Chemical Kinetic Databases for the Simulation of Hydrocarbon Combustion Phenomena

Wing Tsang National Institute of Standards and Technology Gaithersburg, MD 20877 Wing.tsang@nist.gov

Introduction: Progress in the understanding of reactive flows has led to the development of computational fluid dynamics programs that can accommodate increasing amounts of chemistry (1). Fluid dynamics and chemistry is the fundamental basis for combustion. There is the exciting possibility of being able to simulate real situation in real devices. This has led to renewed interest in the chemical kinetic databases that represent the chemical inputs to the new programs. In this presentation we wish to describe activities at the National Institute of Standards and Technology aimed at developing improved databases for this purpose. The paper will begin with a brief historical background. The present situation will be reviewed. We will present some of our recent work in extending the database. Finally we consider extensions to cover more general situations.

Definitions: The elements of a chemical kinetic databases are the individual transferable thermal reactions. Every process is characterized by one specific rate expression. These are usually expressed in the Arrhenius or modified Arrhenius form. Expressing reactions in this form implies reactants are in Boltzmann equilibrium For the high temperatures characteristic of many exothermic processes, rate constants may be so fast that deviations occur. For unimolecular reactions in the most general sense, these departures can be determined. Rate constants become pressure dependent. Most existing combustion kinetics databases have not taken such effects into account. It is only in the last few years that we have been in a position to treat these problems(2). Nevertheless the high pressure rate expression remain the basis upon which all estimates are based. In the description of any real system, physical properties are also important. This presentation will be only concerned with the chemical kinetics.

Background: Exothermic chemical processes lead to many phenomena that are of fundamental and practical interest. It is natural to try to describe such phenomena in terms of the basic chemistry. A natural starting point are systems containing hydrogen and oxygen (3). where the number of species and reactions is limited. The very simplicity of the system makes the specific elements favorite subjects for studies by chemical kineticists. When one goes to a slightly more complex system, for example, the combustion of methane, the generally used database contains 75 species and 325 reactions (4). Even for such a system it is known that the database is unsatisfactory for rich mixture. When one goes to a reference fuel such as heptane, a databases contain over 300 species and 2500 reactions(5,6). The existence of many such kinetics database is evidence of their unsatisfactory nature. In general by suitable adjustment of the elements in the database a variety of observations can be fitted. However for exact quantitative predictions there is much less certainty.

Aside from their size and the effort needed to compile them, another problem with these databases is that validation has almost always been based on fits of situations in oxidative

environments, for example, ignition delays or the regions where negative temperature dependence are reproduced. These are essentially global properties and do not address the issues on the correctness of the individual elements in the database. Chemical kinetics is in many ways still a research area. Older databases represent essentially a snap shot of the chemical kinetics at that time. The large sizes of the database, the enormous effort required to put them together and their fine tuning discourages efforts at improvement. The existing database are really only applicable to pre-mixed system near stoichiometric. Recently, there has been much interest in the particulate forming propensities of combustion system (7). Thus much more attention must be paid to rich situations. In the following we outline recent work on extending the existing heptane kinetics database to cover pyrolytic situations. We then briefly outline some problems with oxidation models and consider the situation of liquid fuels in general

Database for heptane pyrolysis: The reactions characteristic of combustion of any hydrocarbon fuel can be divided four distinct modules (8). They involve [a] the pyrolytic decomposition and [b] the oxidative degradation of the fuel, [c] the destruction of small organic species and [d] PAH or soot formation. The latter represents the oligomerization of the small unsaturated species formed from [a] and [b]. Item [c] is embodied in GRIMECH and contains the reaction set that describe the kinetics of the combustion of methane and small hydrocarbons. There are a number of PAH/soot databases. Item [b] is contained in most existing databases for heptane and similar linear hydrocarbon fuels. Item [a] is the subject of current interest and in our view the least defined at present. Note that items [c] and [d] must be present in any database. Items [a] and [b] deal specifically with the fuel and is necessary for a complete picture.

The mechanism for the pyrolytic decomposition of heptane is summarized in Figure 1.



Figure 1: Mechanism for the pyrolytic breakdown or heptane

It begins with radical attack on the heptyl radical leading to 4 possible heptyl radical. Heptyl radical can isomerize or decompose via beta bond scission. For the latter, data on the decomposition of smaller radicals are available and are used in the present analysis. It is assumed and easily justified that substitution of methylene far from the radical site will have no significant effects on rate constants. The rate constants for isomerization are more difficult to pin down. We have carried out direct experiments. With this data we have now a complete picture of the decomposition of heptyl radicals to smaller alkyl radicals and the 1-olefins. These reactions are competitive with oxygen molecule addition to heptyl radicals and leads to combustion. The database for heptane pyrolysis contains not only heptyl radical decomposition but the kinetics of the breakdown of all the smaller alkyl radicals beginning with pentyl.

A particularly interesting aspect of our work is the resolution of a long standing problem regarding the isomerization reactions of the alkyl radicals (5). These reactions have very large rate constants. They are most conveniently studied near room temperature. The measured A-factors are extremely small and it is difficult to construct a reasonable transition state to accommodate such values. Recent higher temperature measurements lead to much larger A-factors. It is now clear that these effects are a direct consequence of tunneling. Specifically the rate constants at low temperature at almost entirely due to tunneling effects. At 1000 K the tunneling effects represent only 20% of the rate constant, while near room temperature the tunneling effect leads to rate constants that are over an order of magnitude higher than for the case where it is absent. For our purposes the data can be accommodated in terms of an Eckart potential with a width of 1.15 Angstroms. This leads to a non-Arrhenius T^6.5 value. We can rationalize these in terms of the high reaction barrier and the constraints of a cyclic transition state. This work illustrates the problems involved in extrapolating data over extended temperature ranges. They are most important for hydrogen transfer reactions. Nevertheless, an immediate application that comes to mind is the sequence of oxidation reaction $R^* + O_2 = RO_2$ = *QO₂H, in exact analogy to the alkyl radical isomerization case. This has never been taken into account in widely used oxidation databases.

The next step in the pyrolytic decomposition is the decomposition of the 1-olefins. In existing databases, increasing degrees of approximations are used as larger unsaturates are added to the database. There is a tendency to lump them as one compound. This is not justified. The stability of olefins and olefinyl are characterized by resonance energy effects (9). The creation of radicals containing resonance stabilization leads to larger rate constants. If one begins with a resonance stabilized radical, rate constants for decomposition become smaller. In comparison to the heptyl radical, the spread of rate constants is increased. In addition, 1-olefinyl radicals have additional pathways for isomerization. A particularly interesting reaction is the homo-allylic rearrangement (10) that equilibrates certain secondary and primary radicals. The barrier to isomerization is of the order of 60 kJ/mol and the reaction proceeds even at room temperature. The 1-olefinyl radicals with the free electron in the 5 or 6 position can also cyclize to form the cyclopentyl and cyclohexyl radical. We have found that cyclization is much slower than beta bond scission. This is because the latter forms a resonance stabilized radical, allyl. The formation of allyl, will have an inhibitory effect on the overall reaction. The final products in the decomposition of the 1-olefinyl radicals are a variety of 4 and 5 carbon dienes. Together with the small olefins such as ethylene and propene they provide the inputs to existing PAH/Soot model. The new elements introduced with larger fuels are rate constants for isomerization and the effects arising from substitution.

Extensions: The work on the heptane pyrolysis database leads to serious issues regarding the oxidation module. There are vast increases of new species. Thus the 4 heptyl radicals leads directly to the formation of 4 heptylperoxyl radicals. Through internal abstraction of the type described above one can generate 28 hydroperoxyl radical. Each of these can undergo two beta bond scissions and in addition the hydroperoxyl radical can cyclize to form a variety of o-heterocyclics. All of the stable compounds can be attacked by radicals and the entire process will as before start over during the process of molecular size reduction. The existing models are able to reproduce many of the global properties of oxidative systems. Clearly all the possible reactions cannot be of equal importance. Very little effort has been made to quantitatively

reproduce the extensive literature on product distribution from lower temperature oxidative systems. Real time measurement of OH and HO_2 yields during the oxidation of intermediate sized hydrocarbons are beginning to appear (11).

The problem of developing kinetic databases for real liquid fuels is extremely challenging. Real fuels are mixtures that show considerable variations. The use of surrogates have been discussed and there appears to be a consensus that a small set of compounds can be used for this purpose (12). Even in this more limited scope the effort to put together such a database is far larger than that which can be carried out by a single organization. There is a clear need for a JANAF type effort (13). An organization structure for such an effort is being organized. Although the databases can be expected to be large, there is no question for the description of real phenomenon they can be serious reduced. Such reductions must however be based on as complete a database as possible.

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