

PROGRESS IN THE DEVELOPMENT OF A COMBUSTION KINETICS DATABASE FOR LIQUID FUELS

Wing Tsang
National Institute of Standards and Technology
Gaithersburg, MD 20899

ABSTRACT: We describe our progress in the development of chemical kinetics databases for liquid fuels. The intention is to create kinetics databases that can be used to simulate all aspects of combustion across a wide range of equivalence ratios. This paper will include some brief comments on existing databases, a summary of current work and a discussion of future directions. Liquid fuels are complex mixtures containing hundreds of compounds. There are however a limited number of classes. There is general agreement that surrogate mixtures, with a limited number of compounds, can reproduce much of the combustion behavior of real fuels. The largest component in liquid hydrocarbon fuels are the linear alkanes and we have concentrated our work on this type of compound. The discussion will cover work on the development of a database for the cracking of heptane to form the small olefins and dienes that can be used as inputs to PAH/soot models. Primary emphasis has been on the unimolecular reactions that break the larger organic radicals to smaller components used in soot models. Rate constants on the isomerization and breakdown of all alkyl radicals from C₄ to C₇ and 1-olefinyl radicals from C₄ to C₆ have been determined. Recent work has dealt with the chemically activated decomposition of alkyl radicals from H addition to the olefins. These are competitive with the products from hydrogen abstract and will favor olefin as opposed to diolefin yields. The discrepancy between low and high temperature results on isomerization of alkyl radical has been assigned to tunneling effects. Work on the elementary reactions for butylbenzene decomposition was completed. Problems and extensions of this work to more general situation will be discussed.

INTRODUCTION: Fluid dynamics and chemistry are the scientific foundation of combustion. Recent advances in understanding the fluid dynamics of reactive flows[1], particularly in the form of programs with the capability of incorporating increasingly complex chemistry have made simulation of realistic systems a clear possibility. It means that fundamental ideas of fluid dynamics and chemistry can be directly applied to real systems in a quantitative manner. Empirical and expensive test procedures in real or pilot scale systems can have their range of validity increased by simulations. The use of simulations as a design tool is a mark of modern technology. One can scarcely conceive of building new chips or airplanes without the use of simulations. Combustion technology has been a laggard in this regard. Thus, much modern quantitative understanding cannot be used directly in the design process. This is a serious deficiency, since for the foreseeable future the nation's energy needs will continue to depend on combustion sources. Due to the increasing pressures to lower undesirable emissions from combustion devices [2], there are the conflicting problems of increased efficiency and lower emissions. Computer simulation can be a powerful tool for optimization.

In this paper we wish to summarize recent work at NIST aimed at developing the kinetic databases necessary to take advantage of the new technology. We have concentrated particularly on the "fuels" problem. Obviously a description of a realistic system must begin with the fuel. We will begin with a definition of the problem. This will be concerned with the nature of the fuel and the nature of the database. Past work will be summarized and some of the problems

Compound	Mole%
Methylcyclohexane	5%
Cyclooctane	5%
Butylbenzene	5%
Tetralin	5%
Metaxylene	5%
1,2,4,5 tetramethylbenzene	5%
1-methylnaphthalene	5%
Isooctane	5%
Decane	15%
Dodecane	20%
Tetradecane	15%
Hexadecane	10%

Table 1: Composition of a typical JP-8 surrogate mixture [3]

described. The NIST work has been dealt with heptane pyrolysis. The rationale for this approach will be justified and some of the problems encountered described. This will set the basis for extension to larger fuels will be illustrated by considering the inclusion of butylbenzene as a fuel in a "real fuels" kinetics database.

PROBLEM DEFINITION: A serious impediment to the development of databases for computer simulation of the combustion of realistic fuels is the complex nature of such mixtures. Liquid fuels are usually a particular cut from the refinery. There are variations in composition with the season and when regulations change. Since there are literally hundred of compounds in fuel mixtures, it is

obviously impossible to develop databases for such mixtures. Indeed, it is difficult to carry out experimental studies when the starting material is so poorly defined. On the other hand, the large number of compounds can be categorized in terms of a limited classes of molecules. Table 1 is a typical mixture for JP-8[3]. This is obviously a more manageable situation. A recent workshop at NIST has produced an even more limited list[4]. There does appear to be general consensus among all who work on these problems that a limited list of compounds can be used to represent all possible situations. No claim is made that this must be of a particular composition. Instead by appropriate variation of composition all possible situations can be encompassed. It is interesting that the largest component is the linear alkanes and indeed they make up over half of the mixture in Table 1. Thus, there is good justification for starting with such compounds and heptane in particular.

Heptane is a reference fuel. There are a large number of kinetics databases [5-7]. However they have all been validated on the basis of oxidative breakdown. They are characterized by a large number of reactants and thousands of reactions. Recently, there has been increased interest in the soot formation propensities of combustion mixtures[8]. Although existing databases have some of the reactions dealing with pyrolytic decomposition, the subject of the present work, these reactions have only minor effects on the oxidative properties under near stoichiometric conditions. Thus, many of the unjustified assumptions, as well as outdated data have remained in the databases, since their validity has never been tested. It is clear that they cannot be used for applications under rich conditions. This also lead us to suspect that the sizes of these data bases can be significantly reduced. Nevertheless these databases do reproduce many of the aspects of oxidative degradation. Thus our first effort was to bring into the picture the rate constants underlying the pyrolytic decomposition process. Aromatic compounds are an important component of liquid fuel. We have recently extended our analysis to cover butylbenzene. As before we will begin by concentrating on the pyrolytic reactions. Some comments on the oxidative breakdown will also be presented.

NATURE OF THE DATABASE: The essence of the kinetic database are the individual transferable rate expressions that characterize each elementary process. Also of importance are the thermodynamic properties of the molecules and intermediates. These form the boundary conditions in any calculation and in many cases are the basis for estimation. A third element in a complete database is the transport properties. For the present, we concentrate on the chemical kinetics and related thermodynamics. Thermal rate constants represent the first level of transferable information. They involve reactions where the molecules obey thermal distributions. They are most easily represented in the Arrhenius or modified Arrhenius form. Unfortunately, at sufficiently high temperatures for unimolecular reactions the thermal (Boltzmann) distribution can either not be maintained or cannot be attained starting from a reaction that contains excess energy (chemical activation). Fortunately, the treatment of such perturbations can be readily carried out and a great deal of the present effort has been devoted to making such corrections [9]. Thermal rate constants are however the basis of such corrections. The first step in our efforts is devoted to determining these rate constants. Our evaluations are based on the existing experimental data, but not necessarily on direct measurements. Extensive use is made of detailed balance, since in many cases the desired values can be quite accurately determined through those for the reverse reactions. In other cases we use empirical correlations or thermokinetic considerations.

HEPTANE PYROLYSIS DATABASE: Figure 1 contains pathways for pyrolytic decomposition. Together with the oxidative decomposition route we begin with fuel radicals. It is noteworthy that the majority of the reactions involve beta bond scission and isomerization. There is a large amount of data bearing on the former. They are related to radical addition to unsaturated compounds through the equilibrium constant [10]. Although there are in fact very little data bearing on the larger alkyl radicals, the existing data can readily be used for the larger systems of interest since addition of methylene groups far from the reaction site should have minimal effects. The situation is less favorable for isomerization processes. It is known that 1-4 hydrogen transfer is less favored than 1-5 hydrogen transfer. We have obtained rate information on these processes from experimental studies[11]. In addition we have also determined rate constants for 1-6 hydrogen transfer. For the decomposition of heptyl radicals we were able to obtain a complete set of experimental data from which high pressure rate expressions were derived. These can now be projected over the full range of combustion conditions by taking into account energy transfer effects.

The next task is the determination of the rate constants for the creation of the 1-olefinyl radicals. For the radical sites in the 4,5, and 6 position, the rate constants should be the same as those for heptyl radical formation from heptane. Hydrogen in the 3 position in the 1-olefins is weakened by allylic resonance. However, the full value of the resonance energy is not manifested in the rate expression. Data on the actual magnitude of this effect exist in the literature. The consequence is that all the possible 1-olefinyl radicals can be formed from radical attack.

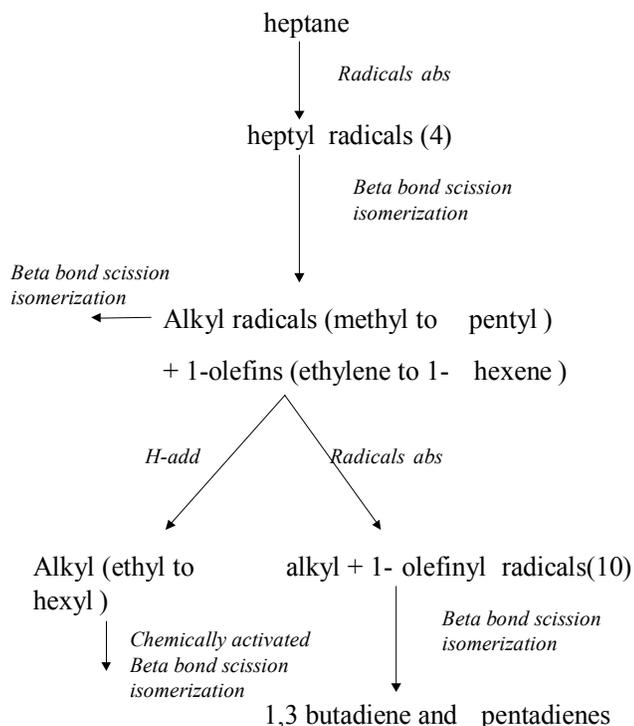


Figure 1: Mechanism for the breakdown of heptyl radical to small unsaturates

decomposition must also include that for pentyl, butyl, propyl and ethyl radicals. In the same way the set of reaction involving 1-hexene and 1-hexenyl, 1-pentene, 1-pentenyl, 1-butene and 1-butenyl must also be present. It is clear that the problem of building an extensive database for cracking is definitely achievable. Probably the real problem is building the database for oxidation, since the number of reactants increases by over an order of magnitude. Nevertheless it is unlikely that all the reactions make equal contributions. Data from product distributions should permit drastic reductions of the reaction pathways.

Chemically activated radical decomposition: In the above, we have created radicals by abstractions. In the following, we describe another channel for radical attack on unsaturates that has the effect of retarding the formation of the dienes. The importance of this reaction is seen in Figure 2. This figure presents data on hydrogen addition to 1 and 2-butene and the rate constant for the abstraction of hydrogens from 1-pentene and n-butane. It can be seen that although there are a large number of hydrogens in the hydrocarbons, in the pressure range of 700-1000 K the addition process is fully competitive with the abstraction reaction. The mechanism is outlined in Figure 3 for the case of non-terminal addition of hydrogen to 1-pentene leading to the formation of 1-pentyl radical. The issue is how much of the 2 pentyl isomers and the decomposition products will be formed as a result of the addition process.

Practically all the past work on chemically activated decompositions has dealt with studies near room temperature [13]. The consequence is that there are no contributions from the thermal decomposition of the stabilized molecule. The aim of the present work is to arrive at a general picture of the case where the chemical activation reaction is occurring under combustion temperatures. At high enough pressures energy transfer will be so fast that chemical activated decomposition cannot occur. On the other hand, if chemical activation is of some importance we will be interested in how rate constants and product distributions will be effected by the high temperatures of interest. Figure 4 gives a picture of the physical situation. At the lowest temperatures, subsequent to an initial induction period and before the attainment of a final steady state distribution one obtains the chemically activated decomposition. However at really long time there are indications that yields are beginning to increase again. The physical picture consists of a certain amount of product being decomposed

The 1-olefinyl radicals decompose by beta bond scission and isomerization. If the 3-position is not involved then the rate constants should be the same as those for alkyl radicals. For reactions involving the 3-position allylic resonance energy will lead to a rate constant for its formation that is smaller than when resonance stabilization is absent. A quantitative value can be derived through the use of the rate constant for the reverse addition of radicals to butadiene and then obtaining rate constants in the beta scission direction through detailed balance. The consequence is activation energies about 12 kJ/mol higher. If a non-resonance stabilized radical leads to the formation of resonance stabilized radicals, the consequence is a higher rate constant with the activation energies about 10 kJ/mol smaller. In comparison to the situation for heptyl radical decomposition, the addition of the vinyl grouping is to spread the range of possible rate constants. It is also interesting that for the 1-olefinyl radicals there is a new type of isomerization, the homoallylic rearrangement [12] that converts a secondary to a primary radical. The rate constants for such processes are extremely large. Indeed, they proceed at room temperature. This means that the appropriate primary and secondary radicals are equilibrated.

Examination of Figure 1 shows the prevalence of beta bond scission reactions involving alkyl radicals. For any large alkyl radicals, their mechanism for degradation must inevitably include decomposition of other smaller alkyl radicals. Thus in the case of heptyl, the database for its

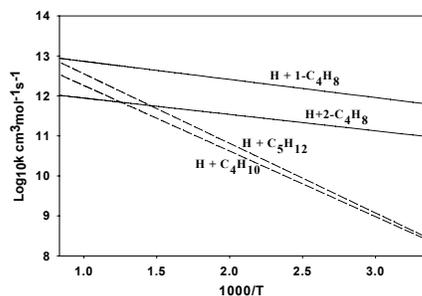


Figure 2: Rate constants for H addition to 1-butene, and 2-butene and H abstraction from 1-pentene and n-butane

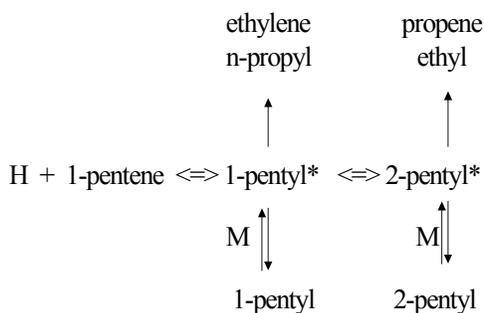


Figure 3: Mechanism for the chemically activated decomposition of 1-pentyl radical

via chemical activation. However much of the activated molecule is being stabilized. As the concentration of stabilized molecule increases, more and more of the molecule will exceed the reaction threshold and begin to decompose. This can be seen in Figure 4 at 400 K for long times and more clearly discerned at 550 K. At the highest temperature the chemical activation and the thermal processes run together and every chemically activated molecule is decomposed. The entire process involves a chemical activation and a thermal component. Note that for the latter the rate constant is the one in the appropriate fall-off region.

Contribution of tunneling to radical isomerization: A particularly interesting aspect of our work is the resolution of a long standing problem regarding the isomerization reactions of the alkyl radicals. These reactions have large rate constants. They are most conveniently studied near room temperature. Surprisingly, the measured A-factors are extremely small [14,15] and it is difficult to construct a reasonable transition state to accommodate such values. Recent higher temperature measurements from this series of studies [11] lead to drastically larger A-factors. It is now clear that these effects are a direct consequence of tunneling. Specifically, the measurements at low temperature are 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 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 value. We can rationalize this in terms of the high reaction barrier and the constraints imposed by the

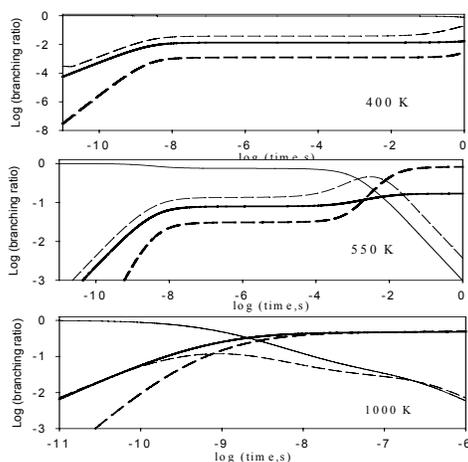


Figure 4: Branching ratio for decomposition and stabilization products during the chemically activated decomposition of 1-pentyl radical from H atom non-terminal addition to 1-pentene. The lines are for 1-pentyl formation (light) and product formation from 1-pentyl (heavy) and 2-pentyl formation (light-dashed) and product formation from 2-pentyl (heavy-dashed). Results are at stated temperature and 1 bar

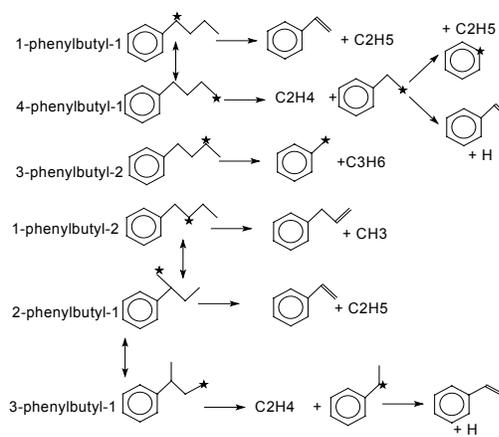


Figure 5: Mechanism for the decomposition of phenylbutyl radicals

cyclic transition state. This work also illustrates the problems involved in extrapolating data over extended temperature range. . Fortunately, they are probably most important for hydrogen transfer reactions. An immediate application that comes to mind is the sequence of oxidation reaction $R^* + O_2 = RO_2 = ^*QO_2H$, in exact analogy to the alkyl radical isomerization case. This has never been taken into account in widely used oxidation databases.

Kinetic database for butylbenzene pyrolysis: Alkylbenzenes are frequently found in fuel mixtures.. Butylbenzene has been suggested as a possible component in surrogate mixtures of JP-8 (see Table 1). Through abstraction reactions 4 phenylbutyl radicals are initially created. Figure 5 presents the mechanism for the decomposition of the phenylbutyl radicals. Note that a neophyl rearrangement[16] transforms 1-phenylbutyl-2 to 2-phenylbutyl-1 and 1,4 isomerization converts the latter to 3-phenylbutyl-1. The special feature of butylbenzene, and indeed any fuel molecule that contains aromatic groupings is the extremely strong C-H bond associated with the aromatic ring and the weak benzyl C-C and C-H bonds. The general situation is outlined in Figure 6. An immediate consequence is that the aromatic ring is preserved while the side chain hydrogens are being abstracted during the initial stages of the decomposition reactions. Thus it is not

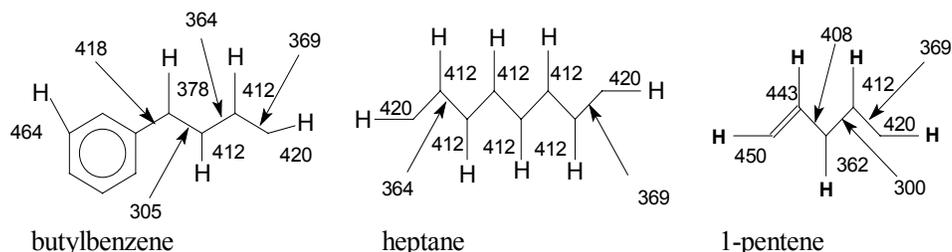


Figure 6: Bond energies in butylbenzene, heptane and 1-pentene (17)

surprising that there are correlations between aromatic content of fuels and their sooting propensities. For the aromatic fuels the first ring is already present. In deriving the rate expressions for the reactions in Figure 5, we follow the same procedure as outlined for the 1-olefinyl radicals. We depend as much as possible on measurements of the reverse radical addition process and derive rate constants on the basis of detailed balance. It soon became clear that there are marked similarities between the phenylbutyl and 1-olefinyl systems. From Figure 6, this is a direct consequence of the similarities in the allylic and benzylic resonance energies. This should not be surprising since the aromatic ring is not disturbed. This is illustrative of the key role that the heptane combustion database can play as the base upon which predictions can be made. Note that the homo-allylic rearrangement for olefinyl radicals is matched by the neophyl rearrangement for branched aromatics and with rate expressions that are close to each other.

Extensions: The results presented here suggest that a pyrolysis kinetic database for real fuels is an achievable goal within a reasonable time frame. The new element that is introduced in comparison to smaller hydrocarbon database is the presence of isomerization processes. We have now carried out studies involving 1-7 isomerization and it is clear that the rate constants are decreasing. Thus for a large linear alkyl radicals, for example a linear C_{16} compound, there appears to be no need to consider isomerizations higher than 1-8 or 1-9 H-atom transfer. There remains of course a great number of beta bond scission reactions that must be specified. The variations in rate constants should not be any larger than those given here. Similarly, for the olefinyl radicals there is a limit above which rate constants will not vary greatly. The effect of methyl substitution could be readily derived from a number of simple experiments using the technique employed to determine branching ratios in normal alkyl decomposition. Since the pyrolytic kinetics database for a large species includes all the smaller alkyl radicals formed as a result of its decomposition, it is clear that the database can cover the full range of possible fuels.

The situation is less favorable in the case of oxidation. This is due to the increased number of possible species. Thus in the case of butylbenzene, the initially formed phenylbutyl radicals can react with oxygen to form 6 peroxy radicals. One can generate 28 hydroperoxy radicals through internal abstraction of the type described above. Each of these can undergo two beta bond scissions and in addition the hydroperoxy 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 start over during the process of molecular size reduction. We estimate the number of species in the oxidative database will be over an order of magnitude larger than the pyrolytic database. Nevertheless, the existing models are able to reproduce many of the global properties of oxidative systems. All the possible reactions cannot be of equal importance. It may well be that combining the pyrolytic database to existing oxidation databases may extend the range of applicability to richer fuel mixtures. Very little effort has been made to quantitatively reproduce the extensive literature on product distribution from lower temperature oxidative systems[18].

Probably a serious deficiency in the information base for oxidative decomposition are the absence of measurements that can be related directly to rate constants. However, real time measurement of OH and HO₂ yields during the oxidation of intermediate sized hydrocarbons are beginning to appear [19]. It is clear that no single group can develop the type of data base that is needed. There is a clear need for a JANAF type effort [20]. 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.

ACKNOWLEDGEMENT: This research was supported by the US Dept. of Defense through the Strategic Environmental and Development Program (SERDP #1198), Charles Pellerin, Scientific Officer.

References:

1. Kee, R. J., Coltrin, M. E. and Glarborg, P., "Chemically Reacting Flow" Theory and Practice, Wiley, Interscience, New York, 2003
2. Yanowitz J, Graboski M.S., McCormick R.L., "Prediction of in-use emissions of heavy-duty diesel vehicles from engine testing" Environ. Sci and Tech. 36: 270-275, 2002
3. Edwards, T., Harrison, W. E. III, and Maurice, L. Q., "Properties and Usage of Air Force Fuel: JP-8", AIAA 2001-0498, 39th AIAA Aerospace Sciences Meeting and Exhibit, January 8-11, 2001 Reno. NV
4. NISTIR 7155 , Workshop on Combustion Simulation Databases for Real Fuels, September 4-5, 2003, Gaithersburg, MD 20899
5. Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K., "A Comprehensive Modeling Study of Heptane Combustion". Comb. and Flame., 1998, 114, 149
6. Lindstedt, R.P., Maurice, L.Q. Detailed Kinetic Modeling of n-Heptane Combustion Comb. Sci. Tech., 1995, 107: 317-353.
7. Bakali, A.E., Delfau, J-L., Vovelle, C., Kinetic Modeling of a Rich Atmospheric Pressure, Premixed n-heptane/O₂/N₂ Flame. Combust.Flame, 1999, 118:381-38
8. Richter H, and Howard J.B., "Formation of polycyclic aromatic hydrocarbons and their growth to soot - a review of chemical reaction pathways ", Prog. Energ. Combust. 2000, 4, 565-608
9. Tsang, W., "A Pre-processor for the Generation of Chemical Kinetics Data for Simulations" AAIA-2001-0359, 39th AIAA Aerospace Sciences Meeting and Exhibit, January 8-11, 2001 Reno. NV
10. Kerr, J. A. and Parsonage, M.J. "Evaluated Kinetic Data on Gas Phase Addition Reactions. Reactions of Atoms and Radicals with Alkenes, Alkynes and Aromatic Compounds" Butterworths, London, 1972
11. Tsang, W, "Heptane Combustion Database" AIAA 42nd AIAA Aerospace Science Meeting and Exhibit, January 4-8 2004, Reno, NV
12. Carter, WPL, and Tardy DC "Homoallylic isomerization of 1-Penten-4-yl and the critical energy for methyl+1,3-butadiene", J. Phys. Chem., 1974, 78,1245-1248
13. Holbrook, K. A., Pilling, M. J., and Robertson, S. H., "Unimolecular Reactions", John Wiley, 1996
14. Watkins, K. W., "Isomerization of 1-Hexyl Radicals in the Gas Phase" J. Phys. Chem., 1973, 77, 2938-2942
15. Dobe, S., Berces T. Reti, F. and Marta, P. "Isomerization of n-Hexyl and s-Octyl Radicals by 1,5 and 1-4 Intramolecular Hydrogen Atom Transfer Reactions", Int. J. Chem. Kin., 1987, 19, 895-921
16. Weber, M. and Fischer, H., J. Absolute rate constants for the beta-scission and hydrogen abstraction reactions of the tert-butoxyl radical and for several radical rearrangements: Evaluating delayed radical formations by time-resolved electron spin resonance Am. Chem. Soc. 1999, 121, 7381-7388
17. Tsang, W. "Heat of formation of organic radicals by kinetic methods" in "Energetic of free radicals" (Simoes, J. A. M., Greenburg, A. and Liebman, J.F, ed) Blackie, London, 1996, 22-58
18. Griffiths J. F. and Mohamed, C. "Experimental and Numerical Studies of Oxidation Chemistry and Spontaneous Ignition Phenomena", in Comprehensive Chemical Kinetics, Low Temperature Combustion and Autoignition (M. J. Pilling, ed) 1997, 545-660
19. DeSain, J. D., Klippenstein S. J. Miller, J. A. , Taatjes, C. A., "Measurements, theory and modeling of OH formation in ethyl plus O₂ and propyl plus O₂ reactions" J. Phys Chem., A, 2003, 107, 4415-4427
20. Chase, MW., "NIST-JANAF thermochemical tables" American Chemical Society ; 1998