Chemical Kinetic Modeling of Higher Hydrocarbon Fuels

Charles K. Westbrook*
Lawrence Livermore National Laboratory, Livermore, California

This paper discusses current efforts directed toward extension of numerical modeling of chemical kinetics to hydrocarbon fuel molecules that are much larger than those treated in the past. The techniques needed are described and illustrated, including the identification of specific product distributions for decompositions of fuel and alkyl radicals, estimation of site-specific H atom abstraction reaction rates, and coupling between the large molecule reactions and those of the H_2-O_2-CO basis reaction mechanism.

Introduction

DURING the past 10–15 years, chemical kinetics modeling of hydrocarbon combustion has established a solid foundation.[1] During this time, the parallel growth in available computer power and in the development of numerical algorithms for solving kinetics equations have been essential elements. However, for three equally important reasons, most of this past research has been limited to rather small hydrocarbon fuel molecules. First, reaction mechanisms are most often constructed in a sequential manner, beginning with the simplest fuels such as hydrogen and methane, then proceeding systematically to C_2 and then C_3 hydrocarbon fuels. This type of development takes a considerable amount of time, since each additional step must be tested and validated extensively before moving on to the next fuel. Second, the very precise types of experiments that are needed to develop and test kinetic models have emphasized the smaller, simpler hydrocarbon fuels such as methane, ethane, and propane. Experiments that measure intermediate species concentrations, radical concentrations, and ignition delays for large fuels have not previously been available. Finally, the computational resources required for the solution of the kinetics equations for large fuel molecules have not been available in the past. The computational costs of these models in terms of computer time and data storage and management increase rapidly according to the number of chemical species in the reaction mechanism. Reaction mechanisms for methane oxidation include roughly 20–30 species, while those for propane require 40–50 species; the propane mechanism requires from 3–5 times more computer time and much more computer storage to solve the rate equations than the methane system. Still, all of these limitations notwithstanding, a considerable body of valuable combustion research has been generated by program efforts in this field. Many fundamental theoretical and practical problems have been addressed and the modeling of chemical kinetics processes has made an important contribution to combustion research.

However, many of the types of combustion problems that are of great practical importance at the present time cannot be adequately addressed by kinetic models for simple fuels. The best current example is the problem of engine knock, which limits the compression ratio at which modern automobile engines can operate. The tendency of an engine to knock under a given set of operating conditions is a very sensitive function of the size and molecular structure of fuel being burned, properties that are related to the octane number of the fuel. Although recent studies with accompanying numerical modeling analyses have addressed[2,3] the knock characteristics of *n*-butane in internal combustion engines, there is a great need to examine the knock properties of fuels that more closely resemble or approximate typical automotive engine fuels. Some kinetic processes that may have important roles in controlling engine knock and the autoignition of typical fuels do not occur to any extent with fuels smaller than pentanes, so there are significant limitations to what can be addressed by kinetic modeling until much larger fuels can be considered. Ignition and oxidation of fuels in gas turbines, industrial safety problems, and many other practical questions also depend on combustion of hydrocarbon fuels much larger and more complex than those for which detailed chemical kinetic reaction mechanisms have existed in the past.

Two important new developments in kinetics modeling are beginning to appear that will soon have significant impacts on combustion research. These are the extension of modeling to much larger hydrocarbon fuel molecules, including those as large as octane, and the analysis of the role that the fuel molecular structure has on combustion properties. With fuels as structurally simple as methane or ethane, the principal kinetic questions are limited. Of course, there are many detailed problems concerning the competitions between different reactions, pressure and temperature dependence of various rates, and identification of the major and minor intermediate species. However, as the fuel molecule being considered becomes larger, many additional questions arise. Beginning with propane, both primary and secondary H atom sites are encountered, which have different binding energies and abstraction rates. The different alkyl radicals decompose at different rates into different products, distinctions that can have a significant effect on overall rates of combustion.

Further extension to include butane brings into consideration the possibility of different isomeric forms of the fuel, *n*-butane and isobutane in the case of butane. It is well known that branched chain fuels generally ignite less rapidly but are more likely to lead to soot formation than straight chain isomers with the same number of C and H atoms. At the present time, kinetics modeling is beginning to shed some light on the detailed kinetic reasons for these distinctions as functions of molecular structure. Current analysis includes side-by-side comparisons between kinetic models for oxidation of *n*-butane vs isobutane and of *n*-octane vs iso-octane (2-2-4 trimethyl pentane), together with comparable experimental data from several experimental environments.

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*Physicist, Computational Physics Division.

This type of modeling analysis is indicating that the vast differences in their combustion behavior are not due to differences in the rate of fuel reaction, since both sets of fuels seem to disappear at roughly the same rate in the experiments examined to date. However, the types of intermediate hydrocarbon species produced during the oxidation of the two types of octane are very different. It appears that the straight chain fuels produce large quantities of primary alkyl radicals that decompose rapidly into H atoms, leading quickly to large rates of chain branching and breakdown of the fuel into small fragments. In contrast, the branched chain fuels produce larger amounts of olefins and methyl radicals, with isobutene being particularly important. These hydrocarbon intermediates are relatively slow and difficult to oxidize, so alternative but usually slower reaction paths leading to chain termination and production of soot precursors can occur at appreciable rates.

In addition to the growing ability of kinetic modeling to examine paraffinic fuels that are much larger and more complex than those dealt with in the recent past, there is one other very important development that has now become possible and will begin to appear in the near future. Application of kinetic modeling to include aromatic fuels has in the past been impossible for two major reasons: 1) the reaction mechanisms were evidently too large to be tractable, and 2) not enough mechanistic information was available on the details of H atom removal from aromatic fuels and the eventual ring-breaking elementary reactions. Current successes in dealing with very large mechanisms such as the octanes provide ample encouragement and reassurance that the computational difficulties to be encountered in dealing with aromatic fuels should not be insurmountable and recent significant progress in identification of major mechanistic paths in aromatic oxidation[4] is providing the fundamental rate data that these models will require.

Combustion chemistry in practical systems, including gas turbines and internal combustion engines, is complicated by the fact that the fuels used in such systems are usually not composed of simple molecules such as methane or propane. Instead, the fuels are generally very large molecules and almost always mixtures of many types of molecules including both paraffinic and aromatic hydrocarbons. From the point of view of kinetics modeling, it is essential that this field grow to the point where the analysis of fuels and fuel mixtures of practical interest and concern becomes possible. Based on past trends and in particular on the work in progress at a number of locations, this capability is rapidly being developed.

Very few earlier kinetic modeling efforts have addressed large hydrocarbon fuels. Coats and Williams[5] modeled ignition of *n*-heptane in shock tubes, using a considerably simplified reaction mechanism for the larger hydrocarbon fragments. In their analysis, all of the H atoms were considered equivalent and the heptyl radicals produced by H atom abstraction from *n*-heptane were all assumed to be consumed by a single sequence of thermal decomposition steps. Using the rules to be described below, this is equivalent to an assumption that all of the heptyl radicals are formed by abstraction of an H atom from a primary site in *n*-heptane and results in an overestimate of the ethylene and methyl radical concentrations in the product distributions. The modeling study was intended to address problems in formation of soot precursors, but the overestimate of CH_3 and C_2H_4 will result in excessive soot precursor production. This approach did not consider the possibility of differences in fragmentation patterns for different classes of heptyl radicals. However, as a demonstration of the feasibility of modeling oxidation of large hydrocarbon fuels, this was a very noteworthy effort.

More recently, Doolan and Mackie[6] presented kinetic modeling results for pyrolysis of *n*-octane behind shock waves. This work did include distinctions between different sites in the hydrocarbon molecule and isomerization reactions between them, enabling it to account for the experimentally observed distributions of C_2-C_7 olefins. A considerable amount of modeling analysis of *n*-alkane pyrolysis at somewhat lower temperatures ($650K \leq T \leq 840K$) has also included site-specific reaction rates of H atom abstraction and isomerization reactions between different alkyl radicals.[7-10] The present paper describes current efforts to combine all of these elements together (treatment of large hydrocarbon fuels, site-specific H atom abstraction, reasonable ways of estimating rates of these site-specific reactions, decomposition reactions of alkyl radicals, and inclusion of both pyrolysis and oxidation reactions) to make a single unified reaction mechanism.

Kinetic Mechanisms

Detailed kinetic reaction mechanisms have a strongly hierarchical structure,[11] with the mechanisms for complex fuels built upon submechanisms for simpler, smaller fuel molecules. The base for all hydrocarbon oxidation is the submechanism for oxidation of hydrogen and carbon monoxide. This submechanism consists of approximately 20–25 elementary reactions between H, O, OH, H_2, O_2, HO_2, H_2O, H_2O_2, CO, and CO_2. The most important of these reactions are those that consume H_2 and CO

$$H_2 + OH = H_2O + H \tag{1}$$

$$CO + OH = CO_2 + H \tag{2}$$

together with the dominant chain branching reaction

$$H + O_2 = O + OH \tag{3}$$

and its primary competitor for H atoms

$$H + O_2 + M = HO_2 + M \tag{4}$$

To a great extent, reactions competing with H_2 and CO for OH will inhibit or retard oxidation of these species as well as the heat release associated with production of water and carbon dioxide, and reactions competing with reaction (3) for H atoms will reduce the rate of chain branching and the overall rate of combustion. Conversely, reactions that produce additional H atoms which can then react with molecular oxygen via reaction (3) will accelerate the overall rate of combustion. During the oxidation of many hydrocarbon fuel molecules, ethyl radicals are produced. Since these radicals decompose rapidly to produce H atoms,

$$C_2H_5(+M) = C_2H_4 + H(+M) \tag{5}$$

the production of ethyl radicals will tend to have a strongly accelerating effect on the overall rate of combustion.

The second major radical species having particular importance is the methyl radical CH_3. Unlike most other hydrocarbon radicals, methyl radicals do not decompose to provide smaller fragments or H atoms. Instead, a considerable fraction recombine through

$$CH_3 + CH_3 = C_2H_6 \tag{6}$$

thereby removing radicals from the available radical pool and resulting in significant amounts of chain termination.

One essential element in modeling the combustion of large hydrocarbon fuels is the identification of the principal radical species produced and the relative rates of production of H atoms and methyl radicals in particular. A good example of this trend is provided by modeling studies of ignition of *n*-alkanes behind reflected shock waves,[12] simulating experimental work of Burcat et al.[13] As illustrated in Fig. 1,

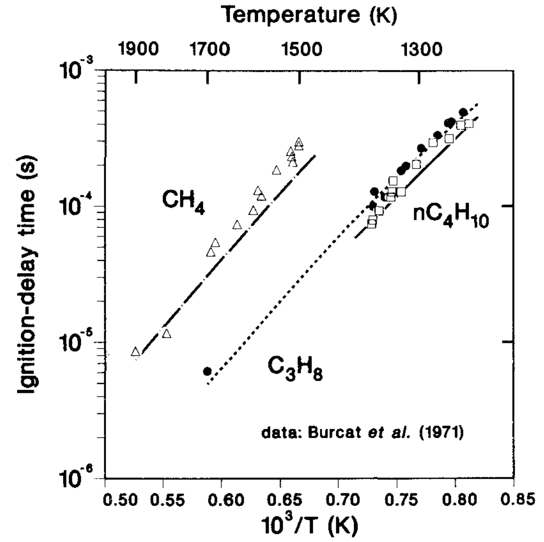


Fig. 1 Comparisons between experimental (open symbols) and computed (lines) ignition delay times for fuel/oxygen/argon behind reflected shock waves.

methane is the slowest of the *n*-alkane fuels to ignite, ethane (not shown) is the fastest, and propane, *n*-butane, and *n*-pentane are approximately equal in ignition rate and rank between methane and ethane. A relatively simple explanation for these trends is provided by the above discussion of the impact of H atoms and CH_3 and C_2H_5 radicals on the overall branching rate. The only major radical produced during methane oxidation is the methyl radical; therefore, methane is relatively very slow to ignite because few H atoms are produced, indirectly during the subsequent slower consumption of the methyl radicals. In contrast, H atom abstraction from ethane yields ethyl radicals, which then decompose to produce H atoms through reaction (5), and few methyl radicals are produced. As a result, ethane ignition is the most rapid. The remaining *n*-alkane fuels produce a mixture of ethyl and methyl radicals following H atom abstraction from the fuel. With propane,[14] there are two distinct propyl radicals, the *n*-propyl radical that decomposes by

$$nC_3H_7 = CH_3 + C_2H_4 \tag{7}$$

and the isopropyl radical that decomposes by

$$iC_3H_7 = H + C_3H_6 \tag{8}$$

Both produce relatively unreactive olefin molecules, but production of the *n*-propyl radical results in a net decrease in the overall rate of combustion due to the subsequent production of methyl radicals. The production of isopropyl radicals conversely leads to an accelerated rate of combustion, since it then provides H atoms that subsequently lead to chain branching from reaction (3).

The same type of behavior is observed for combustion of *n*-butane.[15] In this case, the two radicals formed by H atom abstraction from *n*-butane are primary and secondary butyl radicals that decompose primarily by

$$pC_4H_9 = C_2H_5 + C_2H_4 \tag{9}$$

$$sC_4H_9 = nC_3H_7 + CH_3 \tag{10}$$

With the ethyl radical decomposition producing H atoms, abstraction of primary H atoms from *n*-butane leads to chain branching, while abstraction of secondary H atoms leads to chain termination via the production of methyl radicals.

In the case of *n*-pentane, another element enters this picture. There are the same number of primary H atoms as in propane and *n*-butane and these decompose through

$$1\text{-}C_5H_{11} = C_2H_4 + nC_3H_7 \tag{11}$$

The *n*-propyl radical then decomposes by reaction (7), so the 1-pentyl radical leads to chain termination. The new element is the fact that, although there are six secondary H atoms, they are not all the same. Four of these H atoms are bonded to the second C atom site, while the remaining two H atoms are bonded to the third or central C atom. The two distinct types of secondary pentyl radicals then decompose differently. The four pentyl radicals produced by abstraction of the H atom from the second site decompose by

$$2\text{-}C_5H_{11} = C_3H_6 + C_2H_5 \tag{12}$$

and lead to chain branching, while the last type of pentyl radical decomposes

$$3\text{-}C_5H_{11} = CH_3 + 1C_4H_8 \tag{13}$$

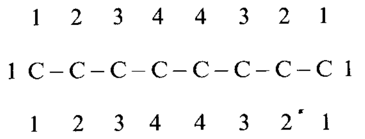
which leads to chain termination.

The above discussion shows that it is essential to be able to keep distinct all of the logically distinct alkyl radicals that can be formed, since they often will lead subsequently to distinct sets of product distributions and differing rates of chain branching, propagation, and termination. For the relatively simple fuels already discussed and for other simple hydrocarbon fuels, the rates of H atom abstraction from specific sites and the rates of alkyl radical decomposition, together with the principal products from those decompositions, have all been studied experimentally. However, none of these data have been determined experimentally for most larger fuel molecules. As a result, it is necessary to develop a systematic and kinetically sound way of estimating these quantities. In the remainder of this paper, the principles being used to carry out these estimations for straight-chain and branched-chain hydrocarbon fuels up to octanes are described and illustrated and the strengths and potential weaknesses of such an approach discussed.

Initiation Reactions

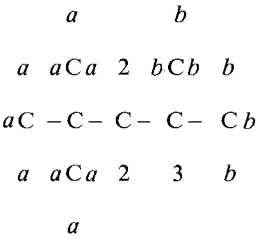
In the majority of combustion environments, transport processes provide an ample supply of radical species that then facilitate the process of fuel consumption. However, in a few cases the fuel-oxidizer mixture must generate this radical pool by itself. Examples of this type of environment are shock tubes, detonations, and some other ignition problems. The reactions that begin the generation of a radical pool are most commonly the thermal decomposition reactions of the fuel molecule itself. For smaller hydrocarbon fuels, these reactions have been extensively studied, both experimentally and theoretically, and the rates of decomposition and the product species have been measured. In the case of methane, a C-H bond must be broken, which has a bond energy of approximately 104 kcal/mole. For ethylene, two sets of products are formed, $C_2H_2 + H_2$ and $C_2H_3 + H$. For the vast majority of larger hydrocarbon fuels and virtually all alkane fuels, a C-C bond is broken with a bond energy of approximately 10-15 kcal/mole less than that for a comparable C-H bond. An observation that can be drawn from initiation reactions studied is that there is a rather strong preference for product alkyl radical products which are approximately equal in size. Thus, for *n*-butane, $C_2H_5 + C_2H_5$ is considerably more likely than $nC_3H_7 + CH_3$ as the primary product channel.

The following examples refer to two isomeric forms of octane. The first, straight-chain *n*-octane, can be represented by



$$\begin{array}{ccccccccccc} & 1 & 2 & 3 & 4 & 4 & 3 & 2 & 1 & \\ 1 & C- & C- & C- & C- & C- & C- & C- & C & 1 \\ & 1 & 2 & 3 & 4 & 4 & 3 & 2' & 1 & \end{array}$$

where the number 1 refers to the H atoms bonded at primary sites, while the numerals 2-4 refer to logically distinct H atoms bonded at secondary sites. For *n*-octane, the major product channels for molecular decomposition should be $1\text{-}C_5H_{11} + nC_3H_7$, followed in importance by two $1\text{-}C_4H_9$ radicals. There should be very little contribution from $CH_3 + 1\text{-}C_7H_{15}$ or the channel $C_2H_5 + 1\text{-}C_6H_{13}$. The second example is that of iso-ocatane (2-2-4 trimethyl pentane), shown schematically as



$$\begin{array}{ccccc} & a & & b & \\ a & aCa & 2 & bCb & b \\ aC & -C- & C- & C- & Cb \\ a & aCa & 2 & 3 & b \\ & a & & & \end{array}$$

Note in this diagram that the H atoms indicated by *a* and *b* are all bonded at primary sites, but those represented by *a* are logically distinct from those represented by *b*. The H atoms indicated by numerals 2 and 3 are at secondary and tertiary sites. Two sets of products should be expected from thermal decomposition of this molecule, using the rule outlined above. These sets of products are distinguished by whether the iso-octane molecule breaks on one side or the other of the secondary C atom. Thus, the expected products should be the terbutyl radical and the isobutyl radical or a neopentyl radical and iC_3H_7. The pieces thus formed then decay following some general rules that will be discussed below. The same overall patterns can be used to predict the product distributions for analogous reactions of any other fuel molecule of interest. The rates of many of these thermal decomposition reactions can also be estimated to a reasonable degree, based on the bond strengths and geometry of the fuel molecule. In large hydrocarbon fuel molecules, structurally similar C-C bonds generally have very similar bond energies, so the activation energies of their decomposition reactions are quite similar. Likewise, the pre-exponential terms in the rate expressions do not vary particularly with molecule size.

Even in those combustion environments in which initiation is essential (such as shock tubes, detonations, and others), the entire initiation phase is almost always a very small fraction of the entire ignition or combustion period. Furthermore, the exact identity of the initiation products and the rate of the specific reactions rarely has a very strong influence on the rate of ignition. For example, during the shock tube ignition of the *n*-alkanes discussed earlier, the initiation phase occupied less than 5% of the total ignition delay time for all of the fuels. Thus, the conclusion is that the initiation reactions play a role only in a few specialized types of combustion problems and, even in those cases, the overall combustion rates are not particularly sensitive to the rates and product distributions of initiation reactions. The primary goal of these initiation steps is to establish a radical pool; this is done rather quickly and it is the radical pool that carries out the bulk of the fuel consumption.

Abstraction Reactions

The oxidation of hydrocarbon fuels actually takes place through the gradual disassembly of the fuel molecule into successively smaller fragments, leading to a considerable degree to C_1 and C_2 species and then to CO and H_2. The first major step is the abstraction of H atoms from the parent fuel molecule. Once a viable radical pool has been established, most of the H atom abstraction is accomplished by reactions between small radical and atomic species and the fuel molecules. The most important such radical species are H, O, OH, HO_2, and CH_3. From previous modeling experience, H atom abstractions by H and OH are dominant for fuel-rich and near-stoichiometric mixtures, while reactions with OH and, to a much lesser extent, O atoms are most important for fuel-lean mixtures.

Rates of H atom abstraction reactions have been studied extensively for many hydrocarbon species, particularly for C_1–C_3 hydrocarbons. A wealth of experimental and theoretical information is available for these steps, especially for reactions with H and OH, which are generally most important. However, again much less is known about rates of reactions of much larger hydrocarbon fuels, including most fuels with more than four or five C atoms. Even less is available for relative rates of H atom abstraction from different sites in the fuel molecule, information which is essential in describing the total rate of fuel oxidation. Fortunately, recent studies have appeared that provide some guidance in this area. For example, work by Tully and coworkers[16,17] has examined the differences in abstraction of H atoms by OH radicals from similar sites in different fuel molecules. In the very detailed experimental work of Tully et al., the rates of primary and secondary H atom abstraction were independently measured in fuels such as ethane, propane, neopentane (tetramethyl methane), cyclohexane, and others. Neopentane is particularly interesting because all 12 H atoms are bonded to primary C atoms, while in cyclohexane all 12 H atoms are bonded to secondary C atoms. Thus, these are examples of relatively large hydrocarbon fuel molecules that can provide unambiguous H atom abstraction rate determinations. This work has found that abstraction of H atoms from a primary site in one molecule is remarkably similar to the abstraction of H atoms from a primary site in many other hydrocarbon fuel molecules.The same observation applies to secondary and tertiary sites. Clearly, the similarities are not exact, since the parent molecules are not identical. However, there is enough similarity from one fuel to another to be able to estimate unknown specific rates with a surprising degree of accuracy. This same idea has been developed over the past 25 years in a number of studies, beginning with Greiner[18] and Baldwin and Walker.[19] The development and predictive accuracy of this approach have recently been reviewed by Atkinson.[20] Using the *n*-octane molecule as an example, it is then possible to estimate that the rate of abstraction of the six primary H atoms will be approximately equal to the rate of primary H atom abstraction in either propane or in *n*-butane, both of which have been measured experimentally and examined in modeling studies. Similarly, the total rate of secondary H atom abstraction in *n*-octane will be 6 times that in propane and 3 times that in *n*-butane (since there are 2 secondary H atoms in propane, 4 in *n*-butane, and 12 in *n*-octane).

The simplest model case that can be used to estimate rates of tertiary H atom abstraction reactions is that of isobutane. Unfortunately, rates of tertiary H atom abstraction from isobutane by H, OH, O, and other radical species at combustion temperatures are much less accurately known than the corresponding model cases (i.e., ethane, propane, and *n*-butane) for primary and secondary H atom abstractions. This results in somewhat greater uncertainty in estimates of tertiary H atom abstraction in other molecules; however, given the current precision available, this is unavoidable. More experimental studies at combustion temperatures are urgently needed to improve this portion of the problem of estimation of H atom abstraction reaction rates.

For each fuel molecule of interest, the total rate of H atom abstraction can be constructed by combining together the appropriate number of primary, secondary, and tertiary rates based on the model cases. In the case of *n*-octane, the rate of primary H atom abstraction should be estimated to be equal to that in *n*-butane. As already noted, the total rate of secondary H atom abstraction should be approximately three times that in *n*-butane. However, there are three logically distinguishable secondary sites in *n*-octane and they must be kept distinct. The subsequent fates of the logically distinguishable *n*-octyl radicals will be discussed below.

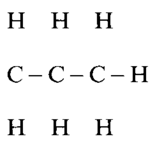
The construction of the total rate of H atom abstraction in iso-octane is somewhat more complex than for *n*-octane, but the principles are exactly the same. Using the diagram presented earlier for iso-octane, there are two distinguishable types of primary H atoms, labeled *a* and *b*. All 15 of these primary H atoms will be assumed to have the same rate of abstraction by reacting radical species, equal to one-sixth of the analogous rate per H atom in *n*-butane or propane. Thus, the total rate of abstraction of type *a* H atoms in iso-octane will be approximately 1.5 times (i.e., 9/6) the total rate of primary H atom abstraction in *n*-butane and the total rate of abstraction of type *b* H atoms will be approximately equal (i.e., 6/6) to that of primary H atom abstraction in *n*-butane. Since there are two secondary H atoms in iso-octane, the total rate of abstraction of these atoms can be estimated to be equal to the rate of secondary H atom abstraction in propane and about half that in *n*-butane, in which there are four such secondary H atoms. Finally, the rate of tertiary H atom abstraction in iso-octane will be approximately equal to that in isobutane, which also has one such H tertiary atom.

The same principles can be used to assemble a total rate of H atom abstraction in any large hydrocarbon molecule. The appropriate numbers of primary, secondary, and tertiary H atom abstraction reactions can be combined, based on model reaction rates for which the rates are well established. Logically distinct alkyl radicals are retained separately and permitted to evolve independently.

Alkyl Radical Decomposition

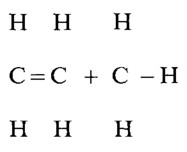
At combustion temperatures above 800–900 K, large alkyl hydrocarbon radicals react primarily by means of thermal decomposition to produce smaller hydrocarbon fragments. Warnatz[21] has shown that, at atmospheric pressures and below, only for alkyl radicals smaller than C_4 species does reaction with molecular oxygen compete to any extent with thermal decomposition. For large alkyl radicals, there are in principle many possible places in the radical at which the bond fission could occur, each leading to different products. However, the great majority of such fragmentations occur at a predictable location that is "one bond away" from the missing H atom.[22] This process, also known as β-scission, can thus be used to identify the probable products of thermal decomposition reactions for radicals that have not been studied specifically.

Examples of β-scission for radicals that have been studied include propyl and butyl radicals. In the case of the *n*-propyl radical



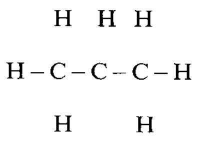
$$\begin{array}{ccccccc} H & & H & & H & & \\ C & - & C & - & C & - & H \\ H & & H & & H & & \end{array}$$

breakage of this radical "one bond away" from the C atom with the free electron will produce as products



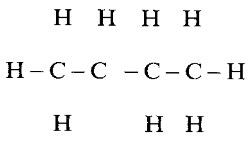
$$\begin{array}{ccccccc} H & & H & & H & & \\ C & = & C & + & C & - & H \\ H & & H & & H & & \end{array}$$

For the isopropyl radical,



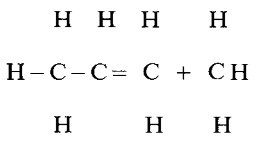
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ H & - & C & - & C & - & C & - & H \\ & & H & & & & H & & \end{array}$$

there is no C-C bond that is one bond away, so a C-H bond will be broken to produce $C_3H_6 + H$. In the case of the sC_4H_9 radical



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & H & & & & H & & H & & \end{array}$$

β-scission yields the products



$$\begin{array}{cccccccc} & & H & & H & & H & & H \\ H & - & C & - & C & = & C & + & CH \\ & & H & & & & H & & H \end{array}$$

Similarly, the same argument applied to the pC_4H_9 radical yields the correct principal products $C_2H_4 + C_2H_5$. In both cases of propane and *n*-butane oxidation,[14,15] the predictions of product distributions and rate estimates agree with experimentally determined values and with results of modeling studies. This agreement provides some confidence in applying the principle to the cases of alkyl radicals for which theoretical and experimental data do not exist.

Using the *n*-octane molecule from above as an example and denoting as 2-C_8H_{17} the *n*-alkyl radical produced by the abstraction of the H atom labeled by the numeral 2, application of β-scission to the *n*-octyl radicals provides the following sets of products:

$$1\text{-}C_8H_{17} = 1\text{-}C_6H_{13} + C_2H_4$$

$$2\text{-}C_8H_{17} = 1\text{-}C_5H_{11} + C_3H_6$$

$$3\text{-}C_8H_{17} = 1\text{-}C_4H_9 + {}_1C_4H_8$$

$$4\text{-}C_8H_{17} = {}_1C_5H_{10} + nC_3H_7$$

$$4\text{-}C_8H_{17} = {}_1C_6H_{12} + C_2H_5$$

In those cases in which two C–C bonds are "one bond away," there is a preference for the formation of the largest possible alkyl radical, which explains why the 3-C_8H_{17} radical does not produce methyl radicals and heptene; however, the selectivity is not so strong that the second alternative for the 4-C_8H_{17} radical would be entirely negligible.

The 1-C_6H_{13} radical produced above will, using the same arguments, quickly decompose to $pC_4H_9 + C_2H_4$, and the butyl radical to $C_2H_4 + C_2H_5$, so the net results from 1-C_8H_{17} are three C_2H_4 molecules and one C_2H_5 radical, resulting in some net chain branching. The other octyl radicals lead to net products of

$$2\text{-}C_8H_{17} = C_3H_6 + 2 \times C_2H_4 + CH_3$$

$$3\text{-}C_3H_{17} = {}_1C_4H_8 + C_2H_4 + C_2H_5$$

$$4\text{-}C_8H_{17} = {}_1C_5H_{10} + C_2H_4 + CH_3$$

$$\text{or } {}_1C_6H_{12} + C_2H_5$$

Taking into account the relative number of each of these radicals that are possible, of the 18 possible H atoms which can be abstracted from *n*-octane, approximately 12 of them lead to chain branching by producing ethyl radicals and ultimately H atoms, while approximately 6 lead to chain termination. This relatively high degree of chain branching is an important factor in the rapidity and ease with which *n*-octane ignites.

Application of the same arguments to the various alkyl radicals produced from iso-octane leads to the following fragments, using the same notational system and applying the principle of β-scission to successive fragments until they are at the level of olefins or C_1 and C_2 radicals:

$$a\text{-}C_8H_{17} = iC_4H_8 + C_3H_6 + CH_3$$

$$b\text{-}C_8H_{17} = iC_4H_8 + C_3H_6 + CH_3$$

$$2\text{-}C_8H_{17} = C_7H_{14} + CH_3$$

$$3\text{-}C_8H_{17} = iC_4H_8 + iC_4H_8 + H$$

where it should be cautioned that the 2- and $3\text{-}C_8H_{17}$ radicals are not the same as those in the discussions of the radicals from *n*-octane. It can be seen here that of the 18 H atoms in iso-octane, only *one* of them leads to chain branching from production of H atoms. All 17 of the rest lead to olefins and methyl radicals and chain termination. This observation is very likely a major factor in the observation that iso-octane is so much more resistant to ignition than *n*-octane, where 12 of the 18 paths led to chain branching.

This same approach can be applied to any number of fuels and their product alkyl radicals. For example, neopentane, with its 12 identical H atoms, yields an alkyl radical that, using β-scission as a guide, would be predicted to lead exclusively to isobutene and methyl radicals, providing no paths to radical chain branching. This suggests that neopentane would be very resistant to ignition.

There are three isomeric forms of methyl heptane, in addition to the straight chain *n*-octane, for which 12 of the 18 H atom abstraction paths led to branching. Of the three singly branched forms, two have five paths leading to branching and the third has nine, all of them less reactive overall than *n*-octane but all more reactive in this sense than iso-octane. These factors correlate fairly well with the observed ignition properties of these different octanes.

As long as there is only one major path for consumption of a given alkyl radical (i.e., thermal decomposition according to β-scission), then uncertainties in the thermal decomposition rate are almost completely insignificant to the computed overall rate of reaction. This is because the radical levels rapidly attain a steady-state, quasiequilibrium level where the rate of consumption approximately equals the rate of production. Thus, the rate of H atom abstraction really determines the rate of production of alkyl decomposition products. At a given H atom abstraction rate, the product of the alkyl radical concentration and the thermal decomposition rate will remain a constant, and an increase in the rate of decomposition will result in a compensating decrease in the alkyl radical concentration, and conversely. The major problem remaining unresolved in the modeling of reactions of large hydrocarbon fuel molecules is the question of the role that radical isomerization plays in redistributing the identities of the alkyl radicals for a given overall composition. If the rates of isomerization are significantly slower than the rates of decomposition, then the product species are correlated by the rates of site-specific H atom abstraction from the fuel. However, if isomerization reactions are relatively rapid, then the various radicals will become redistributed, independent of the paths forming them. This would strongly favor the tertiary alkyl radicals over secondary radicals, which would in turn be preferred over primary radicals, all because of the relative heats of formation of the different radicals. At present, the resolution of this question is a major obstacle to continued profitable application of kinetic modeling of large hydrocarbon combustion to practical problems.

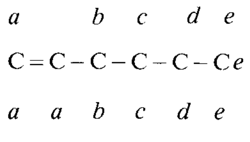
Intermediate Olefins

Modeling studies as well as experimental results all indicate that the oxidation of alkane fuels is accompanied at atmospheric and lower pressures by very little conjugate olefin formation. As already seen, the majority of the olefins produced during large hydrocarbon fuel consumption consist of ethylene, propene, and isobutene, in decreasing order of magnitude. However, there are sufficient amounts of larger olefins formed (see, for example, Dryer and Brezinsky[23] in the cases of *n*-octane and iso-octane) and their consumption must be treated in any numerical model for hydrocarbon combustion. However, like many of the other species already discussed which are encountered during the combustion of large fuels, reaction rates and product species distributions for reactions involving large olefin molecules have not been studied experimentally to any appreciable extent and estimates and assumptions must be made in order to proceed.

Even for small olefinic species such as ethylene and propene, there is considerable uncertainty at present concerning the rates of reactions with radical species at combustion temperatures and in the distributions of reaction products. This is even more true for C_5 and larger olefins. In recent kinetic modeling studies for *n*-butane and propane oxidation,[14,15] it was found that uncertainties in the rates and product distributions of C_3 and C_4 olefins had very little effect on the computed rates of oxidation. It is likely that the same situation will prevail for larger alkane hydrocarbon fuels; that is, it is sufficient to provide only very rough estimates of rates of reactions consuming these large intermediate olefin species and the exact choices of reaction products are not particularly important if overall rates of reaction and fuel consumption are the only quantities of concern.

Still, future experiments will eventually provide enough measured species concentration information to determine the specific reaction paths and rates of reactions between intermediate olefins and other reactive species. With this in mind, it is desirable to make choices for these parameters that are as close as possible to the ultimate answers, choices that make kinetic sense and do not place unreasonable constraints on the kinetic mechanism. The reasoning being used to make these preliminary selections is outlined here for several classes of olefin species.

During the oxidation of normal alkanes, the fragmentation of the common alkyl radicals was seen earlier to lead almost exclusively to 1-olefins, where the double bond was between the first and second C atoms in the chain. With this simplification in mind, it is possible to make a structurally motivated assumption that the interaction of an approaching radical species near one end of the olefin will be nearly independent of the structure at the other end of the molecule. That is, one end of the olefin will "look like" an alkane species with three primary H atom sites and one or more secondary sites nearby. At the other end, the presence of the C=C double bond will dominate the reaction dynamics. Therefore, one can assign reaction rates and product distributions for both ends of the olefin, using data available for smaller alkanes and olefins. Using ${}_1C_6H_{12}$ as an example, one can include the following possible reactions, beginning with an overall picture of the C_6 olefin:



$$\begin{array}{cccccc} a & & b & c & d & e \\ C= & C- & C- & C- & C- & Ce \\ a & a & b & c & d & e \end{array}$$

The H atoms labeled *b, c, d,* and *e* can be abstracted by H, O, and OH. Of course, other radicals could in principle also react with the olefin, but for modeling purposes these are the dominant reactive radicals and, in view of the myriad uncertainties already present in this approach, inclusion of additional reactive species is probably not warranted. Therefore, including the rapid β-scission of the resulting radical produced by this abstraction, the H atom abstraction reactions with O atoms are

$$b\colon\ {}_1C_6H_{12} + O = C_4H_6 + C_2H_5 + OH$$

$$c\colon\ {}_1C_6H_{12} + O = {}_1C_4H_8 + C_2H_3 + OH$$

$$d\colon\ {}_1C_6H_{12} + O = C_3H_5 + C_3H_6 + OH$$

$$e\colon\ {}_1C_6H_{12} + O = C_4H_7 + C_2H_4 + OH$$

Since there are only three primary sites, rather than the six in an alkane molecule, the rate of process *e* has a net rate that is exactly half of the rate of primary H atom abstraction by O atoms in *n*-octane, *n*-butane, or propane, and similarly for the secondary sites. Structural considerations may influence the product distributions of these decompositions (and not all C-C bonds are exactly the same), but these are second-order effects that are beyond the scope of the present discussion.

At the other end of the molecule, the H atoms denoted by a letter *a* are assumed to be associated with the double C = C bond. At this end, it is assumed that the dominant process is addition of the O atom (or H atom) to the double bond in a way that is patterned after better-known processes in ethylene and propene. Lacking any experimental evidence to use as a guideline in providing product species distributions, we assume that the subsequent decomposition of the $O\text{-}{}_1C_6H_{12}$ complex produces either ${}_1C_5H_{11} + HCO$ or $pC_4H_9 + CH_3CO$. Addition of H atoms to this double bond will produce either $1\text{-}C_6H_{13}$ or $2\text{-}C_6H_{13}$ alkyl radicals, which will then decompose by

$$1\text{-}C_6H_{13} = pC_4H_9 + C_2H_4$$

$$2\text{-}C_6H_{13} = nC_3H_7 + C_3H_6$$

again using the principle of β-scission as a guide. At the "alkane" end of the olefin, H atoms are assumed to abstract primary and secondary H atoms, just as illustrated above for abstraction by O atoms.

Application of this approach to other chain olefins is straightforward, with the same limitations as those existing for this example. In addition to the somewhat simplistic picture of molecular structure and reaction theory implicit in the model construction, the approach also depends on the applicability of β-scission to nonalkyl radicals and the absence of rapid radical isomerization reactions. However, it does provide a kinetic model with a kinetically motivated framework with which to at least begin to construct a reaction mechanism, incorporating improvements and conceptual advances as they become available. In addition, the fact that most alkane models are insensitive to the details of the submechanisms for intermediate olefin consumption suggests that the present approach will probably be sufficient for many applications.

Extensions of this approach to branched olefins is even more speculative. Present mechanisms and approaches are little more than weakly educated guesswork and probably should not be represented as anything more sophisticated or appropriate. A great deal of further work is needed in this area to provide modeling programs with sensible guidelines with which to proceed. However, the same insensitivity to the details of intermediate olefin submechanisms also applies in these cases, so it should still be possible to address many problems with these portions of the mechanisms really based on guesswork.

Termination Reactions

In these mechanisms, it is essential to include reaction steps that remove radical species from the system. In the applications being studied at present, by far the most important of these termination steps involves removal of H atoms, since the alternative reactions of H atoms lead to a considerable amount of chain branching via

$$H + O_2 = O + OH$$

One group of such reactions can be represented as

$$H + \text{olefin} = \text{alkyl radical}$$

The product alkyl radical will generally decompose by breaking a C-C bond, leading to product species that may or may not eventually regenerate the H atom. We have seen earlier that H atom addition to ${}_1C_6H_{12}$ produces either ${}_1C_6H_{13}$ or ${}_2C_6H_{13}$. The subsequent β-scission of ${}_1C_6H_{13}$ will provide $C_2H_4 + C_2H_4 + C_2H_5$, with the ethyl radical usually decomposing further to give $H + C_2H_4$. Therefore, this path regenerates the H atom and also breaks the ${}_1C_6H_{12}$ into three ethylene molecules. In contrast, production of ${}_2C_6H_{13}$ leads generally to $CH_3 + C_3H_6 + C_2H_4$. This set of products results in a net reduction in the rate of chain branching and the overall rate of combustion, since the H atom is lost to the radical pool. Therefore, some fraction of these H + olefin reactions will reduce the rate of chain branching and overall rate of combustion.

In the case of branched chain fuels, another very important example of chain termination is the addition of H atoms to isobutene

$$H + iC_4H_8 = iC_4H_9$$

followed by the β-scission of the isobutyl radical

$$iC_4H_9 = CH_3 + C_3H_6$$

which effectively converts the H atom and one olefin into CH_3 and a smaller olefin and reduces the overall rate of chain branching. For both straight and branched chain hydrocarbon fuel molecules, the sequence

$$H + C_3H_6 = nC_3H_7 = CH_3 + C_2H_4$$

is another important example of conversion of reactive H atoms into relatively unreactive methyl radicals.

Another group of radical removal reactions can be represented as

$$H + R = \text{stable alkane or olefin species}$$

or

$$R' + R = \text{stable alkane or olefin species}$$

Examples of these reactions include

$$C_4H_7 + H = {}_1C_4H_8$$

$$C_2H_5 + C_2H_5 = nC_4H_{10}$$

$$pC_4H_9 + C_3H_5 = {}_1C_7H_{14}$$

$$CH_3 + C_2H_5 = C_3H_8$$

as well as the reverse directions of the initiation reactions. Since the decomposition of many of the smaller alkyl and other hydrocarbon radical species lead rather quickly to H atom production, such recombinations also provide a noticeably reduced rate of chain branching.

Discussion

The above presentation is intended to summarize the principles currently being used in the development of very large kinetic reaction mechanisms. When combined together to simulate the combustion of, for example, mixtures of *n*-octane and iso-octane, the mechanism includes more than 75 chemical species and approximately 500 elementary reactions. The very magnitude of these tables makes it very difficult to see any pattern to their construction. Yet, it is impossible to have any confidence in their predictive capabilities without a systematic development, step by step, using sound kinetic principles.

The basic ideas behind the present mechanisms are quite simple and have been used previously in the development and successful applications of kinetic models to much smaller and simpler fuels. When applied to the combustion kinetics of octane, the sheer bulk of the model is sometimes intimidating, but the principles are still the same. Furthermore, the same simple principles provide a rational means of eliminating many additional possibilities that would further clutter up the reaction mechanisms, as well as provide a basis for estimating various quantities for which experimental data are not yet available.

The most speculative areas remaining in these mechanisms have been identified, primarily concerning the reactions of large olefins for both iso-octane and *n*-octane and the questions concerning the importance of radical isomerization reactions. These areas, as well as the presumed alkyl decomposition paths and the assumptions concerning the patterns for primary, secondary and tertiary H atom sites and the rates of H atom abstraction, are presented partially in the hope that they might encourage future experimental and theoretical investigation by others to help in the refinement of the present models.

One result of this process is the realization that reaction mechanisms for large fuel molecules are not qualitatively different from those for smaller fuels, only that they are bigger mechanisms. The principles are the same. More important, present computational resources are entirely sufficient to handle mechanisms that, only two or three years ago, would have been intractable. This encourages the development of detailed reaction mechanisms for the most important class of hydrocarbon fuels not yet addressed to any substantial degree by modeling programs, those for aromatic fuels such as benzene and toluene. For such fuels, the presence of six or more carbon atoms in the fuels has been a roadblock in the development of detailed reaction mechanisms, but the present work can be interpreted as a feasibility study for the treatment of very large mechanisms under combustion conditions.

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