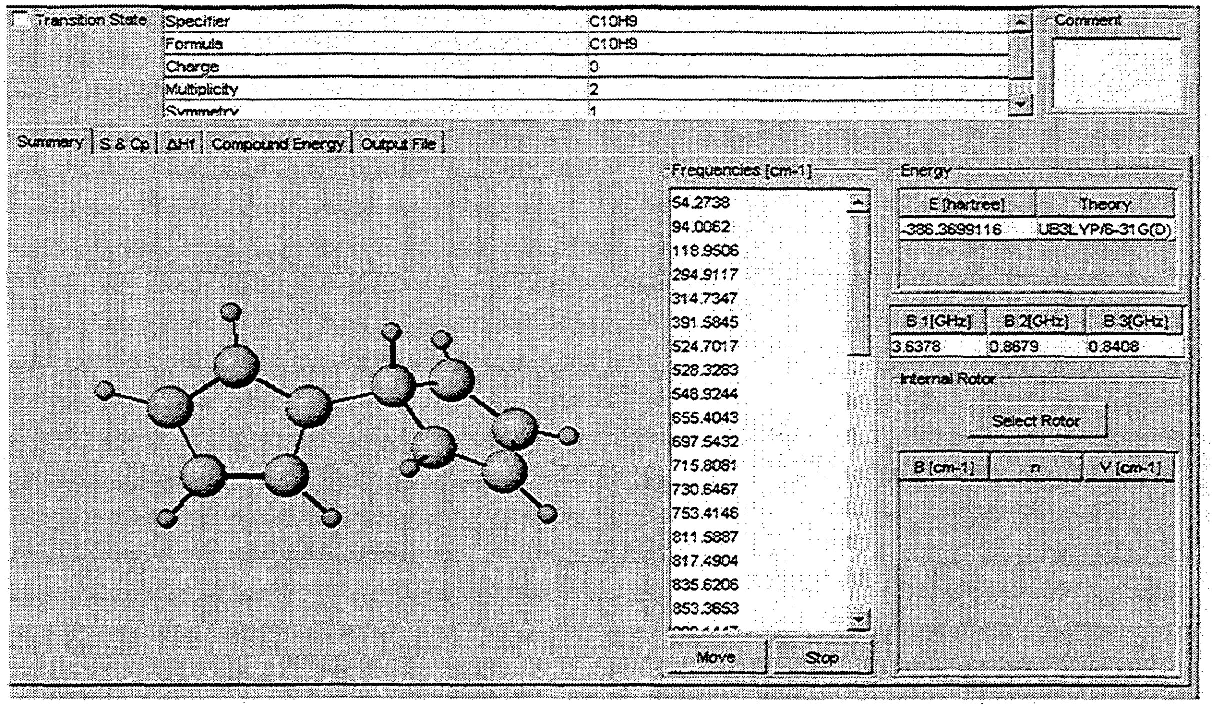
Gaussian can predict energies, molecular structures, and vibrational frequencies of stable species and transition states, used in the prediction of reaction rate.

3.2.1 Data saved

The OpenChem Workbench provides a Gaussian post-processor that parses information from a Gaussian output file, and uses the molecular data to estimate enthalpy, entropy and heat capacity as a function of temperature. This is useful for the creation of thermodynamic fits for molecules used to compare to existing data, and to provide an estimate when other data is unavailable.

The connectivity of a molecule is estimated by proximity, and there is no bond order estimation method, because bond order is ambiguous at the quantum mechanical level and is an occasionally misleading paradigm.

The vibration modes calculated from Gaussian are displayed next to the 3D molecule display panel. Selection of each mode from the list will enable the animation of that mode in the display. This is useful for identifying transition states, and for identifying modes internal rotation modes that are reported as vibrations.



Specifier	C10H9
Formula	C10H9
Charge	0
Multiplicity	2
Symmetry	1

54.2738
94.0062
118.9506
294.9117
314.7347
391.5845
524.7017
528.3283
548.9244
655.4043
697.5432
715.8081
730.6467
753.4146
811.5887
817.4904
835.6206
853.3653

E [hartree]	Theory
-386.3699116	UB3LYP/6-31G(D)

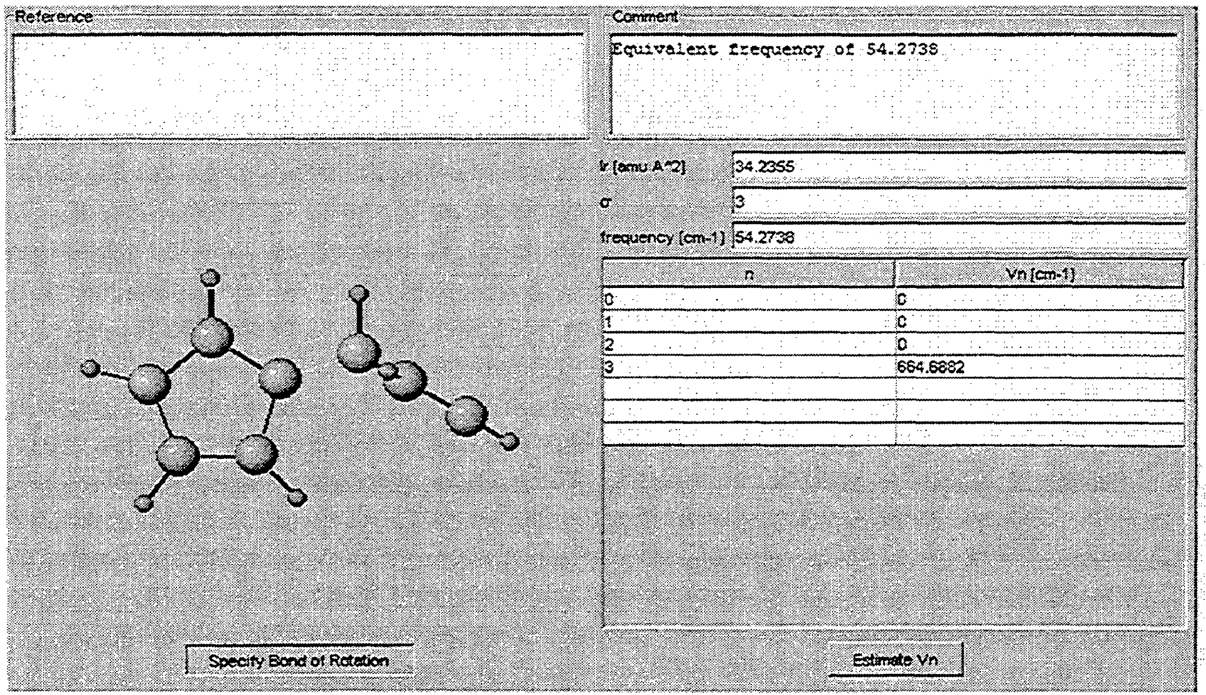
B 1[GHz]	B 2[GHz]	B 3[GHz]
3.6378	0.8679	0.8408

Figure 3.5: Gaussian Summary. Summary of a Gaussian output file.

Estimating the entropy and heat capacity is done using the equations outlined in the Appendix A.1. Enthalpy is estimated in the third tab by using atomization energies[21].

3.2.2 Internal rotor

Internal rotors are important because they are typically active at low temperatures, and because at higher temperatures, the heat capacity of an internal rotor is ½ R, while a harmonic oscillator contributes R to the heat capacity, so there is a guaranteed discrepancy of ½ R to the heat capacity at high temperature. Internal Rotor identification is done by first identifying which mode has been falsely identified as a vibration, and selecting the select rotor button. The next panel will prompt the user to identify parameters such as moment of inertia, and the cosine decomposition of barrier height. This cosine decomposition is done for the modeling of complex barriers to rotation as shown in Appendix A.1.3.1.



Equivalent frequency of 54.2738

Ir [amu A^2] 34.2355

σ 3

frequency [cm-1] 54.2738

n	Vn [cm-1]
0	0
1	0
2	0
3	664.6882

Figure 3.6: Internal Rotation Specification Panel

To estimate the moment of inertia, selecting the Specify Bond of Rotation button, and clicking on the bond, will automatically estimate the moment of inertia around the center of mass axis connecting the two groups.

The potential energy surface of the rotation is modeled with the equation

$$\text{P.E.} = V_0 + \sum_n \frac{V_n}{2}(1 - \cos(n\theta)) \qquad 3.2$$

To estimate the potential surface using a single cosine term from equation 3.2, the program takes the moment of inertia and symmetry of the potential, and calculates the barrier height using the approximation in equation 3.3

$$V_n = \frac{8\pi^2 I_r v^2}{n^2} \qquad 3.3$$

When saved, the Gaussian post processor saves the connectivity, coordinates, energy and theory, calculated entropy, enthalpy, and heat capacity. The contents of the output file are not saved in the database.

3.3 Rate Constant Estimation

Often reaction rate data is difficult to obtain, so the inclusion of an OpenChem Workbench module that would calculate approximate rate constants based on different reaction kinetics theories. Although I designed the user interface for this module, and enabled the multi-well code, the code implementing the reaction rate theory was taken from Hai Wang's RRKM code[22].

The module that performs an estimation of rate constants is designed to be extensible. The currently available rate constant estimation methods include transition state theory, QRRK using strong or weak collisions, and RRKM using strong or weak collisions. These theories are all outlined in Appendix A.2. The abbreviated UML class diagram of the reaction rate estimation module is shown in figure 3.7.

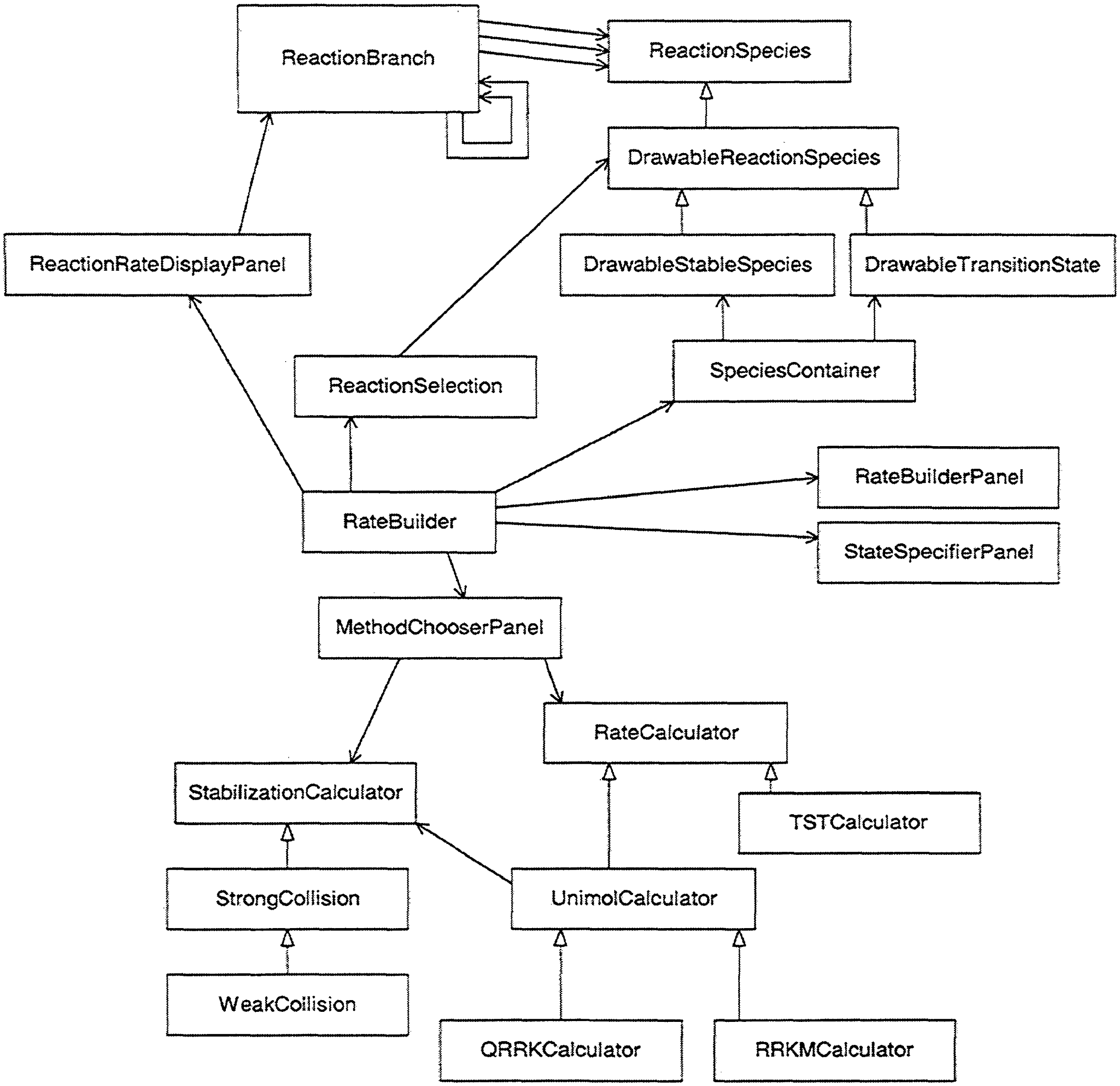


Figure 3.7: **Class Diagram for Reaction Rate Estimation.** The class diagram for the reaction rate estimation module.

The classes important for implementing other reaction rate estimation theories are the RateCalculator, StabilizationCalculator, and the ReactionBranch classes.

To extend a RateCalculator class, implement the setRates(ReactionBranch[]) method. In this method, the rate constant data is set into each branch. The

ReactionBranch class is unique in the figure 3.7 because it has references to all children reaction branches, and the parent reaction branch. The ReactionBranch class has methods for setting forward, reverse, and stabilization rates for intermediate storage of reaction data.

The interface into the reaction module comes in three basic steps: reaction species specification, reaction method specification, and result display. This interface is applied in section 4.3.

The first set of input is the molecules and transition states in the reaction. Reaction species specification involves the setting of vibrational, energy, and internal rotor data for stable species and transition states describing a reaction. The interface displays transition states as ovals, and stable species as squares. To specify the reaction path, the reactant and product species must be connected to the transition state via red lines, activated by clicking on the red arrow on the edge of a transition state object.

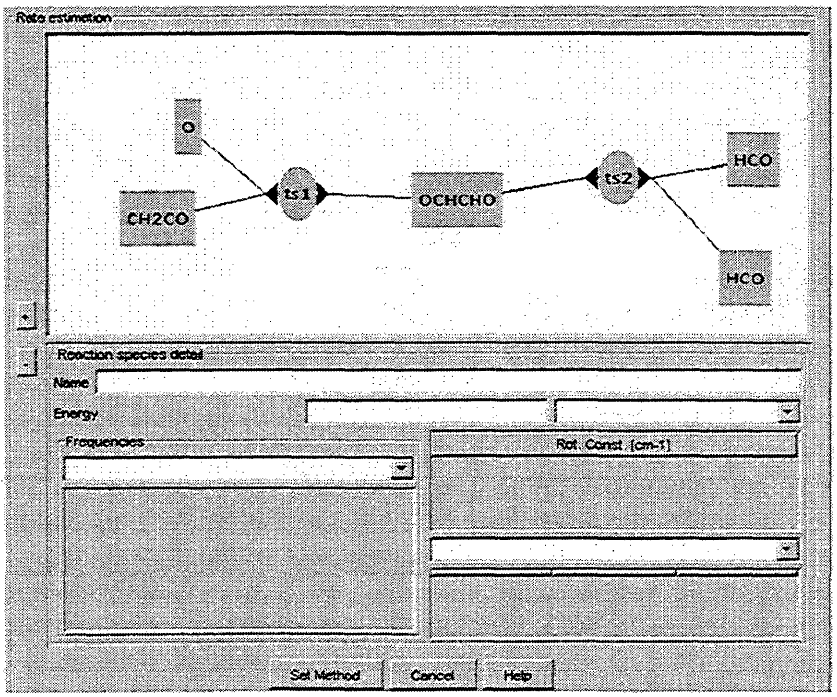
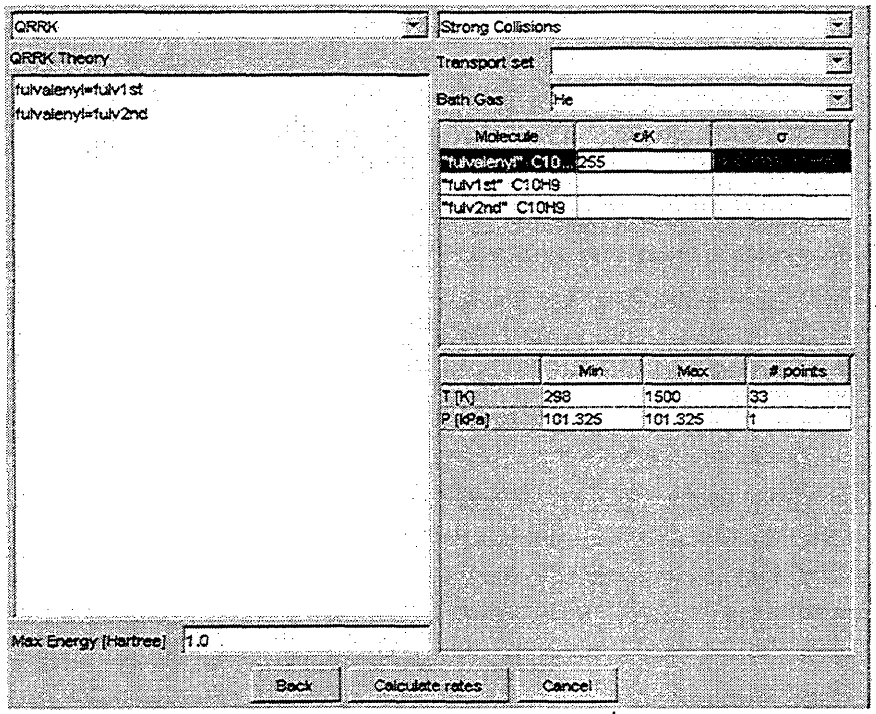


Figure 3.8: Species in a Reaction. The panel for the specification of the species in a reaction.

The second set of input is which rate theory is used, and if necessary, approximate transport properties of unimolecular species in the reaction.

The method of calculation is chosen from the available methods by combo box, and the module displays its own input panel that will prompt for required fields. Any unimolecular method will also require a specification of the method of stabilization rate for all unimolecular intermediates.



QRRK

QRRK Theory

fulvalenyl=fulv1st
fulvalenyl=fulv2nd

Max Energy [Hartree]: 1.0

Strong Collisions

Transport set:

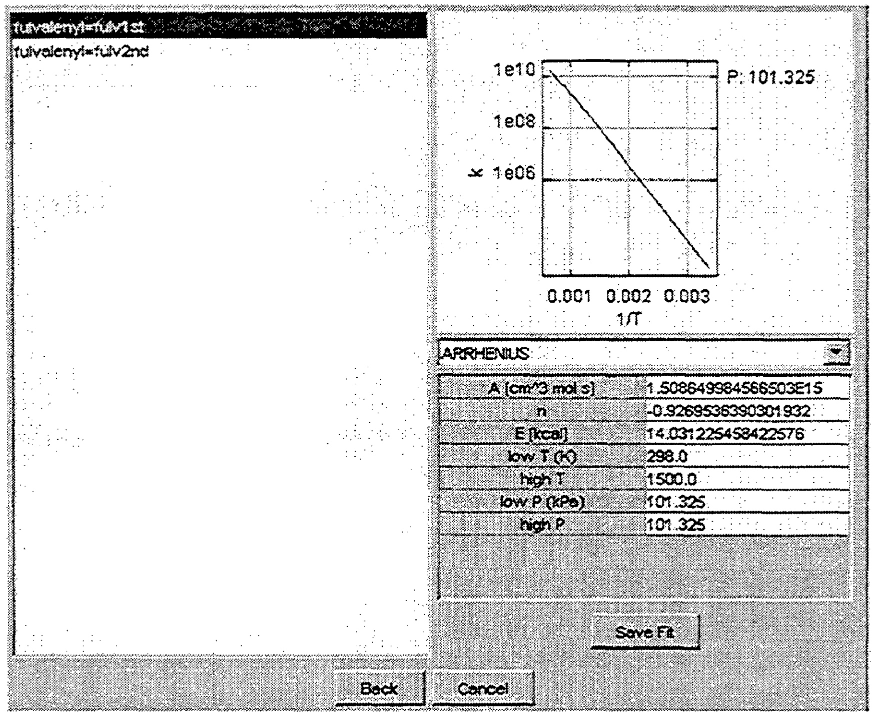
Bath Gas: He

Molecule	ε/K	σ
"fulvalenyl" C10...	255	
"fulv1st" C10H9		
"fulv2nd" C10H9		

	Min	Max	# points
T [K]	298	1500	33
P [kPa]	101.325	101.325	1

Figure 3.9: **Calculating Reaction Rates.** The specification of method for calculating reaction rates. Currently implemented are Transistion state theory, Quantum Rice-Ramsperger-Kassel, and Rice-Ramsperger-Kassel-Marcus theory combined with strong and weak collision.

After the method has been calculated, then the rate constants can be displayed. The rate constants are selected from the available reactions in the list, and their results are displayed. The reaction rate can then be fit with a modified Arrhenius expression, and saved in the database.



fulvalenyl=fulv1st
fulvalenyl=fulv2nd

ARRHENIUS

A [cm^3 mol s]	1.508649984566503E15
n	-0.9269536390301932
E [kcal]	14.031225458422576
low T (K)	298.0
high T	1500.0
low P (kPa)	101.325
high P	101.325

Figure 3.10: Displaying and Saving a Reaction Rate. Panel for displaying and saving a calculated reaction rate.

The reaction rate data calculated here can then be inserted into a mechanism, provided that thermodynamic fits exist for the reacting species, inside the thermodynamic set associated with the mechanism.

3.3.1 Transition State Theory

One method option for rate estimation is through Transition State Theory. The method is explained in the A.2.1. Transition State theory is used for bimolecular reactions such as hydrogen abstraction reactions, but can also be used for estimates of the high pressure rate constant in unimolecular reactions.

3.3.2 Unimolecular reactions

Unimolecular reaction rate constant methods are restricted to the existence of a unimolecular species either as an intermediate or as the initial species. Currently workbench offers RRKM and QRRK estimation techniques, combined with strong collision and modified strong collision for the estimation of unimolecular stabilization, as explained in A.2.

Both QRRK and RRKM make the pseudo steady state approximation on the concentration of the excited unimolecular intermediates. Consequently, there is a consistent pattern to the form of the equation describing the reaction rate formation of product.

3.3.2.1 Equation implementation

For example, for a chemically activated reaction.

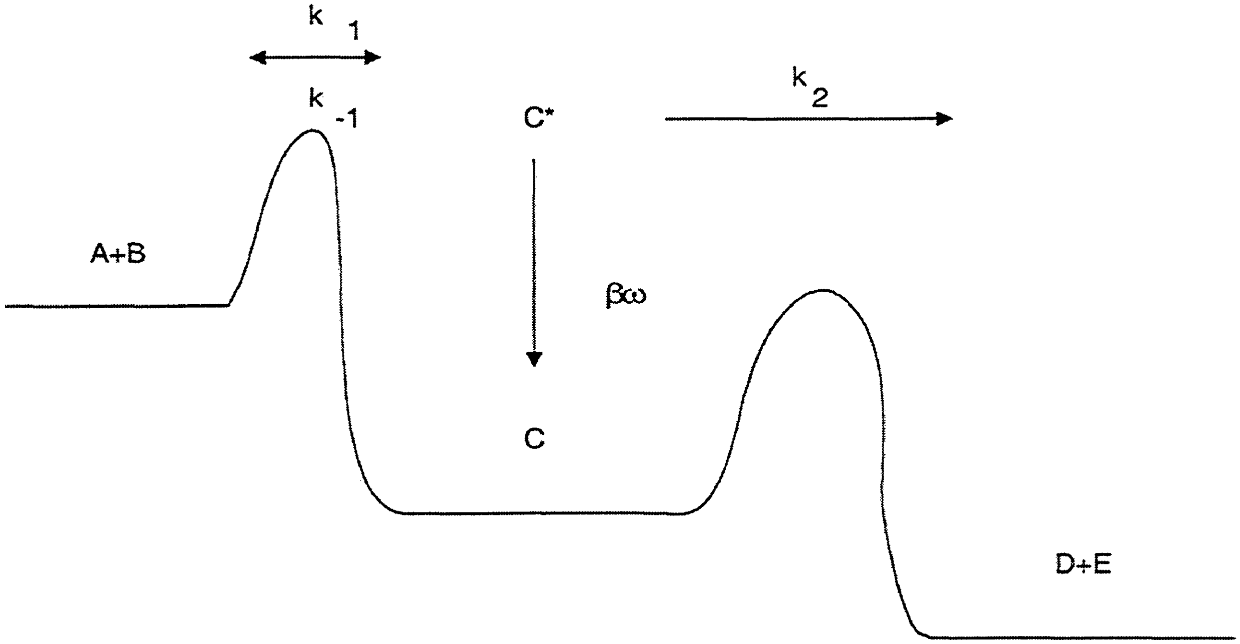


Figure 3.11: Chemical Activation. Potential surface of a chemically activated reaction.

(addition)	A+B <=> C*	$K_{eq}=k_{-1}/k_1$
(stabilization)	C*=>C	βω

(decomposition) $C^* \Rightarrow D+E$ k_2

k_1 is the microcanonical rate constant (i.e. k(E)) of C* going to A+B, and k_{-1} is the rate constant for A+B forming C*. The value of $\beta\omega$ is the collisional stabilization of the unimolecular intermediate.

The population of the excited unimolecular intermediate C can be written:

$$\frac{\partial[C^*]}{\partial t} = -\beta\omega[C^*] - k_1[C^*] - k_2[C^*] + k_{-1}[A][B] \qquad 3.4$$

After assuming steady state on the excited species, an expression for the concentration of excited species can be found:

$$[C^*] = \frac{k_{-1}[A][B]}{\beta\omega + k_1 + k_2} \qquad 3.5$$

The microcanonical rate constant for the formation of C can be written as:

$$k_C = \frac{1}{[A][B]}\frac{\partial[A]}{\partial t} = \frac{\beta\omega[C^*]}{[A][B]} \qquad 3.6$$

Integrating this expression over energy accounting for the statistical weights, gives the overall rate constant for this channel, and then substituting equation 3.5 produces:

$$k_C = \int_{E_0}^{\infty} \frac{\beta\omega K_{eq} k_1 P(E) dE}{\beta\omega + k_1 + k_2} \qquad 3.7$$

The second channel is from the reactants A+B to the decomposition products D+E. The form of the rate constant is found from the equation

$$k_{D+E} = \int_{E_0}^{\infty} \frac{k_2 K_{eq} k_1 P(E) dE}{\beta\omega + k_1 + k_2} \qquad 3.8$$

Formation of this equation is done by using a tree structure, determining the complexity of the equation depending on the depth of the reaction tree. The equation is done by recursion down the reactant tree, following the child reaction branch objects.

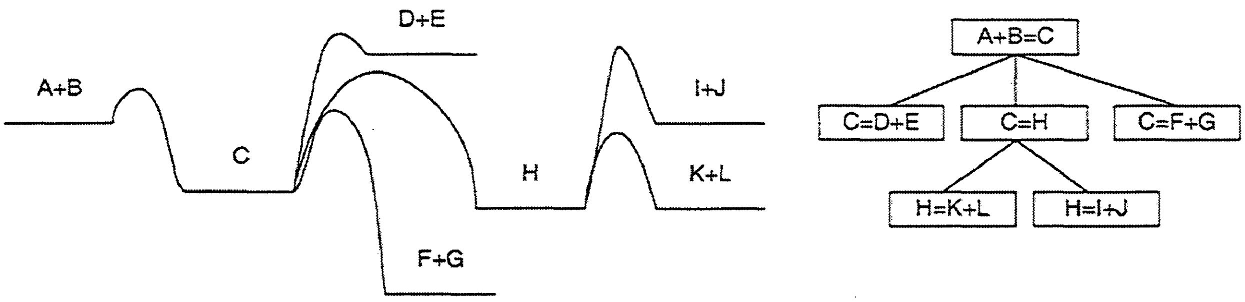


Figure 3.12: Reaction Tree Illustration of the tree structure of a reaction scheme.

The reaction rate estimation module is an important tool in the evaluation of existing reaction rates, and the population of incomplete mechanisms.

3.3.3 Transport parameter estimation

In pressure dependent reactions, the collisional stabilization of excited species is approximated by assuming the molecules are spherical, and then by estimating the number of collisions from their Lennard-Jones binary interaction parameters. σ and ε. The following is one way to estimate these elusive parameters for a molecule.

The L-J radius (σ) is estimated from a linear relationship linking the s to the largest radius of an atom to the center of mass of the molecule.

This relationship was determined from a collection of small species, and the correlation is shown in figure 3.13.

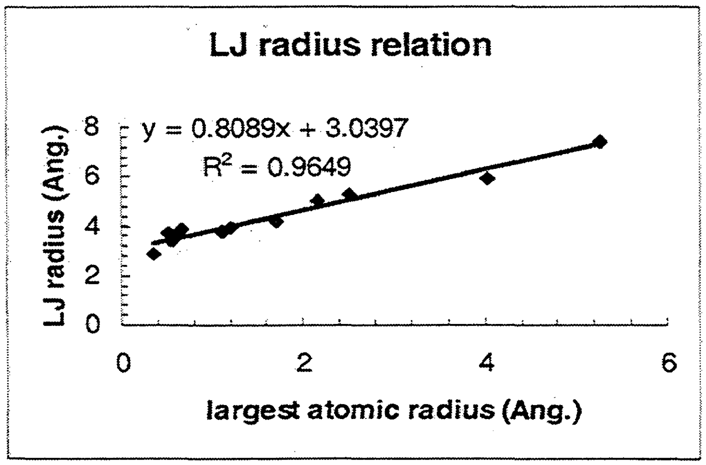


Figure 3.13: Lennard-Jones Correlation. Approximate relationship between largest atomic radius and Lennard Jones radius.

An estimate the well depth (ε), was taken from a relationship relating radius, polarizability, number of effective electrons, and the well depth[23].

The radius is approximately related to the polarizability from the following relation:

$$R_m = 1.767\frac{\alpha_A^{1/3}+\alpha_B^{1/3}}{(\alpha_A\alpha_B)^{\gamma}} \qquad 3.9$$

Where species B is the specified bath gas, and gamma is 0.095. The well depth is then related to an effective long-range interaction term by the following proportionality.

$$\varepsilon \propto C_{6_{eff}} \cdot R_m^{-6} \qquad 3.10$$

Where the long-range interaction term (C_{6eff}) is related to the polarizability and number of effective electrons (N_A, N_B) by the following equation:

$$C_{6_{eff}} = K\frac{\alpha_A\alpha_B}{\sqrt{\alpha_A/N_A}+\sqrt{\alpha_B/N_B}} \qquad 3.11$$

If the long-range interaction term is in meV, the value of K is 15.7E3.

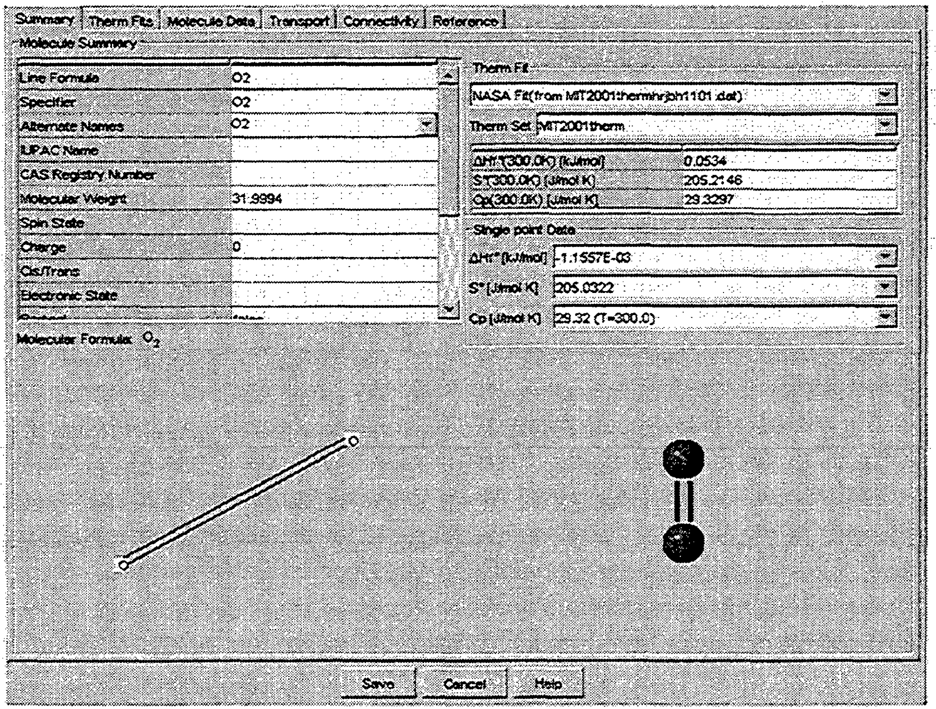
The proportionality constant given by Cambi between the well depth and the long-range interaction term is 0.76. The workbench uses this parameter in the estimation of well depth.

This way of estimating transport properties is reasonable because Lennard-Jones parameters are not unique. For example, the same molecule could use two different parameters for diameter and well depth, and the results would be the same.

3.4 Other modules

Many other modules were implemented in the OpenChem Workbench, performing data organizational and manipulative tasks. What follows are brief descriptions of some of these modules.

The molecule viewer allows manipulation of the data associated with a molecule. The data associated with a molecule was discussed in section 2.3. All data associated with a molecule can be edited in this panel.



Line Formula	O2
Specifier	O2
Alternate Names	O2
IUPAC Name	
CAS Registry Number	
Molecular Weight	31.9994
Spin State	
Charge	0
Cis/Trans	
Electronic State	

Molecular Formula: O_2

NASA Fit(from MIT2001thermhr\pbh1101.dat)

Therm Set: MIT2001therm

ΔHf°(300.0K) [kJ/mol]	0.0534
S°(300.0K) [J/mol K]	205.2146
Cp(300.0K) [J/mol K]	29.3297

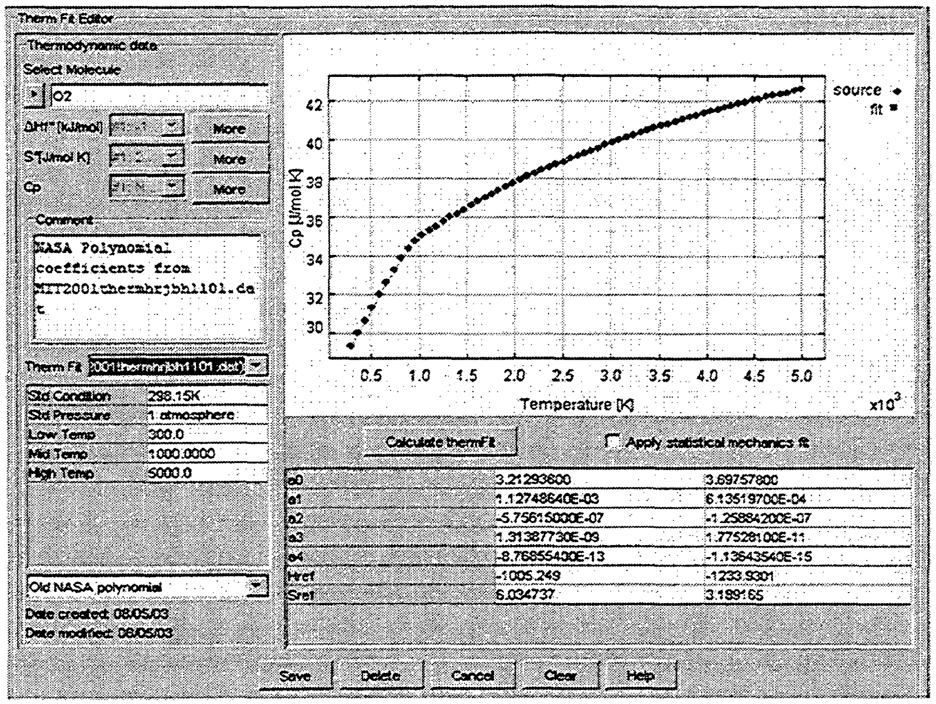
ΔHf° [kJ/mol]: -1.1557E-03

S° [J/mol K]: 205.0322

Cp [J/mol K]: 29.32 (T=300.0)

Figure 3.14: Molecule Editor Panel . Allows for modification of molecular data.

The ThermFit Editor allows manipulation of data in a thermodynamic fit. The polynomial coefficient fit parameters defined in section 2.3 are found with a linear minimization on the heat capacity, and a calculation to match with the reference enthalpy and entropy.



Select Molecule: O2

Comment: NASA Polynomial coefficients from MIT2001thermhrjbh1101.dat

Therm Fit: 2001thermhrjbh1101.dat)

Std Condition	298.15K
Std Pressure	1 atmosphere
Low Temp	300.0
Mid Temp	1000.0000
High Temp	5000.0

Old NASA polynomial

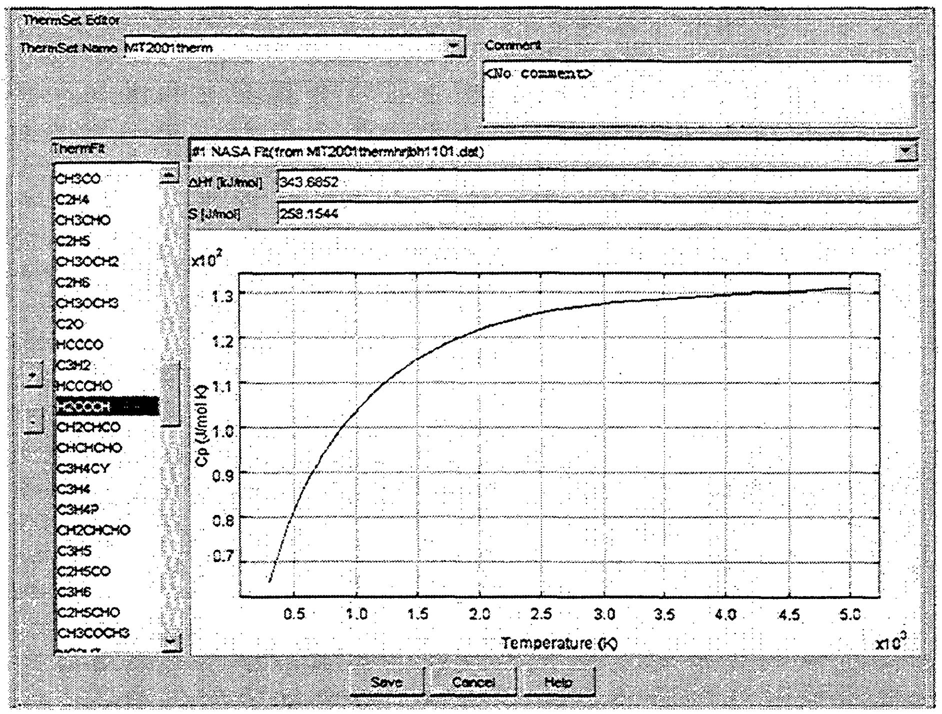
Date created: 08/05/03

Date modified: 08/05/03

a0	3.21293600	3.69757800
a1	1.12748640E-03	6.13519700E-04
a2	-5.75615000E-07	-1.25884200E-07
a3	1.31387730E-09	1.77528100E-11
a4	-8.76855400E-13	-1.13643540E-15
Href	-1005.249	-1233.9301
Sref	6.034737	3.189165

Figure 3.15: Therm Fit Editor. Therm fits are modified and created from existing thermodynamic data.

The ThermSet Editor allows manipulation of ThermFits represented within a set.



ThermSet Name: MIT2001therm

Comment: <No comment>

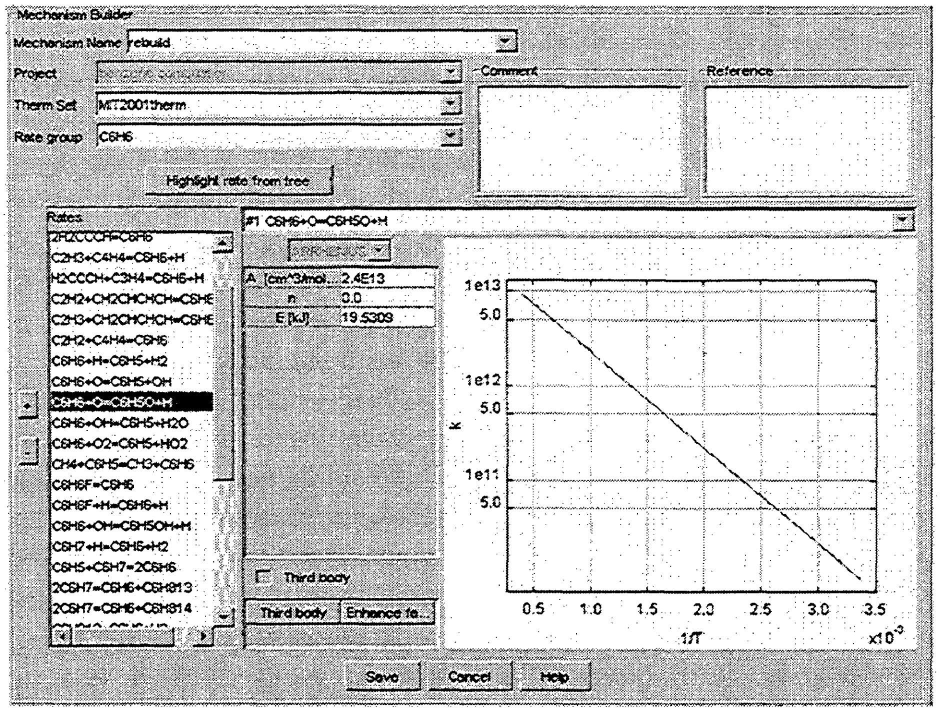
#1 NASA Fit(from MIT2001thermhrjbh1101.dat)

ΔHf [kJ/mol]: 343.6852

S [J/mol]: 258.1544

Figure 3.16: Therm Set Editor. The properties of a ThermSet are edited here.

The mechanism editor allows manipulation of the reaction rates within a mechanism.



Mechanism Name rebuild
Therm Set MIT2001therm
Rate group C6H6

Rates
2H2CCCH=C6H6
C2H3+C4H4=C6H6+H
H2CCCH+C3H4=C6H6+H
C2H2+CH2CHCHCH=C6HE
C2H3+CH2CHCHCH=C6HE
C2H2+C4H4=C6H6
C6H6+H=C6H5+H2
C6H6+O=C6H5+OH
C6H6+O=C6H5O+H
C6H6+OH=C6H5+H2O
C6H6+O2=C6H5+HO2
CH4+C6H5=CH3+C6H6
C6H6F=C6H6
C6H6F+H=C6H6+H
C6H6+OH=C6H5OH+H
C6H7+H=C6H6+H2
C6H5+C6H7=2C6H6
2C6H7=C6H6+C6H813
2C6H7=C6H6+C6H814

#1 C6H6+O=C6H5O+H

A [cm^3/mol...	2.4E13
n	0.0
E [kJ]	19.5309

☐ Third body

Third body | Enhance fa...

Figure 3.17: Mechanism Editor. A mechanism is edited or created new from reactions in the database.

Other modules are designed to run various chemical kinetic integrators, import from various file formats, export to those file formats, compare mechanisms, and run group additivity calculations. My contributions to these modules were minimal, so they are not summarized in this thesis.

CHAPTER 4

BENZENE MECHANISM ANALYSIS

The reason for analyzing the benzene mechanism is two fold. One important reason is to demonstrate the ability of the Workbench to organize complex data. The benzene combustion has been widely studied, and there are plenty of opportunities for the workbench to prove it's worth in the analysis of the resulting data.

The second reason for the analysis of the benzene mechanism is to further our understanding of aromatic chemistry. Research of benzene combustion is important because it is a beginning point for the study of aromatic combustion. It is believed that extension of the benzene mechanism can be used for reactions involving higher molecular weight aromatic species.

Pyrolysis and oxidation of aromatic compounds is a topic of interest from a theoretical standpoint, as well as a practical one. Aromatic compounds released through combustion have been established as an environmental danger, and consequently their mitigation is desired.

This project will be able to simplify the modification of reaction mechanisms, and an improvement in the benzene combustion and pyrolysis mechanism will lead to the development of higher complexity mechanisms involved in the modeling of combustion of the more dangerous aromatic compounds.

There are several existing mechanisms available for comparison, and the OpenChem Workbench provides an easy interface for thermodynamic polynomial display and for modification.

4.1 Thermodynamics analysis

The analysis of the benzene mechanisms began with a thermodynamic analysis of several mechanisms. A few rules were applied in the analysis of the thermodynamic fits.

Rule 1: Heat capacity should not go negative. Negative heat capacity indicates instability.

Rule 2: Heat capacity should approach a constant value at high temperature.

The first mechanism, from Teodorczyk[24] et. al., has thermodynamics that matched poorly to some established enthalpy of formation values. Consequently, the ability to match any of the species in the Teodorczyk mechanism to the species in any other mechanism was greatly hindered.

The thermodynamic properties were taken from two resources, which will be referred to as Glargorg[25] and MIT[26]. The Glarborg benzene combustion mechanism is only recommended for isothermal reaction, and the Glarborg is used for reactive systems lower than 1500 K.

Several reaction thermodynamic entities had corrupted temperature limit parameters in their therm fit. This did not affect any of Glarborg's results , because all of their modelling was limited to temperatures at which the thermodynamic fits remained valid.

Figure 4.1 show an example of the thermodynamic fit found in Glarborg, and the replacement expression.

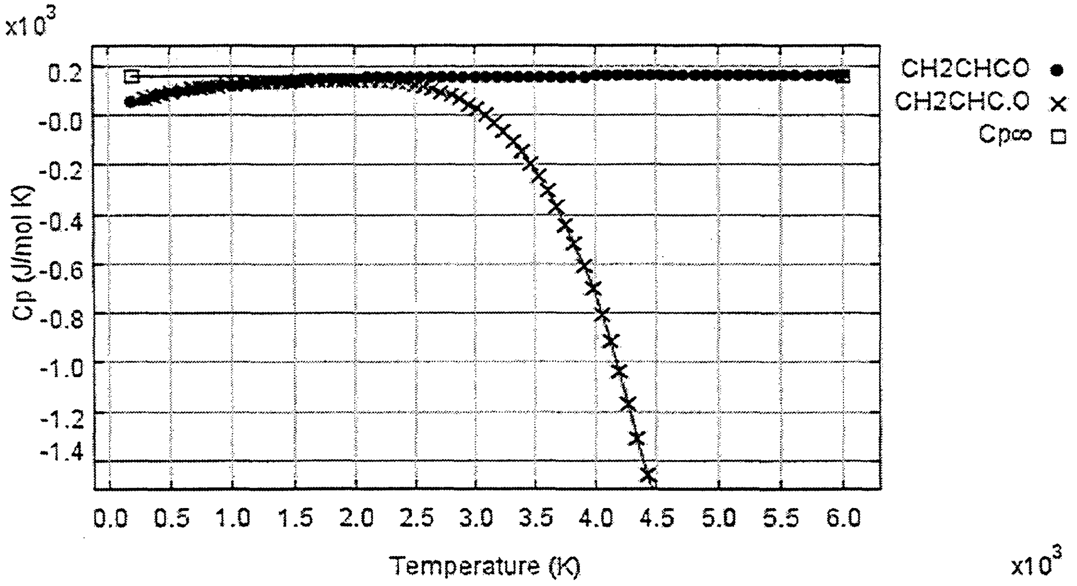


Figure 4.1: Heat capacity for CH2CHCO : Glarborg=x, MIT=•

The following species had corrupted temperature limits on their polynomial expressions.

Table 4.1: Molecules with corrupt temperature limits.

CH2CHC·O
C·HCHCHO
CH2CHCHO
C5H5O
CH2CHC·HCHCH2
CH2CHC·HCHCHOH
CH2CHCHCHC·H2
CHCC·CO
CHCCHCO
CH2CHCHCO
CH2CHC·HCHO
CH2C·CHCO
C5H5OH
C·HCHCHCO

For C2H5CHO, and C2H5CO, although the high temperature heat capacity goes above the vibration/rotation/translation limit this can be explained by low-lying electronic states.

For C6H3O3 the heat capacity goes over 300 kJ/mol K above the vibration/rotation/translation limit. The comparison is to a stoichiometrically identical molecule from the MIT set, with an enthalpy of formation difference of over 200 kJ/mol. Common stoichiometry indicates an identical number of modes of motion, indicating that their infinite heat capacity should approach a similar value, offset by ½ R times the number of internal rotor differences between the two molecules.

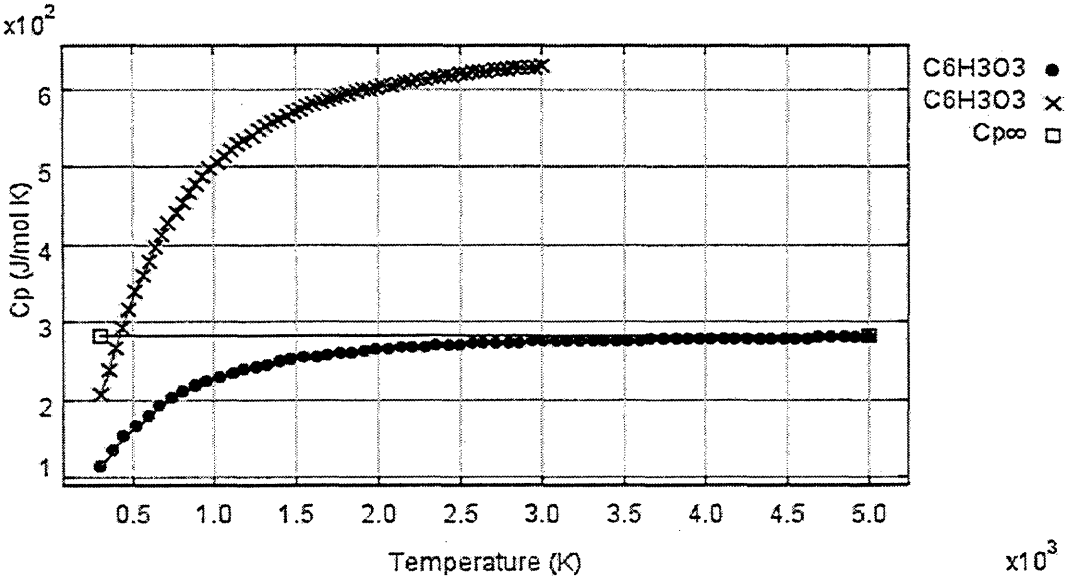


Figure 4.2: Heat capacity for C6H3O3;
Alzueta X, MIT (B3LYP/6-31G**) •

For CHCCHCHC·H2 the high slope of the high temperature heat capacity curve conflicts with that found in the MIT thermodynamic set, for molecules with nearly identical heats of formation.

Occassionally the Glarborg thermodynamic set exhibits polynomial type wavering at high temperatures, indicating that the fits were done with insufficient data points. But this has not been a problem, because the application of this mechanism is restricted to lower temperatures.

In the MIT mechanism, C6H6F (Fulvene) has poor temperature limits in the thermodynamic fit.

After providing reasonable data for thermodynamic polynomial fits, the Transport properties of several species were investigated.

4.2 Transport

The following species contained incorrect transport properties in the transport input file used by the MIT mechanism. The following species had incorrect geometry flags, indicating they were linear.

```
C3H4CY    1  252.000  4.760  0.000  0.000  1.000 ! HR
C3H4      1  252.000  4.760  0.000  0.000  1.000
C3H4P     1  252.000  4.760  0.000  0.000  1.000 ! JAM
C5H2(L)   1  357.000  5.180  0.000  0.000  1.000
C5H3      1  357.000  5.180  0.000  0.000  1.000  !HR,10/00
C5H3(L)   1  357.000  5.180  0.000  0.000  1.000
C5H4      1  357.000  5.180  0.000  0.000  1.000  !HR,10/00
C5H4(L)   1  357.000  5.180  0.000  0.000  1.000  !HR,6/99
C5H5      1  357.000  5.180  0.000  0.000  1.000  !
C5H4H     1  357.000  5.180  0.000  0.000  1.000   !
C5H5(L)   1  357.000  5.180  0.000  0.000  1.000   !
C5H6      1  357.000  5.180  0.000  0.000  1.000   !
C6H       1  357.000  5.180  0.000  0.000  1.000
C6H2      1  357.000  5.180  0.000  0.000  1.000
C6H3      1  357.000  5.180  0.000  0.000  1.000 ! CP
```

The geometric flag for these species was corrected, and transport properties for the following species were estimated by using the method described by Cambi[27].

Table 4.2: Estimates of Transport Properties. Epsilon is the Lennard-Jones well depth in Kelvin, sigma is the Lennard-Jones diameter in Angstroms, and alpha is the polarizability in Angstroms.

	epsilon	sigma	alpha
C.HCHCH3	159.0419	4.043389	4.000049
C.HCHCHCO	154.5522	4.194274	5.621288
C2H2OH	133.0445	3.90933	2.840948
C5H7	179.374	4.30394	7.034723
C5H3O	176.8568	4.320191	7.262286
CH2C.CH3	159.4211	4.052843	4.09138
CH2CHC.HCHCH2	179.374	4.30394	7.034723
CH2CHC.HCHCHOH	185.6668	4.343304	7.594318
CH2CHCHCHC.H2	188.0353	4.30394	7.034723
CHOCH2CH2C.HCHO	199.3173	4.353312	7.741169
CHOCH2CH2C.O	187.7504	4.21786	5.907779
HCOO	131.0528	3.776281	1.921363
O2CCHOO.	181.3652	4.081649	4.377821
CH2C.CHCO	176.8025	4.275841	6.652506
CH2CHC.HCHO	147.3046	4.32309	7.303382
CHCC.CO	171.9541	4.273785	6.625091
C5H5OH	189.6491	4.32509	7.331834
CH2CHCHCHCH2OH	196.3982	4.317315	7.221653
CH2CHCHCHCH3	191.6462	4.281729	6.731428
CH2CHCHCO	180.1356	4.231164	6.073522
CHCCHCO	174.8688	4.182431	5.480938
CHOCH2CH2CHO	189.4987	4.183657	5.495367
CHOCHCHOH	177.3716	4.13924	4.988502
HONO	131.5292	3.76374	1.84552
OC6H4O2	201.8531	4.362763	7.881588
OCHCHO	155.1907	3.935463	3.047672

The modified transport properties can now be used for chemical modeling of complex reactions where the composition of molecules is affected by the ability of a molecule to move in a high concentration and temperature gradient, like the one found in flames.

4.3 Comparison of reaction rates

An important part of mechanism analysis is the evaluation of elementary rate constants. So an analysis of several rate constants in the benzene mechanism was evaluated.

Elementary reactions involved in a mechanism are not easily measured, and there are often differing rate expressions for an identical reaction. The OpenChem workbench provides a quick method for comparing rates in two mechanisms.

The comparison of reaction rates is a quick way to discover which rates are disputed, and which rates have been established as likely candidates for being correct.

$OH+O = H+O_2$

- Arrhenius plot:

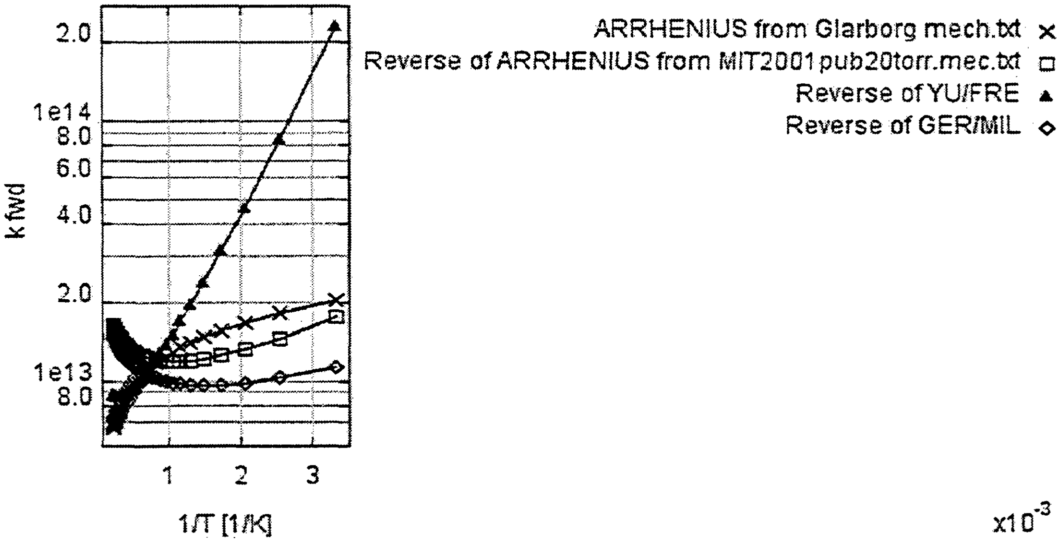


Figure 4.3: Rate Expressions for $OH+O = H+O_2$

- Sensitivity: high
- Rate parameter fit

Glarborg:

A	6.6803E16
n	-0.7862
Ea [kJ]	71.8219

MIT

A	1.9100E14
n	0
Ea [kJ]	68.7882

- General notes: The rate expression in the Alzueta mechanism is written as the reverse reaction relative to the rate expression in the MIT mechanism, and assumes that there is no barrier to a radical-radical addition. Reviews of shock tube studies[28] and transition state theory[29] show no preference for either reaction.
- Recommendation: Do not make any change to the MIT expression.

H_2CCCH+H(+M)=H_2CCCH_2(+M)

- Arrhenius plot:

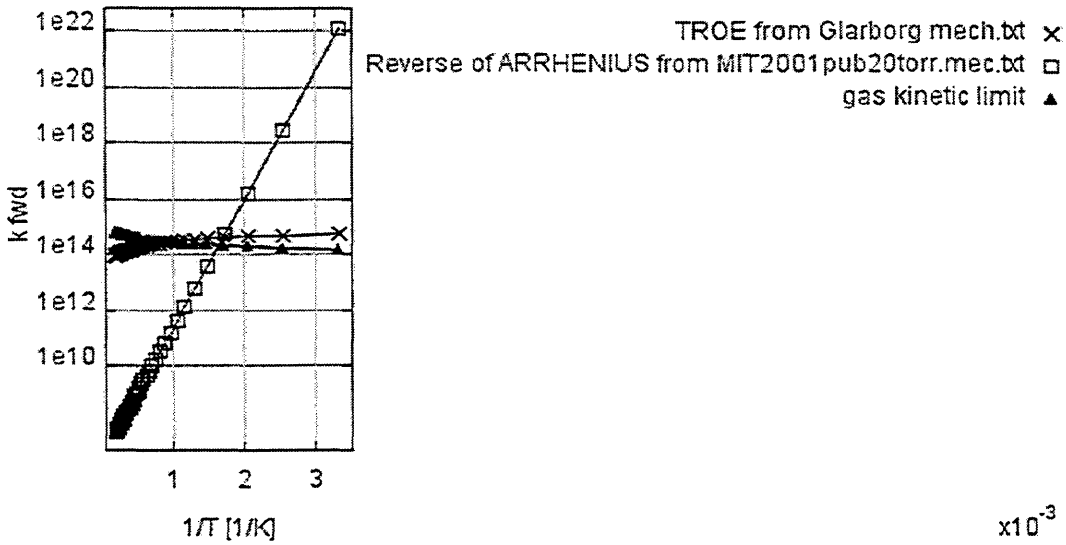


Figure 4.4: Rate Expressions for H_2CCCH+H(+M)=H_2CCCH_2(+M). The (+M) indicates that this is a pressure dependent reaction.

- Sensitivity: high
- Rate parameter fit:

Glarborg

A	9.9580E16
n	-0.8210
Ea [kJ]	1.3075

MIT

A	2.3000E12
n	0
Ea [kJ]	291.5716

- General notes:The rate expression in the Alzueta mechanism is written as the reverse reaction relative to the rate expression in the MIT mechanism. The MIT expression goes above the kinetic limit at low temperatures. The kinetic limit is a theoretical limit to the reaction rate, calculated by assuming that there is no barrier to reaction, and every collision results in reaction. It is calculated with the approximate spherical diameter of the two reacting species (4.9 Angstroms and 2.05 Angstroms), and their mass.
- Recommendation: Use the Glarborg expression.

$H_2CCCH+H(+M)=H_3CCCH(+M)$

- Arrhenius plot:

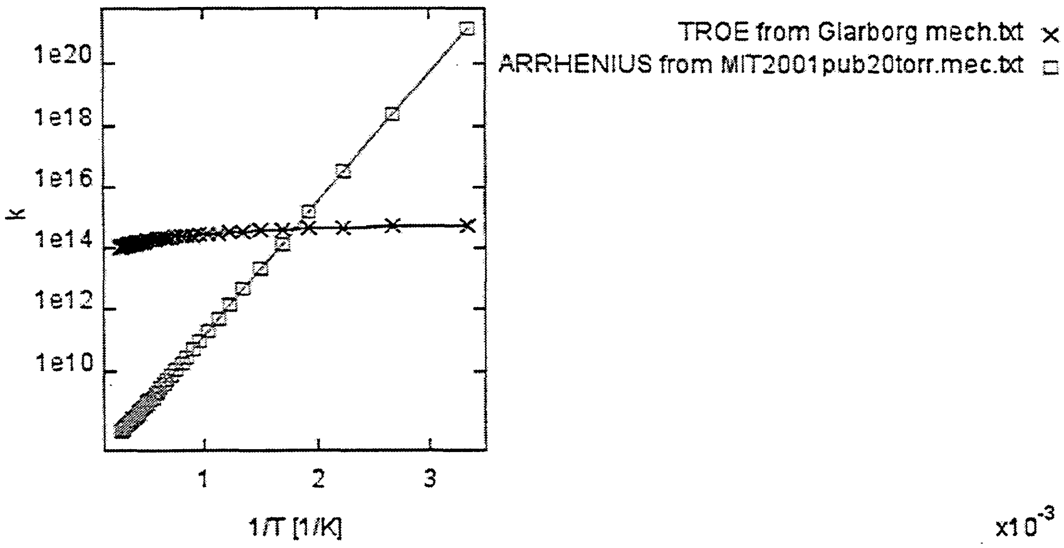


Figure 4.5: Rate Expressions for $H_2CCCH+H(+M)=H_3CCCH(+M)$

- Sensitivity: high
- Rate parameter fit:

Glarborg

A	9.9580E16
n	-0.8210
Ea [kJ]	1.3075

MIT

A	1.3400E12
n	0
Ea [kJ]	292.6511

- General notes: The rate expression in the Alzueta mechanism is written as the reverse reaction relative to the rate expression in the MIT mechanism. Again, the MIT expression goes above the kinetic limit at low temperatures.

- Recommendation: Use the Glarborg expression.

C_5H_5+H=C_5H_6

- Arrhenius plot:

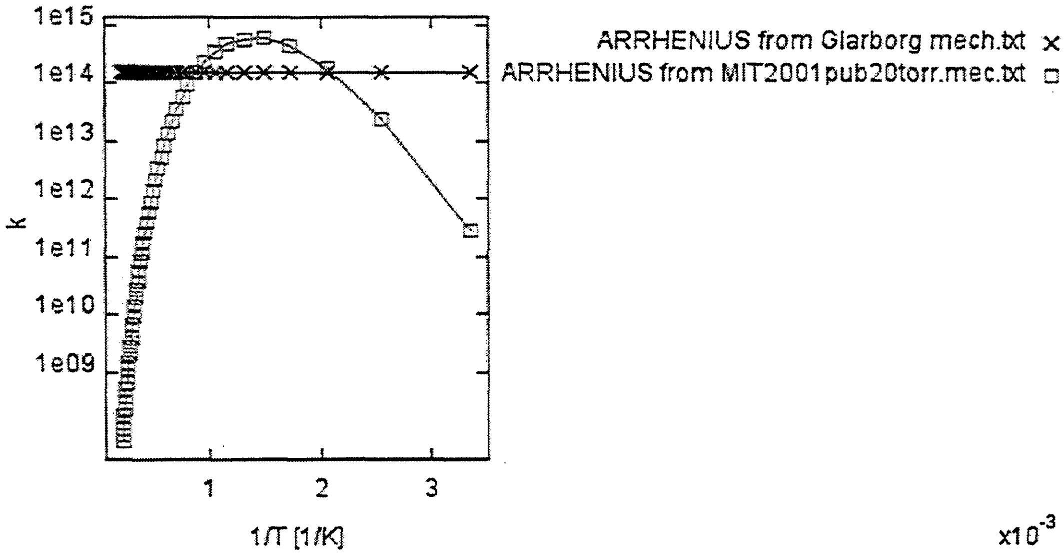


Figure 4.6: Rate Expressions for C_5H_5+H=C_5H_6

- Sensitivity: high.
- Rate parameter fit:

Glarborg

A	1.5000E14
n	0
Ea [kJ]	0

MIT

A	2.7100E63
n	-14.7900
Ea [kJ]	88.0774

- General notes: According to kinetic analysis[30], there is no barrier to a radical-radical recombination for the cyclopentadienyl radical, so the Glarborg expression is more likely.
- Recommendation: Use the Glarborg expression.

C_6H_5O+H=C_6H_5OH

- Arrhenius plot:

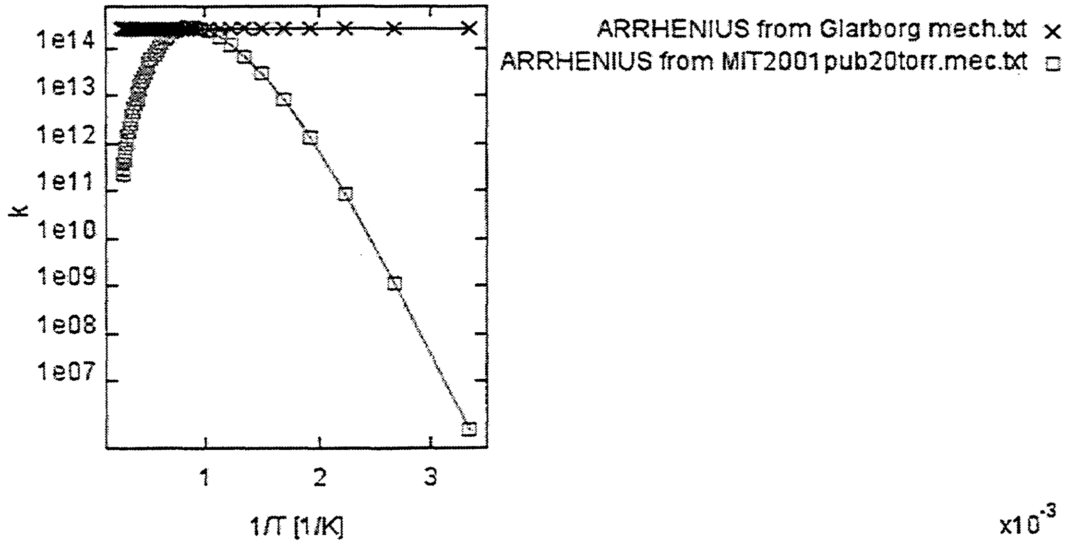


Figure 4.7: Rate Expressions for C6H5O+H=C6H5OH

- Sensitivity: high.
- Rate parameter fit:

Glarborg

A	2.5000E14
n	0
Ea [kJ]	0

MIT

A	4.4300E60
n	-13.2320
Ea [kJ]	125.5678

- General notes: Rate measurement techniques[31] cannot distinguish between the rate expressions, because the range of the rate data is only valid at the overlap of the two rates. But due to the fact that this is radical radical recombination, the Glarborg expression is more likely.
- Recommendation: Use the Glarborg expression

$C_6H_5OH+O=C_6H_5O+OH$

- Arrhenius plot:

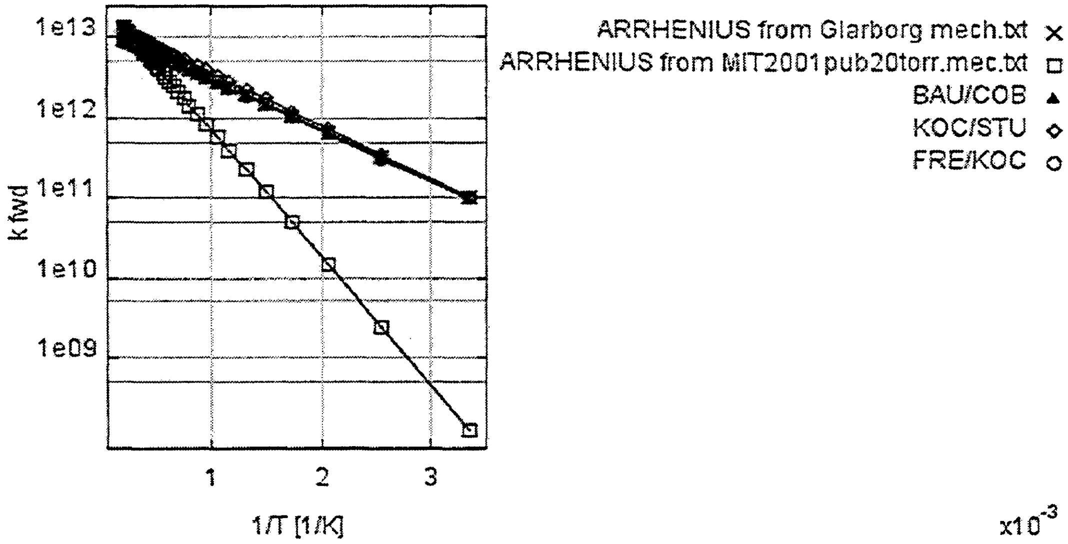


Figure 4.8: Rate Expressions for $C_6H_5OH+O=C_6H_5O+OH$

- Sensitivity: high
- Rate parameter fit:

Glarborg

A	1.3000E13
n	0
Ea [kJ]	12.1342

MIT

A	2.8100E13
n	0
Ea [kJ]	30.7622

- General notes: According to literature review[32], and mass spectrometry results[33,34], the activation energy of this reaction is closer to the Glarborg expression of 3 kcal/mol.

- Recommendation: Use the Glarborg rate expression.

The following reactions showed a difference in their rate expressions, but did not have a large effect on the high concentration species when modified.

4.3.1 Comparison of rates with low sensitivity

H_2O_2+H=HO_2+H_2

- Arrhenius plot:

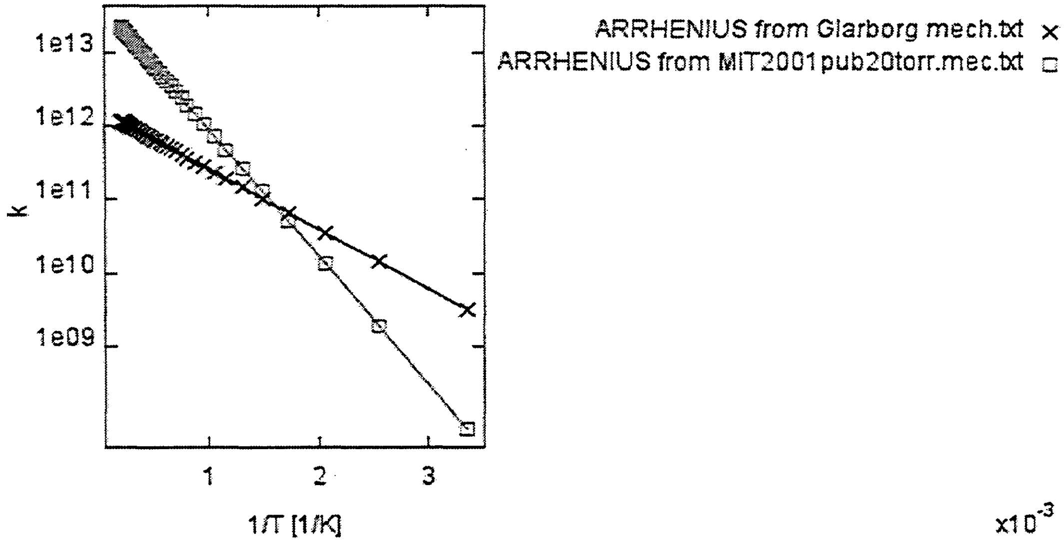


Figure 4.9: Rate Expressions for H_2O_2+H=HO_2+H_2

- Sensitivity: low
- General notes: A literature review done in 1992[32] (E = 3.1 kcal/mol, A = 1.692E12) supports the Glarborg estimate of 3.7 kcal/mol and the pre-exponential of 1.7E12.
- Recommendation: Use the Glarborg rate expression.

CH+H$_2$=HCH+H

- Arrhenius plot:

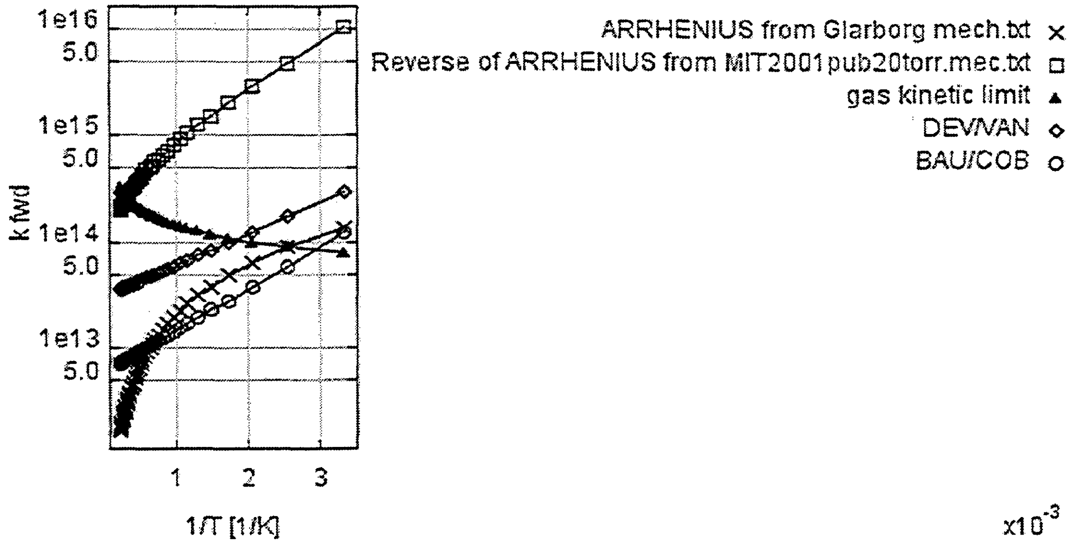


Figure 4.10: Rate Expressions for CH+H$_2$=HCH+H

- Sensitivity: low
- General notes: Glarborg assumes a zero barrier to the radical-radical reverse reaction, which is an assumption valid for recombination, not hydrogen abstraction. Rate parameters found by mass spectrometry[35] and Although, as can be seen in the above plot, the MIT reverse expression goes above the gas kinetic limit.
- Recommendation: Use the Glarborg rate expression.

$CH_2O+O_2=HO_2+CHO$

- Arrhenius plot:

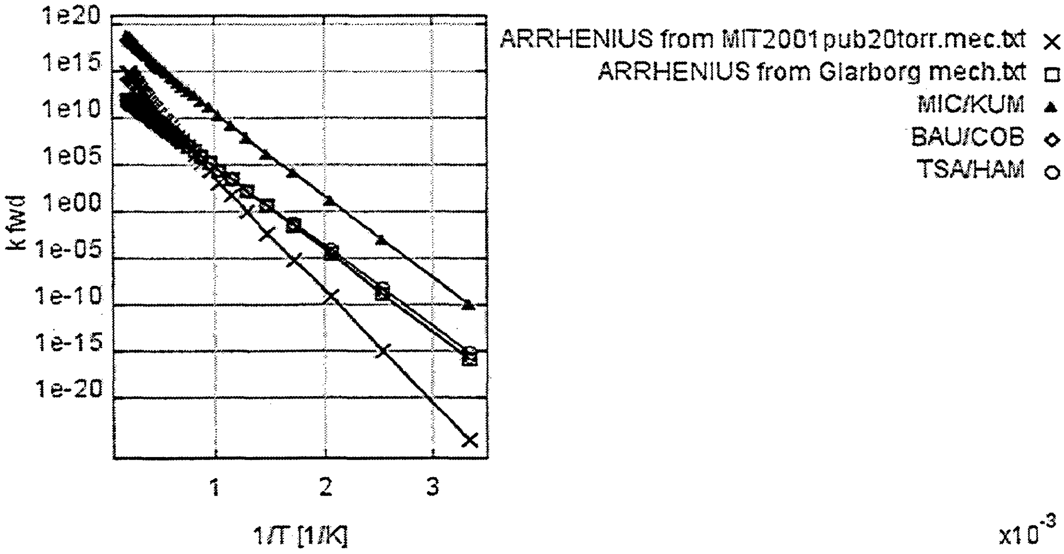


Figure 4.11: Rate Expressions for $CH_2O+O_2=HO_2+CHO$

- Sensitivity: low
- General notes: Glarborg uses a pre-exponential of 6E13, and an activation energy of 40.66 kcal/mol, the MIT mechanism uses a pre-exponential of 9.5E15, and an activation energy of 55.9 kcal/mol. Shock tube studies[36] Literature reviews[32,32] tend to agree with the Glarborg rate expression.
- Recommendation: Use the Glarborg rate expression.

HCH(triplet)+O_2=CO_2+2H

- Arrhenius plot:

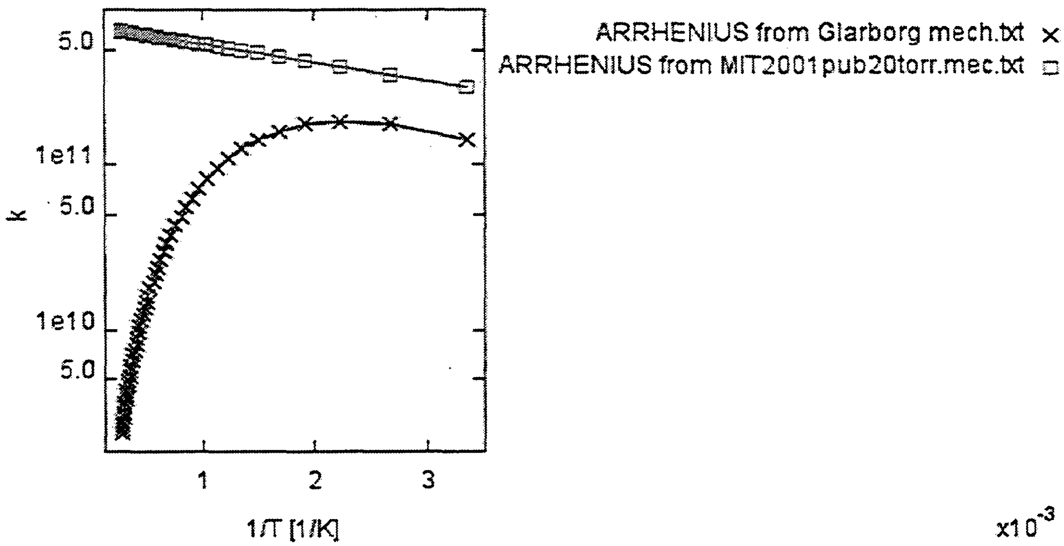


Figure 4.12: Rate Expressions for HCH(triplet)+O_2=CO_2+2H

- Sensitivity: low
- General notes: The two rate expressions produce similar results at low temperature, but the high temperature results indicate a disagreement. At a temperature range of 2100-2600, VIS-UV absorption measures a rate of 5.997E12[37], and in the range of 1000-1700 K the measured rate is 4.99E10[38]. These two data points suggest an increasing rate constant. A paper also published the rate constant expression[39] very similar to the expression used in the Glarborg mechanism.
- Recommendation: Use the Glarborg rate expression.

$CH_2OH+H=CH_3+OH$

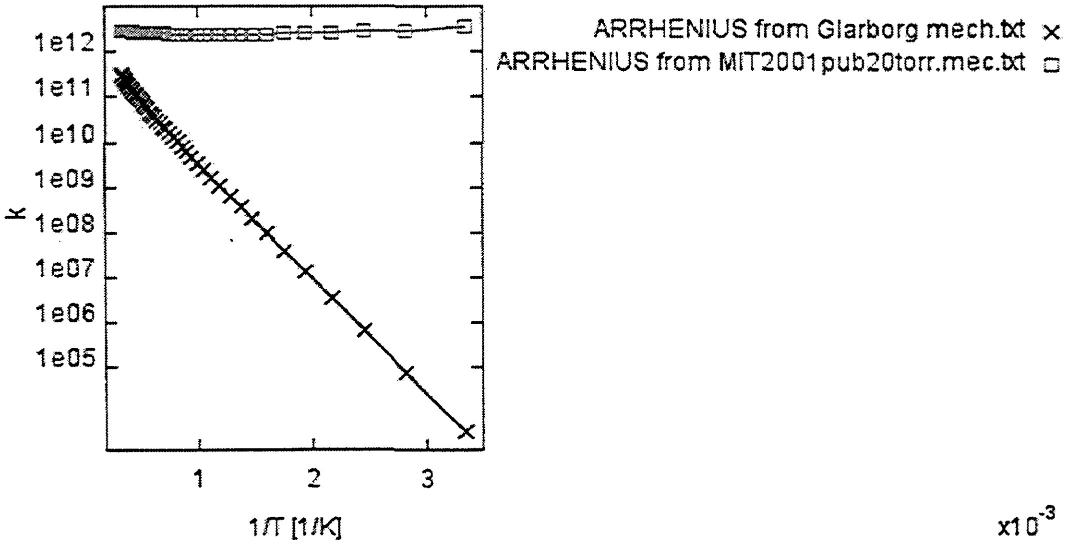


Figure 4.13: Rate Expressions for $CH_2OH+H=CH_3+OH$

- Sensitivity: low
- General notes: In this case, the two reactions are reversed in the two mechanisms. The MIT value has a negative energy of activation, a positive temperature coefficient, and a reverse rate that goes above the collision limit. A literature review[40] agrees with the constant rate used in the Glarborg mechanism.
- Recommendation: Use the Glarborg rate expression.

CH_3+OH = CH_3O+H

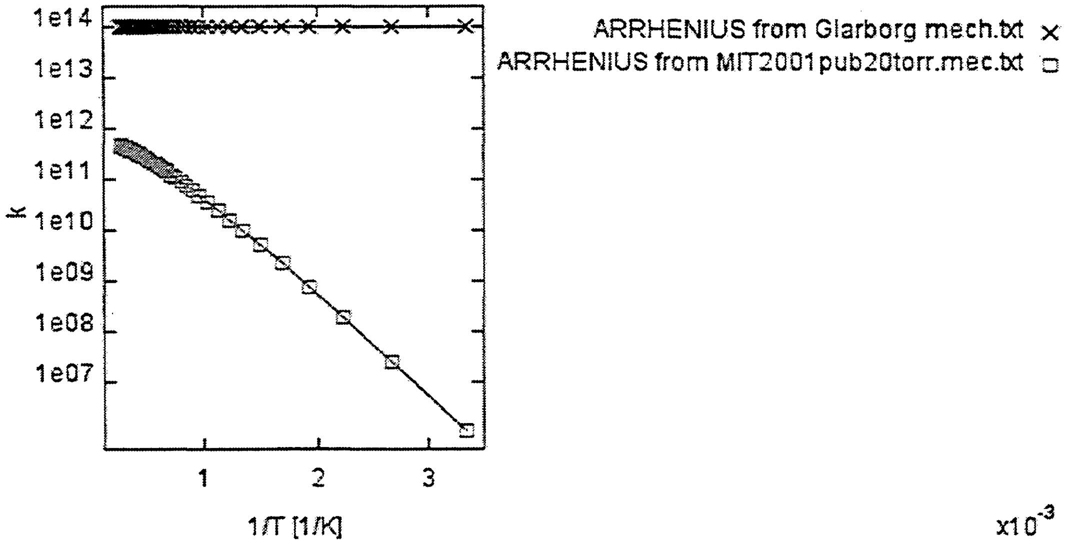


Figure 4.14: Rate Expressions for CH_3+OH = CH_3O+H

- Sensitivity: low
- General notes: These two reactions are reversed in the two mechanisms. Neither rate constants are supported by a QRRK analysis[41]; disagreeing with the magnitude of the Glarborg fit, and the slope of the MIT fit. The high magnitude of the Glarborg expression is unlikely for a radical-radical addition followed by dissociation reaction.
- Recommendation: Use the MIT rate expression.

C_2H_5+H = CH_3+CH_3

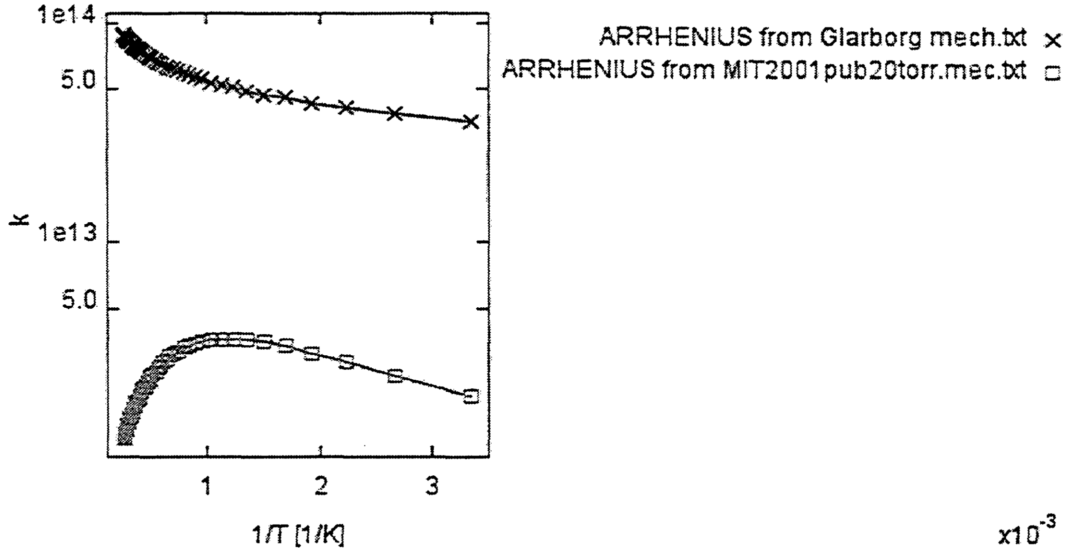


Figure 4.15: Rate Expressions for C_2H_5+H = CH_3+CH_3

- Sensitivity: low
- General notes: According to UV-VIS spectrum data[42] and RRK modeling[43], the rate in the Glarborg mechanism is high. This reaction is likely to be valid only at low pressures, because the competing formation of the stable unimolecular intermediate would reduce the magnitude of this rate.
- Recommendation: Use the MIT rate expression.

C_2H_2+M=C_2H+H+M

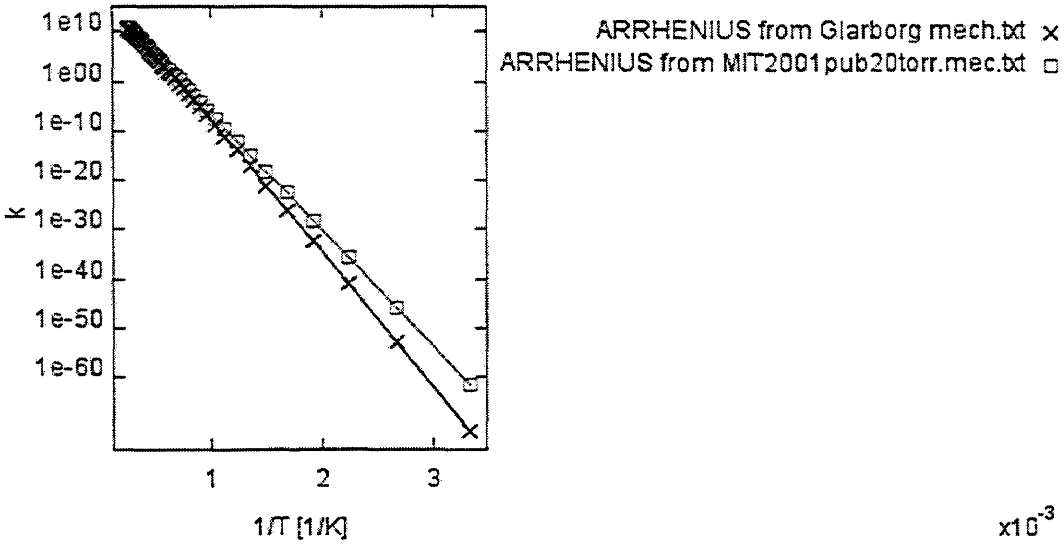


Figure 4.16: Rate Expressions for C_2H_2+M=C_2H+H+M. M is the third body term, exciting the C-H bond of the species C2H2 to dissociate.

- Sensitivity: low
- General notes: Using a 2-parameter fit to the Glarborg rate, the energy of activation was found to be 121 kcal. This value is large compared to the ~107 kcal/mol found from several sources[44,45,46]. Although, the bond dissociation energy for C2H2 is 133.32 kcal[47], indicating that there is support for the Glarborg rate.
- Recommendation: Use the MIT rate expression.

CH+HCH=C_2H_2+H

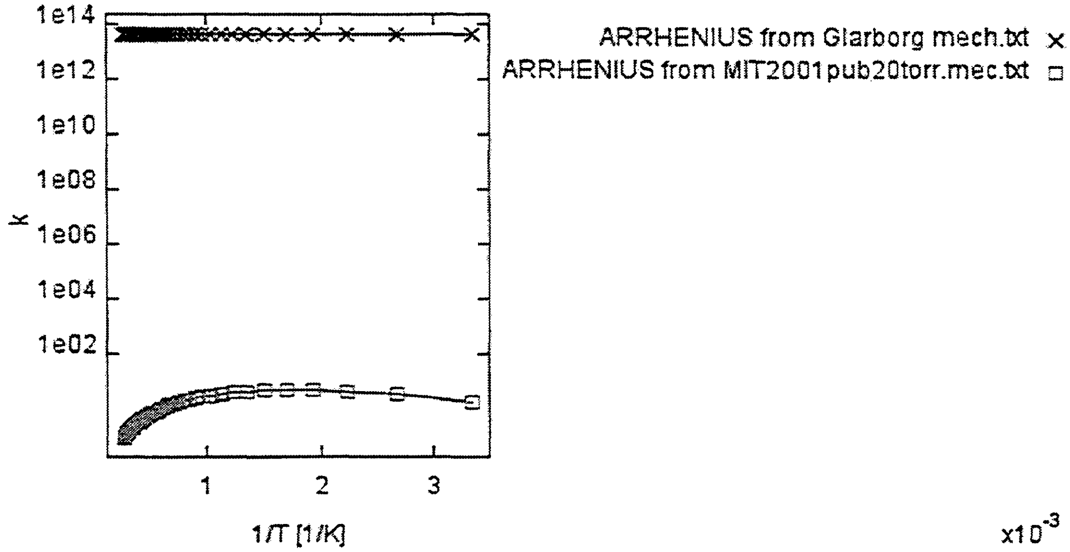


Figure 4.17: Rate Expressions for CH+HCH=C_2H_2+H

- Sensitivity: low
- General notes: The rate expression in the Glarborg mechanism is near the collision limit, which is unlikely to be true for a radical-radical addition followed by beta scission.
- Recommendation: Use the MIT rate expression.

$C_2H_4+CH_3=C_2H_3+CH_4$

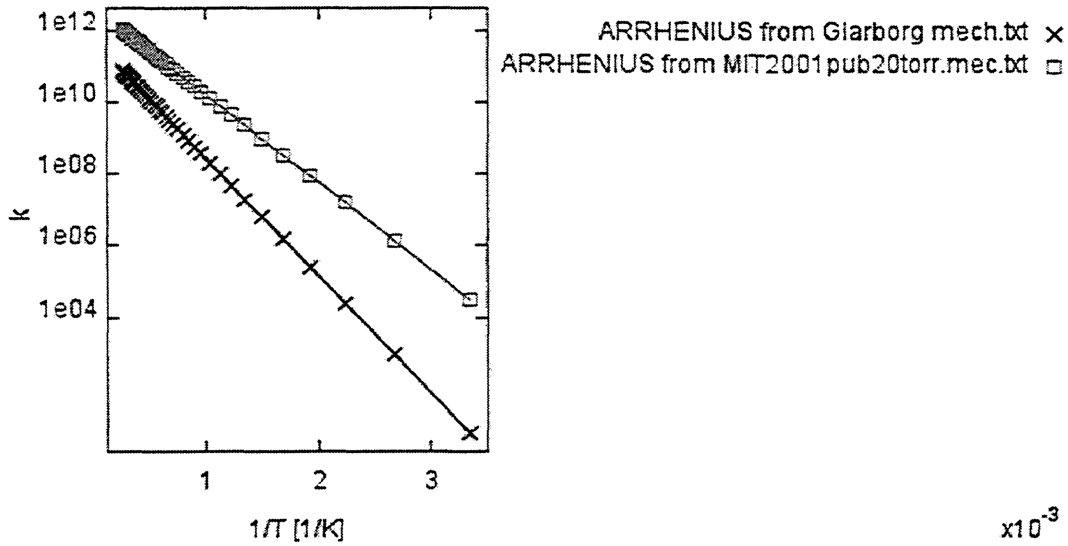


Figure 4.18: Rate Expressions for $C_2H_4+CH_3=C_2H_3+CH_4$

Sensitivity: low

General notes: Both expressions for this rate have support from different papers[32,45,48,49]. Results of a transition state theory calculation for this reaction are given in section 4.3.

Recommendation: Use the MIT rate expression.

$C_2H_4+HO_2=CH_3CHO+OH$

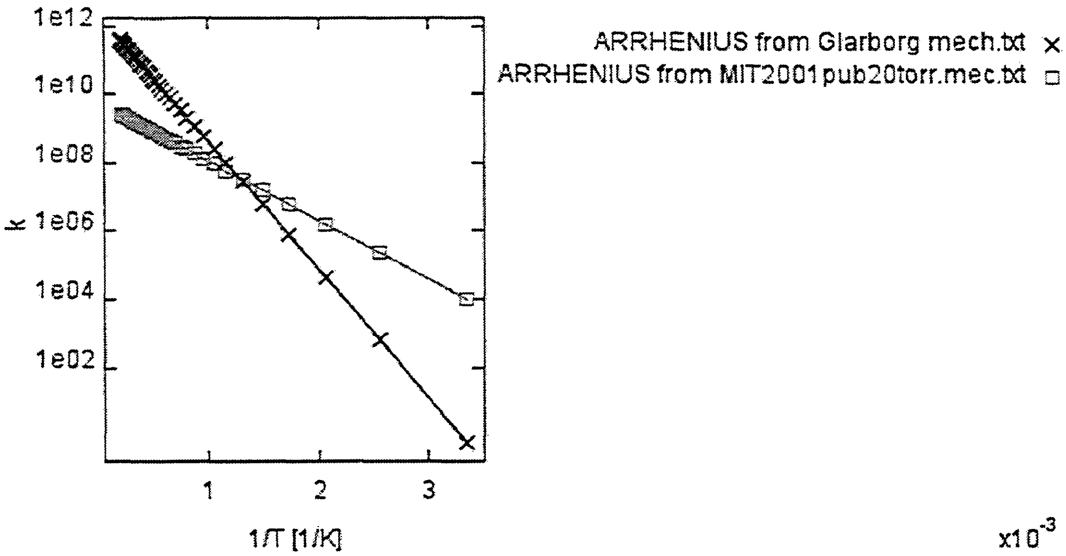


Figure 4.19: Rate Expressions for $C_2H_4+HO_2=CH_3CHO+OH$

Sensitivity: low

General notes: The Glarborg rate is for the formation of oxirane and hydroxyl radical[32], not acetaldehyde and hydroxyl radical[32]. This is an example of how ambiguous structure specification can lead to problems with rate expressions.

Recommendation: Use the MIT rate expression.

$CH_2CHCO = C_2H_3+CO$

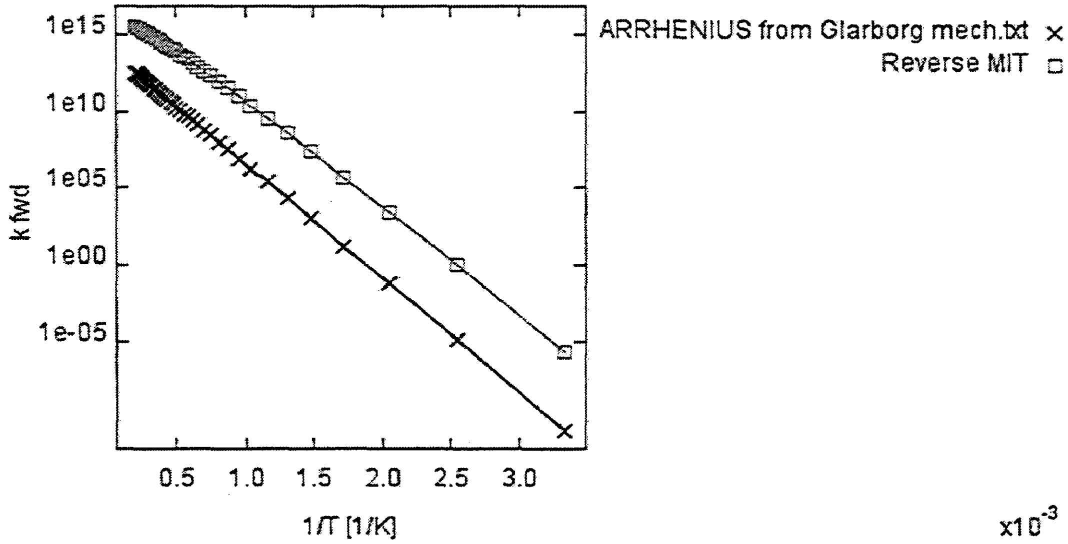


Figure 4.20: Rate Expressions for $CH_2CHCO = C_2H_3+CO$

Sensitivity: low

General notes: The analysis favoring the MIT expression is outlined in the section 4.3.

Recommendation: Use the MIT rate expression.

CH_3+C_2H_2=H_3CCCH+H

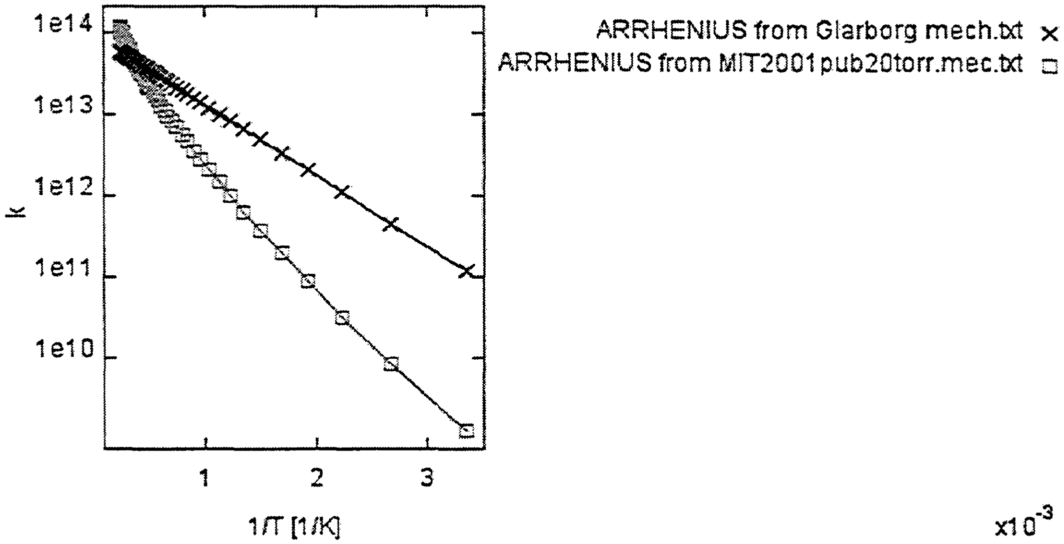


Figure 4.21: Rate Expressions for CH_3+C_2H_2=H_3CCCH+H

- Sensitivity: low
- General notes: In comparison to QRRK analysis[41], the reverse reaction is about 2 orders of magnitude too high in the Glarborg mechanism.
- Recommendation: Use the MIT rate expression.

C_3H_6+O=C_3H_5+OH

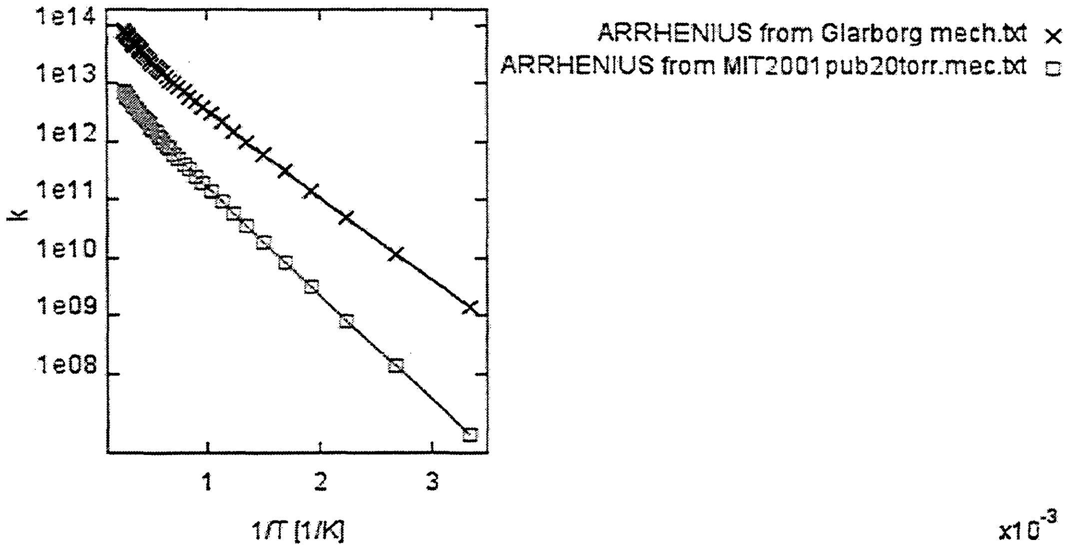


Figure 4.22: Rate Expressions for C_3H_6+O=C_3H_5+OH

- Sensitivity: low
- General notes: The activation energy of the MIT reactions suggests that there was a mistake made with the identity of the C_3H_5 molecule. According to literature reviews[50], the activation energy forming the CH_2=C·CH_3 (Hf ~ 255 kJ/mol) is 7 kcal, compared with the activation energy forming CH_2=CHC·H_2 (Hf ~ 171 kJ/mol) of 5kcal. The heat of formation from the MIT mechanism suggests that the species is with the radical on the third carbon, not the second. A difference of 2 kcal is not enough to distinguish between the two, but it does bring up the point that the identification of species can lead to doubts in rate expressions.
- Recommendation: Use the Glarborg rate expression.

C_3H_6+O=C_2H_5+HCO

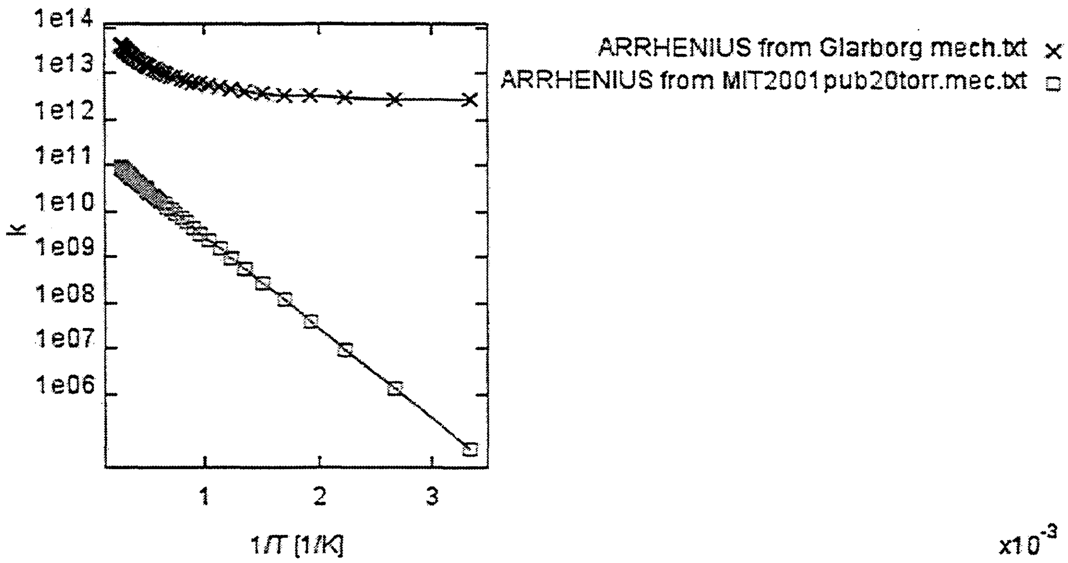


Figure 4.23: Rate Expressions for C_3H_6+O=C_2H_5+HCO

- Sensitivity: low
- General notes: A room temperature flash photolysis measurement[51] shows a very low reaction rate, which would support the MIT expression
- Recommendation: Use the MIT rate expression.

$C_6H_5+O_2=C_6H_5O+O$

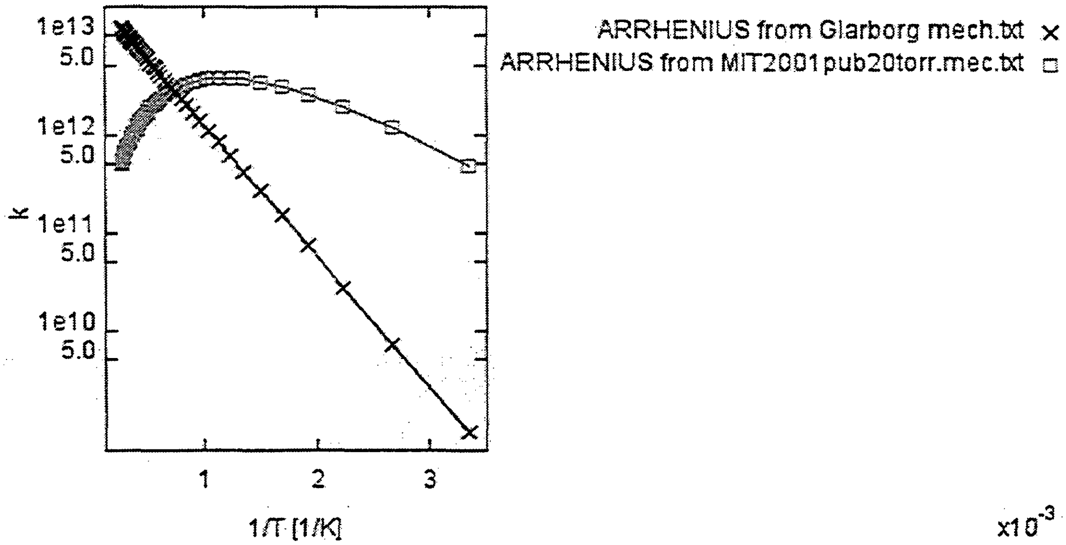


Figure 4.24: Rate Expressions for $C_6H_5+O_2=C_6H_5O+O$

- Sensitivity: low
- General notes: The Glarborg expression is similar in activation energy and pre-exponential to an experimental measurement[52].
- Recommendation: Use the Glarborg rate expression.

$C_6H_5+H=C_6H_4$(benzyne)$+H_2$

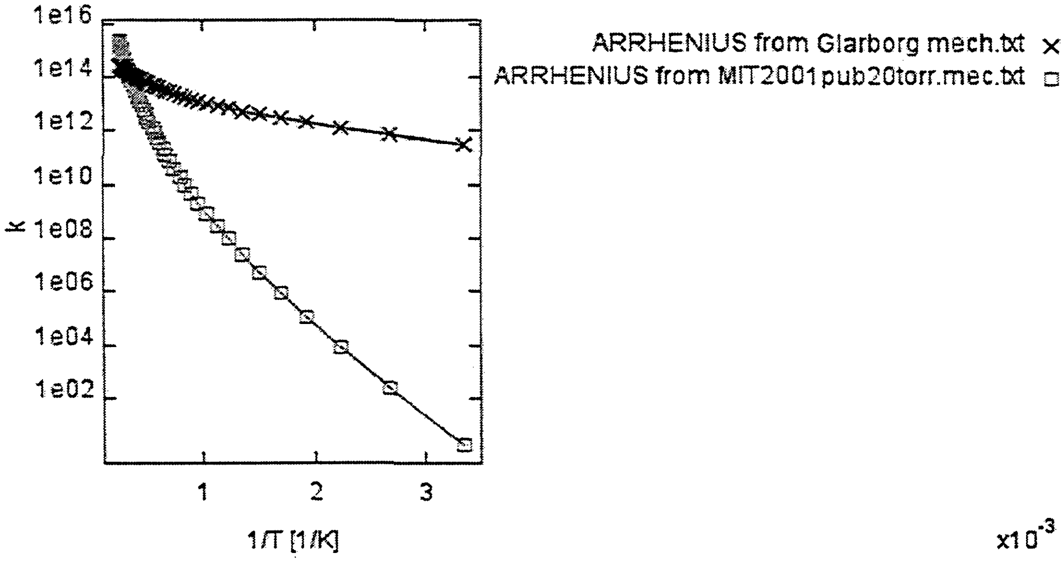


Figure 4.25: Rate expressions for $C_6H_5+H=C_6H_4$(benzyne)$+H_2$

- Sensitivity: low
- General notes: The expression used in the Glarborg mechanism is similar to radical radical addition, but this reaction is a hydrogen abstraction reaction.
- Recommendation: Use the MIT rate expression.

The following reactions were taken from the MIT mechanism, and their reverse rates indicated an inconsistency.

C_3H_6+C_2H=C_4H_6+CH

- Arrhenius plot:

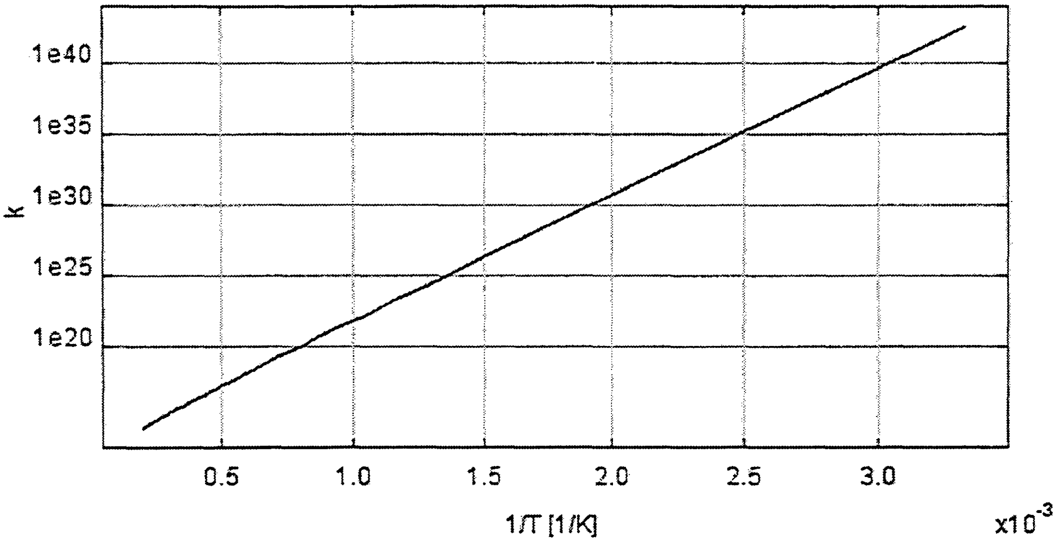


Figure 4.26: Reverse Rate Expression for C_3H_6+C_2H=C_4H_6+CH

- Sensitivity: low
- General notes: The reverse rate of this reaction goes well above the collision limit, so it was replaced with a reverse expression at 1E13, which is an approximation for radical radical addition without a barrier to reaction.
- Recommendation: Use gas kinetic limit expression.

C_2H_2+O=C_2H+OH

- Arrhenius plot:

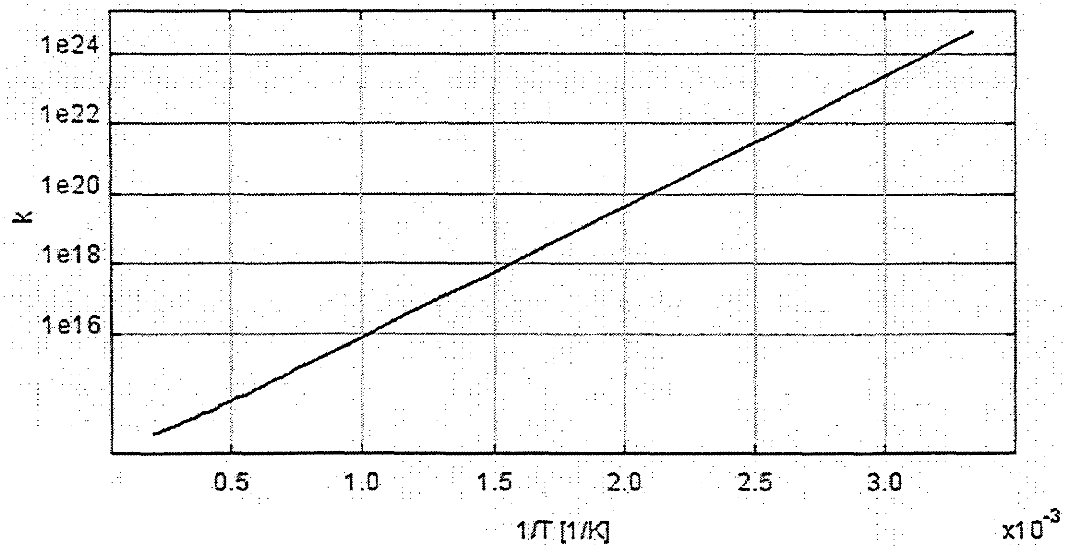


Figure 4.27: Reverse Rate Expression for C_2H_2+O=C_2H+OH

- Sensitivity: low
- General notes: Looking at the reverse expression for this rate, it is well above the collision limit. The reverse rate for this reaction was found by literature review[53].
- Recommendation: Use literature review expression.

4.4 Rate constant evaluation

To demonstrate the abilities of the workbench, and to determine support for conflict between rate constant expressions, the following rates were estimated using Gaussian output file data, being fed into the rate constant estimation module.

- **$CH_3+C_2H_4=C_2H_3+CH_4$**

This reaction has a ~2 order of magnitude disagreement between rate expressions, and both have support from different papers. A transition state theory calculation was made in order to lend support to one or the other expression.

A transition state calculation was made to determine which rate constant was more likely to be correct. The theory and basis set of the electronic structure calculation was B3LYP/6-31G**[54].

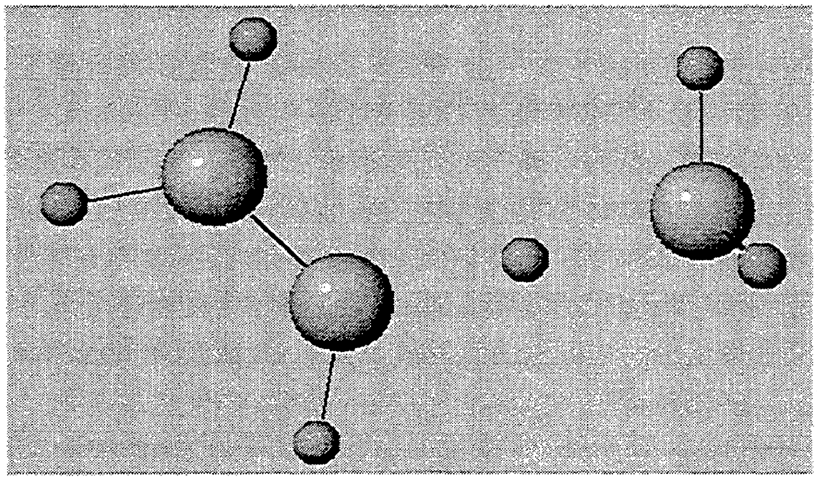


Figure 4.28: Transition State 1. Illustration of the hydrogen abstraction transition state.

Table 4.2: Gaussian Output Set 1. The properties of molecules in the hydrogen abstraction reaction, calculated at B3LYP/6-31G**.

Species	CH_3	C_2H_4	ts CH_2CH-H-CH_2	C_2H_3	CH_4
Energy	-39.84288	-78.5938076	-118.4137048	-77.9063079	-40.5240195
Frequencies	462	831.7	-1576.5	723.1	1356.6
	1420.5	961.1	26.5	815.7	1356.6
	1420.5	976.5	145.7	921.4	1356.6
	3132.3	1069.1	245.6	1062.9	1579.3
	3314.2	1241.6	490.8	1403.8	1579.3
	3314.2	1388.4	550.3	1670.6	3046.9
		1483.3	559.9	3067.3	3163.2
		1714.8	889.1	3166.3	3163.2
		3145.3	919.6	3254.5	3163.2
		3161	966.6		
		3221	1186.5		
		3246.9	1200.5		
			1278.6		
			1390.7		
			1426.8		
			1460.2		
			1475.3		
			1680.7		
			3076.7		
			3108.3		
			3182.9		
			3193.7		
			3207.6		
			3208.7		

This gives a forward barrier of about 14.4 kcal/mol, or 60.3 kJ/mol. Using a path degeneracy of four, corresponding to the four equivalent ways that the methyl radical can abstract a hydrogen from C4H4, the transition state calculation gives a rate expression of:

$k = 1.77E6\ T^{2.283}\exp(-48.5/RT)$

Where the energy is in kJ/mol, ant the pre-exponential factor is in cm^3/mol s. A two-parameter fit over the range of 300 to 1500 K gives a pre-exponential of 5.92E13 and a barrier of 60.8 kJ/mol.

Comparison with the two expressions in the two mechanisms indicates that the slope of the Glarborg fit is correct, but the magnitude of the pre-exponential is closer to values found from the MIT expression.

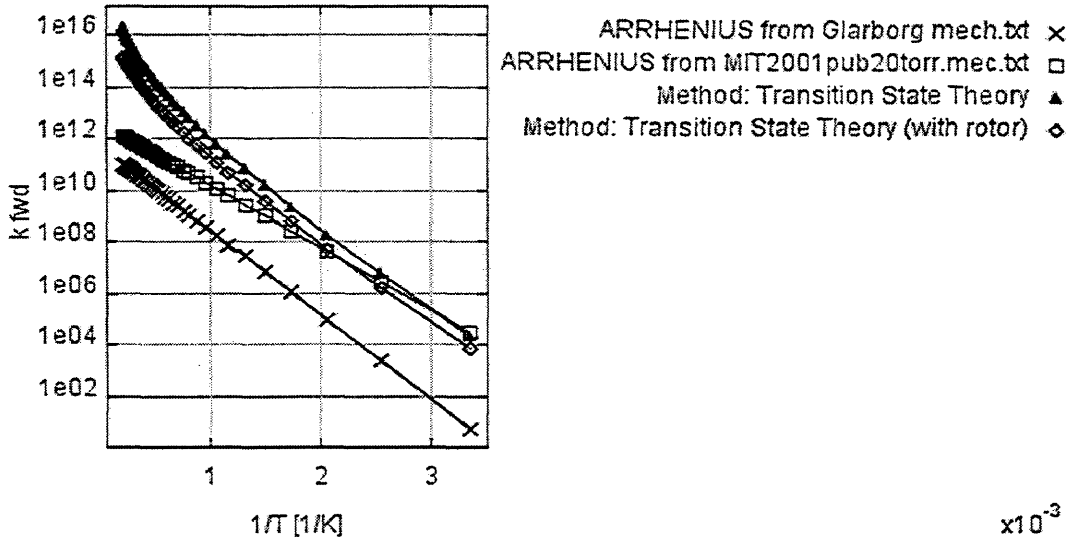


Figure 4.29: Calculated C2H4+CH3=C2H3+CH4. Comparison of rate expressions for C2H4+CH3=C2H3+CH4

The calculation was performed modeling the transition state as both a hindered rotor, and with a harmonic oscillator. Figure 4.53 shows how the magnitude of the difference that a rotation mode versus a harmonic oscillator can make in the calculation. The internal rotor brings the estimated rate closer to the values in the MIT mechanism.

- **$CH_2CHCO = C_2H_3+CO$**

There was a discrepancy between the two rate expressions in the Glarborg and MIT mechanism. There is an approximate 1-2 orders of magnitude difference between the rates.

To determine which rate expression is more likely, an *ab-initio* calculation was done on all reaction species, and the transition state was determined. The level of theory used for calculation was B3LYP/6-31G**.

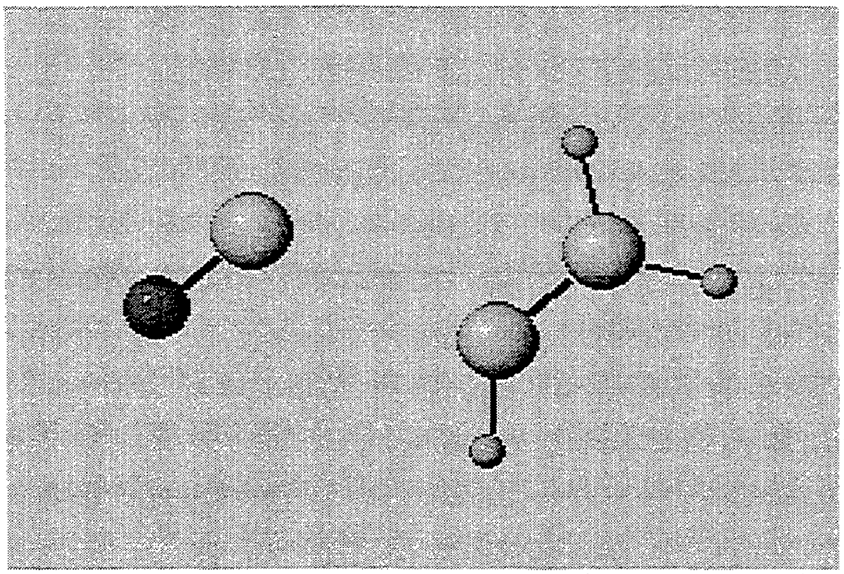


Figure 4.30: Transition state 2. Illustration of the hydroxy elimination transition state.

The following properties were found.

Table 4.3: Gaussian Output Set 2. Properties of the hydroxyl elimination reaction, calculated at B3LYP/6-31G**.

Species	CH2CHC.O	ts ch2chco	C2H3	CO
Energy	-191.2645009	-191.2170593	-77.9063	-113.309
Frequencies	147.2	-117.2	723.1	2208.7
	307.1	52.1	815.7	
	540.9	100.3	921.4	
	638.5	192.2	1062.9	
	891.1	223.3	1403.8	
	1004.3	738.7	1670.6	
	1014.9	820.9	3067.3	
	1112.2	934.7	3166.3	
	1293.9	1063.2	3254.5	
	1431.9	1396.7		
	1686.7	1672.3		
	1903.7	2151.2		
	3134.2	3081.6		
	3167.7	3181.4		
	3259.4	3251.8		

According to the calculated theory, there is a barrier of 26.57 kcal/mol to the formation of products.

The reaction rate theories had similar results, as shown in the Figure 4.56.

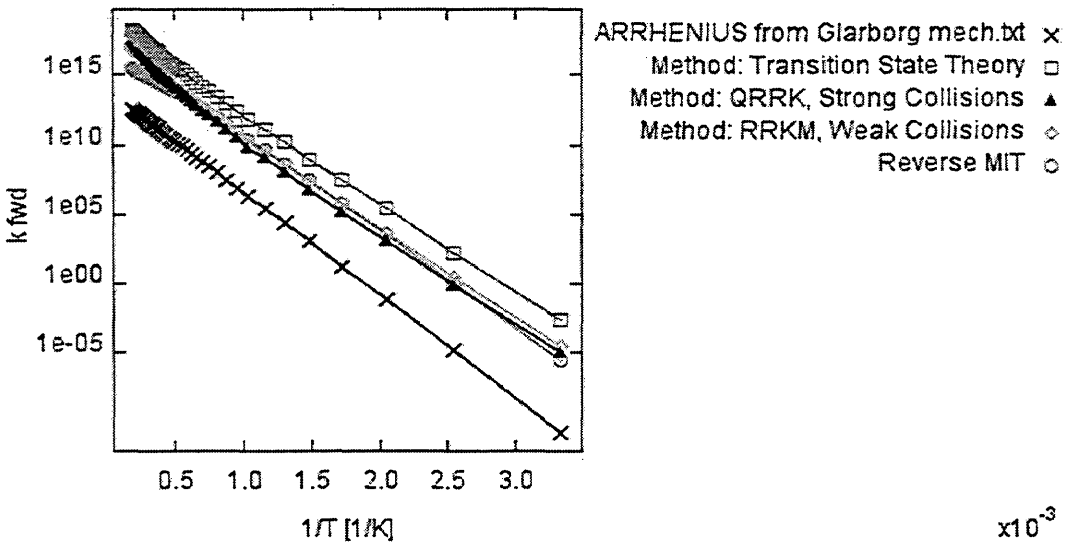


Figure 4.31 Calculated CH2CHCO=CO+C2H3. The three theories at which rates were calculated, and the expressions from the Glarborg and MIT mechanism.

Both calculations done at RRKM and the QRRK theory agree closely with the reverse of the MIT mechanism, so the MIT is the rate recommended by this calculation.

Benzene oxygen addition reaction

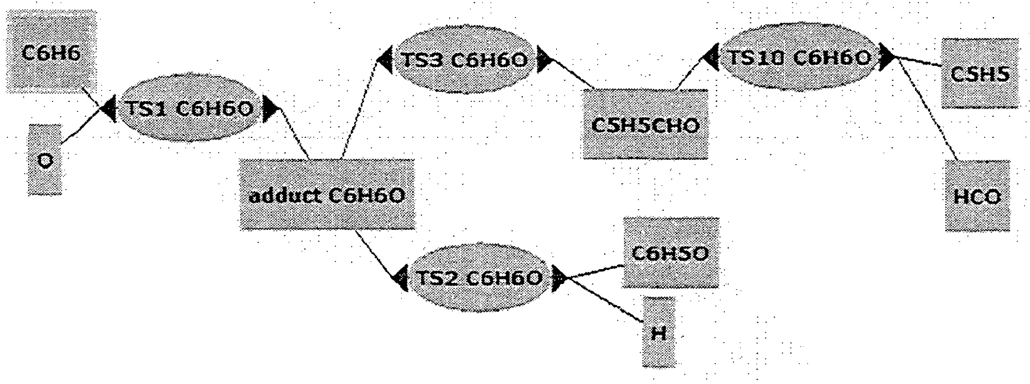
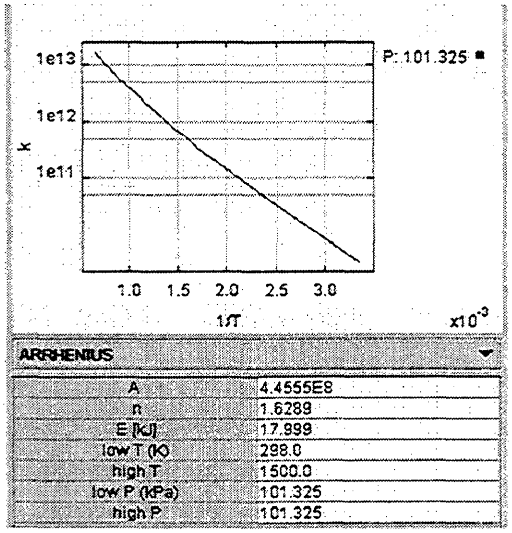


Figure 4.32: Benzene+O Reaction Path. A subset of the reaction surface.

Both mechanisms had an expression for the formation of phenoxy and hydrogen, so a comparison to the existing rate constant could be made.

The RRKM calculation was done with a path degeneracy of 12 (corresponding to the six top and six bottom possible pathways for the addition of oxygen to benzene), using weak collisions at a pressure of 1 atm in molecular nitrogen. The Lennard-Jones parameters of the adduct (206 K, 4.48 A°) and C_5H_5CHO (196 K, 4.46 A°) were estimated from polarization approximations of Cambi et al[55].

The resulting formation of phenoxy and hydrogen gives rate constants similar to expressions found in both mechanisms.



A	4.4555E8
n	1.6289
E [KJ]	17.999
low T (K)	298.0
high T	1500.0
low P (kPa)	101.325
high P	101.325

Figure 4.33: Benzene+O Results to Phenoxy. Rate expression for formation of phenoxy plus hydrogen from oxygen plus benzene.

The calculation verified that the phenoxy channel was the dominant reaction, and provided support for the existing rate expression.

4.5 Result Comparison

In one experiment, data were taken for a Princton flow reactor with a stoichiometric feed mixture of benzene/oxygen[56]. Concentration data taken by gas chromatograph was optimized for monitoring phenol and benzene. CO and oxygen concentration was monitored using continuous fixed gas monitors.

The reactions added to the Glarborg mechanism are found in Appendix B. Along with the added reactions, the following reactions were modified from the Glarborg mechanism.

Table 4.5: Reactions Modified. Modified from the Alzueta et al mechanism.

C2H+O2=2CO+H
C2H+OH=C2H2+O
C2H2+M=C2H+H+M
C2H3+CO=CH2CHCO
C2H4+HO2=CH3HCO+OH
C5H4O+H=C5H4OH
C6H5+H=BENZYNE+H2
C6H5OH+H=C6H6+OH
CH+CH2=C2H2+H
CH2+CO2=CH2O+CO
CH2CHCH3+O=C2H5+HCO
CH3+C2H2=H3CCCH+H
2CH3=C2H5+H
CH3OH+H=CH3O+H2
CH3OH+OH=CH3O+H2O

Modeling the flow reactor as a plug flow reactor, the concentration profiles of all the species is shown in figure 4.34.

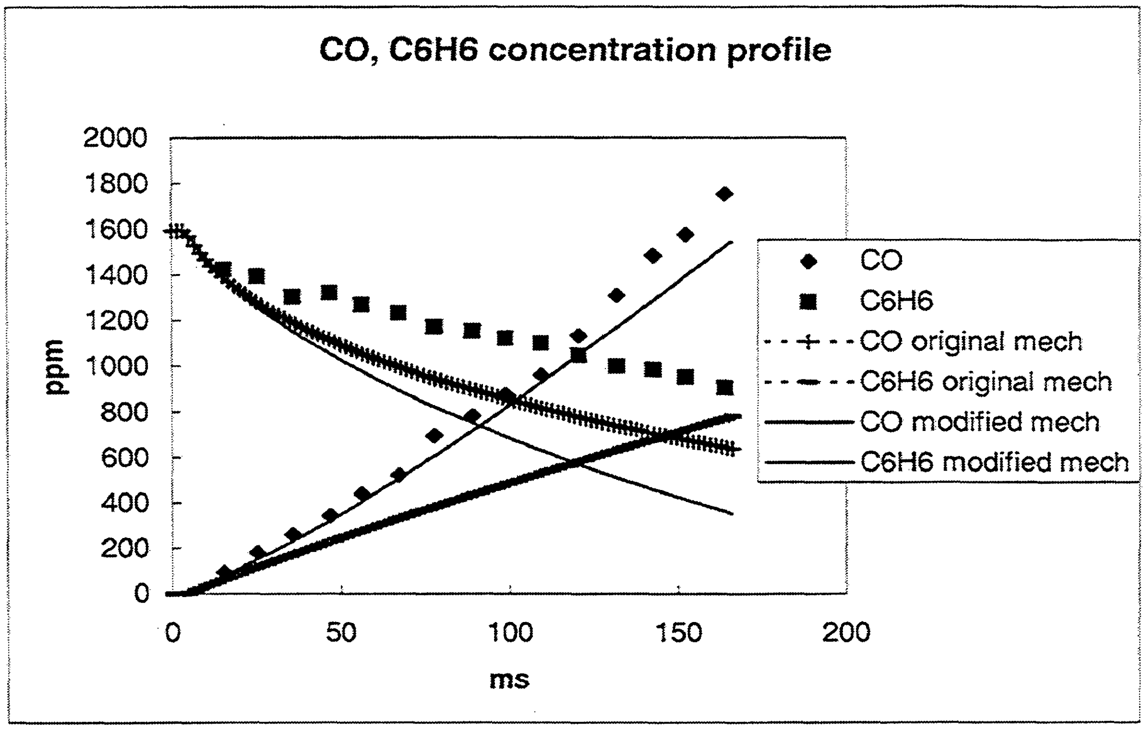


Figure 4.34: CO, C6H6 Profiles. Concentration profile for plug flow reactor compared to experimental results, using the unmodified mechanism, and the modified one.

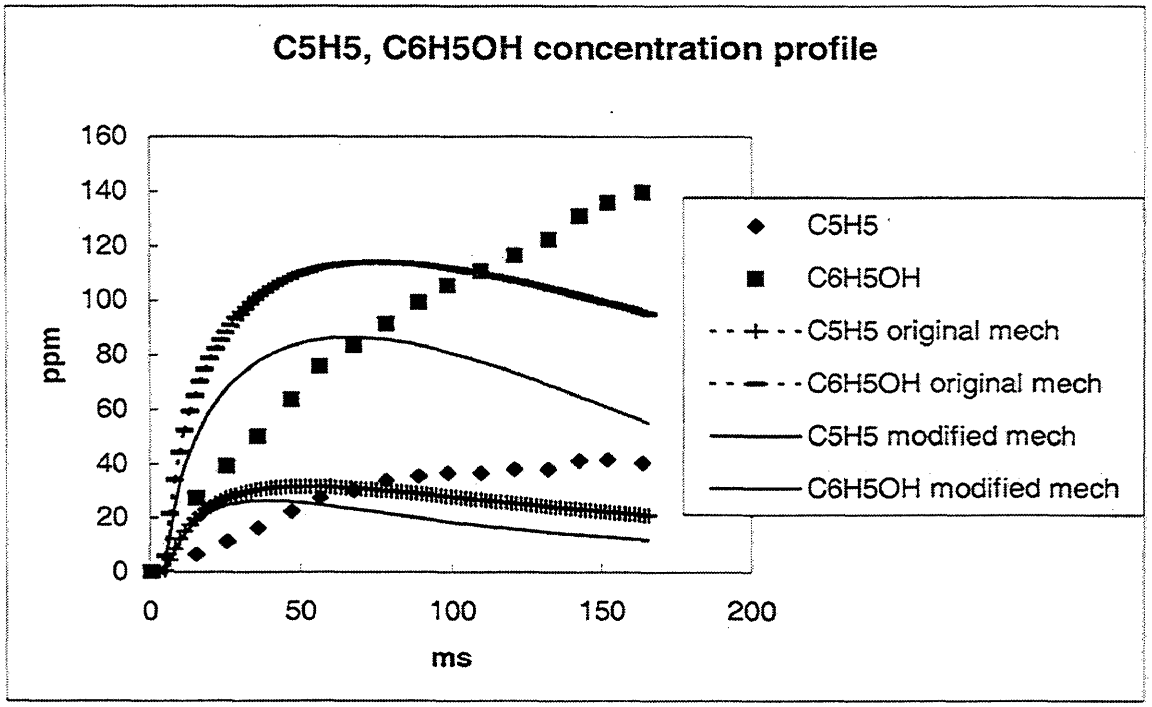


Figure 4.35: C5H5, C6H5OH Profiles. Concentration profiles of cyclopentyl radical and phenol compared to experimental results, for the original and the modified mechanism.

The profile of the carbon monoxide is the only species that is well predicted by this model. An increase on the CO profile has accompanied a decrease in the profile concentrations of the C6H6, C6H5OH, and C5H5 species. This mechanism is still unsatisfactory, because the input benzene concentrations were modeled so poorly. The matching of output carbon monoxide seems to be a direct outcome of consuming more benzene. This indicates that the basis of the carbon monoxide formation is flawed. There should be a stronger formation of carbon monoxide, accompanied with a slight decrease in benzene concentrations.

A sensitivity analysis done on the modified mechanism reveals which reactions have a likely impact on raising the concentration profiles of the underpredicted species. A sensitivity analysis will return a number that indicates how changing a single reaction will affect the magnitude of the concentration of one species.

Table 4.6: Reactions Sensitive to Change
O+OH=O2+H
C6H5O=C5H5+CO
C6H5O+H=C6H5OH
C5H5+HO2=C5H5O+OH
C5H5+H=C5H6
OH+HO2=H2O+O2
C5H4O+OH=C5H3O+H2O
C5H4O+O=CH2CHCCH+CO2
H+HO2=H2+O2
C6H6+OH=C6H5+H2O
H2CCCH+O2=CH2CO+HCO
C6H5OH+O2=C6H5O+HO2
CH2CHC.H2+HO2=CH2CHCHO+H+OH
O+HO2=O2+OH
H2CCCH+H(+M)=H3CCCH(+M)
H2CCCH+H(+M)=H2CCCH2(+M)
CH2CHCHCO+O=CH2HCO+HCCO
C5H5+O2=CH2CHCHCO+HCO
CH2O+OH=HCO+H2O
C6H5OH+H=C6H6+OH
CH2CHC.H2+H=CH2CHCH3
C6H5OH+O=C6H5O+OH
CH2O+O=HCO+OH
C2H2+O=HCCO+H

4.6 Flame experiment comparison

A comparison of the Bittner[57] phi=1.8 benzene/oxygen/30%argon flame was performed with Premix flame code found in the Chemkin Suite.

Many reactive species were well represented by profiles generated by the mechanism. In the following figures, the y-axis is mass fraction, and the x-axis is distance in cm from the burner.

The species that were more than an order of magnitude off of experimental include:

C5H3

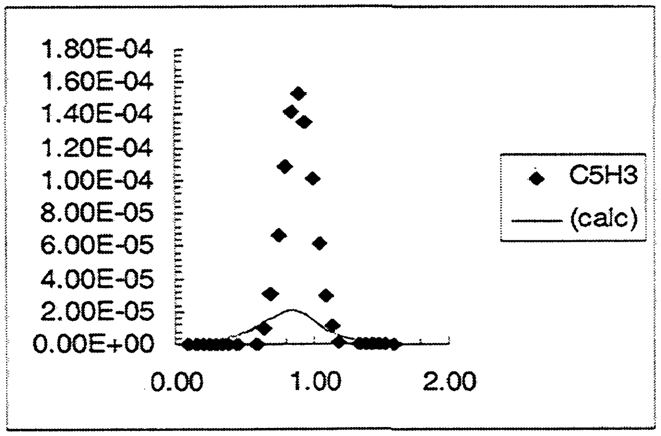


Figure 4.36: C5H3 Profile in Flame. Plotted with experimental measurements.

This pentargyl radical would be likely to display the same resonance stabilization found in the propargyl radical. A high level calculation for determining enthalpy of formation would be useful.

C7H6

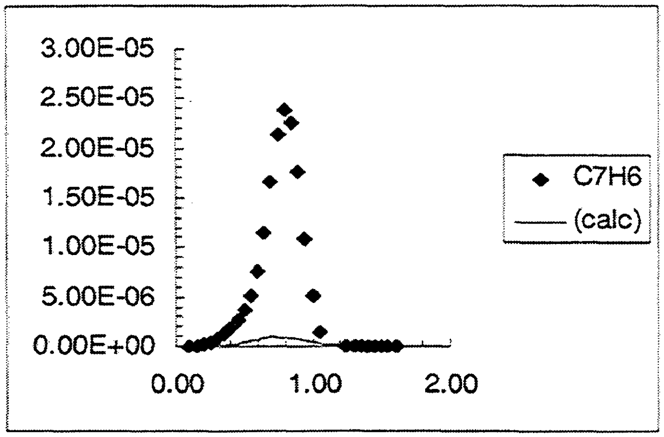


Figure 4.37: C7H6 Profile. An underpredicted concentration profile of the C7H6 radical.

The addition of 5-ethenylidene-1,3 cyclopentadiene to the mechanism from the addition of vinyl radical to cyclopentadiene has not been studied.

C9H8

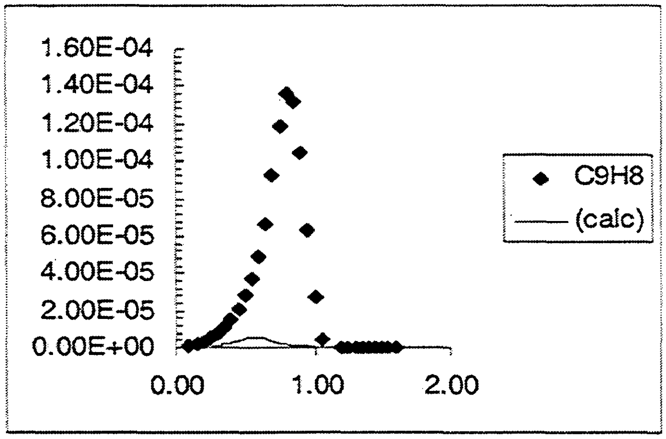


Figure 4.38: C9H8 profile. Comparison of indene concentration to measured shows a large discrepancy.

Propynyl benzene, C_9H_8, is absent from this mechanism, but may prove to be an important precursor to higher molecular weight species. Propynyl benzene is absent from this mechanism.

C10H6

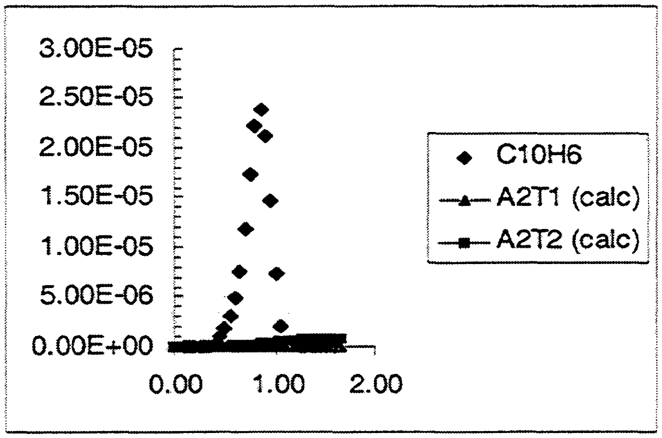


Figure 4.39: C10H6 Profile. Comparison of 1,2-dehydronapthalene and 2,3-dehydronaphtalene concentration profiles.

The 3 ortho, meta, para diethynylbenzene species were not included in this mechanism. Diethynylbenzene also may prove to be an important precursor to high molecular weight species, but it is not included in this mechanism.

C16H10

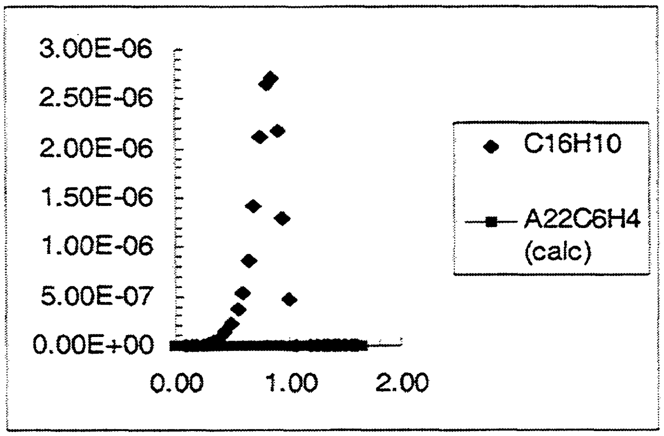


Figure 4.40: C16H10 Profile. Concentration profile calculated for Fluoranthene. Pyrene is not included in this mechanism.

The following species were absent from both mechanisms.

C6H6O2

The high measured concentration of this molecular weight species tends to indicate that there may be a concerted transition state from benzene plus oxygen to 1,2-benzenediol, resorcinol, or hydroquinone. The exact structure of this compound was not measured in the experiment, only the mass is known.

C8H2

This linear species is not represented in the mechanism.

C13H10

(fluorene, benz-indene, and phenalene) and C14H8(diethylnaphthalene, and 9,10-dehydrophenaline) were not in this mechanism.

C14H8

Diethylnaphthalene, and 9,10-dehydrophenaline are not in this mechanism.

The addition of these stable species may provide reasonable agreement with the experimental measurements.

4.7 Benzene reaction path analysis

To analyze the mechanism further, the rate of production of the major species in the reaction was calculated for a plug flow reactor. From this data, figure 4.41 was created, using the arrow thickness as an approximation to the magnitude of the formation channel.

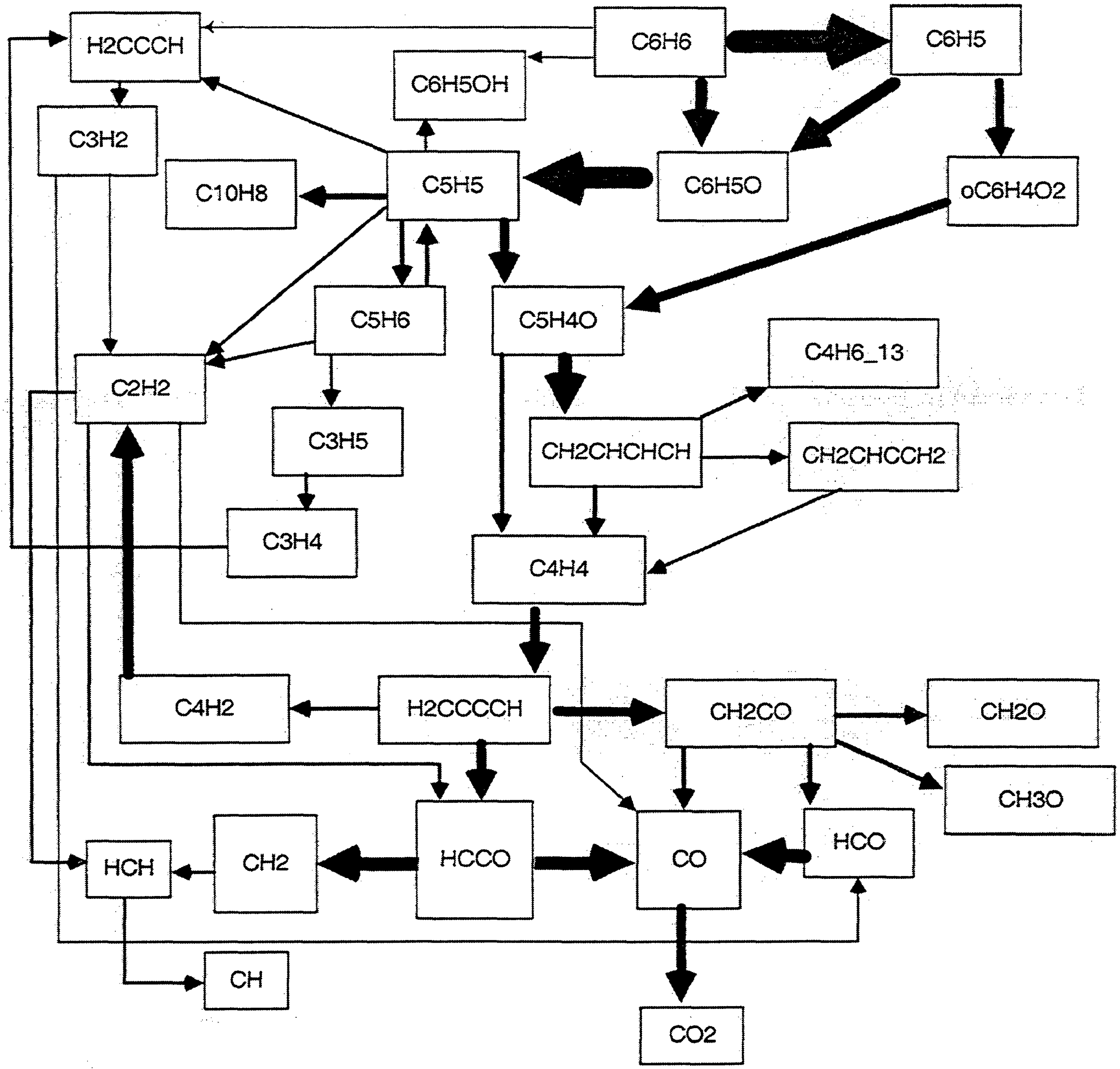


Figure 4.41: Benzene Reaction Pathway Analysis. The major species involved, and the primary pathways taken by the reacting carbon. This is not complete, but it shows the major consumption pathways as predicted by the MIT mechanism.

The use of pathway analysis tells us what the pathways to the formation of species are important, in one graph. With the creation of this pathway analysis, we can see that the C5H4O species seems to be an important pathway toward the decomposition, and the C5H5 radical seems to be an important part of molecular growth.

CHAPTER 5
CONCLUSIONS

The OpenChem workbench has shown that it is a valuable tool in the management of chemical kinetic mechanisms. There is currently no software tool with the functionality offered by the OpenChem Workbench.

The open source nature of the Workbench encourages individuals to extend the functionality to whatever application the programmer needs.

The benzene combustion mechanism has been modified in an attempt to correctly match experimental measurements in a plug flow reactor, and a low-pressure flame. The changes have been documented, but there are still many reactions to add to a mechanism that is getting very large. The plug flow reactor modeling indicates that the mechanism may be flawed, because the consumption of benzene predicted by the mechanism is unusually large. The next step in mechanism analysis would be to attempt to shrink the mechanism before adding the absent and underpredicted species.

The functionality of the workbench greatly enhanced the analysis of the complex benzene mechanism, and provided a quick way to determine which reactions and species are important and sensitive to change.

5.1 Further work

The following species should be added to the mechanism: 1,2-benzenediol, resorcinol, hydroquinone, 5-ethenylidene-1,2 cyclopentadiene, linear HCCCCCCCCH, propynyl benzene, diethynylbenzene, fluorene, benz-indene, phenalene, diethylnaphthalene, 9,10-dehydrophenaline, and pyrene.

The molecular builder currently has no molecular mechanics minimization algorithm. This would be useful in creating estimates for molecular structure that could be used as input to Gaussian or some other high level calculation. The TINKER program was investigated as to its applicability, but because of a lack of parameters describing the force constants between bond length, bond angles, and dihedrals, and an inability to estimate these unknown parameters, this module was not implemented in the release. The existing minimization algorithm is not a chemically rigorous treatment, and implements an inefficient (but free) minimization method.

Additions to the reaction rate estimation include extending the functionality so that parameters for pressure dependent equations like TROE, SRI and Lindemann can be calculated. Currently only modified Arrhenius parameters are calculated. This would require a nonlinear minimization, and verification that the calculated parameters are numerically stable over the region of interest. Additionally, the tunneling correction for rate parameters should also be included in the rate constant estimation algorithm. Quantum mechanical tunneling is the phenomenon that a molecule has a non-negligible probability of being where it does not have enough energy to be. So a molecule could react without having enough energy to cross the barrier. Hence reaction rates are occasionally raised by significant amounts when tunneling is taken into account.

With regards to the Gaussian interface, there are two items that should be implemented. One is that a method for estimating transport properties from polarizability should be included. The second problem is the preprocessor to Gaussian should be put into the Workbench, so that a user can create input files for Gaussian directly. This is a more difficult problem because of the complexity inherent in the formation of Gaussian input files stemming from the variety of abilities available in the Gaussian package. Also, in the Gaussian post-Processor, there is the ability to estimate heat of formation from atomization, this should be generalized to the use of isodesmic reactions as well.

OCWB GLOSSARY

The information in this glossary is taken from the OpenChem Workbench help document glossary. This can be found in the distribution at http://sourceforge.net/projects/openchemwb/

default molecule property

For some molecule properties which have multiplicity (e.g., names) one is considered by the system to be the default. Note the default is user-selectable.

equilibrium product set

The set of all molecules that are allowed to form in an equilibrium calculation.

fundamental property

(of a molecule) These are properties any of which will differentiate two molecules.

- molecular formula
- connectivity
- cis/trans (cis | trans | mixed | other)
- charge
- spin multiplicity
- natural abundance (true | false)

(of a reaction) These are properties any of which will differentiate two reactions.

- reactant molecules
- product molecules

- stoichiometric coefficients

group

A polyvalent atom (ligancy >=2) in a molecule, together with all its ligands (Benson, 1976).

molecule

A chemical species defined by its fundamental properties and including other properties and references.

molecule set

A collection of molecules.

molecular weight

Molecular weight of a molecule is always calculated from the user-supplied atomic weights unless the natural abundance flag is set, in which case the atomic weights in the database are used.

natural abundance flag

A flag on a molecule indicating that all the atomic weights of the molecule are assumed to be given by natural abundance. See molecular weight.

pressure-dependent or "third body" reactions

Reactions for which the rate constant depends explicitly on the pressure or equivalently the concentration of "M", the "third body". Unimolecular decomposition reactions of this type are often called "fall-off" reactions. Bimolecular reactions of this type are often called "chemically activated".

primary name

(of a molecule) See specifier.

pseudo-frequency cp fit

A thermodynamic fit of gas phase heat capacity for a molecule, assuming that translational and external rotation modes are fully activated. The vibrational modes are approximated by three frequencies, and three mode degeneracies.

rate constant

A parameter that, when multiplied by the driving force, determines the rate of disappearance of the reactants. The rate constant is a function of temperature and (sometimes) pressure. The functional form is usually modified Arrhenius (k = A T^n exp(-Ea/RT)), however more complicated expressions are used for pressure-dependent reactions (see www.ReactionXML.org for details). The driving force is typically the product of the reactant concentrations raised to the power of their stoichiometric coefficients.

ratio of reaction rate constants

The average of the ratios of reaction rates calculated from two different rate constants at three temperatures. If a ratio is less than unity, it is defined as the reciprocal of itself. So, a ratio of reaction rate constants will be always larger or equal to unity. The temperatures are starting temperature, ending temperature and middle temperature of the overlap of the valid temperature range of the two reaction rate constants.

reaction

Defined by a group of reactant molecules, a group of product molecules, and their respective stoichiometric coefficients. Often expressed in the form:

aA + bB + ... <-> qQ + rR + ...

The reaction is typically stoichiometrically balanced, but in special cases, unbalanced reactions will be allowed if the "balanced" stoichiometric flag is set to false (e.g., MW growth reactions where tracking hydrogen is not useful or desired).

reaction mechanism

a set of reactions plus: Rate parameters,Specified thermo set, Valid temperature range, Valid Pressure range. See www.ReactionXML.org for a full definition of required and optional properties for mechanisms.

reaction rate

An equation describing the rate at which a chemical reaction occurs in units of mol vol^-1 time^-1.

reaction set

A collection of reactions.

reverse rate constant

Rate constant describing the rate at which products form reactants.

stream

A combination of temperature, pressure, flow rate, and molar composition of molecular species present.

specifier

For a molecule, a unique name for the molecule in the database.

thermfit

A polynomial thermodynamic fit; i.e., thermodynamic data for a molecule. A molecule may have no or many thermfits.

thermset

A collection of thermfits. Each thermfit corresponds to a unique molecule, so that a molecule is represented only once within a thermodynamic set.

APPENDIX A
CALCULATION METHOD

A.1 Thermodynamics

The fundamental properties of matter include mass, volume, energy, and the quantum energy states incurred by the surrounding potential energy surface. From these fundamentals, all other properties are derived.

From the quantum energy states, the partition function (defined in equation A.1) is obtained, and from the canonical partition function entropy (equation A.2) is calculated. Temperature and pressure consequently become derived quantities, rather than the concrete fundamental properties we are accustomed to.

To obtain the heat capacity and entropy for a molecule, we must have an expression for the quantum energy states that occur as a consequence of the potential energy surface. From which, we can obtain the partition function q[58].

$$q = \sum_{i=0}^{\infty} d_i e^{E_i / k_B T} \qquad \text{A.1}$$

Where d_i is the degeneracy of quantum states at Energy level i (ε_i) and k_B is Boltzmann's constant, and T is temperature. The reference energy for the partition function is taken to be the ground state energy plus the zero point energy. Zero point energy is the minimum energy inherent in all vibrations and internal rotations.

$$S = Nk_B + Nk_B \ln\left(\frac{q(V,T)}{N}\right) + Nk_B T \left(\frac{\partial \ln q}{\partial T}\right)_V \qquad \text{A.2}$$

$$E = Nk_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \qquad \text{A.3}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \qquad \text{A.4}$$

One expression is achieved by assuming that all possible modes of motion (translation, external rotation, internal rotation, vibrations, electronic, and atomic) are separable, meaning the population of one mode does not alter the potential surface of another. Atomic contributions are generally considered to be unity, because excited atomic states are so high in energy, they do not normally occur.

$$\begin{aligned} S &= R + R\ln\left(q(V,T)\right) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R\ln\left(q(V,T)e\right) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R\left(\ln(q_t q_e q_r q_v e) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right) \end{aligned} \qquad \text{A.5}$$

A.1.1 Vibration modes

Vibration modes can be modeled by a harmonic oscillator function[58], where the potential energy surface is a parabola. The number of frequencies of a molecule are dependent on the number of atoms, linearity, and number of internal rotors in a molecule. The number of modes is 3N-6 for nonlinear, and 3N-5 for linear, where N is the number of atoms. The number of vibrations is the number of modes minus the number of internal rotations.

The expression for the contribution of vibrations to the partition function is created from the Hamiltonian of a harmonic oscillation.

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + \frac{1}{2}kx^2 \qquad \text{A.6}$$

The energy eigenvalues of a harmonic oscillator are of the form:

$$E_n = (n + \tfrac{1}{2})\hbar\left(\frac{k}{m}\right)^{\frac{1}{2}} \qquad \text{A.7}$$

Assuming that the energy eigenvalues are closely spaced, approaching a continuous function, an approximation to the partition function is determined to be:

$$q_{v,K} = \frac{e^{-\Theta_{v,K}/2T}}{1 - e^{-\Theta_{v,K}/T}} \qquad \text{A.8}$$

$$\Theta_v = \left(\frac{k}{m}\right)^{\frac{1}{2}} \qquad \text{A.9}$$

Since the zero point energy contribution is usually treated separately, the partition function is usually written as

$$q_{v,K} = \frac{1}{1 - e^{-\Theta_{v,K}/T}} \qquad \text{A.10}$$

The combination of all the vibration modes are multiplied together to obtain an overall contribution to the vibration partition function.

$$q_v = \prod_K \frac{1}{1 - e^{-\Theta_{v,K}/T}} \qquad \text{A.11}$$

Thermodynamic contributions from vibrations are expressed through the following equations

$$\begin{aligned}
S_v &= R\left(\ln(q_v) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right) \\
&= R\left(\ln(q_v) + T\left(\sum_K \frac{\Theta_{v,K}}{2T^2} + \sum_K \frac{(\Theta_{v,K}/T^2)e^{-\Theta_{v,K}/T}}{1 - e^{-\Theta_{v,K}/T}}\right)\right) \\
&= R\left(\sum_K \left(\frac{\Theta_{v,K}}{2T} + \ln(1 - e^{-\Theta_{v,K}/T})\right) + T\left(\sum_K \frac{\Theta_{v,K}}{2T^2} + \sum_K \frac{(\Theta_{v,K}/T^2)e^{-\Theta_{v,K}/T}}{1 - e^{-\Theta_{v,K}/T}}\right)\right) \\
&= R\left(\sum_K \ln(1 - e^{-\Theta_{v,K}/T}) + \left(\sum_K \frac{(\Theta_{v,K}/T)e^{-\Theta_{v,K}/T}}{1 - e^{-\Theta_{v,K}/T}}\right)\right) \\
&= R\sum_K \left(\frac{\Theta_{v,K}/T}{e^{\Theta_{v,K}/T} - 1} - \ln(1 - e^{-\Theta_{v,K}/T})\right)
\end{aligned}$$

$$E_v = R\sum_K \Theta_{v,K}\left(\frac{1}{2} + \frac{1}{e^{\Theta_{v,K}/T} - 1}\right) \qquad \text{A.13}$$

$$C_v = R\sum_{K} e^{\Theta_{v,K}/T}\left(\frac{\Theta_{v,K}/T}{e^{-\Theta_{v,K}/T}-1}\right)^2 \qquad \text{A.14}$$

A.1.2 External rotation

There are generally three different cases of increasing complexity when considering rotational kinematics; the one-dimensional free rotor, the rigid rotor, and an oblate or prolate spheroid.

A.1.2.1 One-dimensional free rotor

The free rotor[59] is a spin in a single dimension, without any potential energy hindering that spin. To evaluate a simple system like a one-dimensional free rotor, the Hamiltonian would be:

$$H = \frac{p^2}{2I} \qquad \text{A.15}$$

I is the moment of inertia, and p is the momentum in the θ direction.

For a one-dimensional free rotor, the classical partition function becomes:

$$Q = \frac{1}{h^n}\int\ldots\int d\bar{p}d\bar{q}e^{-\frac{H}{k_BT}} = \frac{1}{\sigma}\sqrt{\frac{\pi k_bT}{B}} \qquad \text{A.16}$$

Where σ is the symmetry number, and B is the rotational constant defined by:

$$B = \frac{h^2}{8\pi^2 I} \qquad \text{A.17}$$

From the partition function, the classical density of states is derived from the inverse Laplace transform relationship. For a one-dimensional free rotor, the density of states is:

$$\rho(E) = \mathcal{L}^{-1}\left\{Q\left(\frac{1}{k_BT}\right)\right\} = \frac{1}{\Gamma(1/2)\sigma}\sqrt{\frac{\pi}{BE}} \qquad \text{A.18}$$

This is the classical approximation, which holds for higher temperatures. Quantum mechanical formulation of the density of states begins again from the Hamiltonian. In polar coordinates, the Hamiltonian is of the form:

$$H = -\frac{\hbar^2}{2I}\frac{\partial^2}{\partial\theta^2} \qquad \text{A.19}$$

Solutions to this wave equation are sine and cosine functions. The boundary conditions are: finite over all θ, and single valued for $0<\theta<2\pi$. Energy eigenvalues for the free rotor are:

$$E_K = \frac{\hbar^2}{2I}K^2 \qquad \text{A.20}$$

where K is an integer. The degeneracy for a one-dimensional free rotor is 2, corresponding to a clockwise and a counter-clockwise spin.

A.1.2.2 Rigid rotor

The rigid rotor[59] has two identical moments of inertia, and the third moment of inertia is zero. An example would be a simple diatomic like hydrogen, because there is one axis passing through both atoms, around which there is no spinning, but two dimensions perpendicular to the first axis both have an identical moment of inertia

Finding the classical approximation to the partition function is similar to the method for the free rotor. From the Hamiltonian for a linear molecule, the partition function is found to be:

$$Q = \frac{1}{\sigma}\frac{k_B T}{B} \qquad \text{A.21}$$

From this expression, the thermodynamic contributions of a rigid rotor are:

$$\begin{aligned} S_r &= R\left(\ln q_r + T\left(\frac{\partial \ln q_r}{\partial T}\right)_V\right) \\ &= R(\ln q_r + 1). \end{aligned} \qquad \text{A.22}$$

$$E_r = RT^2\left(\frac{\partial \ln q_r}{\partial T}\right)_V$$
$$= RT^2\left(\frac{1}{T}\right)$$
$$= RT \qquad \text{A.23}$$
$$C_r = \left(\frac{\partial E_r}{\partial T}\right)_V$$
$$= R. \qquad \text{A.24}$$

Another way of counting the rotational contribution to the density of states is by calculating the quantum energy levels for each rotation, and adding them in with the SR algorithm, outlined in A.2.2.

In polar coordinates, the Hamiltonian for the rigid rotor is:

$$H = -\frac{\hbar^2}{2I}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \qquad \text{A.25}$$

Solutions to the wave equation for the rigid rotor are associated Legendre functions, and the energy eigenvalues for this system are:

$$E_J = J(J+1)\frac{\hbar^2}{2I} \qquad \text{A.26}$$

The degeneracy of states at the energy level corresponding to a quantum number J is 2J+1. This degeneracy is the result of the integer quantum number M, representing the z component of the angular momentum, lying anywhere between –J and J.

A.1.2.3 Oblate or prolate spheroid

The partition function for some number (u) of one-dimensional free rotors and some number (p) of two-dimensional rigid rotors is the product over all the degrees of freedom:

$$Q = \pi^{u/2}(k_b T)^{p+u/2}\prod_{i=1}^{u}\frac{1}{\sigma\sqrt{B_i}}\prod_{j=1}^{p}\frac{1}{\sigma B_j}. \qquad \text{A.27}$$

For an oblate or prolate spheroid, u and p are both one, and the resulting thermodynamic contributions are:

$$\begin{aligned} S_r &= R\left(\ln q_r + T\left(\frac{\partial \ln q_r}{\partial T}\right)_V\right) \\ &= R(\ln q_r + \frac{3}{2}). \end{aligned} \tag{A.28}$$

$$\begin{aligned} E_r &= RT^2\left(\frac{\partial \ln q_r}{\partial T}\right)_V \\ &= RT^2\left(\frac{3}{2T}\right) \\ &= \frac{3}{2}RT \end{aligned} \tag{A.29}$$

$$\begin{aligned} C_r &= \left(\frac{\partial E_r}{\partial T}\right)_V \\ &= \frac{3}{2}R. \end{aligned} \tag{A.30}$$

Taking the Laplace transform of the partition function for the unspecified number of rotors, the density of states is found to be

$$\rho(E) = \frac{\pi^{u/2} E^{p+u/2-1}}{\Gamma(p+u/2)} \prod_{i=1}^{u} \frac{1}{\sigma\sqrt{B_i}} \prod_{j=1}^{p} \frac{1}{\sigma B_j} \tag{A.31}$$

A.1.3 Internal Rotation

Internal rotors occur when two bonded groups counter rotate about a bond. The classic example is the two methyl groups spinning around the carbon-carbon bond of ethane. Unlike free rotation, there is a potential present due to the interactions of the atoms that are not on the rotation axis. This potential function can be expressed by a sum of cosines.

$$\text{P.E.} = V_0 + \sum_n \frac{V_n}{2}(1-\cos(n\theta)) \tag{A.32}$$

Separating an internal rotational mode from other modes is an incomplete solution when off-diagonal "Coriolis coupling" terms occur in the rotational kinematics matrix[60]. For the majority of cases, the coupling of external and internal modes can be neglected [61].

Determining the moment of inertia of the separable internal rotation mode is complicated when the bond of rotation does not coincide with the center of mass of the molecule (e.g. CH2Cl-CH2Cl). An approximation to the moment of inertia of the internal rotor is done by determining the axis connecting the centers of mass of the two rotating groups, and calculating the reduced moment from the respective moments about the center of mass axis.

Several solutions have been presented for the approximation of internal rotation modes, which were first presented by Pitzer, Knyazev, Truhlar, and McClurg-Flagan-Goddard.

A.1.3.1 Pitzer, Knyazev, Truhlar, and McClurg-Flagan-Goddard

Pitzer's solution assumes that the wave equation is of a Fourier series form, and solves for the energy eigenvalues. The resulting energy levels are used to calculate the partition function.

Knyazev assumes a continuous function on the density of states, and solves for a single parameter V_n in the potential energy equation.

$$P.E. = \frac{1}{2} V_n (1 - \cos n\phi) \qquad \text{A.33}$$

There was no analytic solution for a complex barrier with more than one parameter. This approximation of a single parameter has been shown to cause more error than the assumption of internal rotation as a separable mode.[61]

$$Q_{rot} = \frac{1}{\sigma_{pew}} \left(\frac{\pi k_b T}{B} \right)^{1/2} exp\left(\frac{-V_o}{2k_B T} \right) I_o \left(\frac{V_0}{2k_B T} \right) \qquad \text{A.34}$$

Both Truhlar and McClurg-Flagan-Goddard approaches the partition function approximation by a factor multiplying the partition function of the equivalent vibration mode.

Tuhlar[62] uses the approximations:

$$
\begin{aligned}
&Q^{hr} \approx Q^{ho}_{quant} f_m \\
&f_m = \tanh(Q^{fr}_{class} u_m) \\
&u_m = \frac{\hbar\omega_m}{kT}
\end{aligned}
\qquad \text{A.35}
$$

McClurg-Flagan-Goddard[63] uses the approximations:

$$
\begin{aligned}
&Q^{hr} \approx f\, Q^{ho} \\
&f = P \exp[\Delta E^{zp} / kT] \\
&\Delta E^{zp} = \frac{\hbar\omega}{2+16r} \\
&P = \left(\frac{\pi r}{\Theta}\right)^{1/2} \exp\left[\frac{-r}{2\Theta}\right] I_0\left(\frac{r}{2\Theta}\right)
\end{aligned}
\qquad \text{A.36}
$$

$$
\omega = n\sqrt{\frac{V_n}{2I_m}} \quad r = \frac{V_n}{\hbar\omega} \qquad \text{A.37}
$$

Applying these theories to a series of simple rotors, the root mean squared error and the error standard deviation were calculated for entropy and heat capacity. The comparison of these methods was performed by comparing calculated properties with values derived from NASA polynomial thermodynamic fits, taken from the Sandia thermodynamic database.

Using parameters made at B3LYP/6-31G*, from a temperature range of 300 to 1000 K, using classical approximations to the contribution modes, with no frequency scaling factor, ignoring electronic contributions, the following errors were found:

Table A.1: Entropy RMS Error B3LYP/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	4.5430	6.2067	5.8503	2.0402	14.7327
1-2 dichloroethane	18.2149	12.1990	18.5319	13.9680	46.3076
1,2,3 trichloroethane	6.4514	8.0559	7.6007	4.1897	16.8761
Chloroethane	3.5074	4.7430	4.8361	1.2121	15.1694
Propene	5.8741	6.7963	6.8574	4.2544	19.7072
Acetaldehyde	5.9361	5.1206	5.2135	4.4831	20.8615
Methanol	6.8695	7.1327	6.9440	4.2521	15.0423
Ethanedial	4.0602	3.6563	4.7793	2.6819	21.2310
Formic Acid	7.4244	9.0074		4.5351	
Hydrogen Peroxide	4.7122	9.3563	5.2495	1.7377	13.3371

Table A.2 Entropy Standard Deviation of Error B3LYP/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	1.9160	2.4639	2.0876	1.5994	7.8479
1-2 dichloroethane	1.1445	0.8322	2.2601	2.4338	1.3068
1,2,3 trichloroethane	0.4934	1.0310	1.2194	1.3057	5.2718
Chloroethane	1.3317	1.1487	1.0570	0.4541	3.1797
Propene	0.2012	0.5748	0.5501	0.9117	3.7546
Acetaldehyde	0.1343	1.1963	1.2437	0.5825	2.9234
Methanol	0.6340	0.3821	0.2349	1.2371	3.7342
Ethanedial	0.6693	1.2194	0.2834	0.2268	3.8978
Formic Acid	0.4898	0.7239		1.0892	
Hydrogen Peroxide	0.3772	1.1531	0.2966	0.2210	4.1716

Table A.3 Heat Capacity RMS Error B3LYP/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	0.8892	0.9779	0.7373	0.3406	3.3374
1-2 dichloroethane	2.4411	2.3700	5.2422	5.5773	3.6285
1,2,3 trichloroethane	1.0768	2.2104	2.6705	3.0915	12.2810
Chloroethane	2.9011	2.8517	2.7929	1.1886	7.3542
Propene	0.9110	1.5149	1.5301		
Acetaldehyde	0.6285	2.7976	2.8954	1.3358	6.9454
Methanol	1.6886	1.0703	1.1226	3.3190	8.9389
Ethanedial	1.4120	3.5373	0.9535	0.8443	9.6117
Formic Acid	1.1558	2.7121		2.6617	
Hydrogen Peroxide	0.8722	2.6806	0.8310	1.1653	10.2486

Table A.4 Heat Capacity Standard Deviation of Error B3LYP/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	0.8255	0.7607	1.1553	1.7096	0.6485
1-2 dichloroethane	0.8118	2.0190	1.2699	0.9734	1.4069
1,2,3 trichloroethane	0.2955	0.7348	0.7674	1.3173	1.5768
Chloroethane	0.7148	0.6799	1.1791	0.8146	0.6058
Propene	0.9315	0.4791	0.7326		
Acetaldehyde	0.5440	0.3527	0.3772	0.6389	0.8382
Methanol	0.5543	0.5700	1.0978	1.8298	0.9953
Ethanedial	0.7148	2.0006	1.0127	0.7912	0.5489
Formic Acid	0.0843	1.9203		2.1714	
Hydrogen Peroxide	0.0678	0.2237	0.2424	1.2457	1.9771

For a complex molecule like 1-2 Dichloroethane, the barrier height is a more complex function than a simple sinusoid.

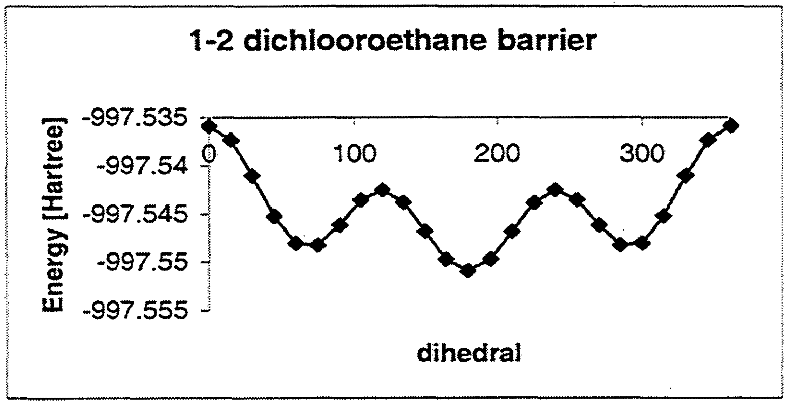


Figure A.1 Dichloroethane Internal Rotation Potential Surface.

The error from modeling this molecule as an internal rotor is shown in the following plot.

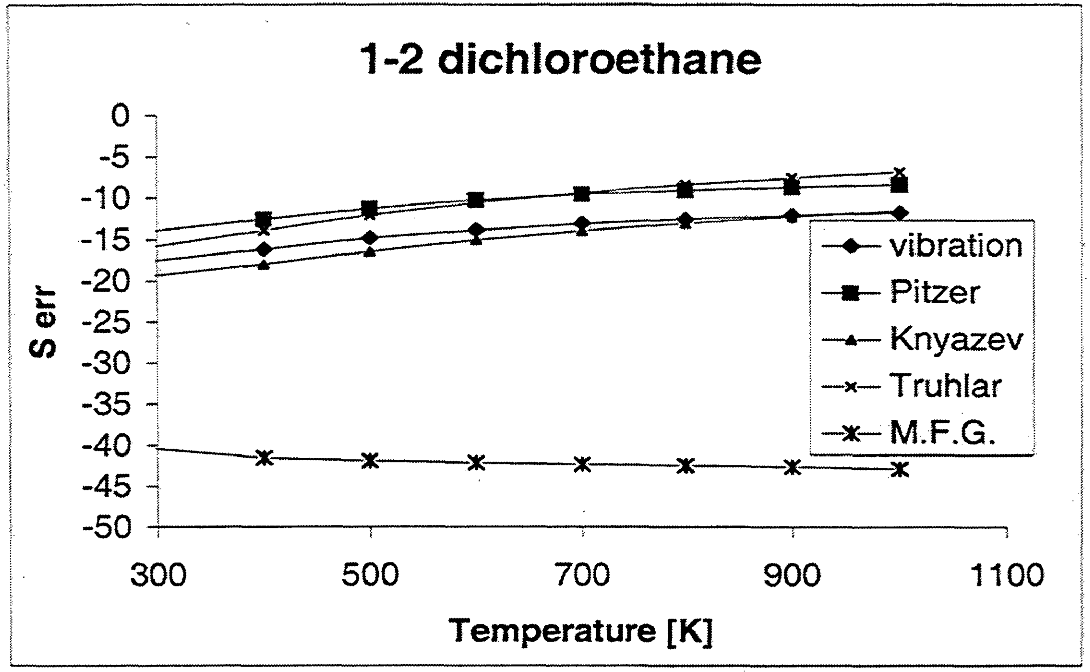


Figure A.2: CH2ClCH2Cl Entropy Error. Error between calculated and experimental entropy for dichloroethane.

McClurg-Flagan-Goddard (M.F.G.) tends to be the worst approximation, and Pitzer seems to be roughly equal to treating the internal rotation as a vibration.

For ethanedial, the barrier to rotation is another complex one

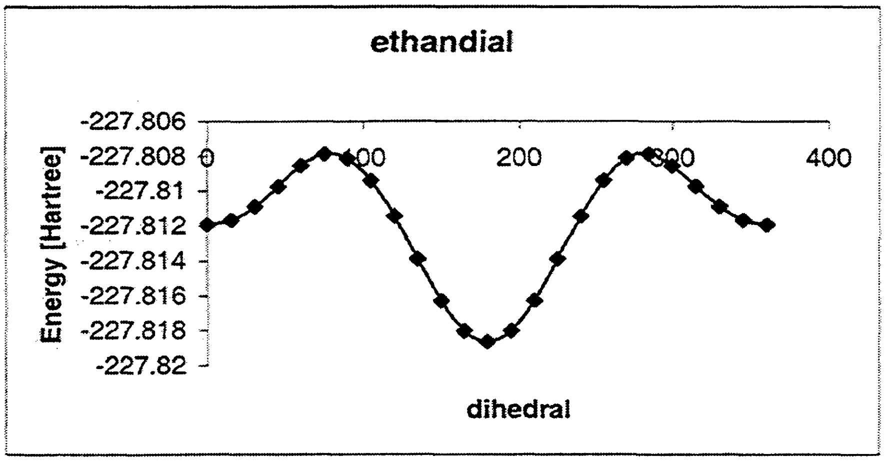


Figure A.3: Ethanedial Internal Rotor Ppotential Surface.

And the thermodynamic errors are similar.

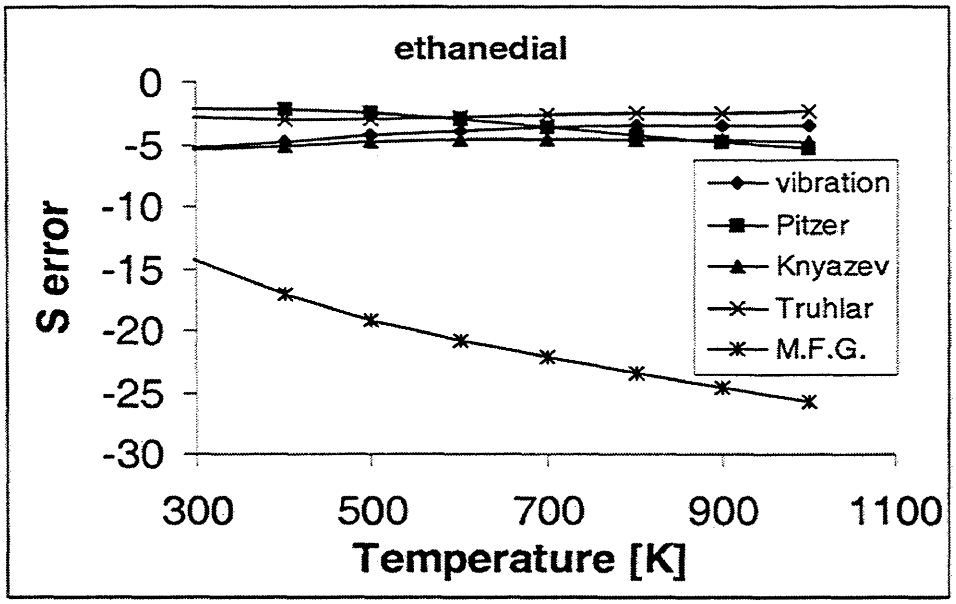


Figure A.4: CHOCHO Entropy Error. Errors between calculated and experimental entropy for ethanedial.

Using parameters made at MP3FC/6-31G*, from a temperature range of 300 to 1000 K, using classical approximations to the contribution modes, with no frequency scaling factor, ignoring electronic contributions, the following errors were found:

Table A.5 Entropy RMS Error MP3FC/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	4.5430	6.2067	5.8503	2.0402	14.7327
1-2 dichloroethane	14.0820	8.2919	14.8795	10.5304	41.7336
1,2,3 trichloroethane	1.1627	2.4606	2.0398	1.4982	10.8429
Chloroethane	2.0453	2.5071	2.5155	2.0748	11.7752
Propene	5.3780	6.0735	6.2159	3.7324	19.4195
Acetaldehyde	5.6514	4.5794	4.6618	4.1565	20.7077
Methanol	6.2069	6.6406	6.4174	3.5366	14.2709
Ethanedial	3.4921	3.2392	4.1075	2.0892	20.1887
Formic Acid	7.5666	8.5807		4.6524	
Hydrogen Peroxide	5.2015	9.5793	5.8409	2.2385	14.2943

Table A.6: Entropy Standard Deviation of Error MP3FC/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	0.8892	0.9779	0.7373	0.3406	3.3374
1-2 dichloroethane	2.0681	0.3588	2.9958	3.2602	0.6011
1,2,3 trichloroethane	0.4154	0.1771	0.3395	0.4543	4.3131
Chloroethane	2.1101	1.8229	1.6802	1.2491	2.4964
Propene	0.4240	1.1090	1.1362	0.4309	3.1521
Acetaldehyde	0.3165	1.6643	1.7077	0.1656	2.4213
Methanol	0.3158	0.6648	0.4762	0.9138	3.4377
Ethanedial	0.7560	1.1186	0.3948	0.2301	3.8015
Formic Acid	0.5437	0.4820		1.0750	
Hydrogen Peroxide	0.3572	1.1517	0.3256	0.1988	4.2717

Table A.7Heat Capacity RMS Error MP3FC/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	1.9160	2.4639	2.0876	1.5994	7.8479
1-2 dichloroethane	4.4941	1.5790	6.8860	7.4171	2.2786
1,2,3 trichloroethane	1.0718	0.7125	0.7776	1.9200	10.3681
Chloroethane	4.6831	4.3251	4.1211	2.8987	5.8245
Propene	1.0195	2.7910	2.8787	0.9536	7.3095
Acetaldehyde	0.6986	3.8934	3.9831	0.7764	5.7946
Methanol	0.8909	1.7969	1.6976	2.5948	8.2066
Ethanedial	1.6053	3.4508	1.0906	0.7410	9.3984
Formic Acid	1.2967	2.2637		2.6359	
Hydrogen Peroxide	0.8285	2.6774	0.8676	1.0204	10.3910

Table A.8 Heat Capacity Standard Deviation of Error MP3FC/6-31G*

Species	vibration	Pitzer	Knyazev	Truhlar	McClurg
Ethane	0.8255	0.7607	1.1553	1.7096	0.6485
1-2 dichloroethane	1.1186	1.5244	1.3999	1.1342	1.5457
1,2,3 trichloroethane	0.5035	0.7253	0.3442	1.8969	2.1641
Chloroethane	0.8599	0.4914	1.0329	1.0472	0.4181
Propene	0.6840	0.6652	0.8853	0.4848	1.0754
Acetaldehyde	0.4543	0.3988	0.4083	0.8293	0.8921
Methanol	0.3584	0.8137	1.3764	1.6986	0.8136
Ethanedial	0.7634	2.1971	1.0969	0.6235	0.5770
Formic Acid	0.1285	1.8958		2.1403	
Hydrogen Peroxide	0.0779	0.2249	0.2219	1.0898	1.8036

The error can be attributed to an incorrect barrier height, and a neglect of the electronic contribution. All methods gave similar errors, and the time for calculations are relatively similar, but the Pitzer method is the only one to allow an expression for the barrier height of greater complexity than a sinusoidal potential. That is the reason it was implemented in the OpenChem Workbench.

The error tables support the approximation of an internal rotor as a harmonic oscillator. The reason for not treating the internal rotor as a vibration is because at high temperatures, the internal rotor contributes R/2 to the heat capacity, but a vibration contributes a factor of R. If the model approximates the vibration, then the value for heat capacity is guaranteed to be off by R/2 as temperature increases.

A.1.4 Electronic

The electronic contribution is calculated by a sum of all excited electronic states[58]. A more rigorous expression would include their rotational contributions multiplying them, but this method is sufficient for most application. The electronic contribution to the partition function is:

$$g_e = \omega_0 e^{-\epsilon_0/k_B T} + \omega_1 e^{-\epsilon_1/k_B T} + \omega_2 e^{-\epsilon_2/k_B T} + \cdots \qquad \text{A.38}$$

The thermodynamic contributions are calculated through equations A.2-A.5.

Small molecules will have a non-negligible contribution to the heat capacity caused by electronic contributions, so ignoring this contribution can occasionally lead to significant errors. This occurs in small molecules because the contribution from electronic states is not dwarfed by the other modes in a molecule. The small magnitude of the heat capacity in small molecules means that a larger percentage of the heat capacity comes from the electronic energy levels, and the energy contribution cannot be glossed over, like is normally done with larger molecules.

Excited electronic energy levels are determined experimentally through optical spectroscopy. Calculation of estimates for these excited states can also be done in Gaussian.

A.1.5 Analysis of technique

The errors in heat capacity encountered by using the previous statistical mechanical methods were around 3% for the examples cited. This indicates that either the results are close to reality, or the errors in each mode are canceling. An individual analysis of each mode is not possible without an extensive statistical analysis.

A.1.6 Translation mode

Translational contributions to the partition function of a molecule are generally derived via the classical method[64], assuming that there are no interactions between particles. The Hamiltonian in radial coordinates is given as:

$$H = \frac{p_r^2 + p_\theta^2 + p_\phi^2}{2m} \qquad \text{A.39}$$

And the classical approximation to the partition function is determined by the following:

$$Q = \frac{1}{h^3} \iiint_V e^{\frac{-H}{kT}} dp_r dp_\theta dp_\phi dr\, r d\theta\ r \sin\theta d\phi \qquad \text{A.40}$$

This results in a translation contribution to partition function of

$$q_t = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V. \qquad \text{A.41}$$

$$\left(\frac{\partial \ln q_t}{\partial T}\right)_V = \frac{3}{2T} \qquad \text{A.42}$$

This leads to the following thermodynamic contributions:

$$\begin{aligned} S_t &= R\left(\ln(q_t e) + T\left(\frac{3}{2T}\right)\right) \\ &= R(\ln q_t + 1 + 3/2). \end{aligned} \qquad \text{A.43}$$

$$\begin{aligned} E_t &= N_A k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= RT^2\left(\frac{3}{2T}\right) \\ &= \frac{3}{2}RT \end{aligned} \qquad \text{A.44}$$

$$\begin{aligned} C_t &= \frac{\partial E_t}{\partial T} \\ &= \frac{3}{2}R. \end{aligned} \qquad \text{A.45}$$

During the implementation of the OpenChem Workbench, the low temperature spike in heat capacity caused by electronic contributions caused a problem with the statistical mechanical thermodynamic fitting method, so it was hypothesized that a negative temperature dependence of heat capacity was the result of a potential distribution in the translational component. What follows is the mathematics and results behind this conjecture.

The generalized potential function for a Lennard-Jones type interaction is of the form:

$$\Phi = \frac{\beta}{r^\alpha} \qquad \text{A.46}$$

Adding this term to the Hamiltonian, and deriving the new partition function for translation, the result is:

$$Q^* = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{3}{\alpha} E_{\frac{3}{\alpha}+1}\left(\frac{\beta}{r_0^{\alpha} kT}\right) \qquad \text{A.47}$$

Where the function $E_{3/\alpha+1}$ is the exponential integral. The exponential integral converges rapidly[65] by using the continued fraction:

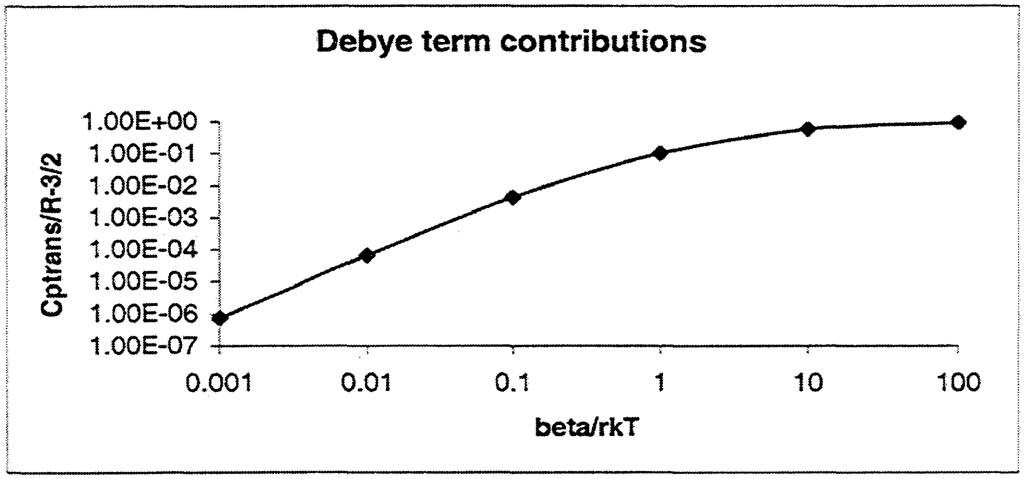
$$E_\nu(z)=\cfrac{e^{-z}}{z+\left(\cfrac{\nu}{1+\left(\cfrac{1}{z+\left(\cfrac{\nu+1}{1+\left(\cfrac{2}{z+(\ldots)}\right)}\right)}\right)}\right)}. \qquad \text{A.48}$$

For the simple case when α is 1, such as in Debye-Huckel type interactions, the heat capacity contribution is as follows:

$$c_{ptrans*}=\frac{3}{2}R+R\beta\left[\frac{\beta E_2\left(\frac{\beta}{r_0kT}\right)}{r_0^2k^2T^2E_4\left(\frac{\beta}{r_0kT}\right)}-\frac{\beta E_3\left(\frac{\beta}{r_0kT}\right)^2}{r_0^2k^2T^2E_4\left(\frac{\beta}{r_0kT}\right)^2}\right] \qquad \text{A.49}$$

Depending on the magnitude of the potential function, this causes a decrease in the partition function, and can cause the curvature of the partition function to decrease at lower temperature, subsequently causing a negative temperature dependence of the heat capacity with temperature.

When calculating this contribution, it turned out to be negligible over most values of the radial potential term beta.



The radial potential term beta had to be larger than 8E-5 eV before the term becomes non-negligable.

A.1.7 Statistical mechanical fitting technique

As a guide for fitting thermodynamics when only a few data points exist, a method of statistical mechanical fitting was employed. This method makes the following assumptions:

1. The electronic energy level is high, so that mode is inactive over the range of interest.
2. The external rotors are active, meaning they each contribute ½ R to the heat capacity.
3. The translations are active, indicating another ½ R for each dimension is added to the heat capacity.
4. The vibrations can be approximated by three frequencies. A high, low and middle frequency and their corresponding integer degeneracies will describe the vibrational contribution to heat capacity.

This statistical mechanical fitting is used for Group Additivity, when there are only 5 data points and a value of the infinite temperature heat capacity, and we must use those data points to create a 14+ parameter polynomial fit.

A.2 Reaction Kinetics

The estimation of the kinetic rate of a reaction is entirely dependent upon the Gibbs free energy surface it encounters in normal atomic motion. For gas phase, this term can be evaluated from the partition functions and the relative energies of the reaction species and the corresponding transition state, because as seen in section A.1, the thermodynamics is directly related to the partition function and relative ground state energy. The simplest definition of the transition state is the molecular configuration that minimizes the probability of species traveling along the reaction coordinate through the transition state. It is the molecular configuration at the maximum of the Gibbs energy surface connecting the reactants and products along the reaction coordinate.

There are three rate calculation methods of increasing complexity that can be easily calculated. They are Transition State Theory, Quantum Rice-Ramsperger-Kassel, and Rice-Ramsperger-Kassel-Marcus theories. The last two are restricted to unimolecular or chemically activated reactions, meaning they require a stable activated complex, or they cannot be used. The rate of stabilization of the activated complex can be estimated by strong collision or modified strong collision.

Because the Master equation[59] method does not evaluate the individual rate channels, and because there are multiple methods for the evaluation of the collisional energy transfer, this method was not implemented in the OpenChem Workbench.

A.2.1 Transition State Theory

In Transition State Theory[66], the rate constant is determined by the ratio of the transition state partition functions to the reactant partition functions.

$$A + B \xleftrightarrow{\ddagger} C + D$$

$$k = \frac{k_B T}{h} K^{\ddagger} \qquad \text{A.50}$$

$$K^{\ddagger} = \frac{q^{\ddagger}}{q_A q_B} e^{\frac{-E_o}{k_B T}}$$

The partition functions are evaluated as given in section A.1. The term E_o is the relative difference of the ground state of the transition state relative to the ground state of the stable reactants. Although the partition functions can be expressed including this energy difference, the exponential term is written explicitly here.

The partition function of the transition state is evaluated the same as for a stable species, except that one mode (the reaction coordinate) is neglected.

A.2.2 Quantum Rice-Ramspurger-Kassel

Multi-well unimolecular and chemically activated reactions, like the one shown in figure A.5, are not modeled well by transition state theory, because there is no explicit consideration for collisional stabilization.

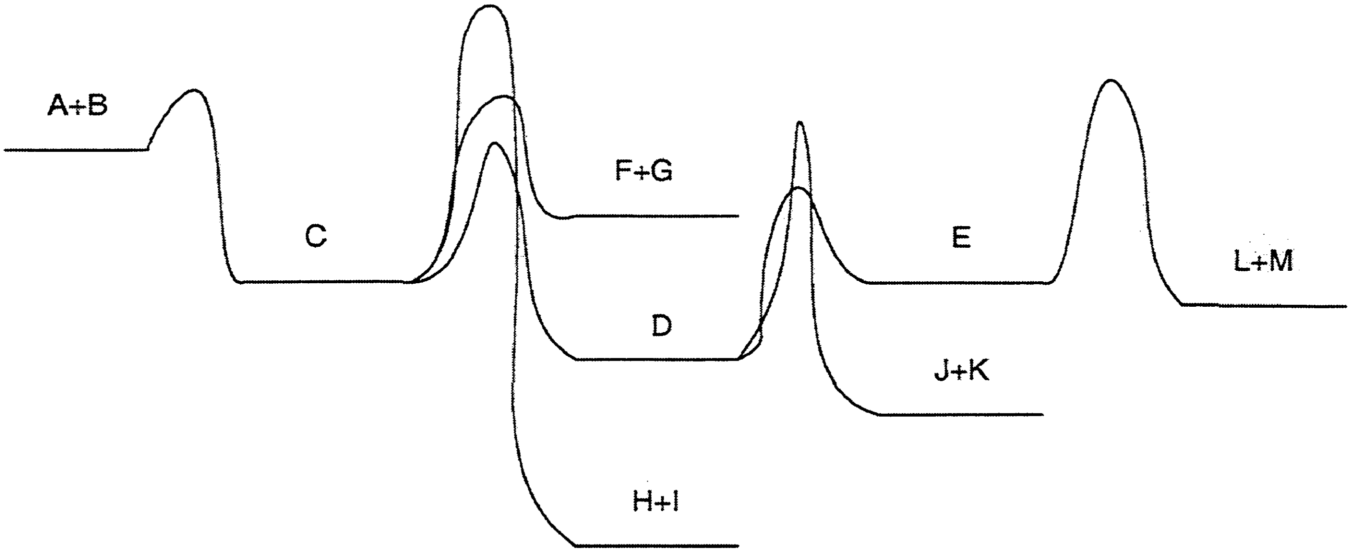


Figure A.5: Illustration of a multi-well reaction.

Quantum Rice-Ramspurger-Kassel[67] method assumes that there are s identical oscillators in a reacting molecule, with a total of n quanta, with one oscillator containing m quanta. The variable s is equal to the number of modes in a molecule, 3N-6 for nonlinear, and 3N-5 for linear, where N is the number of atoms in the molecule.

The rate of reaction of an excited species at a specified energy spacing is expressed as

$$k_a(nh\nu) = k^{\ddagger}\frac{n!(n-m+s-1)!}{(n-m)!(n+s-1)!} \quad \text{A.51}$$

And the fraction of elements with energy above n is given as:

$$f^* = \alpha^n (1-\alpha)^s \frac{(n+s-1)!}{n!(s-1)!} \quad \text{A.52}$$

$$\alpha = e^{\frac{-h\nu}{k_B T}}$$

In the Workbench implementation, the reaction rate $k^{\ddagger}$ is calculated from transition state theory, using a geometric mean frequency for the s oscillators. The frequencies are required input for the calculation.

A.2.2 Rice-Ramsperger-Kassel-Marcus

RRKM[68] is an extension of the RRK theory implemented in QRRK, and evaluates the microcanonical rate constant with increased rigor. RRKM theory requires a more detailed expansion of the density of states of a molecule. Density of states is the number of quantum states that occur within some energy granularity.

The energy eigenvalues of the contributing modes (including vibration, internal rotation, and the external moment of inertia coupling with internal rotors) are evaluated from the equations given in section A.1.3. The convolution of energy modes is achieved by using the Stein-Rabinovich algorithm[69], outlined in figure A.5.

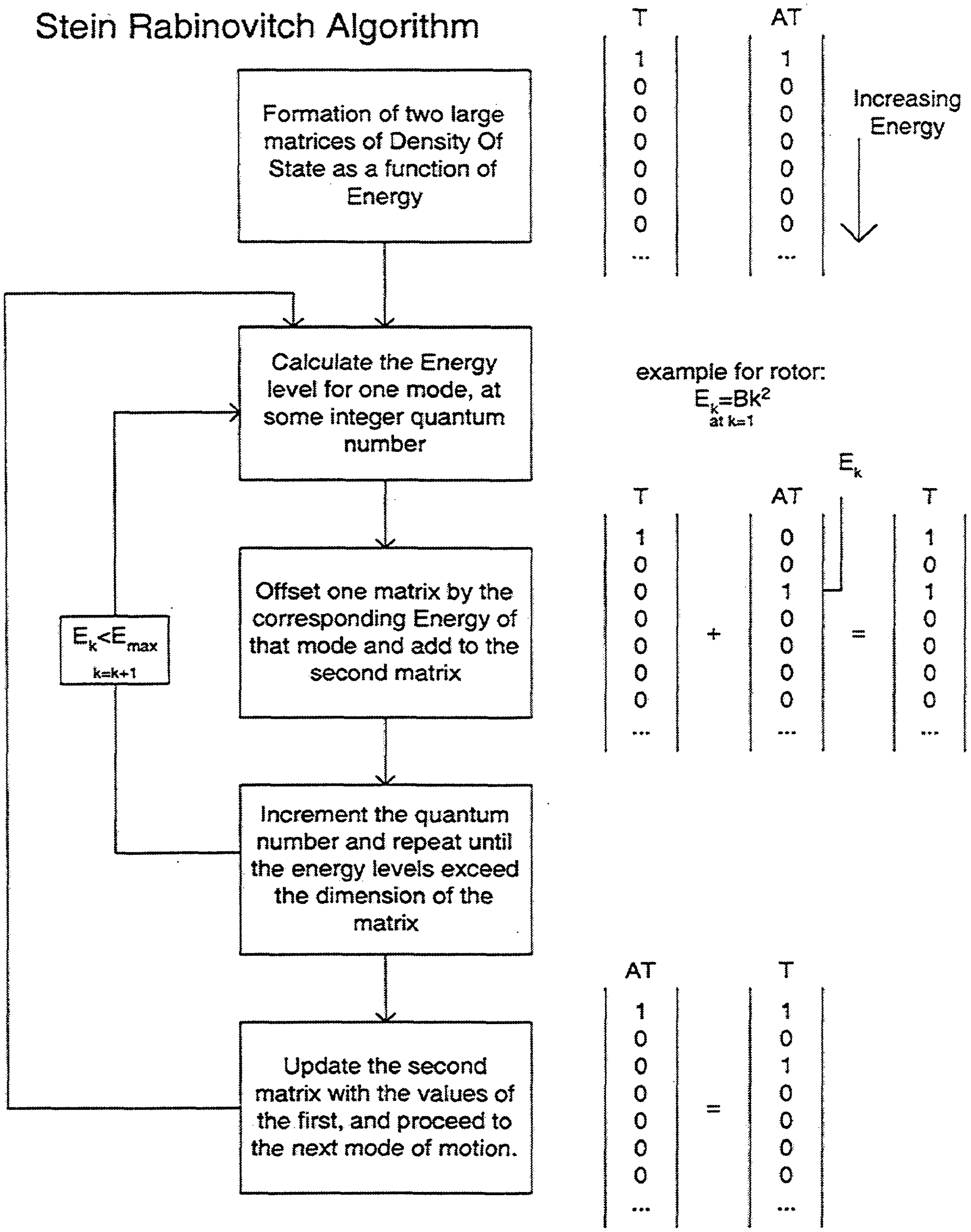


Figure A.5: SR Algorithm. The algorithm formulated by Stein-Rabinovich for convoluting energy eigenvalues from different modes.

The RRKM reaction rate is evaluated by using the following reaction rate expression

$$k_a(E) = L^{\ddagger} \frac{Q_r^{\ddagger}}{Q_r^{A}} \frac{W^{\ddagger}(E)}{h\rho(E)} \qquad \text{A.53}$$

Where r is the density of states of the unimolecular species, $W^{\ddagger}$ is the sum of states of the transition state, $L^{\ddagger}$ is the reaction path degeneracy, and $Q^{\ddagger}_r$ is the external rotation partition function contribution, inserted because of conservation of momentum.

The fraction of elements with energy above a given value is:

$$f^* = \frac{\rho(\varepsilon^*) e^{\frac{-\varepsilon}{k_B T}} d\varepsilon}{\int_0^{\infty} \rho(\varepsilon^*) e^{\frac{-\varepsilon}{k_B T}} d\varepsilon} \qquad \text{A.54}$$

A.2.4 Strong collision

Strong collision assumes that every collision will deactivate an excited species. From the characteristic properties of the bath gas, and the reactant molecule, the collision frequency can be found from the general expression:

$\omega = \theta v[M]$

Where θ is the collisional cross section, v is the average velocity calculated from equation A.57, and [M] is the concentration of the bath gas. The collisional cross section can be estimated from Lennard Jones diameter of the reactant and the bath gas σ_{A-M}, and the collision integral Λ, which is approximated with the empirical equation[59]:

$$\Lambda = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{e^{0.77327T^*}} + \frac{2.16178}{e^{2.4378877T^*}} \qquad \text{A.55}$$

$$T^* = k_b T/\varepsilon_{A-M} \qquad \text{A.56}$$

Where ε_{A-M} is the geometric mean Lennard Jones well depth of the reactant and bath gas.

Average velocity is calculated from the relationship:

$$v = \sqrt{\frac{8k_bT}{\pi\mu_{A-M}}} \qquad \text{A.57}$$

Where $\mu_{A\text{-}M}$ is the reduced mass of the two interacting particles. Determining the collisional frequency can now be found with the equation:

$$\omega = \sigma_{A-M}{}^2 \sqrt{\frac{8k_bT}{\pi\mu_{A-M}}} \Lambda_{A-M}[M] \qquad \text{A.58}$$

A.2.5 Weak Collision

Weak collision is an approximation that brings us closer to reality. In reality a collision can energize, or de-energize some reaction species by an amount that may or may not be enough to rise above the barrier to reaction. The weak collision uses an empirical expression to describe this behavior.

Troe[70] derived the relation between the collision factor to the average energy lost per collision (<E>) to the following equations:

$$\frac{\beta}{1-\sqrt{\beta}} = \frac{-<E>}{F_e k_b T} \qquad \text{A.59}$$

$$\beta \approx \left(\frac{<E_{down}>}{<E_{down}> + F_e k_b T} \right)^2 \qquad \text{A.60}$$

Where F_e is the function:

$$F_e = \frac{\int_{E_o}^{\infty} \rho(E) e^{-E/k_bT} dE}{\rho(E_o) e^{-E_o/k_bT} k_bT} \qquad \text{A.61}$$

Because larger molecules and higher temperatures were not represented well by this equation, Gilbert[71] made a modification to the derived equation, resulting in a final equation of:

$$\beta \approx \frac{\left(\frac{<E_{down}>}{<E_{down}>+F_e k_b T}\right)^2}{\int_0^{E_o} \rho(E)\, e^{-E/k_b T}\left(1-\frac{F_e}{1-F_e} e^{E_o - E/F_e}\right) dE} \qquad \text{A.62}$$

APPENDIX B

ADDED REACTIONS

The Following reactions were added to the Glarborg mechanism to create a more comprehensive in temperature mechanism. Reactions modified from the Glarborg mechanism are listed in table 4.5.

H2+O2=OH+OH	1.7E13	0.0	47780.0	! [Miller and Melius 1992]
2H+H2=2H2	9.2E16	-0.6	0.0	! [Miller and Melius 1992]
2H+CO2=H2+CO2	5.49E20	-2.0	0.0	! [Miller and Melius 1992]
O+OH+M=HO2+M	1.0E17	0.0	0.0	! [Zhang and McKinnon 1995]
HO2 peroxyl reactions				
H2O2+O=O2+H2O	9550000.0	2.0	3970.0	! [Emdee et al. 1992]
HCO (aldehyde) reactions				
HCO+O2=CO2+OH	3.31E12	-0.4	0.0	! [Baulch et al. 1992]
HCO+HO2=CO2+OH+H	3.0E13	0.0	0.0	! [Zhang and McKinnon 1995]
HCO+CH3O=CH3OH+CO	9.04E13	0.0	0.0	! [Tsang and Hampson 1986]
2HCO=CH2O+CO	4.52E13	0.0	0.0	! [Baggott 1986]
2HCO=2CO+H2	3.01E12	0.0	0.0	! [Zhang and McKinnon 1995]
CO, CO2 reactions				
CH+H2=CH3	3.19E25	-4.99	2710.0	! [QRRK-HR, 20 torr]
CH+O=C+OH	1.52E13	0.0	4732.0	! [Murrel and Rodriguez 1986]
CH+O2=CO+OH	3.3E13	0.0	0.0	! [Baulch et al. 1992]
CH+H2O=CH2OH	5.71E12	0.0	-755.0	! [Zabarnick et al. 1986]
CH2+O=H2+CO	7.83E12	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+O2=CO2+2H	7.83E12	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+O2=O+CH2O	7.83E12	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+O2=H2+CO2	7.83E12	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+HO2=CH2O+OH	3.01E13	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+H2O2=CH3O+OH	3.01E13	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+HCO=CO+CH3	1.81E13	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+CH2O=HCO+CH3	1.2E12	0.0	0.0	! [Zhang and McKinnon 1995]
CH2+O=CH+OH	3.0E14	0.0	11923.0	! [Frank and Just 1984]
Triplet Methylene reactions				
HCH+O2=HCO+OH	4.3E10	0.0	-500.0	! [Miller and Melius 1992]
HCH+HCO=CH3+CO	1.81E13	0.0	0.0	! [Zhang and McKinnon 1995]
HCH+CH3O=CH3+CH2O	1.81E13	0.0	0.0	! [Zhang and McKinnon 1995]
CH3 methyl reactions				
CH3+M=HCH+H+M	2.72E36	-5.309	117084.0	! [Su and Teitelbaum '94, l.p. limit]
CH3+O=HCO+H2	1.26E13	0.0	0.0	! [Lim/Michael '93, Marcy et al. '01]
CH3+O=CH3O	1.78E14	-2.14	603.0	! [Dean and Westmoreland 1987]
CH3+OH=CH2O+H2	3.98E10	-0.02	8765.0	! [Dean and Westmoreland 1987]

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CH3+CH2OH=CH4+CH2O          2.41E12  0.0     0.0     ! [Tsang 1987]
CH3+CH3O=CH4+CH2O           2.41E13  0.0     0.0     ! [Tsang et al. 1986]
CH3+CH3=C2H4+H2             1.0E16   0.0     32030.0 ! [Warnatz 1984]
CH2OH+HO2=CH2O+H2O2         1.2E13   0.0     0.0     ! [Zhang and McKinnon 1995]
CH2OH+HCO=CH3OH+CO          1.2E14   0.0     0.0     ! [Zhang and McKinnon 1995]
CH2OH+CH2O=CH3OH+HCO        5540.0   2.81    5682.0  ! [Zhang and McKinnon 1995]
2CH2OH=CH3OH+CH2O           4.82E12  0.0     0.0     ! [Zhang and McKinnon 1995]
CH2OH+HCO=2CH2O             1.81E14  0.0     0.0     ! [Tsang 1987]
CH3O methoxy radical reactions[CH3O C2H5O-> alkoxy radicals]
CH3O+HO2=CH2O+H2O2          3.01E11  0.0     0.0     ! [Zhang and McKinnon 1995]
CH3O+CO=CH3+CO2             1.57E13  0.0     11797.0 ! [Zhang and McKinnon 1995]
CH3OH methanol reactions
CH3OH+M=CH3+OH+M            3.5E16   0.0     66444.0 ! [Zhang and McKinnon 1995]
CH3OH+M=CH2OH+H+M           1.75E15  0.0     66444.0 ! [Zhang and McKinnon 1995]
CH3OH+M=CH2+H2O+M           7.0E15   0.0     66444.0 ! [Zhang and McKinnon 1995]
CH3OH+CH3=CH2OH+CH4         31.9     3.17    7172.0  ! [Zhang and McKinnon 1995]
CH3OH+CH3=CH3O+CH4          14.5     3.1     6935.0  ! [Zhang and McKinnon 1995]
CH3OH+O=OH+CH3O             1.0E13   0.0     4684.0  ! [Warnatz 1984]
CH3OH+O2=CH2OH+HO2          2.05E13  0.0     44717.0 ! [Zhang and McKinnon 1995]
CH3OH+CH2OH=CH3OH+CH3O      7.83E9   0.0     12062.0 ! [Tsang 1987]
CH3OH+HCH=CH2OH+CH3         1.58E12  0.0     5736.0  ! [Zhang and McKinnon 1995]
CH4 Methane reactions
C2H+M=C2+H+M                4.68E16  0.0     124000.0 ! [Colket 1986]
C2H+O2=HCO+CO               2.41E12  0.0     0.0     ! [Zhang and McKinnon 1995]
C2H+OH=CH2+CO               1.81E13  0.0     0.0     ! [Tsang et al. 1986]
CH+HCH=C2H+2H               5.49E22  -2.41   11520.0 ! [Westmoreland 1986]
HCCO+H=HCCOH                1.85E39  -8.521  6430.0  ! [QRRK, HR, 20 torr]
HO2+C2H=HCCO+OH             1.81E13  0.0     0.0     ! [Tsang et al. 1986]
C2H+O2=HCCO+O               5.0E13   0.0     1500.0  ! [Baulch et al. 1992]
CH2CO+O=HCO+HCO             2.0E13   0.0     2293.0  ! [Zhang and McKinnon 1995]
CH2CO+O=CH2+CO2             1.75E12  0.0     1350.0  ! [Miller and Melius 1992]
CH2+CO=CH2CO                6.0E8    0.0     0.0     ! [QRRK, HR, 20 torr]
CH2CO+OH=CH2O+HCO           2.8E13   0.0     0.0     ! [Zhang and McKinnon 1995]
CH2CO+OH=CH3O+CO            2.8E13   0.0     0.0     ! [Baulch et al. 1992]
HCCOH+H=CH2CO+H             1.0E13   0.0     0.0     ! [Miller and Melius 1992]
C2H2 acetylene reactions
C2H2+O2=C2H+HO2             1.2E13   0.0     74475.0 ! [Zhang and McKinnon 1995]
C2H2+H=CH+CH2               1.02E16  0.0     125076.0 ! [Lee et al. 1993]
CH3OH+C2H=CH3O+C2H2         1.21E12  0.0     0.0     ! [Tsang 1987]
CH3OH+C2H=CH2OH+C2H2        6.03E12  0.0     0.0     ! [Tsang 1987]
HO2+C2H2=CH2CO+OH           6.03E9   0.0     7949.0  ! [Tsang et al. 1986]
HCO+C2H=C2H2+CO             6.03E13  0.0     0.0     ! [Tsang et al. 1986]
CH2+C2H2=HCH+C2H2           4.0E13   0.0     0.0     ! [Miller and Melius 1992]
CH2+CH2=C2H2+H2             3.01E13  0.0     0.0     ! [Zhang and McKinnon 1995]
CH3O+C2H=CH2O+C2H2          2.41E13  0.0     0.0     ! [Zhang and McKinnon 1995]
2HCH=C2H2+H2                4.02E14  -0.47   480.0   ! [Westmoreland 1986]
C2H+CH2OH=C2H2+CH2O         3.61E13  0.0     0.0     ! [Tsang 1987]
C2H+C2H=C2H2+C2             1.81E12  0.0     0.0     ! [Tsang et al. 1986]
C2H+CH2=CH+C2H2             1.81E13  0.0     0.0     ! [Tsang et al. 1986]
HCH+C2H=CH+C2H2             1.81E13  0.0     0.0     ! [Zhang and McKinnon 1995]
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C2H3 vinyl radical or ethenyl reactions
C2H3+O=C2H2+OH             3.0E13   0.0      0.0      ! [Baulch et al. 1992]
C2H3+O=CO+CH3              3.0E13   0.0      0.0      ! [Baulch et al. 1992]
CH+HCH=C2H3               3.09E14  -1.98    620.0     ! [Westmoreland 1986]
CH2+CH2=C2H3+H             2.0E13   0.0      0.0      ! [Frank and Just 1984]
2HCH=C2H3+H              7.12E21  -3.9    2460.0    ! [Westmoreland 1986]
CH2OH+C2H2=C2H3+CH2O         7.3E11    0.0     9004.0   ! [Tsang 1987]
C2H3+O=HCO+CH2              3.0E13   0.0      0.0      ! [Baulch et al. 1992]
C2H3+C2H=2C2H2             3.0E13   0.0      0.0      ! [Miller and Melius 1992]
C2H3+CH=HCH+C2H2             5.0E13   0.0      0.0      ! [Miller and Melius 1992]
C2H3+CH2=CH3+C2H2            1.81E13  0.0      0.0      ! [Tsang et al. 1986]
HCH+C2H3=CH3+C2H2            1.81E13  0.0      0.0      ! [Zhang and McKinnon 1995]
C2H4 ethylene reactions
2HCH=C2H4                1.11E20  -3.43    2070.0   ! [Westmoreland 1986]
CH3O+C2H3=CH2O+C2H4           2.41E13  0.0      0.0      ! [Zhang and McKinnon 1995]
C2H3+H2O2=C2H4+HO2           1.21E10  0.0     -596.0    ! [Tsang et al. 1986]
C2H3+CH2OH=C2H4+CH2O          3.01E13  0.0      0.0      ! [Tsang 1987]
C2H4+OH=CH3+CH2O             1.05E12  0.0     -916.0    ! [Zhang and McKinnon 1995]
C2H4+O2=C2H3+HO2            4.22E13  0.0     57594.0   ! [Zhang and McKinnon 1995]
HO2+C2H5=C2H4+H2O2            3.01E11  0.0      0.0      ! [Tsang et al. 1986]
HCH+CH3=C2H5              2.53E20  -3.49    2030.0   ! [Westmoreland 1986]
CH3+CH2=C2H5              1.11E19  -3.2     1780.0   ! [Westmoreland 1986]
C2H+C2H5=C2H2+C2H4            1.81E12  0.0      0.0      ! [Tsang et al. 1986]
C2H5+H=C2H4+H2             1.81E12  0.0      0.0      ! [Tsang and Hampson 1986]
2C2H4=C2H5+C2H3             4.82E14  0.0     71539.0   ! [Tsang et al. 1986]
C2H5+HO2=CH3+CH2O+OH          2.4E13   0.0      0.0      ! [Zhang and McKinnon 1995]
CH2+C2H5=C2H4+CH3            9.03E12  0.0      0.0      ! [Zhang and McKinnon 1995]
HCH+C2H5=CH3+C2H4            1.81E13  0.0      0.0      ! [Zhang and McKinnon 1995]
C2H6 ethane reactions
C2H4+C2H5=C2H3+C2H6          632.0    3.13     18010.0   ! [Tsang and Hampson 1986]
C2H3+C2H5=C2H6+C2H2          4.82E11  0.0      0.0      ! [Zhang and McKinnon 1995]
C2H2+C2H5=C2H6+C2H           2.71E11  0.0     23446.0   ! [Zhang and McKinnon 1995]
Dimethylether (CH3OCH3): Formation and Consumption
CH3+CH3O=CH3OCH3             1.21E13  0.0      0.0      ! [Tsang/Hampson '86]
CH3OCH3+H=CH3OCH2+H2          1.9E13   0.0     5166.0    ! [Faubel et al. '79]
CH3OCH3+OH=CH3OCH2+H2O         6.27E12  0.0      739.0    ! [Tully/Droege '87]
CH3OCH3+O=CH3OCH2+OH          5.0E13   0.0     4571.0    ! [Herron '88]
CH3OCH3+CH3=CH3OCH2+CH4        3.55E12  0.0     11800.0   ! [Batt et al. '82]
CH3OCH2=CH3+CH2O            1.6E13   0.0     25440.0   ! [Sehested et al. 1997]
Formation and Consumption of the Acetaldehyde Radical (CH2CHO)
CH+CH2O=CH2CHO             9.64E13  0.0     -517.0    ! [Baulch '92]
C3H6+O=CH2CHO+CH3            1080000.0 2.15    -795.0    ! [Tsang '91; Knyazev '92]
C4H8+O=CH2CHO+C2H5           5140000.0 1.95    -596.0    ! [Ko et al.'91/Koda et al.'91]
CH2CHO=CH2CO+H             1.58E13  0.0     34970.0   ! [Colket et al. '75]
CH2CHO=CH3CO              1.0E13   0.0     47100.0   ! [Colket et al. '75]
CH3CO Formation and Consumption
CH3CO+CH3=CH3COCH3           4.04E15  -0.8     0.0      ! [Tsang/Hampson '86]
CH3CO+CH3=CH2CO+CH4           6.06E14  -0.8     0.0      ! [Hassinen et al. '90]
IC3H7+HO2=CH3CHO+CH3+OH        2.41E13  0.0      0.0      ! [Tsang '88]
IC3H7+O=CH3CHO+CH3           4.82E13  0.0      0.0      ! [Tsang '88]
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IC3H7+O=CH3COCH3+H          4.82E13  0.0      0.0      ! [Tsang '88]
C2H5+O2=CH3CHO+OH           4.55E13  -1.03    9665.0   ! [Bozzelli/Dean '90, 0.01 atm]
C2H3+OH=CH3CHO              3.01E13  0.0      0.0      ! [Tsang/Hampson '86]
CH3CHO+CH3=CH3COCH3+H        1.66E10  0.0     12398.0  ! [Liu/Laidler '68]
C3H2 propynylidene reactions
C3H2+O=C2H+HCO              6.8E13   0.0      0.0      ! [Warnatz et al. 1982]
C3H2+OH=CHCHCHO             3.01E13  0.0      0.0      ! [Tsang/Hampson '86]
H2CCCH  reactions
H2CCCH=C3H2+H               5.2E12   0.0      78447.0  ! [Scherer et al. 2000]
H2CCCH+O=C3H2+OH            3.2E12   0.0      0.0      ! [Warnatz et al. 1982]
CH3+C2H=H2CCCH+H            2.41E13  0.0      0.0      ! [Tsang et al. 1986]
C2H+CH2OH=H2CCCH+OH          1.21E13  0.0      0.0      ! [Tsang 1987]
C2H+C2H5=CH3+H2CCCH          1.81E13  0.0      0.0      ! [Tsang et al. 1986]
C2H2+HCCO=H2CCCH+CO          1.1E11   0.0      3000.0   ! [Miller and Melius 1992]
CH2+C2H2=H2CCCH+H           8.48E25  -3.736   3774.0   ! [QRRK-HR, 20 torr]
HCH+C2H2=H2CCCH+H           1.2E13   0.0      6600.0   ! [Boehland et al. 1986]
H2CCCH+O=HCCCHO+H           6.03E13  0.0      0.0      ! [Tsang '91 for C3H5+O]
C3H2+O=HCCCHO               6.62E12  0.0      3060.0   ! [Aleksandrov et al. '80 for C3H4+O]
CHCHCHO+H=HCCCHO+H2          1.21E13  0.0      0.0      ! [Baulch et al. '92 for C2H3]
CHCHCHO+OH=HCCCHO+H2O         2.0E13   0.0      0.0      ! [Miller and Melius '92 for C2H3]
C2H+CH3CO=CH3+HCCCO          1.81E13  0.0      0.0      ! [Tsang/Hampson '86 for C2H3]
HCCCHO=C2H2+CO              8.51E14  0.0      70940.0  ! [Saito et al. '90]
HCCCHO+O=HCCCO+OH            5.68E12  0.0      1542.0   ! [Singleton et al. '77 for C2H5CHO]
HCCCHO+OH=HCCCO+H2O           1.6E13   0.0      0.0      ! [Maldotti et al. '92 for C2H3CHO+OH]
C2H+CO=HCCCO                1.51E11  0.0      4810.0   ! [Tsang/Hampson '86 for C2H3+CO]
2-propenal (acrolein): CH2CHCHO Formation and Consumption
H2CCCH+OH=CH2CHCHO           3.01E13  0.0      0.0      ! [Tsang/Hampson '86 for
C2H3+OH=CH3CHO]
HCO+C2H3=CH2CHCHO            1.81E13  0.0      0.0      ! [Tsang/Hampson '86]
C3H4+O=CH2CHCO+H            6.62E12  0.0      3060.0   ! [Aleksandrov et al. '80]
C2H3+CH3CO=CH3+CH2CHCO        1.81E13  0.0      0.0      ! [Tsang/Hampson '86]
CH2CHCHO+C2H5=CH2CHCO+C2H6   1.2E13   0.0      12647.0  !
[McAdam/Walker'87+Tsang/Hamp.'86 for C2H5CHO]
CH2CHCHO+IC3H7=CH2CHCO+C3H8  1.02E10  0.0      6840.0   ! [Szirovicza '85]
CH2CHCHO+H=CHCHCHO+H2         5.07E7   1.93     12951.0  ! [Knyazev et al. 1996a for C2H4]
CH2CHCHO+OH=CHCHCHO+H2O       2.02E13  0.0      5955.0   ! [Miller and Melius '92 for C2H4]
CH2CHCHO+CH3=CHCHCHO+CH4      4.16E12  0.0      11128.0  ! [Baulch '92 for C2H4]
CHCHCHO+H=CH2CHCHO            5.36E14  0.0      982.0    ! [Duran et al. '88 for C2H3]
CHCHCHO=C2H2+HCO             2.95E12  0.0      11110.0  ! [Cadman et al. '70 for
C2H5CO=C2H5+CO]
Propanal and its radical: C2H5CHO and C2H5CO
NC3H7+O=C2H5CHO+H            9.64E13  0.0      0.0      ! [Tsang '88]
NC3H7+O2=C2H5CHO+OH           1.1E8    0.0      0.0      ! [Baker et al. '71]
C3H5+OH=C2H5CHO              3.01E13  0.0      0.0      ! [C2H3+OH: Tsang/Hampson '86]
C2H5CHO+C2H5=C2H5CO+C2H6      1.2E13   0.0      12647.0  !
[McAdam/Walker'87+Tsang/Hamp.'86]
CH+C2H4=C3H4+H              1.75E15  -0.38    100.0    ! [QRRK-HR, 20 torr]
CH2+C2H2=C3H4CY              1.66E38  -8.65    6090.0   ! [QRRK-HR, 20 torr]
CH2+C2H2=C3H4               7.46E39  -8.78    6350.0   ! [QRRK-HR, 20 torr]
CH2+C2H2=C3H4P              2.62E40  -8.86    6410.0   ! [QRRK-HR, 20 torr]
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C3H4CY=C3H4                1.51E14  0.0      50400.0  ! [Karni et al. '88]
C3H4CY=C3H4P               7.08E13  0.0      43700.0  ! [Karni et al. '88]
C3H4+OH=HCO+C2H4           1.0E12   0.0      0.0      ! [Westbrook and Dryer 1984]
C3H4+CH3=H2CCCH+CH4        2.0E12   0.0      7700.0   ! [Kern et al. 1991]
C3H4P+CH3=H2CCCH+CH4       2.0E12   0.0      7700.0   ! [Kern et al. 1991]
C3H4+H=C2H2+CH3            2.0E13   0.0      2400.0   ! [Kern et al. 1991]
C2H+CH3=C3H4P              8.07E49  -11.305  43800.0  ! [QRRK-HR, 20 torr]
C2H3+HCH=C3H4+H            3.0E13   0.0      0.0      ! [Miller and Melius 1992]
C3H4P+C2H=C2H2+H2CCCH      1.0E13   0.0      0.0      ! [Kern et al. 1991]
C3H4+C2H=C2H2+H2CCCH       1.0E13   0.0      0.0      ! [Kern et al. 1991]
C3H4+O=CH2O+C2H2           9.0E12   0.0      1870.0   ! [Zhang and McKinnon 1995]
C3H4+O=HCO+C2H3            9.0E12   0.0      1870.0   ! [Zhang and McKinnon 1995]
C3H4P+O=CH2O+C2H2          7.5E12   0.0      2102.0   ! [Zhang and McKinnon 1995]
C3H4P+O=HCO+C2H3           7.5E12   0.0      2102.0   ! [Zhang and McKinnon 1995]
C3H4+OH=CH2CO+CH3          3.37E12  0.0      -304.0   ! [Zhang and McKinnon 1995]
C3H4P+OH=CH2CO+CH3         4.28E11  0.0      -843.0   ! [Zhang and McKinnon 1995]
CH+C2H4=C3H5               1.67E34  -7.6     3690.0   ! [QRRK-HR, 20 torr]
C3H5+CH2=C4H613+H          3.01E13  0.0      0.0      ! [Tsang 1991]
C2H+C3H5=C2H2+C3H4         0.15     0.0      0.0      ! [Tsang 1991]
C2H+C3H5=C2H3+H2CCCH       20.0     0.0      0.0      ! [Tsang 1991]
C3H5+C2H3=C3H4+C2H4        2.41E12  0.0      0.0      ! [Tsang 1991]
C3H5+C2H5=C3H4+C2H6        9.64E11  0.0      -131.0   ! [Tsang 1991]
C2H3+CH2OH=C3H5+OH         1.21E13  0.0      0.0      ! [Tsang 1987]
C2H4+HCH=C3H5+H            3.19E12  0.0      5285.4   ! [Zhang and McKinnon 1995]
CH3+C2H2=C3H5              14000.0  2.21     16500.0  ! [Diau et al. 1994]
C2H3+CH3=C3H5+H            7.2E13   0.0      0.0      ! [Fahr et al. 1999]
C3H6 = Propylene reactions
C3H6+CH3=C3H5+CH4          2.21     3.5      5675.0   ! [Tsang 1991]
C3H6+CH2OH=C3H5+CH3OH      60.3     2.95     11989.0  ! [Tsang 1991]
C3H6+CH3O=C3H5+CH3OH       90.0     2.95     11987.0  ! [Tsang 1991]
C3H6+C2H=C3H4P+C2H3        1.21E13  0.0      0.0      ! [Tsang 1991]
C3H6+CH2=C3H5+CH3          7.23E11  0.0      6192.0   ! [Tsang 1991]
C3H6+HCO=C3H5+CH2O         1.08E7   1.9      17006.0  ! [Zhang and McKinnon 1995]
C3H6+C2H5=C3H5+C2H6        2.23     3.5      6637.0   ! [Tsang 1991]
C3H6+C2H3=C3H5+C2H4        2.21     3.5      4682.0   ! [Tsang 1991]
C3H5+HCO=C3H6+CO           6.03E13  0.0      0.0      ! [Tsang 1991]
C3H5+CH2OH=C3H6+CH2O       1.81E13  0.0      0.0      ! [Tsang 1991]
C3H5+CH3O=C3H6+CH2O        3.01E13  0.0      0.0      ! [Tsang 1991]
C3H5+C2H3=C3H6+C2H2        4.82E12  0.0      0.0      ! [Tsang 1991]
C3H5+C2H5=C3H6+C2H4        2.59E12  0.0      -131.0   ! [Tsang 1991]
2C3H5=C3H4+C3H6            8.43E10  0.0      -262.0   ! [Tsang 1991]
CH2+C2H5=C3H6+H            9.03E12  0.0      0.0      ! [Zhang and McKinnon 1995]
CH2+C2H4=C3H6              9.03E13  0.0      0.0      ! [Zhang and McKinnon 1995]
NC3H7+H=C3H6+H2            1.81E12  0.0      0.0      ! [Tsang '88]
NC3H7+OH=C3H6+H2O          2.41E13  0.0      0.0      ! [Tsang '88]
NC3H7+HCH=C3H6+CH3         1.81E12  0.0      0.0      ! [Tsang '88]
NC3H7+CH3=C3H6+CH4         1.14E13  -0.32    0.0      ! [Tsang '88]
NC3H7+O2=C3H6+HO2          1.0E12   0.0      5020.0   ! [Warnatz '84]
NC3H7+CH2OH=C3H6+CH3OH     4.82E11  0.0      0.0      ! [Tsang '88]
NC3H7+C2H=C3H6+C2H2        6.03E12  0.0      0.0      ! [Tsang '88]
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NC3H7+C2H3=C3H6+C2H4        1.21E12  0.0     0.0     ! [Tsang '88]
NC3H7+C2H5=C3H6+C2H6        1.45E12  0.0     0.0     ! [Tsang '88]
NC3H7+C3H5=2C3H6         1.45E12  0.0     -131.0  ! [Tsang '91]
IC3H7+H=C3H6+H2          3.61E12  0.0     0.0     ! [Tsang '88]
IC3H7+CH3=C3H6+CH4         9.41E10  0.68    0.0     ! [Tsang '88]
IC3H7+O2=C3H6+HO2          1.26E11  0.0     0.0     ! [Tsang '88]
IC3H7+OH=C3H6+H2O          2.41E13  0.0     0.0     ! [Tsang '88]
IC3H7+C2H=C3H6+C2H2         3.61E12  0.0     0.0     ! [Tsang '88]
IC3H7+CH2OH=C3H6+CH3OH       2.89E12  0.0     0.0     ! [Tsang '88]
IC3H7+C2H3=C3H6+C2H4        1.52E14  -0.7    0.0     ! [Tsang '88]
IC3H7+C2H5=C3H6+C2H6        2.3E13   -0.35   0.0     ! [Tsang '88]
IC3H7+C3H5=2C3H6          2.29E13  -0.35   -131.0  ! [Tsang '91]
Formation/Consumption of n- and i-propyl (n-/i-C3H7)
NC3H7=C2H4+CH3           1.2E13   0.0     30303.0  ! [Tsang '88]
IC3H7=CH3+C2H4           1.0E12   0.0     34580.0  ! [Konar et al. '68]
C3H6+H=NC3H7            1.3E13   0.0     3261.0   ! [Tsang '92]
C3H6+H=IC3H7            1.3E13   0.0     1560.0   ! [Tsang '92]
C3H8+H=NC3H7+H2          1330000.0 2.54    6756.0   ! [Tsang '88]
C3H8+OH=NC3H7+H2O          3.16E7   1.8     934.0    ! [Cohen '91]
C3H8+O=NC3H7+OH           193000.0 2.68    3716.0   ! [Tsang '88]
C3H8+CH3=NC3H7+CH4          0.904    3.65    7154.0   ! [Tsang '88]
C3H8+H=IC3H7+H2          1300000.0 2.4     4471.0   ! [Tsang '88]
C3H8+OH=IC3H7+H2O          7080000.0 1.9    -159.0   ! [Cohen '91]
C3H8+O=IC3H7+OH          47700.0  2.71    2106.0   ! [Tsang '88]
C3H8+CH3=IC3H7+CH4          1.51     3.46    5481.0   ! [Tsang '88]
NC3H7+HCH=C2H4+C2H5         1.81E13  0.0     0.0     ! [Tsang '88]
IC3H7+C2H2=C4H613+CH3        2.77E10  0.0     6504.0   ! [Tsang '88]
NC3H7+C2H=H2CCCH+C2H5        1.21E13  0.0     0.0     ! [Tsang '88]
Propane (C3H8) chemistry
CH3+C2H5=C3H8           3.37E13  0.0     0.0     ! [Baulch et al. '94]
NC3H7+H2O2=C3H8+HO2         18700.0  2.11    2571.0   ! [Tsang '88]
NC3H7+C2H3=C2H2+C3H8        1.21E12  0.0     0.0     ! [Tsang '88]
NC3H7+HCO=C3H8+CO          6.03E13  0.0     0.0     ! [Tsang '88]
NC3H7+CH2OH=C3H8+CH2O        9.64E11  0.0     0.0     ! [Tsang '88]
NC3H7+CH3O=C3H8+CH2O        2.41E13  0.0     0.0     ! [Tsang '88]
NC3H7+CH3OH=C3H8+CH2OH       33.7     3.17    9161.0   ! [Tsang '88]
NC3H7+CH3OH=C3H8+CH3O        14.5     3.1     8942.0   ! [Tsang '88]
NC3H7+CH2O=C3H8+HCO         3010.0   2.9     5862.0   ! [Tsang '88]
NC3H7+C2H5=C3H8+C2H4        1.15E12  0.0     0.0     ! [Tsang '88]
NC3H7+C2H6=C3H8+C2H5        0.253    3.82    9042.0   ! [Tsang '88]
NC3H7+NC3H7=C3H8+C3H6        1.69E12  0.0     0.0     ! [Tsang '88]
NC3H7+C3H5=C3H4+C3H8        7.23E11  0.0     -131.0  ! [Tsang '91]
NC3H7+C3H6=C3H8+C3H5        2.23     3.5     6637.0   ! [Tsang '91]
NC3H7+C3H8=C3H8+IC3H7        8.44E-4  4.0     4726.0   ! [Tsang '88]
IC3H7+C2H5=C2H4+C3H8        1.84E13  -0.35   0.0     ! [Tsang '88]
IC3H7+C2H6=C3H8+C2H5        0.844    4.2     8716.0   ! [Tsang '88]
IC3H7+CH3OH=C3H8+CH2OH       31.9     3.7     10532.0  ! [Tsang '88]
IC3H7+CH3OH=C3H8+CH3O        14.5     3.1     10333.0  ! [Tsang '88]
IC3H7+CH2O=C3H8+HCO         1.08E11  0.0     6955.0   ! [Tsang '88]
IC3H7+H=C3H8            2.0E13   0.0     0.0     ! [Warnatz '84]
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IC3H7+H2O2=C3H8+HO2          289.0    2.83    4048.0   ! [Tsang '88]
IC3H7+HCO=C3H8+CO          1.21E14   0.0      0.0     ! [Tsang '88]
IC3H7+CH2OH=C3H8+CH2O        2.35E12  0.0      0.0      ! [Tsang '88]
IC3H7+CH3O=C3H8+CH2O        1.21E13   0.0      0.0     ! [Tsang '88]
IC3H7+C2H3=C3H8+C2H2        1.52E14  -0.7     0.0     ! [Tsang '88]
IC3H7+NC3H7=C3H8+C3H6        5.13E13  -0.35    0.0      ! [Tsang '88]
IC3H7+IC3H7=C3H8+C3H6       2.11E14  -0.7     0.0     ! [Tsang '88]
IC3H7+C3H5=C3H8+C3H4        4.58E12  -0.35   -131.0   ! [Tsang '91]
IC3H7+C3H6=C3H8+C3H5        0.0662   4.0     8070.0   ! [Tsang '91]
C4H2 = H-CC-CC-H : Diacetylene reactions. C4H, butadiynyl
2C3H2=C4H2+C2H2            2.0E13   0.0      85000.0  ! [Kern et al. 1991]
C2H2+C2H=C4H2+H            4.12E15  -0.49   740.0    ! [QRRK-HR, 20 torr]
C4H2+M=C4H+H+M              3.5E17   0.0     80065.0  ! [Frenklach and Warnatz 1987]
C4H2+C2H=C4H+C2H2            2.0E13   0.0     0.0      ! [Frenklach and Warnatz 1987]
C4H4+C2H=C4H2+C2H3           1.0E13   0.0     0.0      ! [Frenklach and Warnatz 1987]
C4H3 = H2CCCCH & HCCHCCH reactions
HCCHCCH+H=C4H2+H2            2.5E13   0.0     0.0      ! [0.5*Miller and Melius 1992 for n-]
H2CCCCH+H2=C2H2+C2H3          5.01E10  0.0     20000.0  ! [Colket 1986]
H2CCCCH+HCH=C3H4+C2H          2.0E13   0.0     0.0      ! [Miller and Melius 1992]
C2H2+C2H=HCCHCCH            1.09E32  -6.577   4090.0   ! [QRRK-HR, 20 torr]
H2CCCH+CH=H2CCCCH+H           7.0E13   0.0     0.0      ! [Miller and Melius 1992]
H2CCCH+CH=HCCHCCH+H           7.0E13   0.0     0.0      ! [Miller and Melius 1992]
C2H2+C2H2=HCCHCCH+H          1.0E12   0.0     65980.0  ! [Benson 1989]
C4H4 = H-CC-CHCH2 : Vinyl acetylene reactions
C2H2+C2H2=C4H4             1.89E58  -13.6   62790.0  ! [QRRK-HR, 20 torr]
C2H3+C2H3=C4H4+2H            7.83E12  0.0     0.0      ! [Knyazev et al. 1996c]
C2H3+C2H2=C4H4+H            1.91E15  -0.74   10500.0  ! [QRRK-HR, 20 torr]
C4H4+C2H=H2CCCCH+C2H2         4.0E13   0.0     0.0      ! [Kiefer et al. 1985]
C4H4+C2H=HCCHCCH+C2H2         4.0E13   0.0     0.0      ! [Kiefer et al. 1985]
H2CCCH+HCH=C4H4+H            4.0E13   0.0     0.0      ! [Miller and Melius 1992]
C2H3+C2H=C4H4              2.12E60  -13.452  27550.0  ! [QRRK, HR, 20 torr]
C2H4+C2H=C4H4+H            1.21E13   0.0     0.0      ! [Tsang et al. 1986]
Formation of n-C4H3
C4H4+C2H3=C2H4+HCCHCCH        5.0E11   0.0     16300.0  ! [Colket 1986]
Formation of i-C4H3
C4H4+C2H3=C2H4+H2CCCCH        5.0E11   0.0     16300.0  ! [Colket 1986]
C4H5 = CH2CHCHCH & CH2CHCCH2 : Butadienyl reactions
C2H3+C2H2=CH2CHCHCH          3.45E45  -11.13   15980.0  ! [QRRK-HR, 20 torr]
CH2CHCHCH+H=C4H613           1.21E14  0.0     0.0      ! [Fahr et al. 1991 for C2H3+H]
CH2CHCCH2+O2=C4H4+HO2         1.2E11   0.0     0.0      ! [Emdee et al. 1992]
2C2H3=CH2CHCCH2+H            4.0E13   0.0     0.0      ! [Miller and Melius 1992]
CH2CHCCH2+H=C4H4+H2          3.0E7    2.0     1000.0   ! [Miller and Melius 1992]
C4H613 (1,3-Butadiene) and i-C4H7 (CH2=CHCHCH3) reactions
C2H3+C2H4=C4H613+H           2.27E12  -0.17   3380.0   ! [QRRK-HR, 20 torr]
C2H3+C2H4=I-C4H7           2.11E22  -4.7    1190.0   ! [QRRK-HR, 20 torr]
I-C4H7=C4H613+H            3.16E13  0.0     34800.0  ! [Weissman and Benson 1984]
I-C4H7+H=C4H613+H2           1.81E12  0.0     0.0      ! [Tsang1986] c2h5+h=c2h4+h2
I-C4H7+OH=C4H613+H2O          2.41E13  0.0     0.0      ! [Tsang1986] c2h5+oh=c2h4+h2o
C2H3+C2H3=C4H613           2.0E13   0.0     0.0      ! [Colket et al. 1989]
C3H6+C2H3=C4H613+CH3          7.23E11  0.0     5010.0   ! [Tsang 1991]
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C4H613+H2CCCH=CH2CHCHCH+C3H4  1.0E13   0.0     22500.0  ! [Kern et al. 1988]
C4H613+O=C2H4+CH2CO         1.0E12   0.0      0.0      ! [Pitz and Westbrook 1986]
C4H613+O=C3H4+CH2O          1.0E12   0.0      0.0      ! [Pitz and Westbrook 1986]
C4H613+OH=C3H5+CH2O         1.0E12   0.0      0.0      ! [Pitz and Westbrook 1986]
C4H613+OH=C2H5+CH2CO        1.0E12   0.0      0.0      ! [Pitz and Westbrook 1986]
1-butyne Formation and Consumption
H2CCCH+CH3=C4H6-1           5.42E13  0.0      0.0      ! [Fahr and Nayak '2000: 60% of total]
C3H6+C2H=C4H6-1+CH          1.21E13  0.0      0.0      ! [Tsang '91]
C4H6-1=C4H612           2.5E13   0.0     65000.0  ! [Hidaka et al. 1995a]
C4H6-1+O=C3H6+CO            2.0E13   0.0      1659.0   ! [Cvetanovic '87]
1,2-butadiene Formation and Consumption
H2CCCH+CH3=C4H612           3.61E13  0.0      0.0      ! [Fahr and Nayak '2000: 40% of total]
C4H612=C4H613           2.5E13   0.0     63000.0  ! [Hidaka et al. 1995b]
C4H612+H=C3H4+CH3           6.0E12   0.0      2100.0   ! [Hidaka et al. 1995b]
C4H612+H=C3H4P+CH3          6.0E12   0.0      2100.0   ! [Hidaka et al. 1995b]
Formation of C4H8 (1-butene)
I-C4H7+H=C4H8           1.0E14   0.0      0.0      ! [Sillesen et al. 93 for C2H5+H]
C4H8=C3H5+CH3            1.1E16   0.0     77692.0  ! [Knyazev/Slagle 2001]
H2C4O reactions
C4H2+HCH=C5H3(L)+H          1.3E13   0.0      0.0      ! [Miller and Melius 1992]
C4H2+CH2=C5H3(L)+H          3.0E13   0.0      0.0      ! [Miller and Melius 1992]
C4H2+CH=C5H2(L)+H           1.0E14   0.0      0.0      ! [Miller and Melius 1992]
C5H3(L)+H=C5H2(L)+H2        6.03E13  0.0     15103.0   ! [CH3+H, Baulch et al. 1992]
C5H4 (cyclopentatriene), also formed by p-C6h4O2 decay
C5H5+H=C5H4+H2          3.23E7   2.095   15842.0  ! [Mebel et al. 1997, C6H6+H]
C5H5+OH=C5H4+H2O            2.11E13  0.0      4571.0   ! [Madronich/Felder 1985, C6H6+OH]
C5H5+O=C5H4+OH          2.0E13   0.0     14694.0  ! [Lindstedt/Skevis 1994, C6H6+O]
C5H5+CH3=C5H4+CH4           2.0E12   0.0     15060.0  ! [Zhang et al. 1989, C6H6+CH3]
C5H4H+H=C5H4+H2         2.8E13   0.0      2259.0   ! [Roy et al. 1998 for C5H6+H]
C5H4H+OH=C5H4+H2O           3080000.0 2.0      0.0      ! [Zhong and Bozzelli'98,C5H6+H]
C5H4H+O=C5H4+OH         47700.0  2.71     1106.0   ! [Zhong and Bozzelli'98,C5H6+H]
C5H4=C5H4(L)            1.0E13   0.0      6000.0   ! [estimate, present work]
C5H4(L) (1,2-pentadiene-4-yne, CH2=C=CH-CCH)
C5H5(L)+H=C5H4(L)+H2        1.81E12  0.0      0.0      ! [C2H5+H, Tsang/Hampson '86]
C5H5(L)+OH=C5H4(L)+H2O      2.41E13  0.0      0.0      ! [C2H5+OH, Tsang/Hampson '86]
C5H5(L)+CH3=C5H4(L)+CH4     1.95E13  -0.5     0.0      ! [C2H5+CH3, Tsang/Hampson '86]
C5H5/C5H4H/C5H5(L) = cyclic and acyclic C5H5 reactions
C5H5=H2CCCH+C2H2            2.79E79  -18.3   130834.0  ! [Moskaleva and Lin 2000, 100 torr]
C5H5=C5H4H              5.17E80  -20.4    96185.0  ! [Moskaleva and Lin 2000, 100 torr]
C5H4H=H2CCCH+C2H2           3.4E80   -19.2   102265.0  ! [Moskaleva and Lin 2000, 100 torr]
C5H5+O=C5H5O            1840.0   1.03    -6960.0  ! [Zhong and Bozzelli 1998, QRRK-HR]
C5H5+CH3=C5H5CH3            3.43E52  -12.49  12000.0  ! [QRRK-HR]
C5H4O, C5H4OH and C5H5OH reactions
C5H6+H=C5H4H+H2         2.8E13   0.0     35139.0  ! [p.w., C5H4H/C5H5 energies]
C5H6+H=C3H5+C2H2            6.6E14   0.0     12345.0  ! [Roy et al. 1998]
C5H6+OH=C5H4H+H2O           3080000.0 2.0     32880.0  ! [p.w., C5H4H/C5H5 energies]
C5H6+O=C5H4H+OH         47700.0  2.71    33986.0  ! [p.w., C5H4H/C5H5 energies]
C5H6+CH3=C5H4H+CH4          0.18     4.0     32880.0  ! [p.w., C5H4H/C5H5 energies]
C5H6+C10H7*1=C5H5+C10H8     0.1      4.0      0.0      ! [p.w., sim. to C5H6 + C6H5]
C5H6+C10H7*2=C5H5+C10H8     0.1      4.0      0.0      ! [p.w., sim. to C5H6 + C6H5]
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C5H6+CH2CHCHCH=C5H5+C4H613    0.12     4.0      0.0      ! [Zhong and Bozzelli 1998]
C5H6+C3H5=C5H5+C3H6           0.2      4.0      0.0      ! [Zhong and Bozzelli 1998]
C3H5+C5H5=C5H6+C3H4           1.0E12   0.0      0.0      ! [Dean 1990]
C6H2 = H-CC-CC-CC-H Triacetylene reactions
C6H2+M=C6H+H+M                5.0E16   0.0      80065.0  ! [Frenklach and Warnatz 1987]
C6H2+OH=C6H+H2O               1.1E13   0.0      7002.7   ! [Frenklach and Warnatz 1987]
C6H2+C2H=C6H+C2H2             2.0E13   0.0      0.0      ! [Frenklach and Warnatz 1987]
C6H2+C2H=C4H+C4H2             1.0E13   0.0      0.0      ! [Frenklach and Warnatz 1987]
C4H2+C2H=C6H2+H               4.98E40  -7.66    21910.0  ! [QRRK-HR, 20 torr]
2C3H2=C6H2+H2                 2.0E13   0.0      85000.0  ! [Kern et al. 1991]
C6H3 = HCCCCCHCH hexenediynyl reactions
C4H2+C2H=C6H3                 3.76E63  -14.722  27250.0  ! [QRRK-HR, 20 torr]
C6H2+H=C6H3                   2.74E56  -12.585  29690.0  ! [QRRK-HR, 20 torr]
C6H3+H=C6H2+H2                2.0E13   0.0      0.0      ! [Frenklach and Warnatz 1987]
C6H4: HCCCHCHCCH cis-3-hexen-1,5-diyne and benzyne reactions
C6H4+H=C6H3+H2                1.5E14   0.0      10205.3  ! [Frenklach and Warnatz 1987]
C6H3+H=C6H4                   9.55E67  -15.959  31510.0  ! [QRRK-HR, 20 torr]
C6H4+OH=C6H3+H2O              7.0E13   0.0      3011.4   ! [Frenklach and Warnatz 1987]
C6H4+C2H=C6H3+C2H2            2.0E13   0.0      0.0      ! [Frenklach and Warnatz 1987]
HCCHCCH+C2H2=BENZYNE+H        1.64E9   0.73     12180.0  ! [Westmoreland et al. 1989, 20 torr]
HCCHCCH+C2H2=C6H4+H           296.0    3.33     9620.0   ! [Westmoreland et al. 1989, 20 torr]
C6H4+H=C6H5(L)                1.41E67  -15.609  20940.0  ! [QRRK-HR, 20 torr]
C6H5 reactions
C6H5(L)+H=C6H4+H2             2.0E13   0.0      0.0      ! [Frenklach and Warnatz 1987]
HCCHCCH+C2H2=C6H5(L)          1.73E11  -0.41    4030.0   ! [Westmoreland et al. 1989, 20 torr]
H2CCCCH+C2H3=C6H5+H           6.0E12   0.0      0.0      ! [Pope and Miller 2000]
C6H5(L)=C6H5                  1.66E11  0.0      16350.0  ! [Dewar et al. 1987]
C6H5+CH2O=C6H6+HCO            1.75E10  0.0      0.0      ! [Yu  and Lin 1993]
C6H5=C6H4+H                   1.45E77  -17.1    129500.0 ! [Madden et al. 1997, 380 torr]
C6H6 reactions
H2CCCH+H2CCCH=C6H6            3.0E12   0.0      0.0      ! [Marinov et al. 1996]
C4H4+C2H3=C6H6+H              1.9E12   0.0      2510.0   ! [Kubitza et al. '94, in Lindstedt/Skevis '97]
C3H4+H2CCCH=C6H6+H            2.2E11   0.0      2000.0   ! [Wu and Kern 1987]
CH2CHCHCH+C2H2=C6H6+H         1.9E7    1.47     4910.0   ! [Westmoreland et al. 1989, 20 torr]
CH2CHCHCH+C2H3=C6H6+H2        2.8E-7   5.63     -1890.0  ! [Westmoreland et al. 1989, 20 torr]
C4H4+C2H2=C6H6                4.47E11  0.0      30010.0  ! [Chanmugathas/Heicklen '1986]
C6H5+CH4=C6H6+CH3             6.0E12   0.0      12320.0  ! [Tokmakov et al. 1999]
C6H6F=C6H6                    7.59E13  0.0      73853.0  ! [Melius et al. 1992]
C6H6F+H=C6H6+H                3.0E12   0.5      2000.0   ! [Marinov et al. 1997]
CH2CHCHCH+C2H2=C6H7           1.96E19  -3.35    5240.0   ! [Westmoreland et al. 1989, 20 torr]
CH3+C5H5=C6H7+H               2.44E41  -7.989   39259.0  ! [Dean 1990]
C6H7+H=C6H6+H2                1.0E13   0.0      0.0      ! [Louw and Lucas 1973]
C6H7+C6H5=2C6H6               1.0E12   0.0      0.0      ! [Louw and Lucas 1973]
C6H7+H=C6H813                 6.0E13   0.0      0.0      ! [Berho et al. 1999]
C6H7+H=C6H814                 6.0E13   0.0      0.0      ! [Berho et al. 1999]
2C6H7=C6H813+C6H6             1.94E15  -1.0     0.0      ! [Berho et al. '99/James and Suart '68]
2C6H7=C6H814+C6H6             1.67E15  -1.0     0.0      ! [Berho et al. '99/James and Suart '68]
C6H813+O2=C6H7+HO2            8.13E11  0.0      24840.0  ! [Mulder and Louw 1985]
C6H814+H=C6H7+H2              2.8E13   0.0      2259.0   ! [Roy et al. 1998, C5H6+H=C5H5+H2]
C6H813=C6H6+H2                4.7E13   0.0      61600.0  ! [Orchard and Thrush 1974]
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C6H814=C6H6+H2              1.05E12  0.0     42690.0  ! [Ellis and Frey 1966]
C2H3+CH2CHCHCH=C6H813         5.5E15   -1.67    1470.0   ! [Westmoreland et al. 1989, 20 torr]
C4H613+C2H2=C6H814            2.3E12   0.0      35000.0  ! [Westmoreland et al. 1989, h. p. limit]
C6H5O phenoxy reactions
C6H5OH+CH2CHCHCH=C4H613+C6H5O 6.0E12   0.0      0.0      ! [Emdee et al. 1992]
C6H5OH+OH=H2O+C6H4OH          1.41E13  0.0      4571.0   ! [Shandross et al. 1996]
C6H5OH+H=H2+C6H4OH            1.67E14  0.0      16000.0  ! [Shandross et al. 1996]
C5H5+CO=C6H4OH                3.77E42  -9.865   73120.0  ! [QRRK-HR, 20 torr]
Benzoquinone (o-C6H4O2 and p-C6H4O2) reactions
C6H5+CH3=C7H7+H               4.44E33  -5.45    24290.0  ! [QRRK-HR, 20 torr]
C4H4+H2CCCH=C7H7              5.39E51  -12.2    7120.0   ! [QRRK-HR, 20 torr]
C7H7+C6H5OH=C7H8+C6H5O        1.05E11  0.0      9500.0   ! [Emdee et al. 1992]
C7H7+HO2=C6H5+CH2O+OH         5.0E12   0.0      0.0      ! [Hippler et al. 1990]
C7H8 = C6H5CH3 TOLUENE
C7H7+H=C7H8                   2.59E14  0.0      0.0      ! [Baulch et al. 1994]
C6H5+CH3=C7H8                 1.07E65  -15.64   22720.0  ! [QRRK-HR, 20 torr]
C7H8+O2=C7H7+HO2              3.0E14   0.0      41400.0  ! [Emdee et al. 1992]
C7H8+OH=C7H7+H2O              1.26E13  0.0      2583.0   ! [Emdee et al. 1992]
C7H8+H=C7H7+H2                1.2E14   0.0      8235.0   ! [Emdee et al. 1992]
C7H8+H=C6H6+CH3               1.2E13   0.0      5148.0   ! [Emdee et al. 1992]
C7H8+CH3=C7H7+CH4             3.16E11  0.0      9500.0   ! [Emdee et al. 1992]
C7H8+C6H5=C7H7+C6H6           2.1E12   0.0      4400.0   ! [Emdee et al. 1992]
C7H8+C2H3=C7H7+C2H4           3.98E12  0.0      8000.0   ! [Zhang and McKinnon 1995]
CH2CHCHCH+C3H4=C7H8+H         2.0E11   0.0      3700.0   ! [Kern et al. 1988]
CH2CHCHCH+C3H4P=C7H8+H        3.16E11  0.0      3700.0   ! [Cole et al. 1984]
HYDROXYTOLUENE (C7H8O)
C6H5O+CH3=C7H8O               1.0E12   0.0      0.0      ! [Lin and Lin 1986]
C7H8O+H=C7H8+OH               2.21E13  0.0      7910.0   ! [Emdee et al. 1992]
C7H8O+H=C6H5OH+CH3            1.2E13   0.0      5148.0   ! [Emdee et al. 1992]
Benzaldehyde (C6H5CHO) and benzoyl (C6H5CO)
C7H7+O=C6H5CHO+H              1.58E13  0.0      0.0      ! [Brezinsky et al. '84]
C6H5CHO=C6H5CO+H              3.98E15  0.0      83660.0  ! [Grela and Colussi '86]
C6H5CHO+O=C6H5CO+OH           6.03E12  0.0      1810.0   ! [Baulch et al. '94]
C6H5CHO+OH=C6H5CO+H2O         7.83E12  0.0      0.0      ! [Baulch et al. '94]
C6H5CO=C6H5+CO                3.98E14  0.0      29410.0  ! [Solly and Benson '71]
Benzylalcohol (C6H5CH2OH)
C7H7+OH=C6H5CH2OH             2.0E13   0.0      0.0      ! [Hippler et al. 1990]
Methylphenylether (C6H5OCH3)
C6H5O+CH3=C6H5OCH3            1.21E13  0.0      0.0      ! [Tsang/Hampson '86 for CH3+CH3O]
C6H5+CH3O=C6H5OCH3            1.21E13  0.0      0.0      ! [Tsang/Hampson '86 for CH3+CH3O]
Biphenylether (C6H5OC6H5)
C6H5+C6H5O=C6H5OC6H5          1.21E13  0.0      0.0      ! [Tsang/Hampson '86 for CH3+CH3O]
PHENYLACETYLENE (C8H6 = C6H5C2H)and phenylcarbene (C6H5CH)
C6H6+C2H=C8H6+H               1.0E12   0.0      0.0      ! [Colket 1986]
C6H5+C2H2=C8H6+H              8.32E22  -2.68    17400.0  ! [QRRK-HR, 20 torr]
C8H6+H=A1C2H*2+H2             3.23E7   2.095    15842.0  ! [Mebel et al. 1997, for C6H6+H]
C8H6+OH=A1C2H*2+H2O           2.11E13  0.0      4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
C8H6+CH3=A1C2H*2+CH4          1.67E12  0.0      15057.0  ! [Marinov et al. 1996]
A1C2H*2+H=C8H6                8.02E19  -2.011   1968.0   ! [c6h5+h=c6h6]
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C6H5+C2H=C8H6             2.54E17  -1.489   1541.0  ! [Zhang and McKinnon 1995]
C6H5+C4H4=C8H6+C2H3          3.2E11   0.0      1350.0   ! [Harris et al. 1988]
CH2CHCHCH+C4H2=C8H6+H          3.16E11  0.0      1800.0   ! [Cole et al. 1984]
HCCHCCH+C4H2=A1C2H*2            3.33E24  -3.89    9210.0   ! [n-C4H3+C2H2,Westmoreland et al.
1989, 20 torr]
C6H5+C2H2=C6H5CHCH           8.56E44  -10.5    13220.0  ! [QRRK-HR, 20 torr]
C6H5CHCH+H=C8H6+H2            1.21E14  0.0      0.0      ! [QRRK-HR, 20 torr]
C6H5CHCH=C8H6+H            2.7399999999999998E22 -4.061 37040.0 ! [Knyazev et al. 1996b for
C2H3=C2H2+H]
C8H6+O=C6H5CH+CO            3.6E12   0.0      633.0    ! [Eichholtz et al. '94]
C6H5CH+H=C7H7            1.0E13   0.0      0.0      ! [guess, p.w.]
C7H7+H=C6H5CH+H2            6.03E13  0.0      15103.0  ! [Baulch et al. 1992 for
CH3+H=HCH(T)+H2]
C6H5CH+O=C6H6+CO            1.0E13   0.0      0.0      ! [guess, p.w.]
C6H5CH+OH=C6H6+HCO            1.0E13   0.0      0.0      ! [guess, p.w.]
STYRENE (C8H8 = C6H5C2H3 PHENYLETHYLENE)
C6H5+C2H3=C8H8            1.75E49  -10.314  24270.0  ! [QRRK-HR, 20 torr]
C6H5CHCH+H=C8H8            4.8E10   -0.74    -7630.0  ! [QRRK-HR, 20 torr]
C6H5+C4H4=C8H8+C2H            3.2E11   0.0      1900.0   ! [Harris et al. 1988]
C6H5+C4H613=C8H8+C2H3            3.2E11   0.0      1900.0   ! [Harris et al. 1988]
C4H4+C4H4=C8H8            1.5E14   0.0      38000.0  ! [Lundgard and Heicklen 1984]
CH2CHCHCH+C4H4=C8H8+H            3.16E11  0.0      600.0    ! [Cole et al. 1984]
C8H8=C6H6+C2H2            1.58E11  0.0      58440.0  ! [Mueller-Markgraf/Troe 1988]
C6H5+C2H4=C8H8+H            2.51E12  0.0      6200.0   ! [Fahr and Stein, '88]
C8H8+H=C6H5CHCH+H2            5.07E7   1.93     12951.0  ! [Knyazev et al. 1996a for C2H4+H]
C8H8+OH=C6H5CHCH+H2O            2.02E13  0.0      5955.0   ! [Miller and Melius 1992 for
C2H4+OH]
C6H6+C2H3=C8H8+H            7.94E11  0.0      6400.0   ! [Fahr and Stein 1988]
C6H5+C2H2=C8H7*2            7.9E51   -12.41   17770.0  ! [QRRK-HR, 20 torr]
C8H7*2+H=C8H8            8.02E19  -2.011   1968.0   ! [c6h5+h=c6h6]
PHENYLETHANE
C7H7+CH3=C8H10            1.19E13  0.0      221.0    ! [Brand et al. 1990]
C8H10+H=C6H6+C2H5            1.2E13   0.0      5100.0   ! [Zhang and McKinnon 1995]
C8H10+OH=C8H8+H2O+H            8.34E12  0.0      2583.0   ! [Emdee et al. 1992]
C8H10+H=C8H8+H2+H            8.0E13   0.0      8235.0   ! [Emdee et al. 1992]
C8H10+O2=C8H8+HO2+H            2.0E14   0.0      41400.0  ! [Emdee et al. 1992]
C8H10=C8H8+H2            5.01E12  0.0      64000.0  ! [Clark and Price 1970]
BIPHENYL
C6H5+C6H5=C12H10            5.94E42  -8.83    13830.0  ! [QRRK-HR, 20 torr]
C6H5+C6H6=C12H10+H            1.9E76   -18.9    39470.0  ! [Park et al. 1999, 40 torr]
C12H10+H=C12H9+H2            3.23E7   2.095    15842.0  ! [Mebel et al. 1997 for C6H6+H]
C12H10+OH=C12H9+H2O            2.11E13  0.0      4571.0   ! [Madronich and Felder 1985 for
C6H6+OH]
C6H5+H2CCCH=C6H5C3H2+H            3.0E12   0.0      0.0      ! [D'Anna and Violi 1998]
C6H5C3H2+H2CCCH=C12H9+H            3.0E12   0.0      0.0      ! [D'Anna and Violi 1998]
C12H9+H=C12H10            1.17E33  -5.57    8760.0   ! [QRRK-HR, 20 torr]
Naphthalene (C10H8)
2C5H5=C10H8+2H            5.0E12   0.0      8000.0   ! [0.25 * Marinov et al. 1998]
C6H5+HCCHCCH=C10H8            1.51E75  -17.845  39600.0  ! [QRRK-HR, 20 torr]
C7H7+H2CCCH=C10H8+H+H            3.0E12   0.0      0.0      ! [D'Anna and Violi 1998]
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 A1C2H*2+C2H2=C10H7*1          4670000.0 1.787     3262.0    ! [HP-limit for C10H7*1+C2H2/4]
 C6H5+HCCHCCH=C10H7*2+H          1.84E72   -16.129   57630.0   ! [QRRK-HR, 20 torr]
 C10H8+H=C10H7*1+H2            3.23E7    2.095      15842.0   ! [Mebel et al. 1997 for C6H6+H]
 C10H8+H=C10H7*2+H2            3.23E7    2.095      15842.0   ! [Mebel et al. 1997 for C6H6 + H]
 C10H8+OH=C10H7*1+H2O          2.11E13   0.0        4571.0    ! [Madronich and Felder 1985 for
C6H6+OH]
 C10H8+OH=C10H7*2+H2O          2.11E13   0.0        4571.0    ! [Madronich and Felder 1985 for
C6H6+OH]
 C10H8+CH3=C10H7*1+CH4         2.0E12    0.0        15060.0   ! [Zhang et al. 1989, C6H6+CH3]
 C10H8+CH3=C10H7*2+CH4         2.0E12    0.0        15060.0   ! [Zhang et al. 1989, C6H6+CH3]
 C10H7*1+H=C10H8             8.02E19   -2.011    1968.0    ! [Mebel et al. 2001, C6H5, 100 torr]
 C10H7*1+H=A2T1+H2             4.4E-13   7.831     9261.0    ! [Mebel et al. 2001, C6H5, 100 torr]
 C10H7*2+H=C10H8             8.02E19   -2.011    1968.0    ! [Mebel et al. 2001, C6H5, 100 torr]
 C10H7*2+H=A2T2+H2             4.4E-13   7.831     9261.0    ! [Mebel et al. 2001, C6H5, 100 torr]
 Formation of A21C6H4 and A22C6H4
 A2T1+BENZYNE=A21C6H4          4.58E41   -8.73     12740.0   ! [QRRK-HR, 20 torr]
 A2T2+BENZYNE=A22C6H4          4.58E41   -8.73     12740.0   ! [QRRK-HR, 20 torr]
 Naphthol and indene
 C10H7*1+O2=C10H7O-1+O         2.39E21   -2.62     4400.0    ! [QRRK-HR, 20 torr, for C6H5+O2]
 C10H7*1+OH=C10H7O-1+H         5.0E13    0.0       0.0       ! [Miller and Melius 1992, for C6H5+OH]
 C10H7*2+O2=C10H7O-2+O         2.39E21   -2.62     4400.0    ! [QRRK-HR, 20 torr, for C6H5+O2]
 C10H7*2+OH=C10H7O-2+H         5.0E13    0.0       0.0       ! [Miller and Melius 1992, for C6H5+OH]
 C10H7O-1+H=C10H7OH-1          4.43E60   -13.232   30010.0   ! [QRRK, 20 torr,for C6H5O+H]
 C10H7OH-1+H=C10H7O-1+H2         1.15E14   0.0       12400.0   ! [rxn. 674.]
 C10H8+OH=C10H7OH-1+H          1.59E19   -1.82     12800.0   ! [QRRK-HR, 20 torr, for C6H6+OH]
 C10H7OH-1+OH=C10H7O-1+H2O       1.39E8    1.43      -962.0    ! [Shandross et al. 1996,
C6H5OH+OH]
 C10H7O-2+H=C10H7OH-2          4.43E60   -13.232   30010.0   ! [QRRK, 20 torr,for C6H5O+H]
 C10H7OH-2+H=C10H7O-2+H2         1.15E14   0.0       12400.0   ! [rxn. 674.]
 C10H8+OH=C10H7OH-2+H          1.59E19   -1.82     12800.0   ! [QRRK-HR, 20 torr, for C6H6+OH]
 C10H7OH-2+OH=C10H7O-2+H2O       1.39E8    1.43      -962.0    ! [Shandross et al. 1996,
C6H5OH+OH]
 C10H7O-1=INDENE*+CO           2.51E11   0.0       43900.0   ! [Lin and Lin 1986, for C6H5O]
 C10H7O-2=INDENE*+CO           2.51E11   0.0       43900.0   ! [Lin and Lin 1986, for C6H5O]
 INDENE+H=INDENE*+H2           1.48E14   0.0       13585.0   ! [Knyazev et al. 1996a for CH4+H]
 INDENE+OH=INDENE*+H2O           1.57E7    1.83      2780.0    ! [Baulch et al. 1992 for CH4+OH]
 INDENE+O=INDENE*+OH           6.92E8    1.56      8490.0    ! [Baulch et al. 1992 for CH4+O]
 INDENE*+H=INDENE            2.0E14    0.0       0.0       ! [Marinov et al. 1996]
 C7H7+C2H2=INDENE+H            3.2E11    0.0       7000.0    ! [Marinov et al. 1996]
 INDENE*+O=C6H5CHCH+CO           1.0E14    0.0       0.0       ! [Marinov et al. 1996]
 Methylnapththalene Formation
 C10H7*1+CH3=A2CH2-1+H         1.7E36    -5.91     34630.0   ! [QRRK-HR, 20 torr]
 C10H7*2+CH3=A2CH2-2+H         1.7E36    -5.91     34630.0   ! [QRRK-HR, 20 torr]
 C10H7*1+CH3=A2CH3-1           3.05E52   -11.8     17660.0   ! [QRRK-HR, 20 torr]
 C10H7*2+CH3=A2CH3-2           3.05E52   -11.8     17660.0   ! [QRRK-HR, 20 torr]
 A2CH2-1+H=A2CH3-1             1.0E14    0.0       0.0       ! [Marinov et al. 1996]
 A2CH2-2+H=A2CH3-2             1.0E14    0.0       0.0       ! [Marinov et al. 1996]
 A2CH3-1+H=C10H8+CH3           1.2E13    0.0       5148.0    ! [Marinov et al. 1996]
 A2CH3-2+H=C10H8+CH3           1.2E13    0.0       5148.0    ! [Marinov et al. 1996]
 1-and-2-naphthylacetylene
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C10H7*1+C2H2=A2C2H-1+H       9.6E-9   6.44    8620.0   ! [QRRK-HR, w/isom., 20 torr]
C10H7*2+C2H2=A2C2H-2+H       1.01E26  -3.44   20230.0  ! [QRRK-HR, w/o is., 20 torr]
A2VINP+H=A2C2H-2+H2          1.21E14  0.0     0.0      ! [QRRK-HR, 20 torr, for C6H5CHCH+H]
2-vinylnaphthalene and its radical
C10H7*2+C2H4=A2C2H3-2+H      2.51E12  0.0     6200.0   ! [Fahr and Stein 1988, for C6H5+C2H4]
C10H8+C2H3=A2C2H3-2+H        7.94E11  0.0     6399.0   ! [Fahr and Stein 1988, for C6H6+C2H3]
C10H7*2+C2H2=A2VINP          2.77E46  -10.9   14210.0  ! [QRRK-HR, 20 torr]
A2VINP=A2C2H-2+H             2.7399999999999998E22 -4.061 37040.0 ! [Knyazev et al. 1996b for
C2H3=C2H2+H]
A2VINP+H=A2C2H3-2            4.8E10   -0.74   -7630.0  ! [QRRK-HR, 20 torr, for C6H5CHCH+H]
Biphenylene and Acenaphthylene
BENZYNE+BENZYNE=BIPHEN       4.6E12   0.0     0.0      ! [Porter and Steinfeld 1968]
BIPHENH=BIPHEN+H             1.3E16   0.0     33203.0  ! [Mebel et al. 1997 for C6H7=C6H6+H]
BIPHENH+H=BIPHEN+H2          6.02E12  0.0     0.0      ! [Mebel et al. 1997 for
C6H7+H=C6H6+H2]
BIPHENH=A2R5+H               1.0E13   0.0     20000.0  ! [estimate]
C10H7*1+C2H2=A2R5+H          3.57E24  -3.176  14861.0  ! [QRRK-HR, 20 torr]
Acenaphthene
C10H7*1+C2H4=A2R5H2+H        2.51E12  0.0     6200.0   ! [Fahr and Stein 1988, for C6H5+C2H4]
C10H7*1+C2H2=HA2R5           7.74E45  -10.85  13470.0  ! [QRRK-HR, 20 torr]
HA2R5+H=A2R5+H2              1.81E12  0.0     0.0      ! [Tsang et al. 1986, for C2H5+H]
HA2R5+OH=A2R5+H2O            2.41E13  0.0     0.0      ! [Tsang et al. 1986, for C2H5+OH]
HA2R5+H=A2R5H2               1.0E14   0.0     0.0      ! [Sillesen 1993, for C2H5+H=C2H6]
A2R5H2+H=HA2R5+H2            540.0    3.5     5210.0   ! [Miller and Melius 1992, for C2H6+H]
A2R5H2+OH=HA2R5+H2O          8.7E9    1.05    1810.0   ! [Miller and Melius 1992, for C2H6+OH]
A2R5H2=A2R5+H2               4.7E13   0.0     61600.0  ! [Orchard and Thrush 1973 for 1,3-
cycohexadiene=C6H6+H2]
PHENANTHRENE (A3)
C12H9+C2H2=A3+H              1.87E7   1.787   3262.0   ! [HP-limit for 1-C10H7+C2H2, O. Mazyar in
Richter et al. 2001]
INDENE*+C5H5=A3+2H           5.0E12   0.0     8000.0   ! [0.5*Marinov et al 1997]
A2C2H-2+H=A2C2H-2*1+H2       3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A2C2H-2+OH=A2C2H-2*1+H2O     2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A2C2H-2*1+C2H2=A3*1          4670000.0 1.787  3262.0   ! [HP-limit for C10H7*1+C2H2/4]
A2C2H-1+H=A2C2H-1*2+H2       3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A2C2H-1+OH=A2C2H-1*2+H2O     2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A2C2H-1*2+C2H2=A3*4          4670000.0 1.787  3262.0   ! [HP-limit for C10H7*1+C2H2/4]
C8H6+C6H5=A3+H               9.55E11  0.0     4308.0   ! [Park et al. 1999 for C6H5+C6H6]
A1C2H*2+C6H6=A3+H            9.55E11  0.0     4308.0   ! [Park et al. 1999 for C6H5+C6H6]
A3+H=A3*1+H2                 3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3+H=A3*2+H2                 3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3+H=A3*4+H2                 3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3+H=A3*9+H2                 3.23E7   2.095   15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3+OH=A3*1+H2O               2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for C6H6+OH]
A3+OH=A3*2+H2O               2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for C6H6+OH]
A3+OH=A3*4+H2O               2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for C6H6+OH]
A3+OH=A3*9+H2O               2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for C6H6+OH]
A3*1+H=A3                    2.15E19  -1.55   1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
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A3*2+H=A3                2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
A3*4+H=A3                2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
A3*9+H=A3                2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
ANTHRACENE
A2C2H-2+H=A2C2H-2*3+H2        3.23E7   2.095    15842.0  ! [Mebel et al. 1997 for C6H6+H]
A2C2H-2+OH=A2C2H-2*3+H2O       2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A2C2H-2*3+C2H2=A3L*1         4670000.0 1.787    3262.0   ! [HP-limit for C10H7*1+C2H2/4]
C10H7*2+C4H2=A3L*2          4670000.0 1.787    3262.0   ! [HP-limit for C10H7*1+C2H2/4]
A3L+H=A3L*1+H2             3.23E7   2.095    15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3L+OH=A3L*1+H2O             2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A3L*1+H=A3L              2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
A3L+H=A3L*2+H2             3.23E7   2.095    15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3L+OH=A3L*2+H2O             2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A3L*2+H=A3L              2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
A3L+H=A3L*9+H2             3.23E7   2.095    15842.0  ! [Mebel et al. 1997 for C6H6+H]
A3L+OH=A3L*9+H2O             2.11E13  0.0     4571.0   ! [Madronich and Felder 1985, for
C6H6+OH]
A3L*9+H=A3L              2.15E19  -1.55    1700.0   ! [QRRK-HR, 20 torr, for A3*1+H=A3]
A3L=A3                7.94E12  0.0     65000.0  ! [Colket and Seery 1994]
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