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COMBUSTION REACTIONS OF PARAFFIN COMPONENTS IN LIQUID TRANSPORTATION FUELS USING GENERIC RATES

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The approach of mechanism generation is the accepted one of assigning generic rates to reactions in the same class. The procedure has been successfully applied to higher paraffins that include detailed sub-models of n-hexane, cyclohexane, n-heptane, n-decane, n-dodecane, and n-hexadecane and semi-detailed submodels of iso-octane and methyl cyclohexane, in addition to reactions of aromatic formation and oxidation. Comparison between predictions and experimental data were found to be satisfactory for n-heptane, iso-octane, n-decane and gasoline premixed flames. The mechanism was also able to reproduce the measured concentrations for a n-hexadecane experiment in a jet stirred reactor. The numerical accuracy in predicting the flame structures of soot precursors, including acetylene and benzene, is one of the major foci of this study. The predicted maximum concentrations of acetylene and benzene are within 20% for most flames in this study.

Keywords: cyclohexanes reaction mechanism, gasoline surrogate and gasoline reaction mechanism, normal paraffin reaction mechanism, premixed flames

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INTRODUCTION

The study is motivated by the need for the chemical kinetics for compounds used in surrogate formulations (Eddings et al., 2005; Agosta et al., 2004; Cooke et al., 2005) for liquid fuels, particularly jet fuels. Edwards (2002) has shown that jet fuels have a range of compositions. The aromatic content range from 8 to 26% by volume (mean 18%), cyclo-paraffins range from 0 to 26% (mean 11%), and the sum of isoand n-paraffins range from 34 to 78% (mean 59%). An analysis of a Jet-A (Violi et al., 2002) showed approximately equal concentrations of iso- and n-paraffins. The present study is focused on the developing kinetic models of the paraffins - cvclo-, iso- and normal - that account for a large percentage of the fuels. The kinetics are here developed for premixed, atmospheric pressure flames and well-stirred reactors because of the availability of detailed concentration profiles in these flames and because of the authors' interest in modeling pool fires at atmospheric pressure. This study is intended to extend to higher temperatures other studies in the literature on the modeling of the mechanism and kinetics of paraffins (Curran et al., 1998; Ranzi et al., 2001). The chemical kinetics for the paraffins have been included in the formulation of a more general Utah Surrogate Mechanism, which was used to model flames of three composite fuels (natural gas, gasoline and kerosene) recently (Zhang et al., 2007).

Combustion Studies of Large Paraffins

The building block for the mechanisms of large paraffins is the detailed mechanism for n-heptane as reviewed by Simmie (2003). For higher hydrocarbons the number of reactions increases markedly and lumping procedures are often used to make the problem manageable, as reviewed by Ranzi et al. (2001). The present paper follows similar procedures.

Other experimental studies are that of Bales-Gueret and coworkers (1992) on the oxidation of normal decane in a jet stirred reactor (JSR) at atmospheric pressure and temperatures between 873 and 1033 K. Concentration profiles of about 20 species were measured and a quasiglobal chemical kinetic mechanism was developed to reproduce the experimental data. A JSR experiment of n-decane oxidation was also studied by Cathonnet and coworkers (1990) at intermediate and high temperatures with pressures up to several atmospheres. Three sets of premixed laminar flames of normal decane were investigated by Vovelle and coworkers. In the first experiment (Delfau et al., 1991), normal decane was diluted with argon at a low pressure of 6 kPa and the experimental data were modeled by a reaction mechanism extended from a formerly validated C₂ mechanism. Vovelle and coworkers (Vovelle et al., 1994; Doute et al., 1995a) also studied the flame structures in atmospheric-pressure flames of n-decane and kerosene, reporting profiles of more than 20 species. Experimental studies have also been reported of the combustion of normal hexadecane in a jet stirred reactor (Fournet et al., 2001) and mole fraction profiles of species at three different equivalence ratios have been reported.

Additional modeling of the combustion of n-decane, an important surrogate component of liquid aviation and transportation fuels, has been proposed by Bales-Gueret and coworkers (1992) in JSR and premixed flames. Battin-Leclerc and coworkers (Battin-Leclerc et al., 2000; Glaude et al., 1998) obtained satisfactory agreement, using an automatically generated mechanism with 7920 reactions, between simulated results and measured concentrations of selected species from a JSR experiment and a premixed flame. Cathonnet and coworkers (1999) modeled a JSR kerosene experiment assuming a surrogate fuel composed of cyclohexane, toluene, and n-decane. The detailed normal decane model proposed by Dagaut and coworkers (1994) with 573 reactions and 90 species for one of their earlier JSR experiments was reduced into a skeletal mechanism involving 283 reactions and 78 species. The skeletal mechanism was further reduced to a model with only 30 species assuming pseudo-equilibrium for intermediates; the reduced mechanism predicted the extinction limits with sufficient accuracy. Vovelle and coworkers measured concentration profiles of nearly two dozen species in their n-decane premixed flames at reduced (Delfau et al., 1991) or atmospheric pressures (Doute et al., 1995a). These data provided insights for the development and validation of detailed mechanisms of n-decane. The same Orleans group who measured the flame structures proposed a reaction mechanism (Vovelle et al., 1994) to simulate both the low-pressure n-decane flames and a kerosene flame assuming a surrogate of 90% n-decane and 10% toluene. Later on, they extended their mechanism to include 638 reactions and 78 species (Doute et al., 1997) in order to reproduce the concentration profiles of more than 20 species in an atmospheric premixed flame, including the fuel, oxidizer, inert (N₂), and major products (H₂, H₂O, CO, and CO₂), as well as olefins

(ethylene, propylene, 1-butene, 2-butene, iso-butene, 1-pentene, 1-hexene, and 1-heptene), alkynes (acetylene and propyne), diene, diyne, and enyne (allene, di-acetylene, and vinyl acetylene), paraffins (CH₄, C_2H_6 , and C_3H_8), and benzene. Bikas and Peters (2001) modeled the same atmospheric premixed flame of n-decane using a mechanism of 600 reactions and 67 species, and the proposed mechanism was also tested with experimental data from shock-tube ignition experiments, JSR experiments, and a freely propagating premixed flame.

Decane mechanisms proposed by Doute et al. (1997) and Bikas and Peters (2001) were intended to reproduce concentration profiles of olefins and gave better results for smaller olefins than for larger ones. The decomposition of normal decane mainly via β scission forms large olefins. Hydrogen addition reactions that will be discussed later in this paper lead to their decomposition to smaller olefins. Errors in the predicted concentrations of larger olefins will therefore propagate to smaller olefins. Other compounds that will be impacted by the errors in the predicted concentration of large olefins are allylic radicals produced by thermal decomposition, and other aromatic precursors formed from allylic radicals, such as propyne, butyne, and butene isomers. Thus a weakness in the chemistry of higher olefins may result in incorrect kinetic rates for smaller olefins and benzene, and thus make the model vulnerable to changes in experimental conditions.

Numerical Mechanism and Experimental Data

In this study, the base normal heptane mechanism, which consisted of 176 species and 840 reactions (Zhang, 2005), was extended to include detailed sub-mechanisms of n-hexane, cyclohexane, n-heptane, n-decane, n-dodecane, and n-hexadecane and semi-detailed sub-mechanisms of iso-octane and methyl cyclohexane so that the resulting Utah Surrogate Mechanism (Zhang et al., 2006) can be used to model the combustion of liquid transportation fuels.

The Utah Surrogate Mechanism will be validated with the atmospheric laminar premixed flame structures of: n-heptane with equivalence ratios of 1.9 (El Bakali et al., 1999) and 1.0 (Vovelle, 2001), iso-octane ($\Phi = 1.9$; El Bakali et al., 1998), and n-decane ($\Phi = 1.7$; Doute et al., 1995a). In addition, the mechanism will be validated with the experimental mole fraction profiles of a n-hexadecane flame in a jet stirred reactor ($\Phi = 1.5$; Fournet et al., 2001). A premixed gasoline flame ($\Phi = 1.0$; Hakansson et al., 2001) at 30-torr will also be modeled in the current study to test the mechanism for composite fuels.

The simulator used was CHEMKIN III (Kee et al., 2003) and the thermodynamics data for the gaseous species were obtained from the CHEMKIN thermodynamic database (Kee et al., 1993) or estimated by THERGAS (Muller et al., 1995) employing Benson's additivity theory (Benson et al., 1969). The transport properties of species were obtained from the CHEMKIN transport database (Kee et al., 1986) or estimated from those of similar species.

DEVELOPMENT OF PARAFFIN COMBUSTION MECHANISMS

The fundamental pathway for the decomposition of higher paraffins by thermal decomposition or hydrogen abstraction to form radicals that subsequently decomposes via β scission to an olefin and a radical is well established (Zhang, 2005; Ranzi et al., 2001; Curran et al., 1998). The inclusion of such fuel consumption reactions is the first step in extending the base heptane mechanism to fit the structure of higher paraffin flames; such reactions also serve to provide a cascade from the higher paraffins down to species with seven carbons or less included in the base heptane mechanism. The generic rates for these reactions will be used in the mechanism generation process. Reactions involving paraffins, olefins, and alkyl radicals in the same class are assigned similar rates with adjustments for different reaction sites, and the generic rates of these reactions are summarized in Table 1.

Normal Paraffins

Large paraffins decompose during combustion via hydrogen abstraction and thermal decomposition. Hydrogen abstraction reactions of higher paraffins by six different abstractors, including H, OH, O, CH₃, HO₂ and O₂, were added in the extended mechanism, and their rates were taken from mechanisms proposed by Lawrence Livermore National Laboratory (Curran et al., 1998; Tamura, 1987). All conjugate alkyl radicals of normal paraffins (up to C₁₆) are included to describe the decomposition of the fuel more accurately. Thermal decomposition reactions took the rates of similar reactions from a chemical kinetics table for n-paraffin decomposition compiled by Allara and Shaw (1980). The cleavage of the C-C σ bond is treated similarly for all reactions except those forming C₂H₅ and CH₃ radicals. The reaction energy barrier when CH₃ is a

	$\mathbf{k} = \mathbf{AT}^{\mathbf{r}}$ mole	° exp(− E ●cm●s●c	E/RT) cal	
Reaction Classes	А	n	Е	Reference
Hydrogen Abstraction from Paraffin per H				
1° Hydrogen by H Radical	3.13E + 04	2.75	6280.11	Curran, 98
2° Hydrogen by H Radical	6.50E + 05	2.4	4471.08	Curran, 98
3° Hydrogen by H Radical	6.02E + 05	2.4	2583	Curran, 98
1° Hydrogen by OH Radical	1.75E + 09	0.97	1590.11	Tamura, 87
2° Hydrogen by OH Radical	2.35E + 07	1.61	-34.89	Tamura, 87
3° Hydrogen by OH Radical	1.70E + 06	1.9	-1451	Curran, 98
1° Hydrogen by O Radical	7.25E + 05	2.4	5500	Tamura, 87
2° Hydrogen by O Radical	1.55E + 05	2.5	2230	Tamura, 87
1° Hydrogen by CH ₃ Radical	1.51E-01	3.65	7153.92	Curran, 98
2° Hydrogen by CH ₃ Radical	1.35E + 04	2.26	7287.05	Curran, 98
1° Hydrogen by O ₂ Radical	1.00E + 13	0	52800	Curran, 98
2° Hydrogen by O ₂ Radical	1.00E + 13	0	50150.1	Curran, 98
1° Hydrogen by HO ₂ Radical	1.680e + 13	0	20440	Curran, 98
2° Hydrogen by HO ₂ Radical	1.120e + 13	0	17690	Curran, 98
Thermal Decomposition of Paraffins	3.16E+16	0	81900	Allara, 80
Except that toward $C_2H_5 + alkyl$	6.31E+16	0	81900	Allara, 80
Except that toward CH_3 + alkyl	6.31E+16	0	85400	Allara, 80
Isomerization of Alkyl Radicals per	1.00E + 11	0	14102.9	Doute, 94
H Via 6-Membered Transition State				,
Via 5-membered Transition State			+4000	Doute, 94
Via 7-membered Transition State			+4000	Doute, 94
1° radical $\rightarrow 2^{\circ}$ radical			-3000	Doute, 94
β Scission Reaction				
Forming C_2H_4 + alkyl	3.20E + 13	0	28400	Allara, 80
Forming C_2H_4 + alkyl	4.00E + 13	0	28800	Allara, 80
Forming $C_4H_{e-1} + alkyl$	2.50E + 13	0	28800	Allara, 80
Forming $CH_2 + olefin$	1.03E + 14	-0.42	28690.0	Curran, 98
All other reactions	1.60E + 13	0	28300	Allara 80
Hydrogen Abstraction Reaction by	1.00 ± 12	Ő	4251 19	Doute 94
O2 from Alkyl Radical per H	1.002 12	Ū	1201117	Doute, 71
Except that $1_{alkyl} \rightarrow 1_{alkene}$	$1.00 E \pm 12$	0	2000	Doute 94
Except that 1 -alkyl $\rightarrow 1$ -alkene	1.00E + 12 1.00E + 12	0	2000 4500	Doute 94
Thermal Decomposition of Olefins	1.00L + 12 3 16E + 16	0	80927 3	Doute 97
Olefin $\pm \mathbf{X} = \mathbf{H}\mathbf{X} \pm \beta$ Scission Products per H	5.100 + 10	v	30727.3	Doutt, 97
1° Hydrogen by H Radical	933E + 04	2	7700	Curran 00
2° Hydrogen by H Dadical	$7.55E \pm 00$	2	5000	Curron 00
2 myurugen by fi Kadical	4.33E+00	2	3000	Curran, 98

Table 1. Generic reaction rates of paraffins, olefins, and alkyl radicals

(Continued)

	$k = AT^n$ mole	exp(−E cm●s●c	/RT) al	
Reaction Classes	Α	n	Е	Reference
1° Hydrogen by OH Radical	1.75E+09	0.97	1590.11	Tamura, 87
2° Hydrogen by OH Radical	2.35E + 07	1.61	-34.89	Tamura, 87
$Olefin + H = \beta \ Scission \ Products$	2.27E + 13	0	1873.20	Doute, 95b
via primary alkyl radical	2.27E + 13	0	3569.38	Doute, 95b

Table 1. Continued

product is increased by 3.5 kcal (Allara and Shaw, 1980) as seen in Table 1; when C_2H_5 is a product, the pre-exponential factor is increased by a factor of two.

Isomerization of the conjugate alkyl radicals is assumed to be described by the rate of Doute and coworkers (1994). A preferred transition state of a six-membered intra-molecular ring of carbon and hydrogen atoms is modeled by a reaction energy barrier 4 kcal lower than those of other isomerization reactions (Doute et al., 1994) as seen in Table 1. Also, the isomerization reactions from the primary radical toward secondary radicals are favored by a reduction of 3 kcal in the energy barrier (Doute et al., 1994) due to the less stable nature of the primary radical.

The conjugate alkyl radicals decompose via β scission with rates taken from the kinetics table compiled by Allara and Shaw (1980), except for those of reactions forming CH₃ and olefins, which were assigned the rate from a similar reaction of 3-heptyl radical in the LLNL n-heptane mechanism (Curran et al., 1998); this rate is comparable to those of similar reactions in the n-decane mechanisms developed by Doute et al. (1997) and Bikas and Peters (2001). Olefins formed from β scission always have the double bond at the end of carbon string.

The rates of formation of conjugate olefins produced via hydrogen abstraction from the fuel alkyl radicals by O_2 were taken from the values proposed by Doute and coworkers (1994) as summarized in Table 1. Isomers of a conjugate olefin in the extended mechanism are lumped into one species to reduce the size of the mechanism, with the pre-factors of their reactions appropriately adjusted.

In summary, reaction rates of abstraction of hydrogen by O_2 , isomerization, and β scission of conjugate alkyl radicals are listed in Table 1.

The consumption reactions of conjugate olefin isomers, and smaller olefins and alkyl radicals formed in the fuel decomposition are added in the extended mechanism using rates in Table 1. The olefins are consumed via thermal decomposition, the rate of which was taken from similar reactions of paraffins suggested by Allara and Shaw (1980), with a decrease of 1 kcal in the reaction energy barrier to account for the effect of resonantly stabilized structures for one of the products due to the neighboring double bond of the radical site. The adjusted rate was used by Doute and coworkers (1997) in their n-decane mechanism. Other important competing pathways of olefin decomposition include hydrogen addition reactions. The intermediate alkyl radicals are consumed by β scission with generic rates as listed in Table 1. The base mechanism for n-heptane comes the chemistry of olefins and alkyl radicals with seven carbons or less, with the exception of hexyl radicals.

Cyclohexane

Cyclohexane and its derivatives belong to a class of paraffinic species with mostly secondary carbon atoms, and likely decompose via the major fuel consumption routes as discussed for normal paraffins. In the extended mechanism, cyclohexane is to be consumed by H, OH, and O radicals, which forms cyclohexyl radical as shown in Figure 1a. These hydrogen abstraction reactions use generic rates at secondary carbon sites to account for twelve possible reaction sites of hydrogen atoms. The formation of linear 1-hexen-6-yl radical via β scission is the major decomposition pathway of cyclohexyl radical, and competes with the unimolecular dehydrogenation that is the exclusive formation pathway of cyclohexene.

Isomerization among linear hexenyl radicals after the ring-opening step directs the product distribution of cyclohexane decomposition. Isomerization of the 1-hexen-6-yl radical goes forward via an internal hydrogen migration over four-six carbon atoms. Mechanisms that do not include isomerization reactions of conjugate fuel radicals will likely misrepresent the entire fuel decomposition chemistry. For example, the isomerization reaction that forms 1-hexen-3-yl radical competes favorably with the direct decomposition of 1-hexen-6-yl radical because the resonant structures of 1-hexen-3-yl radical make the hydrogen migration more preferred.



Figure 1. Major reaction pathways of cyclohexane and its derivatives. (a) product distribution in flames with cyclohexane; (b) a representative composite reaction of methyl cyclohexane via hydrogen abstraction followed by ring opening, isomerization and β scission; (c) interweaving dehydrogenation between sub-mechanisms of cyclohexane and its derivatives.

Cascading dehydrogenation was also included as a competing decomposition pathway of the conjugate cyclohexyl radical. Cyclohexyl radical can be consumed via unimolecular dehydrogenation or via hydrogen abstraction by O_2 that leads to cyclohexene. Cyclohexene is consumed mainly by hydrogen abstraction with H, OH, and O radicals, which forms the cyclohexenyl radical. Generic rates at the secondary carbon sites were assigned to hydrogen abstraction reactions. Dehydrogenation and β scission reactions consume the cyclohexenyl radical, and primarily lead to the formation of cyclohexadiene.

The hydrogen abstraction reactions with H, OH, and O radicals were considered to provide the major decomposition pathways of cyclohexadiene. No ring opening of the resulting $C-C_6H_7$ radical, however, was included in the extended mechanism since these reactions involve the breakage of a double bond or the formation of vinylic radicals. Benzene is formed mainly via unimolecular dehydrogenation, which is also the major consumption route of $C-C_6H_7$ radical.

In summary, the formation of the first aromatic ring in flames with cyclohexane and its derivatives involves exclusively the cascading dehydrogenation of the fuel.

Methyl Cyclohexane

Sometimes, a lumped approach is necessary in generating combustion mechanisms, either for mechanism size control or due to the paucity in the literature of the kinetics of this species. Less detail was included in the methyl cyclohexane sub-mechanism, for example, which was built upon major fuel consumption reaction classes of normal paraffins. In comparison with detailed decomposition mechanisms of normal paraffins, major consumption pathways of any conjugate methyl cyclohexyl isomer represent combined reactions, and each composite reaction describes the consecutive hydrogen abstraction and subsequent ring opening, isomerization and β scission reactions. One example of the formation of 1,3-butadiene and 1-propyl radical is presented in Figure 1b.

The methyl cyclohexane sub-mechanism includes hydrogen abstraction reactions with H and OH radicals, which account for the majority of the fuel consumption. Generic rates of hydrogen abstraction at secondary carbon abstraction sites (see Table 1) were assigned to these reactions, by assuming that the concentration of the intermediate methyl cyclohexyl radical is in pseudo equilibrium and that the following β scission is instantaneous. Sometimes, the heptenyl radicals formed from the rupture of the ring undergo isomerization before they decompose into smaller species. In the extended mechanism, isomerization of alkyl radicals is described by an internal hydrogen migration via a fiveto seven-membered ring. Isomerization reactions are also assumed to be instantaneous, and the pre-factors of their rates are adjusted to account for combined rates of different reaction channels that lead to the same products.

Lumped elementary reactions that include a ring-opening step and subsequent β scission and isomerization reactions are also included to represent thermal decomposition. Two additional reactions are also included and consist of a ring-opening step after the rupture of the C-C sigma bond between the ring and the methyl group. Those reactions were assigned the generic rates in Table 1 with the pre-factors appropriately adjusted to account for combined rates of different reaction channels that result in the same products.

Also, benzene formation from methyl cyclohexane via a set of reactions of cascading hydrogen abstraction followed by dehydrogenation was included. Dehydrogenation reactions of cyclohexane have been discussed in detail earlier; therefore, only those that involve a demethylation step that interweaves together the sub-mechanisms of cyclohexane and its derivatives are illustrated in Figure 1c.

Interweaving dehydrogenation complements combination reactions between methyl and cyclic radicals $(C-C_6H_{11}, C-C_6H_9, \text{ and } C-C_6H_7)$ that also coordinate the sub-mechanisms of cyclohexane and its derivatives. Interweaving dehydrogenation steps are, therefore, vital additions to the cascading dehydrogenation mechanism in benzene formation.

Lumped species were used to represent different isomers, such as the three methyl-cyclohexenes, in order to obtain a smaller reaction mechanism. The radical sites shown in Figure 1c, therefore, are not the exact location since these radicals are lumped species as well. The hydrogen abstraction/dehydrogenation reactions were assigned generic rates of hydrogen abstraction by assuming the concentration of the radical intermediate to be in pseudo equilibrium. Statistical factors have been adjusted to account for the number of hydrogen atoms on the ring being abstracted. For example, a hydrogen abstraction rate from methyl cyclohexane to form methyl cyclohexyl radical is assigned a value that is 11.5 times the generic rate at the secondary carbon sites because, in addition to ten other hydrogen atoms on the secondary carbons, the rate of the reaction involving the hydrogen on the tertiary carbon is weighed by a factor of 1.5 in order to account for its weaker C-H bond relative to those on other sites. This value is also reflected in the energy barrier of the abstraction from a tertiary carbon by H radical that is about 2 kcal lower than from secondary carbons (Curran et al., 1998; Table 1).

The rates of cascading hydrogen abstraction reactions on the decomposing ring have also been adjusted in the statistical factor and activation energy. The statistical factors of the reactions involving methyl cyclohexene are two thirds of the corresponding reactions involving methyl cyclohexane, and only one third for the reactions involving methyl cyclohexadiene to account for the decreasing reaction sites on sp^3 carbons. The energy barrier of the generic rate is reduced by 0.5 kcal for the reactions involving methyl cyclohexene and by 1 kcal for those involving methyl cyclohexadiene to account for the greater stability resulting from the delocalization of the electron on the radical sites (emerging aromaticity).

Also, a reduction of 0.5 kcal is applied to the energy barriers of reactions breaking the methyl radical from the ring, since a C–C sigma bond is weaker than a C–H sigma bond (Kerr and Stocker, 2000–2001). Two reactions of hydrogen addition followed by decomposition (Figure 1c) that involve methyl cyclohexene and methyl cyclohexadiene and use generic rates of olefins, are added to the extended mechanism to form the methyl radical and cyclohexene or cyclohexadiene. Thus, all important decomposition routes summarized from normal paraffin reaction mechanisms have been included in the methyl cyclohexane sub-mechanism.

TEMPERATURE PROFILES

The ability to predict the concentrations of the reactant species (fuel and oxygen) is the first step in combustion simulations that usually target the concentration profiles of other important intermediates and products. Simulation results probably have no significance if the measured concentrations of fuel and oxygen, assumed to be among the most accurately measured, cannot be reproduced. Uncertainty in temperature measurements in premixed flames, due to probe effects and flame disturbance, is, however, a major concern for model validation, because the predicted reactant concentrations using the measured temperature profile, very often, do not match the experimental data. In this study, the measured temperature profiles of the five premixed flames were shifted downstream. In Figure 2, the thin solid lines represent the measured



Figure 2. The shifted temperature profiles used in the simulations and the effects on the concentrations of fuel and oxygen. Thin solid lines: the results using the measured temperatures; dotted lines: those using profiles suggested by Vovelle (2001); Heavy solid lines: those using modified profiles.

temperatures and the resulting concentration profiles of fuel and oxygen in the simulations. The dotted lines represent the profiles suggested by Vovelle (2001), whose research group measured the structures for four of the flames, and the corresponding predicted concentration profiles of fuel and oxygen (using these temperatures and the Utah Surrogate Mechanism). The heavy solid lines correspond to what are the temperature profiles used and the concentrations obtained in the modeling of this work. The quality of predicted concentrations of fuel and oxygen are improved dramatically using the modified temperature profiles. The temperature profile of the stoichiometric n-heptane flame has not been reported in the literature and the profile suggested by Vovelle (2001) was used in this study. Iso-octane is a major fraction in composite gasoline fuels, and is also one of the largest fractions in the surrogate fuel for gasoline used in this study; the concentration profile of iso-octane is, therefore, chosen to represent the gasoline fuel consumption rate in Figure 2. The concentrations of oxygen were not reported for this flame.

The pattern of temperature shift reported for the gasoline flame in Figure 2 is a simple but effective way for better prediction of flame structures. The differences between the peak positions of measured concentration profiles of major intermediates and those predicted by the model using the experimental temperature profile usually suggest the amount of shift needed for the temperature profile. A temperature modification is, therefore, made accordingly, as shown in Figure 2 for the gasoline flame by shifting the temperature peak downstream. The measured or extrapolated temperature at the burner surface is kept intact so that estimations of the temperatures between the burner surface and the shifted profile fall into the straight line connecting the burner surface and the first shifted point. Further temperature adjustments may be necessary, however, for better predictions. The effectiveness of this technique in modeling other flames of natural gas (Turbiez et al., 2004), ethylene (Bhargava and Westmoreland, 1998a, b) and methanol (Vandooren and van Tiggelen, 1981) is shown in Figure 3.

NUMERICAL PERFORMANCE OF THE UTAH SURROGATE MECHANISM

New reactions added in the extended mechanism include major decomposition routes of large paraffins, and consumption reactions for each new species formed from the fuel decomposition. In this study,



Figure 3. The shifted temperature profiles used in the simulations and the effects on the concentrations of fuel and oxygen for natural gas (Turbiez et al., 2004), ethylene (Bhargava and Westmoreland, 1998a, b), and methanol (Vandooren and van Tiggelen, 1981) flames. Thin lines: the results using the measured temperatures; Heavy lines: those using modified profiles.

the resulting Utah Surrogate Mechanism was used to simulate the species concentrations in five premixed flames of higher paraffin and composite fuels, and in one JSR experiment of normal hexadecane. These flames, with a range of equivalence ratios from 1.0 to 1.9, are all at atmospheric pressure, with the exception of the gasoline flame that was operated at 30 torr.

Premixed Flames of Large Paraffins

The simulation results of the iso-octane, n-decane and two n-heptane flames are in satisfactory agreement with the experimental data. The measured concentration profiles of the fuels, oxidizer, inert species and major products are successfully reproduced, for example, as seen in Figure 4 for the n-heptane ($\Phi = 1.9$) and n-decane ($\Phi = 1.7$) flames. Detailed comparisons between the measured and predicted concentration profiles of intermediates in these two flames were reported elsewhere (Zhang, 2005); and comparisons for a set of representative species have been shown in Figure 5. The predicted peak concentrations of nine species in these two flames, including acetylene, 1-butyne, 1-pentene, and benzene in the n-heptane flame, and propylene, di-acetylene, 2-butene, iso-butene, and 1-pentene in the n-decane flame, are within 5% of the measured values. Those of vinyl acetylene in the n-heptane flame and benzene in the n-decane flame are within 10% of the measured values. The predicted peak concentrations of three species (n-heptane flame: ethylene, 1-butene, and 1-heptene) are within 15% of the measured values; eight species (n-heptane flame: 1,3-butadiene, 1-hexene, and 2-heptene; n-decane flame: acetylene, allene, 1,3-butadiene, 1-butene, and 1-hexene) are within 20%; four species (n-heptane flame: 3-heptene; n-decane flame: methane, ethylene, and 1-heptene) are within 30%; and four species (n-heptane flame: methane, ethane, propylene, and propyne) are within 50%. The numerical results for two species (n-heptane flame: allene; n-decane flame: ethane) have higher deviations but are still within a factor of three of the measured values. The predicted peak concentration of propane in the n-decane flame is one order of magnitude lower than the experimental value. The numerical performance of the iso-octane ($\Phi = 1.9$) and the stoichiometric n-heptane flames have been discussed elsewhere (Zhang, 2005), and comparisons for a set of six species in each flame have been provided in Figure 6. The deviation of each species of these four premixed flames using the Utah Surrogate Mechanism, however, is tabulated in Table 2.



Figure 4. Comparison with experimental results (data points) of simulations of the concentrations of the fuels, oxidizer, inert species and major products (solid lines) in the n-heptane ($\Phi = 1.9$) and the n-decane flames ($\Phi = 1.7$).



Figure 5. Predicted and experimental concentration profiles of selected species in the n-heptane flame (upper, $\Phi = 1.9$, 760 torr) measured by El Bakali and coworkers (1999) and n-decane flame (lower, $\Phi = 1.7$, 760 torr) by Doute and coworkers (1995a). The symbols represent the experimental data and the lines the simulations.



Figure 6. Predicted and experimental concentration profiles of selected species in the iso-octane flame (upper, $\Phi = 1.9$, 760 torr) measured by El Bakali and coworkers (1998) and the n-heptane flame (lower, $\Phi = 1.0$, 760 torr) by Vovelle and coworkers (2001). The symbols represent the experimental data and the lines the simulations.

			n-Decane Premixe	d Flame $\Phi = 1.7$		
	1-C ₇ H ₁₄	1-C ₆ H ₁₂	$1-C_{5}H_{10}$	$1-C_4H_8$	$2-C_4H_8$	i-C4H8
MPC* Deviation,%	5.20E-4 + 20.58	8.38E-4 - 17.54	9.65E-4 - 4.97	2.72E-3 - 18.38	3.00E-5 - 2.67	3.50E-5 +4
	C_3H_6	C_2H_4	p-C ₃ H ₄	C_2H_2	a-C ₃ H ₄	C_4H_2
MPC Deviation,%	6.70E-3 + 0.15	4.08E-2 - 26.72	4.80E-4 - 13.96	1.66E-2 - 17.47	4.28E-4 - 17.99	2.00E-4 - 4.25
	C_6H_6	CH_4	C_2H_6	C_3H_8		
MPC Deviation,%	6.50E-5 + 8.31	1.20E-2 - 28	4.00E-3 - 73.75	9.70E-4 - 93.29		
			n-Heptane Premixe	d Flame $\Phi = 1.9$		
	1-C ₇ H ₁₄	$2-C_7H_{14}$	$3-C_7H_{14}$	$1-C_{6}H_{12}$	$1-C_5H_{10}$	$1-C_4H_8$
MPC Deviation,%	1.28E-5 - 10.94	2.40E-5 + 19.17	1.63E-5 + 26.99	2.35E-4 + 19.15	5.00E-4 - 3.8	1.20E-3 + 11.67
	C_3H_6	C_2H_4	$1 \# C_4 H_6$	$p-C_3H_4$	C_2H_2	
MPC Deviation,%	3.30E-3 +33.94	2.45E-2 + 10.20	1.88E-5 + 3.19	2.70E-4 + 35.93	1.60E-2 - 0.63	
	$13-C_4H_6$	$a-C_3H_4$	C_4H_4	C_6H_6	CH_4	C_2H_6
MPC Deviation,%	5.30E-4 + 15.28	1.50E-4 + 97.33	1.30E-4 - 8.46	7.50E-5 + 1.2	1.42E-2 - 31.69	1.60E-3 - 30.63

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			i-Octane Premixee	I Flame $\Phi = 1.9$		
	C_2H_4	C ₃ H ₆	$i-C_4H_8$	C_4H_8-1	C_4H_8-2	C_6H_6
MPC Deviation,%	9.50E-3 + 26.32	7.00E-3 +12.71	7.90E-3 + 40.51	5.50E-4 - 30	7.55E-5 - 21.99	2.92E-4 + 55.82
	CH_4	C_2H_6	C_3H_8	C_2H_2	PC_3H_4	C4H6#1
MPC Deviation,%	2.28E-2 - 7.46	2.93E-3 18.43	9.40E-5 - 61.28	1.85E-2 - 21.62	1.36E-3 + 26.47	8.60E-5 - 42.09
	AC_3H_4	$12-C_4H_6$	$13-C_4H_6$	C_4H_2	C_4H_4	
MPC Deviation,%	1.20E-3 + 20	6.60E-5 +169.70	4.20E-4 - 35.95	1.95E-4 + 40.51	2.35E-4 - 34.89	
			n-Heptane Premixe	td Flame $\Phi = 1.0$		
	C_2H_4	C ₃ H ₆	C_4H_8-1	C ₅ H ₁₀ -1	C ₆ H ₁₂ -1	$C_7H_{14}-1$
MPC Deviation,%	1.03E-2 - 2.91	2.00E-3 +25.5	7.17E-4 - 4.04	3.22E-4 - 13.04	1.40E-4 + 8.57	4.91E-6 - 4.89
	C_2H_2	PC_3H_4	AC_3H_4	$13-C_4H_6$	C_4H_4	C_6H_6
MPC Deviation,%	1.83E-3 - 15.85	5.12E-5 +151.95	6.33E-5 + 132.23	1.70E-4 + 39.41	1.15E-5 + 193.04	1.20E-5 - 83.42
	CH_4	C_2H_6	C_3H_8	C_4H_{10}		
MPC Deviation,%	1.21E-3 - 33.72	1.36E-3 - 42.72	2.79E-4 - 85.73	3.50E-5 - 49.71		
*Measured Peal	k Concentration (repo	orted as mole fraction)				

JSR Flames of Large Paraffins

The predicted concentration profiles of selected species as functions of temperature are compared with experimental data in Figure 7 for a jet stirred reactor experiment with normal hexadecane. The fuel conversion rates of normal hexadecane have been well reproduced at all temperatures and the predicted conversion rates of oxygen are in good agreement with the measured values at temperatures lower than 1200 K. The model fails to predict the concentration profile of oxygen at temperatures higher than 1200 K, and further investigation is needed to resolve the difference.

The predicted concentration profiles of olefins capture the trends of the experimental profiles very well. For example, the predicted peak concentrations of ethylene and propylene are 26% and 23% lower than the measured values, respectively, with the peak positions correctly estimated; the deviations are within the experimental uncertainties for these species. The simulated concentration profile of 1-butene, which is



Figure 7. Predicted and measured concentration profiles of selected species in the fuel-rich normal hexadecane JSR experiment ($\Phi = 1.5$, 760 torr) measured by Fournet and coworkers (2001). The symbols represent the experimental data and the lines with a corresponding symbol represent the simulations.

formed mainly via the β scission of alkyl radicals, is shifted 30 K to higher temperatures with the predicted maximum concentration 38% lower than the measured value. The experimental maximum concentration of iso-butene, which is formed via the recombination reaction of the CH₃ radical and C₃H₅ isomers, is well predicted with a deviation of only -7.6%; however, the unexpected flat plateau in the measured concentration profile of iso-butene makes it more difficult for the Utah Surrogate Mechanism to capture the trend of the experimental data.

The measured concentration profiles of acetylenes are also well reproduced in the simulation. For example, the maximum concentration of acetylene, one of the most important soot precursors, is under-predicted by only 24.7% with the peak concentration temperature predicted correctly. The predicted peak concentration of propyne, another important soot carbon source via dehydrogenation to propargyl radical, is in good agreement with the measured value with a deviation of 32.2%.

The Utah Surrogate Mechanism successfully captures the trends of the measured concentration profiles of the two C₄ diene isomers as seen in Figure 7. The maximum concentration of 1,3-butadiene is underpredicted by 45.7% with the temperature of the peak concentration 30 K higher than the measured value. The predicted peak concentration of the other isomer 1,2-butadiene is 30.9% higher than the experimental measurement with the temperature of the peak position predicted correctly. The deviations in the concentrations of the two isomers are likely due to uncertainties in their isomerization reactions.

The model is also able to capture the trends of the measured concentration profiles of other minor intermediates such as ethane and acrolein $(CH_2=CH-CHO)$. The peak concentration of ethane is under-predicted by a factor of two with the temperature of the maximum concentration predicted correctly. The Utah Surrogate Mechanism over-predicts the maximum concentration of acrolein, a species of olefinic aldehyde, by only 16.0% but with the predicted temperature of the maximum concentration 40–50 K higher.

Premixed Flames of Composite Fuels

The flame structures of three composite fuels have also been studied using the Utah Surrogate Mechanism (Zhang et al., 2007). A detailed discussion of the numerical results in a premixed kerosene flame has also been reported elsewhere (Zhang, 2005). In Figure 8, the predicted



Figure 8. Predicted and experimental concentration profiles of selected species in the gasoline flame ($\Phi = 1.0$, 30 torr) measured by Hakansson and coworkers (2001). The symbols represent the experimental data and the lines the simulations.

concentration profiles of selected species are compared to the experimental data in a stoichiometric premixed gasoline flame. The surrogate used in the simulation of the gasoline flame includes 15.5% n-butane, 13.9% xylene isomers, 12.7% n-hexane, 11.9% toluene, 10.3% isooctane, 9.5% methyl cyclohexane, 8.7% ethylbenzene, 7.2% methyl ethylbenzene, 6.0% n-heptane, 1.9% benzene and a small fraction of olefins from C₄ to C₉. A more detailed study of this gasoline flame with a refined surrogate formulation is given elsewhere (Zhang et al., 2007).

The measured fuel consumption rate in the gasoline flame is successfully reproduced, inferred by the measured and simulated concentration profiles of iso-octane and toluene in Figure 8, two of the major components in the composite gasoline fuel. The comparisons of predicted and measured concentrations of major olefins show that the peak concentration of ethylene is over-predicted by 29.0% and that of iso-butene is under-predicted by 12.7%. The model yields benzene concentrations that are within experimental uncertainties (Hakansson et al. reported the uncertainty for major species to be 25%); the benzene in the gasoline fuel accounts for the anomalous high values of concentrations at the burner surface. The maximum concentration of acetylene is underpredicted by a factor of 2.9, which is probably due to the semi-detailed nature of the sub-mechanisms for a few major components, likely missing critical species in the surrogate fuel, and possible uncertainties in the kinetics involving C_4 species formed from the decomposition of paraffin components. We have found that reactions involving C_4H_5 isomers were critical in acetylene formation in a modeling study of a stoichiometric premixed cyclohexane flame measured by Law (2005), and these findings will be reported in a separate publication.

SUMMARY

A reaction mechanism was generated and extended to fit five premixed flames of large paraffin and composite fuels with a range of equivalence ratios from 1.0–1.9. The mechanism was also tested with JSR experimental data of normal hexadecane. H and OH radicals are the most important hydrogen abstractors accounting for most of the fuel consumption followed by molecular O_2 , O, HO₂ and CH₃ radicals. Thermal decomposition is usually not important under the conditions of the premixed laminar flames studied due to the depletion of fuels at these temperatures, but can be important in diffusion flames, since, unlike premixed flames, the fuel survives to high temperatures (Zhang, 2005).

Alkyl radicals are the products of hydrogen abstraction or thermal decomposition, and each alkyl radical decomposes via β scission to form a smaller alkyl radical and an olefin. Olefin decomposes mainly via hydrogen addition followed by β scission to form a smaller olefin and an alkyl radical. The inclusion of the reaction class of hydrogen addition followed by β scission is one of the contributions of this study to fuel combustion chemistry, since the importance of this reaction class is not fully recognized in many mechanisms in the literature on modeling of higher paraffin or composite fuels. Thermal decomposition and hydrogen abstraction are also included as the minor consumption routes of olefins.

In premixed flames, normal paraffins react by a cascading mechanism involving hydrogen addition, isomerization, and β scission reactions of olefins and alkyl radicals, as illustrated by the shaded area in Figure 9. Generic rates are assigned to reactions in the same class of paraffins, olefins and alkyl radicals as summarized in Table 1. Reactions involving alkynes, allylic radicals and other unsaturated species



Figure 9. The decomposition mechanism of normal paraffins can be presented as a collection of cascading decomposition sub-mechanisms of homologous series of olefin species and alkyl radicals.

are assigned rates carefully estimated from literature values for similar reactions. Most of these reactions have already been included in the gas phase core mechanism and involve mostly smaller species, and there is probably no need to reevaluate them, with the exception of species that involve fuel-dependent reactions, in the future generation of large paraffin mechanisms.

The same technique has been applied in generating mechanisms for iso- and cyclo-paraffins. Ring-opening reactions compete with those of cascading dehydrogenation for decomposition of the conjugate cyclohexyl radicals. The major ring opening pathways produce 1-buten-4-yl and ethyl radicals, molecular ethylene, and 1,3-butadiene. Cascading dehydrogenation also makes an important contribution to the fuel decomposition, and provides the exclusive formation pathway of benzene. The extension has been proved to be successful as seen in comparisons between the simulated and measured concentration profiles of the iso-octane flame and the gasoline flame, in which iso- and cyclo-paraffins are major fractions. The use of generic rates of reaction classes has greatly reduced mechanism generation efforts, yet still leads to generally good agreement between numerical and experimental results.

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