

An Investigation of the Thermochemical Parameter and Rate Coefficient Assignments for the Low-Temperature Oxidation Pathways of Alkanes: A Case Study using the Pentane Isomers

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Abstract

This paper describes our developing understanding of low-temperature oxidation kinetics. We have investigated the ignition of the three pentane isomers in a rapid compression machine over a wide range of temperatures and pressures including the negative temperature coefficient temperature range. The pentane isomers are small alkanes, yet have structures that are complex enough to allow for the application of their kinetic and thermochemical rules to larger molecules. Updates to the thermochemistry of the species important in the low-temperature oxidation of hydrocarbons have been made based on a thorough literature review. An evaluation of recent quantum-chemically derived rate coefficients from the literature pertinent to important low-temperature oxidation reaction classes has been performed, and new rate rules are recommended for these classes. Several reaction classes have also been included to investigate their importance with regard to simulation results, and we find that they should be included when developing future chemical kinetic mechanisms. A comparison of the model simulations with pressure-time histories from experiments in a rapid compression machine shows very good agreement for both ignition delay time and pressure rise for both the first- and second-stage ignition events. We show that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well. The results of this study enhance our understanding of the combustion of straight- and branched-chained alkanes.

Introduction

Alkanes are the simplest type of hydrocarbon, so knowledge of the combustion of these compounds is essential to the fundamental understanding of the combustion of all hydrocarbons and oxygenated fuels (e.g. alcohols, large methyl esters, etc.). The low-temperature oxidation of alkanes is of practical importance to the advancement of technologies such as homogeneous-charge compression-ignition (HCCI), premixed-charge compression-ignition (PCCI), and reactivity-controlled compression-ignition (RCCI) engines. Construction of detailed mechanisms describing low-temperature oxidation can be difficult due to the large number of chemical species and reactions involved. Group additivity [1] and rate rule [2,3] methods are convenient solutions to this problem. In this study we discuss the implementation of both methods, and improved values used therein, for current and future development of detailed chemical kinetic models.

The first low-temperature reaction channels for the oxidation of alkanes were proposed in the late 1960s by Knox [4] and Fish [5]. An improved understanding was developed by Pollard [6], Cox and Cole [7] and Walker and Morley [8]. Curran et al. applied rate coefficients based on rate estimation rules for different reaction classes and had success in modelling the oxidation of n-heptane and iso-octane at low temperatures [2,3]. However, some reaction classes were excluded from the low-temperature reaction pathways of these mechanisms due to limitations in knowledge at the time. These involve peroxy-hydroperoxy-alkyl (O_2QOOH) radicals undergoing reactions similar to those included

for alkyl-peroxy (RO_2) radicals, such as the direct elimination of HO_2 radicals from the alkyl-peroxy radicals (also forming olefins), and isomerization reactions like those of RO_2 to produce hydroperoxy-alkyl ($QOOH$) radicals, but instead resulting in the formation of di-hydroperoxy alkyl radicals. These can undergo reactions similar to those of $QOOH$ radicals, such as cyclic ether formation, and β -scission reactions, Fig. 1 (R, Q and P represent alkyl radicals or structures C_nH_{2n+1} , C_nH_{2n} and C_nH_{2n-1} , respectively). Inclusion of these “alternative” reaction classes are of particular importance for the mechanisms of branched alkanes, as previously [3], the chain of reactions proceeding from tertiary alkyl radical addition to molecular oxygen came to a “dead end” upon formation of an O_2QOOH radical. An example of this for iso-pentane is shown in Fig. 2.

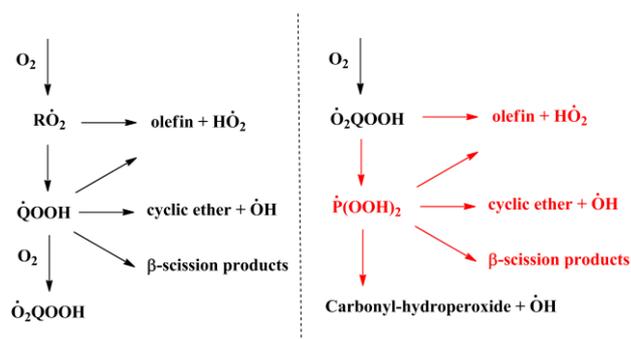


Figure 1. Lumped kinetic scheme of the primary oxidation reactions of alkanes. Species and arrows highlighted in red represent pathways not previously considered for the pentane isomers.

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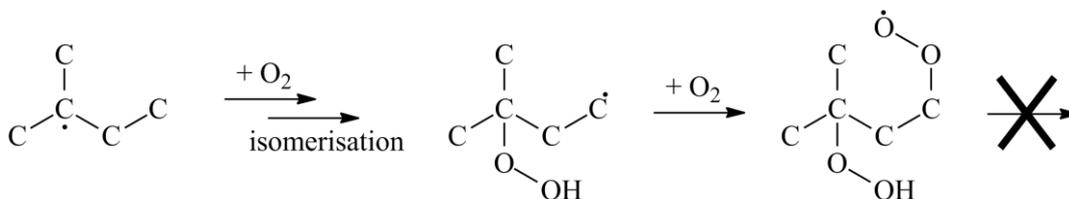


Figure 2. Example of “dead end” in low-temperature pathways of iso-pentane.

Silke [9] and Glaude *et al.* [10] have performed studies of some of these alternative reaction classes for the low-temperature oxidation of *n*-heptane. A simplified scheme for the primary oxidation reactions of alkanes, including these “alternative” reaction classes is shown in Fig. 1. Silke [9] added the following reaction classes to the *n*-heptane mechanism previously published by Curran *et al.* [2]:

- $O_2QOOH \rightleftharpoons P(OOH)_2$
- $P(OOH)_2 \leftrightarrow \text{cyclic ether} + OH$
- $RO_2 + OH \leftrightarrow RO + HO_2$
- $RO_2 + HO_2 \leftrightarrow ROOH + O_2$
- QOOH intramolecular isomerization
- $RO_2 \leftrightarrow \text{olefin} + HO_2$

Silke found that, of the classes added, those that had the largest effect on simulated ignition delay times (IDTs) were $O_2QOOH \rightleftharpoons P(OOH)_2$ and $P(OOH)_2 \leftrightarrow \text{cyclic ether} + OH$. Examples of these types of reactions for *n*-pentane are shown in Fig. 3.

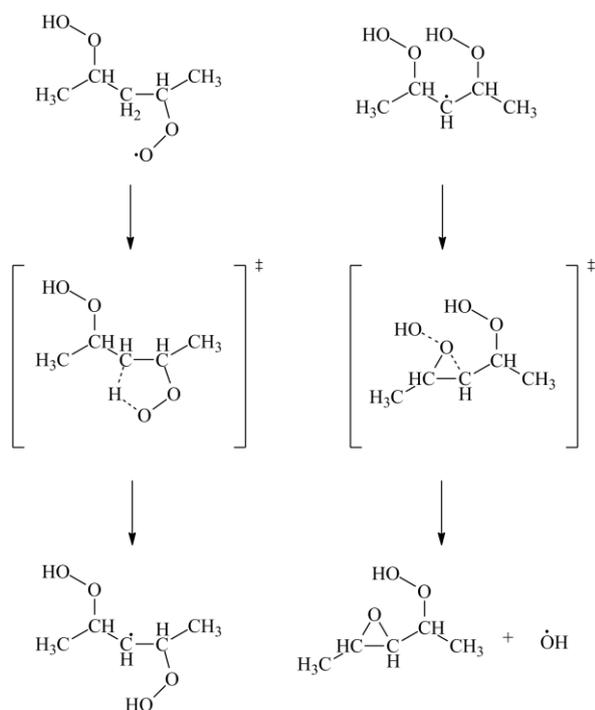


Figure 3. Examples of reaction classes applied to *n*-pentane in this work previously added to Silke [9] *n*-heptane mechanism (a) “Alternative” isomerization of O_2QOOH . (b) Hydroperoxy cyclic ether formation from $P(OOH)_2$.

Silke [9] assigned rate coefficients to the new reaction classes by making analogies to similar reactions, i.e., rate coefficients for $O_2QOOH \rightleftharpoons P(OOH)_2$ isomerization reactions were based on those of for $RO_2 \rightleftharpoons QOOH$. For the reactions $P(OOH)_2 \leftrightarrow \text{cyclic ether} + OH$ the rate coefficients used for $QOOH \leftrightarrow \text{cyclic ether} + OH$ were adopted. The rate coefficients used were those recommended by Curran *et al.* [2,3]. Inclusion of these classes led to large changes in simulated IDTs, to the extent that the model no longer predicted the experimental measurements. Thus, the rate rules used were not compatible with the consideration of these alternative reactions. However, it is essential that these pathways are included to ensure a detailed understanding of a fuel’s oxidation. The fact that the rate rules of Curran *et al.* [2,3] were not suitable for application to the alternative pathways, yet the predictions of the *n*-heptane [2] and *iso*-octane [3] models reproduced data very well, points to a lack of fundamental understanding of the thermochemical parameters, rate coefficients, and/or both in the previous studies.

In their work on *iso*-octane, Curran *et al.* [3] reduced the rate coefficients for the isomerization reactions of RO_2 and O_2QOOH radicals by a factor of three relative to those employed in *n*-heptane in order to match experimental data at low temperatures (600–770 K). It was postulated that there must be a reason that these reactions were slower for *iso*-octane than for *n*-heptane, or that there must have been pathways missing in the mechanism. With such discrepancies existing for the primary reference fuels (PRFs), it was clear that a re-examination of the thermochemistry and rate coefficients pertaining to the low-temperature oxidation pathways of alkanes was needed in order to reconcile these differences. It is for this reason that the pentane isomers were selected in this study. They are small enough to allow for an in-depth study of their low-temperature oxidation pathways, yet large enough to be representative of larger alkanes. The proximity of the outermost secondary carbons in *n*-pentane makes it an ideal analogue for longer *n*-alkanes, due to isomerization reactions of RO_2 and of O_2QOOH radicals between these carbons being dominant controlling pathways at low temperatures. The different levels of structural branching of *iso*- and *neo*-pentane make them suitable analogues for longer branched-chained alkanes, such as *iso*-octane, with both isomers being representative of the varyingly branched ends of the *iso*-octane molecule.

There have been a number of recent systematic studies which have used various computational quantum

chemical methods for rate coefficient calculations for reactions relevant to the low-temperature oxidation of alkanes [12–17]. These studies have calculated high-pressure limit rate coefficients for sets of training reactions so that they can be used directly in chemical kinetic mechanisms for combustion relevant applications. To our knowledge, these rate coefficients have not been applied to all of the important reaction classes in the low-temperature regime in a hydrocarbon oxidation mechanism. In this work, the rate coefficients from these studies are compared and have been applied to the mechanisms of the pentane isomers. The model simulations are compared to sample ignition delay times in addition to pressure-time histories obtained in a rapid compression machine (RCM) [18]. Based on these theoretical studies, new recommended rate rules are proposed, and are also tested in mechanisms to evaluate their performance against ignition delay times.

A more thorough validation of the mechanisms across a broader range of temperatures, pressures, and with data is planned. This study provides a systematic evaluation of the rate rules in the literature and their suitability for application to mechanisms for the low-temperature oxidation of straight-chained, branched-chained and highly-branched alkanes, and will propose new rate rule recommendations for application to larger alkanes. This will be particularly important for the construction of gasoline surrogate mechanisms.

Model Development

Healy *et al.* [19] developed a mechanism to describe *n*-pentane oxidation based on rate rules recommended by Curran *et al.* [2,3]. This mechanism did not include any of the alternative reaction classes but has served as a starting point for the current investigation.

Thermochemistry

Previously [2,3,9,19,20], the thermochemical data for species were estimated using group additivity rules derived by Benson [1] and implemented in THERM [21]. Due to improved computational methods for calculation of thermochemical properties and a growing amount of literature data, a thorough literature review of thermochemical properties was undertaken for C₁–C₄ alkanes, alkenes, alcohols, hydroperoxides, alcoholic hydroperoxides, and their associated radicals [22]. A variety of sources, including high level ab initio studies, experimental studies, online databases, and review studies has led to updated THERM group values which have been used to update the thermochemistry of the following classes of C₅ species: fuel (RH), fuel radicals (R), olefins, alkyl hydroperoxides (RO₂H), alkyl-peroxy radicals (RO₂), hydroperoxy alkyl radicals (QOOH), cyclic ethers, hydroperoxy alkyl-peroxy radicals (O₂QOOH) and carbonyl-hydroperoxides, as well as any species produced through pathways which have been added to the mechanisms, which will be discussed in detail later.

Table 1. Comparison of original and updated THERM group values at 298 K for selected groups.

| | Original | | Updated | |
|------------------|--|--|--|--|
| | Enthalpy, H° (kcal mol ⁻¹) | Entropy, S° (cal K ⁻¹ mol ⁻¹) | Enthalpy, H° (kcal mol ⁻¹) | Entropy, S° (cal K ⁻¹ mol ⁻¹) |
| C/C/H2/OO | -7.89 | 9.65 | -8.02 | 6.62 |
| C/C2/H/OO | -6.08 | -11.96 | -7.03 | -15.46 |
| OO/C/H | -23.50 | 36.84 | -20.60 | 38.64 |
| ALPEROX | 86.30 | 0.22 | 85.27 | -0.48 |

The most significant changes are to the values of the groups listed in Table 1. The C/C/H2/OO and C/C2/H/OO groups were optimised based the newly recommended values for ethyl, *n*-propyl, iso-propyl, *n*-butyl and *s*-butyl hydroperoxides and their associated peroxy radicals. The enthalpies increased from those previously used, and the entropies decreased for all of these species, resulting in the Gibbs energies increasing by approximately 2.1–3.4 kcal mol⁻¹ at 298 K when the new group values are applied. The OO/C/H group was optimised also based on the aforementioned alkyl hydroperoxide and alkyl-peroxy radical species, but also based on hydroperoxy-ethanol and hydroperoxy-*n*-propanol, and their associated peroxy radicals. Both the enthalpies and entropies for the hydroperoxy alcohols and their associated peroxy radicals decreased from those which had previously been used. This resulted in the Gibbs energies of these species varying by approximately -0.6–+0.5 kcal mol⁻¹ at 298 K. The optimisation of the ALPEROX group was based on the updated values of the aforementioned alkyl-peroxy radical species, the enthalpy and entropy values of which (as mentioned previously) increased and decreased, respectively, resulting in an increase in Gibbs energy values of approximately 2.1–2.5 kcal mol⁻¹ at 298 K.

Figure 4 illustrates the changes in values of thermochemical properties for species important in the low-temperature combustion regime for *n*-pentane, as well as the shifts in equilibria for the main reaction pathways they participate in, brought about by the changes in the thermochemical values.

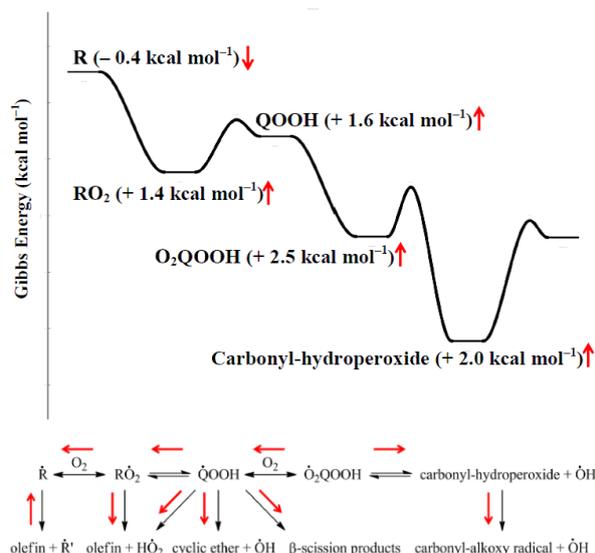


Figure 4. Representation of average change in Gibbs energy at 298 K for important classes of species due to updated THERM group values for n-pentane, and subsequent shifts in equilibria for important reaction classes.

The inclusion of the updated thermochemistry results in a significant decrease in reactivity (Fig. 5) due to a change in the equilibria of the reactions involving the updated species, Fig. 4. The main shifts in equilibria are for the reactions of RO_2 , QOOH and O_2QOOH radicals, with dissociation of RO_2 and O_2QOOH radicals back to their respective alkyl and hydroperoxy-alkyl radicals and molecular oxygen becoming more dominant, as well as the chain propagating reactions of RO_2 and QOOH radicals (which curtail progression towards chain branching reactions) also becoming more dominant. With the updated thermochemistry, there is more flux from O_2QOOH species to produce carbonyl-hydroperoxides + OH, and subsequently the decomposition of carbonyl-hydroperoxides to yield a second hydroxyl radical and a carbonyl-alkoxy radical. These steps constitute chain branching as three radicals are formed from the initial O_2QOOH species, but the effect of the shifts in equilibria on reactivity is minimal due to the large changes in flux earlier in the chain of reactions, involving R, RO_2 , and QOOH radicals, leading to their formation. These results show that, with the adjusted thermochemistry of species relevant to the low-temperature combustion of n-pentane, updates to the rate coefficients important to low-temperature oxidation were necessary. This began with an update to the C_0 - C_4 [23–26] sub-mechanism, with the results showing a relatively minor influence when compared to that of the updated thermochemistry, Fig. 5. It is clear that major changes were needed in the rate coefficients used for the C_5 reactions. These updates will form the basis of our later discussion.

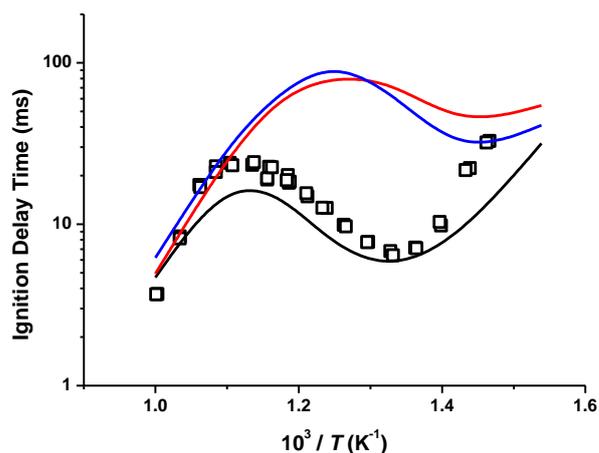


Figure 5. Effect of updated thermochemistry and sub-mechanism. n-pentane, $\Phi = 1.0$ in 'air', 10 atm. — Model predictions using original thermochemistry; — Model predictions using updated thermochemistry; — Model predictions using updated thermochemistry and C_0 - C_4 [23–26] sub-mechanism. All simulations were performed assuming constant volume conditions.

Chemical Kinetic Mechanism

Villano *et al.* [12,13] systematically calculated high-pressure limit rate coefficients for the low-temperature oxidation reactions of alkanes, including n-pentane, at the CBS-QB3 level of theory combined with canonical transition state theory calculations. Karwat *et al.* [27] studied the oxidation of n-heptane in a rapid compression facility and demonstrated success in applying the Villano *et al.* rate rules. However, Villano *et al.* [12,13] did not calculate rate coefficients for the alternative reaction classes that were investigated in the work presented here, and so rate coefficients for these reactions are based by analogy with similar reactions. Rate coefficients for each reaction in the following reaction classes have been applied directly from the papers of Villano *et al.* [12,13].

- Concerted elimination of HO_2 from alkyl-peroxy radical ($RO_2 \leftrightarrow$ olefin + HO_2)
- β -scission of hydroperoxy alkyl radical to give an olefin + HO_2 ($QOOH \leftrightarrow$ olefin + HO_2)
- Cyclic ether formation ($QOOH \leftrightarrow$ cyclic ether + OH)
- β -scission of hydroperoxy alkyl radical to give other products ($QOOH \leftrightarrow$ β -scission products)

$R + O_2$ and $QOOH + O_2$ addition reactions

Miyoshi [14] used variational transition state theory (VTST) and Rice-Ramsperger-Kassel-Marcus theory (RRKM)/master equation calculations based on the CASPT2(7,5)/aug-cc-pVDZ//B3LYP/6-311G(d,p) potential energy curves and B3LYP/6-311G(d,p) geometries and vibrational frequencies, for archetypal

alkyl radical (C_2H_5 , $i-C_3H_7$, $n-C_4H_9$, $s-C_4H_9$ and $t-C_4H_9$) + O_2 reactions, and obtained class-specific high-pressure limit rate coefficients for these systems, which we adopt in this work. Rate coefficients for the addition of R to O_2 , and QOOH to O_2 have been calculated by Goldsmith *et al.* [15] for the propyl + O_2 system, also using VTST calculations. We find that using the rate coefficients calculated by Goldsmith *et al.* [15] results in ignition delay time simulations that are faster than experimental measurements for the pentane isomers. Instead, the rate coefficients used for addition of QOOH to O_2 are based on those used for addition of the fuel radicals to O_2 calculated by Miyoshi [14], with the A-factor scaled based on the results of Goldsmith *et al.* [15]. Their work reported that the QOOH + O_2 reaction is typically slower than the analogous R + O_2 reaction by approximately a factor of two, with the exception of the addition of $HOOCH(CH_3)CH_2$, which is faster than the analogous first addition to O_2 . For each of the pentanes, we find that a reduction of the second addition to O_2 by approximately a factor of two results in experimental data being well reproduced by model simulation results.

RO_2 and O_2QOOH isomerization reactions

Miyoshi [16] and Sharma *et al.* [17] calculated rate coefficients for $RO_2 \rightleftharpoons QOOH$ isomerization reactions for sets of sample reactions at the CBS-QB3 level of theory. There is good agreement between the literature values, most being within a factor of 2–3 of one another, with a maximum discrepancy of approximately a factor of 5 for reactions proceeding through an 8-membered transition state (TS) ring at 1000 K. When applied to the mechanisms of the pentane isomers the rate coefficients for the H-shift reactions of $RO_2 \rightleftharpoons QOOH$ through 6-membered TS rings are the most important, with a relatively high flux proceeding through these pathways.

Miyoshi and Sharma *et al.* also calculated rate coefficients for $O_2QOOH \rightleftharpoons$ carbonyl-hydroperoxide + OH isomerization reactions at the CBS-QB3 level of theory. However, Sharma *et al.* propose an alternative hindered-rotor treatment for O_2QOOH radicals due to these molecules having multiple internal rotors with potentials that are not independent of each other. They find that interactions between the oxygen and hydrogen atoms within the molecule results in a lowest energy conformer that has a ring shape, with the peroxy group forming a hydrogen bond with the OOH group. Comparisons of the rate coefficients show general trends. Rate coefficients calculated by Sharma *et al.* for reactions which proceed through 5-membered TS rings are, in general, faster than those calculated by Miyoshi, whereas reactions proceeding through 6-, 7- and 8-membered rings are generally slower.

We have found that for each of the pentane isomers that using Miyoshi’s rate coefficients for both the first and second isomerization reactions, yields similar results to using Miyoshi’s first isomerization rate coefficients and treating the second isomerization reactions by analogy to these (i.e. by using the same

pre-exponential factors as the reaction being used in the analogy (while at the same time accounting for degeneracy) and reducing the activation energy by 3 kcal mol⁻¹). While similar results are seen when applying the rate coefficients of Miyoshi [16] and Sharma *et al.* [17] to *n*- and *neo*-pentane, simulated ignition delay times are significantly longer when applying the directly calculated rate coefficients of Sharma *et al.* to the first and second isomerization reactions of *iso*-pentane. When facility effects are included (i.e. ignition delay times are simulated using non-reactive pressure-time profiles from the RCM) it is shown that the model is in very good agreement with the experimental data, Fig. 6.

Results and discussion

RCM experiments were simulated using the closed homogeneous batch reactor module in CHEMKIN-PRO [28]. For the simulation of RCM experiments, the calculations use volume profiles generated from non-reactive pressure traces. The volume history is used to simulate reaction during the compression stroke, and the heat losses that occur during the experiments.

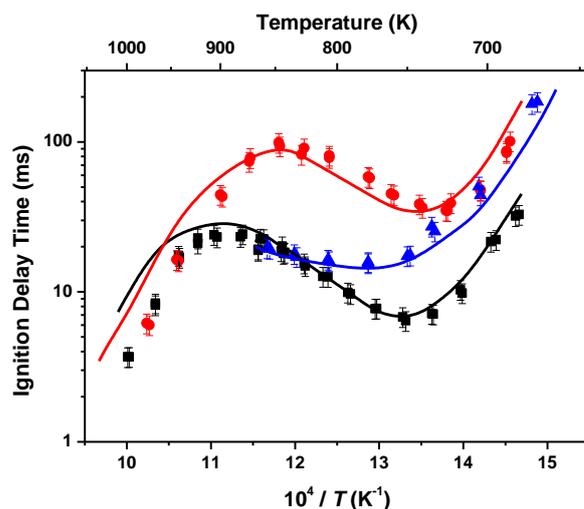


Figure 6. Comparison of model simulations with experimental data. Black symbols and lines represent *n*-pentane, red represents *iso*-pentane, and blue represents *neo*-pentane. All simulations shown have included facility effects. $\Phi = 1.0$ in ‘air’. $p_C = 10$ atm.

Conclusions

There have been significant changes to the thermochemical properties values and rate coefficients for the species and reactions important to low-temperature oxidation, respectively. By using the most up-to-date thermochemistry group values and rate coefficients from several recent publications, the current model shows very good agreement with experimental data. We show that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well.

Past models that used the rate rule estimates of Curran *et al.* [2,3] for reaction classes, replicated experimental data very well. However, it would seem that this is due to a series of compensating errors in terms of both thermochemistry and rate coefficient assignments, which may have been overcome in certain instances by not allowing thermochemical equilibrium to hold (i.e. by definition of rate coefficients in both the forward and reverse directions). Previous thermochemistry generated utilising group additivity rules used by Curran *et al.* most likely hindered a more accurate estimation of rate rules for the reaction classes.

This work represents a major change in the understanding of the low-temperature oxidation of alkanes, and shows that careful consideration of both thermochemistry and rate coefficients is essential in order to accurately replicate experimental data.

With major updates to thermochemical properties values and recommended rate rules, along with solutions to the long-standing discrepancies in the mechanisms of the PRFs, future work would entail applying the updated thermochemistry values, rate rules, and pathways used in this work to larger straight- and branched-chained alkanes. The oxidation of biofuels should also be reconsidered in light of our results.

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References

- [1] S. W. Benson, *Thermochemical Kinetics*, 2nd ed., Wiley: New York, 1976.
- [2] H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook, *Combust. Flame* 114 (1–2) (1998) 149–177.
- [3] H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook, *Combust. Flame* 129 (3) (2002) 253–280.
- [4] J. H. Knox, In: P. G. Ashmore, T. M. Sugden, F. S. Dainton, (Eds.), *Photochemistry and reaction kinetics*, Cambridge: Cambridge University Press; 1967.
- [5] A. Fish, *Oxidation of organic compounds*, vol. 2. *Adv. Chem. Ser.* 1968; 76: 69.
- [6] R. T. Pollard, *Hydrocarbons*, In: C. H. Bamford, C. F. H. Tipper, (Eds.), *Comprehensive chemical kinetics: gas-phase combustion*, vol. 17. Amsterdam: Elsevier; 1977.
- [7] R. A. Cox, J. A. Cole, *Combust. Flame* 60 (1985) 109–123.
- [8] R. W. Walker, C. Morley, *Basic chemistry of combustion*, In: M. J. Pilling, (Ed.), *Comprehensive chemical kinetics: low-temperature combustion and autoignition*, vol. 35. Amsterdam: Elsevier; 1997.
- [9] E. J. Silke, *The Influence of Fuel Structure on Combustion as Demonstrated by the Isomers of*

Heptane: a Rapid Compression Machine Study & Detailed Kinetic Modelling of n-Heptane, PhD thesis, School of Chemistry, NUI Galway, 2005.

- [10] P. A. Glaude, F. Battin-Leclerc, R. Fournet, V. Warth, G. M. Côme, G. Scacchi, *Combust. Flame* 122 (4) (2000) 451–462.
- [11] H. K. Ciezki, G. Adomeit, *Combust. Flame* 93 (4) (1993) 421–433.
- [12] S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean, *J. Phys. Chem. A* 115 (46) (2011) 13425–13442.
- [13] S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean, *J. Phys. Chem. A* 116 (21) (2012) 5068–5089.
- [14] A. Miyoshi, *Int. J. Chem. Kin.* 44 (1) (2012) 59–74.
- [15] C. F. Goldsmith, W. H. Green, S. J. Klippenstein, *J. Phys. Chem. A* 116 (13) (2012) 3325–3346.
- [16] A. Miyoshi, *J. Phys. Chem. A* 115 (15) (2011) 3301–3325.
- [17] S. Sharma, S. Raman, W. H. Green, *J. Phys. Chem. A* 114 (18) (2010) 5689–5701.
- [18] L. Brett, *Re-commissioning of a rapid compression machine and computer modelling of hydrogen and methane autoignition*, PhD thesis, School of Chemistry, NUI Galway 1999.
- [19] D. Healy, D. M. Kalitan, C. J. Aul, E. L. Petersen, G. Bourque, H. J. Curran, *Energy & Fuels* 24 (3) (2010) 1521–1528.
- [20] M. Ribaucour, R. Minetti, L. R. Sochet, H. J. Curran, W. J. Pitz, C. K. Westbrook, *Proc. Combust. Inst.* 28 (2) (2000) 1671–1678.
- [21] E. R. Ritter, J. W. Bozzelli, *Int. J. Chem. Kin.* 23 (9) (1991) 767–778.
- [22] S. M. Burke, *Development of a Chemical Kinetic Mechanism for Small Hydrocarbons*, PhD thesis, School of Chemistry, NUI Galway 2014.
- [23] A. Kéromnès, W. K. Metcalfe, K. A. Heufer, N. Donohoe, A. K. Das, C. -J. Sung, J. Herzler, C. Naumann, P. Griebel, O. Mathieu, M. C. Krejci, E. L. Petersen, W. J. Pitz, H. J. Curran, *Combust. Flame* 160 (6) (2013) 995–1011.
- [24] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, H. J. Curran, *Int. J. Chem. Kin.* 45 (10) (2013) 638–675.
- [25] S. M. Burke, W. K. Metcalfe, O. Herbinet, F. Battin-Leclerc, F. M. Haas, J. Santner, F. L. Dryer, H. J. Curran, *Combust. Flame* 161 (11) 2765–2784.
- [26] U. Burke, K. P. Somers, P. O’Toole, C. M. Zinner, N. Marquet, G. Bourque, E. L. Petersen, W. K. Metcalfe, Z. Serinyel, H. J. Curran, *Combust. Flame* (2014) in press.
- [27] D. M. A. Karwat, S. W. Wagnon, M. S. Wooldridge, C. K. Westbrook, *Combust. Flame* 160 (12) (2013) 2693–2706.
- [28] CHEMKIN-PRO 15101, *Reaction Design*, San Diego, 2010.