Chemical Kinetic Modeling of 2-Methylhexane Combustion

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Abstract
Accurate chemical kinetic combustion models of lightly branched alkanes (e.g., 2-methylalkanes) are important for investigating the combustion behavior of diesel, gasoline, and aviation fuels. Improving the fidelity of existing kinetic models is a necessity, as new experiments and advanced theories show inaccuracy in certain portions of the models. This study focuses on updating thermodynamic data and kinetic model for a gasoline surrogate fuel, 2-methylhexane, with recently published group values and rate rules. These update provides a better agreement with rapid compression machine measurements of ignition delay time, while also strengthening the fundamental basis of the model.

Introduction

Accurate kinetic models of fuel oxidation at high and low temperatures offer better prediction of combustion properties, hence, enabling improvements in the engine combustion efficiency with less emission. Current kinetic model validation is achieved by comparison with a wide range of experimental data. However, kinetic models require continuous improvement with recent, more accurate calculated or experimental data to eliminate or reduce uncertainty.

Models are developed based on the rate rules and group additivity methods for reaction classes and thermodynamic data, respectively. Group additivity method is a trustworthy method for determining thermochemical data provided accurate group values are available. On the other hand, especially at low-temperatures, few of the assigned rate rules are experimentally determined, while the rest are approximated, which increases the uncertainty. Therefore, accurate theoretically calculated rate rules are needed [1]. Computational chemistry is a flexible and reliable method for predicting rates at conditions inaccessible by experiments [2].

Improving a kinetic model requires both updating the thermodynamic and kinetic data, including the introduction of alternative pathways or adding pressure dependent rates [2].

The aim of this study is to update the thermodynamic data and the reaction rate rules for 2-methylhexane, based on a previously published model by Sarathy et al [3]. This is combined with adding alternative pathways of OOQOOH isomerization. Most of the rates used in this work to replace old rate rules are based on computational calculations available in the literature.

The importance of 2-methylhexane refers to the fact that it is a proposed surrogate component for gasoline fuels. It is one of iso-alkane constituents which can represent up to 84% in some gasoline surrogates [4]. Accurate prediction of ignition from each component in the surrogate will result in an accurate surrogate kinetic model [4].

Chemical kinetic model:

The mechanism used is a high and low temperature 2-methylhexane mechanism by Sarathy et al [3] based on Curran et al.'s [5, 6] rate rules.

Model Validation:

The updated model is validated against ignition delay time data, which is widely used as a mechanism validation tool. Ignition delay time is commonly measured in a shock tube or rapid compression machine (RCM). It is defined as the time difference between the end of compression and the start of ignition [7], identified as a maximum change in pressure or temperature with respect to time ((max dT/dt ≡ max dp/dt) [8].

The model has been validated against RCM data from Silke et al [8]. The experiment was held at an equivalence ratio of phi=1. Different initial temperature, pressure and diluent fraction were used to achieve at the end of compression, a pressure of 13.5-15 atm at a temperature range of 640-960K.

The effect of updating the thermodynamic data and each updated class is simulated in a constant volume model using CHEMKIN PRO in a homogeneous batch reactor to estimate the ignition delay time. The simulations are performed for a temperature range of 650 to 1450 K at 15 atm and phi=1.

Thermodynamic data:

The thermodynamic data is calculated using the THERM software [9]. It is based on the group additivity method (GA) which is proposed by Benson and co-workers [10]. This method breaks the molecule into groups, each having its own contribution to the thermodynamic properties. We use a second order estimation method in which corrections for 1,4 and 1,5 interactions, optical isomers, cyclization, etc. are accounted for [9].

New updated group values are used to estimate the thermodynamic data of all 2-methylhexane species. Attention was given to the optical isomers and the effect of the non-next-nearest neighbor interactions (NNI)

(gauche interaction) as proposed by Sabbe et al. [11, 12].

One optical isomer is added for each chiral carbon (carbon attached to four different groups). This is the case when a primary radical in C1 makes C2 a chiral center. Moreover, in ROO, QOOH and OOQOOH species an optical isomer is added for each OOH group (pseudochiral OOH center) in addition to the chiral sites [1].

Three different types of gauche interactions are accounted for:

• Alkane gauche interaction (AG): when a tertiary and a secondary sites are adjacent, i.e. C2 and C3 in figure 1, one gauche (0.8 kcal/mol) is added [11].

• Radical gauche 1 interaction (RG1): when a radical exists in one of the gauche center carbon, C2 or C3, it is neglected and one gauche is assumed [11, 12].

• Radical gauche 2 interaction (RG2): when a radical exists on sites neighboring the central carbons C2 or C3, i.e. C1 or C4, the number of gauche interaction is, AG − RG2. Therefore, no gauche effect is assumed [11, 12].

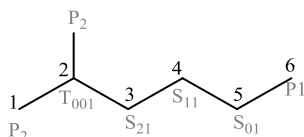Radicals on the remaining sites have negligible effect in gauche corrections.

Figure 1: 2-methylhexane structure

Updated group values, especially alperox and OO/C/H, were used based on the work of Burke et. al. [13]. These impacted thermochemical properties of low temperature species, leading to significant alteration in the enthalpy, entropy and consequently the Gibbs energy. This affects the reverse rate of reaction and ignition delay predictions, as shown in figure 2, wherein the ignition delay time slower than that of the original mechanism.
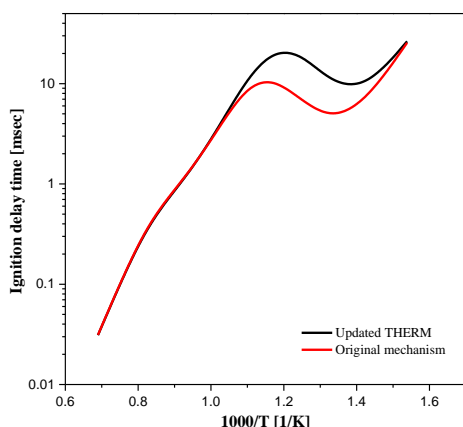

Figure 2: Ignition delay time simulated at constant volume at 15atm, phi=1.

Chemical kinetic mechanism:
Some important reaction classes have been revised and modified by more accurate calculated and measured rate

rules. This leads to a better model performance in extended operating conditions.
Updates and additional pathways were made according to the sequence below.

1 ($R + OH \leftrightarrow R^.$)
2 (1+($R^. + O_2 \leftrightarrow ROO^.$)
3 (2+(ROO$^.$ $\leftrightarrow$ $^.$QOOH)
4 (3+(ROO$^.$ $\leftrightarrow$ alkene + HO$_2$))
5 (4+($^.$QOOH $\leftrightarrow$ cyclic ether + OH))
6 (5+($^.$QOOH $\leftrightarrow$ alkene + HO$_2$))
7 (6+($^.$QOOH + O$_2$ $\leftrightarrow$ $^.$OOQOOH))
8 (7+($^.$OOQOOH $\leftrightarrow$ ketohydroperoxide +OH))

Added Classes:
9 (8+(P($^.$OOH)$_2$ formation, P(OOH)$_2$$\leftrightarrow$alkene+HO$_2$))
10 (9+(P($^.$OOH)$_2$ $\leftrightarrow$ cyclic ether + OH))
11 (10+(Cyclic ether decomposition))
12 (11+(C0-C4 and C5 updates))

For example, the 7th update is $^.$QOOH+O$_2$ updated with all the precedent reactions (1-6) and thermodynamic date also updated. The 12th update is the final updated model.

H-atom abstraction from the fuel by OH
The next-nearest-neighbor (NNN) estimation method proposed by Cohen et al. [14] was used to assign a unique rate constant for each site based on the number of the next neighbor of the considered site.
The subscripts in figure 1 show the NNN of each site. The rate constants of P1, P2, S01, and S11 were obtained from Sivaramakrishnan et al.'s [15] measurements at a wide range of temperatures, while S21 and T001 were obtained from Badra et al.'s [16] measurements.

Addition of O$_2$ to alkyl radicals ($R^. + O_2 = ROO^.$) and Addition of O$_2$ to$^.$ QOOH ($^.$QOOH + O$_2$ = OOQOOH)
This was updated using Miyoshi et al.'s [17] rates estimated by the variational transition-state theory for different radicals + O$_2$. However, QOOH + O$_2$ was updated using Miyoshi rates with a pre-exponential factor A divided by 2, based on Goldsmith et al.'s [18] recommendation, which determined that the rate of R$^.$+O$_2$ is faster than the corresponding $^.$QOOH +O$_2$.

Alkyl peroxy radical isomerization (ROO$^.$ = $^.$QOOH) and Concerted eliminations (ROO$^.$ = alkene + HO2)
This was updated using Villano et al.'s [1] rates calculated at CBS-QB3 level of theory along with transition state theory for reactions involving C1-C5 and few selected C6 and C7 alkyl peroxy radicals.

Cyclic ether formation ($^.$QOOH = cyclic ether + OH)
This was updated using Villano et al.'s [2] rates calculated at CBS-QB3 level of theory along with the transition state theory. The activation energy is formulated as a function of the heat of reaction at 298°C which is evaluated for each reaction using the updated heat of formation values obtained from THERM.

$\cdot$QOOH = alkene + HO$_2$ (radical site beta to OOH group).

This was updated using Villano et al.'s [19] rates calculated at CBS-QB3 level of theory along with the transition state theory.

Isomerization of OOQOOH (OOQOOH $\leftrightarrow$ ketohydroperoxide + OH)

This was updated using rates calculated at CBS-QB3 method with a special treatment of hindered rotors, by Sharma et al. [20]. They found that the difference between the activation energy of ROO isomerization and $\cdot$QOOH isomerization varies with the transition state's ring size. It was estimated as 8.6, 2.2 and 0 kcal/mol for 5, 6 and 7 members ring respectively. Therefore, the activation energy of ROO isomerization – 3 kcal used in the original mechanism, as suggested by Curran et al. [6], is not valid for $\cdot$QOOH isomerization.

Updating this class of reaction resulted in up to eight msec difference on the ignition delay time, as shown on figure 3. This is considered as the major effect relative to all other previous updates, which were all within three msec difference of the original mechanism.
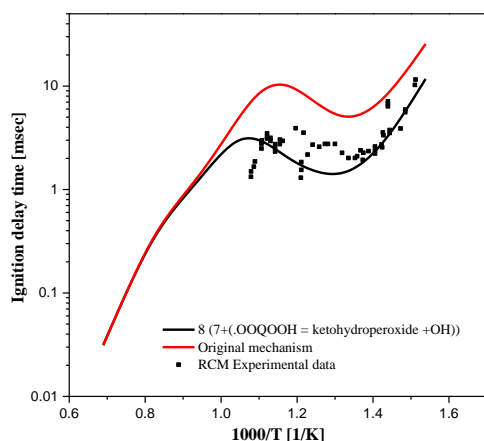

Figure 3: Ignition delay time simulated at constant volume at 15atm, phi=1.

Although the predicted ignition delay time qualitatively matches the experimental data, it was faster than expected. Therefore, alternative pathways of OOQOOH that are competitive to ketohydroperoxide formation (the most important low temperature, chain branching reaction) were considered. This is to eliminate the over prediction of the formation of ketohydroperoxide, which is the cause of accelerating ignition.

Alternative isomerization

Figure 4 below shows the conventional and alternative pathways of OOQOOH that were considered. Since no rate rules are estimated for these reactions explicitly, functional group analogy was used to assign rate constants.

The added classes are:

- Alternative isomerization, P$\cdot$(OOH)$_2$ formation, where P$\cdot$ is C_nH_{2n-1}. In this class the OO$\cdot$ group abstracts H from carbons other than the weakest

carbon, which is bonded to the OOH group. Only six member ring reactions are included in this work.

- P$\cdot$(OOH)$_2$ $\leftrightarrow$ alkene+HO$_2$. This is added in analogy to alkene production from R$\cdot$OO and $\cdot$QOOH.

- P$\cdot$(OOH)$_2$ $\leftrightarrow$ cyclic ether + OH, which is similar to the cyclic ether formation from $\cdot$QOOH.

- Cyclic ether decomposition, this is a chain branching pathway which is added to investigate the effect of OH radical produced.
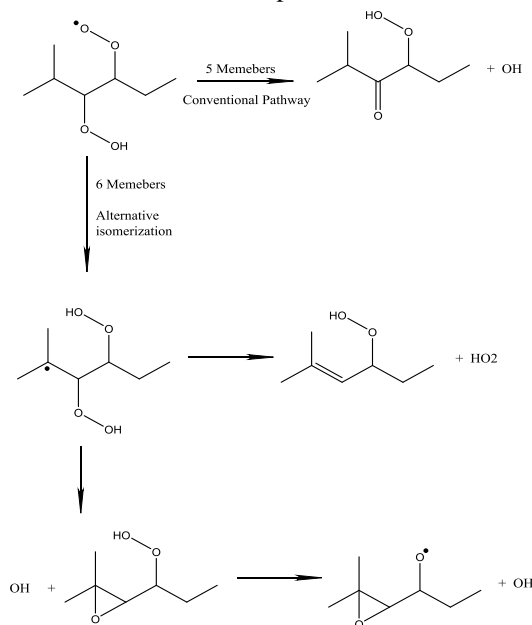

Figure 4: Conventional and alternative pathways of OOQOOH isomerization

Estimated ignition delay times after alternative isomerization were compared to the updated model without these pathways as shown in figure 5.
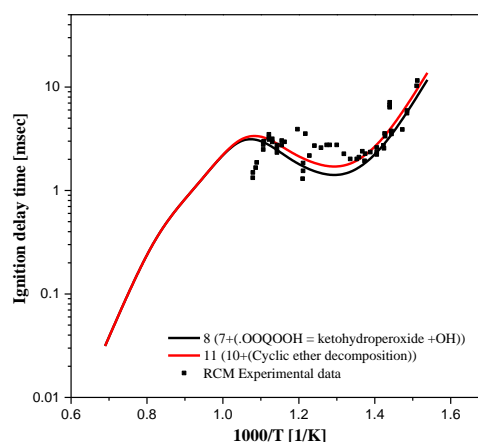

Figure 5: Effect of adding alternative isomerization pathway

Figure 5 shows a very minor effect in the ignition behavior after adding alternative pathways. Both P$\cdot$(OOH)$_2$ $\leftrightarrow$ cyclic ether + OH and cyclic ether decomposition are chain branching reactions producing

two OH radicals, thus, adding these pathways will maintain the reactivity of the conventional model in which OOQOOH isomerizes to ketohydroperoxide only. However, the rate of $P^.(OOH)_2 \leftrightarrow$ alkene+HO_2 was much faster than $P^.(OOH)_2 \leftrightarrow$ cyclic ether + OH by an average of eight orders of magnitude at low temperature. Thus, alkene + HO_2 is the dominant pathway producing HO_2 radicals, which are responsible for the decreased reactivity and slower ignition delay times observed.

Finally the base chemistry was updated by using an updated C0-C4 and C5 sub-mechanism by Burke at al [21] and Sarathy et al. [22] respectively. The final updated model is shown in figure 6 below.

The final model agrees well with the RCM data; however more validation is required especially at intermediate and high temperatures in a shock tube.
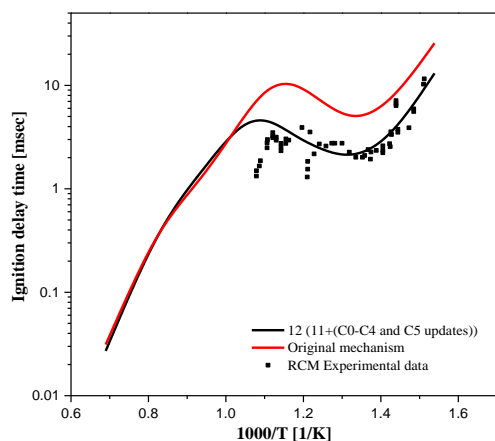

Figure 6: Final model after applying all updates

Conclusion:

In this work, thermodynamic data and kinetic mechanism for 2-methylhexane are updated using new updated group values and accurately measured and calculated rate rules, respectively. The model updates for both thermodynamic and rate rule data showed a significant variation in the model behavior especially at low temperatures. The new predicted ignition delay time is in a better agreement with the RCM experimental data. Further validation will be held by measuring the ignition delay time in a shock tube experiment.

Acknowledgment:

References:

1.   S. M. Villano; L. K. Huynh; H. H. Carstensen; A. M. Dean, The journal of physical chemistry. A 115 (46) (2011) 13425-42 10.1021/jp2079204.
2.   S. M. Villano; L. K. Huynh; H. H. Carstensen; A. M. Dean, The journal of physical chemistry. A 116 (21) (2012) 5068-89 10.1021/jp3023887.
3.   S. M. Sarathy; C. K. Westbrook; M. Mehl; W. J. Pitz; C. Togbe; P. Dagaut; H. Wang; M. A. Oehlschlaeger; U. Niemann; K. Seshadri; P. S. Veloo; C. Ji; F. N. Egolfopoulos; T. Lu, Combustion and Flame 158 (12) (2011) 2338-2357 10.1016/j.combustflame.2011.05.007.
4.   S. M. Sarathy; G. Kukkadapu; M. Mehl; W. Wang; T. Javed; S. Park; M. A. Oehlschlaeger; A. Farooq; W. J. Pitz; C.-J. Sung, Proceedings of the Combustion Institute (0)) http://dx.doi.org/10.1016/j.proci.2014.05.122.
5.   H. J. Curran; P. Gaffuri; W. J. Pitz; C. K. Westbrook, Combustion and Flame 114 (1–2) (1998) 149-177 http://dx.doi.org/10.1016/S0010-2180(97)00282-4.
6.   H. J. Curran; P. Gaffuri; W. J. Pitz; C. K. Westbrook, Combustion and Flame 129 (3) (2002) 253-280 http://dx.doi.org/10.1016/S0010-2180(01)00373-X.
7.   B. W. Weber; C.-J. Sung, Energy & Fuels 27 (3) (2013) 1688-1698 10.1021/ef302195c.
8.   E. J. Silke; H. J. Curran; J. M. Simmie, Proceedings of the Combustion Institute 30 (2) (2005) 2639-2647 http://dx.doi.org/10.1016/j.proci.2004.08.180.
9.   E. R. Ritter, Journal of Chemical Information and Computer Sciences 31 (3) (1991) 400-408 10.1021/ci00003a006.
10.   S. W. Benson; J. H. Buss, The Journal of Chemical Physics 29 (3) (1958) 546 10.1063/1.1744539.
11.   M. K. Sabbe; M. Saeys; M.-F. Reyniers; G. B. Marin; V. Van Speybroeck; M. Waroquier, The Journal of Physical Chemistry A 109 (33) (2005) 7466-7480 10.1021/jp050484r.
12.   M. K. Sabbe; F. De Vleeschouwer; M.-F. Reyniers; M. Waroquier; G. B. Marin, The Journal of Physical Chemistry A 112 (47) (2008) 12235-12251 10.1021/jp807526n.
13.   S. M. Burke; J. M. Simmie; H. J. Curran, J. Phys. Chem. Ref. Data   (Accepted Sept 2014)
14.   N. Cohen, International Journal of Chemical Kinetics 23 (5) (1991) 397-417 10.1002/kin.550230506.
15.   R. Sivaramakrishnan; J. V. Michael, The Journal of Physical Chemistry A 113 (17) (2009) 5047-5060 10.1021/jp810987u.
16.   J. Badra; A. Elwardany; A. Farooq, Proceedings of the Combustion Institute (0)) http://dx.doi.org/10.1016/j.proci.2014.05.098.
17.   A. Miyoshi, The journal of physical chemistry. A 115 (15) (2011) 3301-25 10.1021/jp112152n.
18.   C. F. Goldsmith; W. H. Green; S. J. Klippenstein, The journal of physical chemistry. A 116 (13) (2012) 3325-46 10.1021/jp210722w.
19.   S. M. Villano; H. H. Carstensen; A. M. Dean, The journal of physical chemistry. A 117 (30) (2013) 6458-73 10.1021/jp405262r.
20.   S. Sharma; S. Raman; W. H. Green, The Journal of Physical Chemistry A 114 (18) (2010) 5689-5701 10.1021/jp9098792.
21.   S. M. Burke; W. Metcalfe; O. Herbinet; F. Battin-Leclerc; F. M. Haas; J. Santner; F. L. Dryer; H. J. Curran, Combustion and Flame 161 (11) (2014) 2765-

2784
http://dx.doi.org/10.1016/j.combustflame.2014.05.010.
22. S. M. Sarathy; T. Javed; F. Karsenty; A. Heufer; W. Wang; S. Park; A. Elwardany; A. Farooq; C. K. Westbrook; W. J. Pitz; M. A. Oehlschlaeger; G. Dayma; H. J. Curran; P. Dagaut, Combustion and Flame 161 (6) (2014) 1444-1459 http://dx.doi.org/10.1016/j.combustflame.2013.12.010.