

Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes

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Abstract— This study probes our developing understanding of low-temperature oxidation kinetics. We have investigated the ignition of the pentane isomers in a rapid compression machine over a wide range of temperatures and pressures including the negative temperature coefficient behaviour 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.

I. 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 hydroperoxyl-alkyl-peroxyl ($\dot{O}_2\text{QOOH}$) radicals undergoing reactions similar to those included for alkyl-peroxyl ($\text{R}\dot{O}_2$) species, such as the direct elimination of $\text{H}\dot{O}_2$ radicals from the alkyl-peroxyl radicals (also forming olefins), and isomerisation reactions like those of $\text{R}\dot{O}_2$ radicals to produce hydroperoxyl-alkyl ($\dot{Q}\text{OOH}$) radicals, but resulting in the formation of dihydroperoxyl-alkyl radicals. These can undergo reactions similar to those of $\dot{Q}\text{OOH}$ radicals, such as cyclic ether formation, and β -scission reactions, Fig. 1 (R, Q and P represent alkyl radicals or structures $\text{C}_n\text{H}_{2n+1}$, C_nH_{2n} and $\text{C}_n\text{H}_{2n-1}$, 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 $\dot{O}_2\text{QOOH}$ radical, as these radicals cannot proceed to formation of a carbonyl-hydroperoxide + $\dot{O}\text{H}$. An example of this for iso-pentane is shown in Fig. 2. This means that any $\dot{O}_2\text{QOOH}$ species formed from successive pathways stemming from a tertiary alkyl radical had no mechanism to decompose other than dissociation back to $\dot{Q}\text{OOH} + \text{O}_2$. This represents quite a mechanistic oversight in the modelling of branched alkanes.

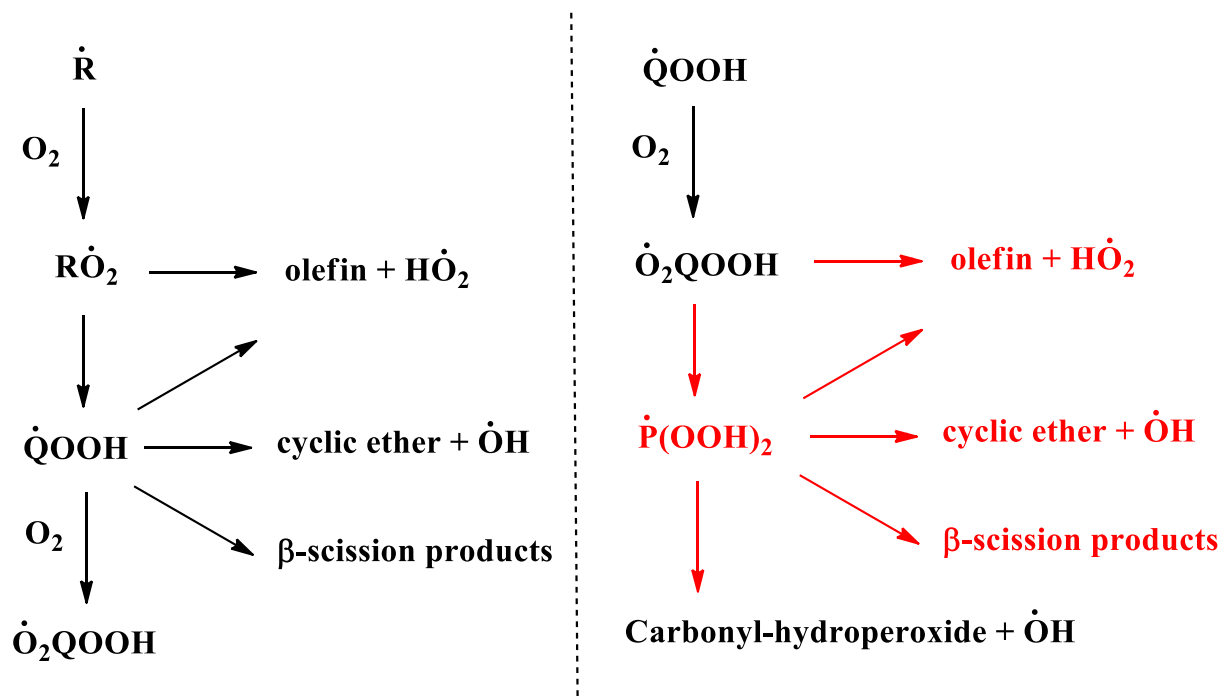


Figure 1. Lumped kinetic scheme of the primary oxidation reactions of alkanes. Species and arrows highlighted in red represent pathways not previously considered for the pentane isomers.

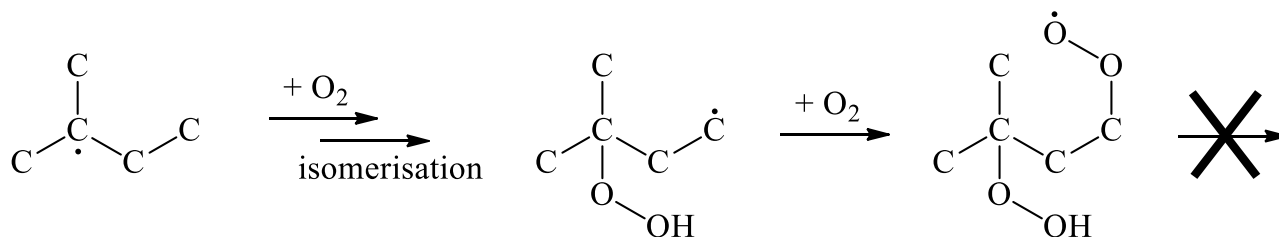


Figure 2. Example of a “dead end” in low-temperature pathways of *iso*-pentane. The example $\dot{O}_2\text{QOOH}$ shown cannot form a carbonyl-hydroperoxide + \dot{OH}

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.

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REFERENCES

- [1] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.
- [2] Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. A Comprehensive Modeling Study of *n*-Heptane Oxidation. *Combust. Flame* 1998, 114, 149–177.
- [3] Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. A Comprehensive Modeling Study of *iso*-Octane Oxidation. *Combust. Flame* 2002, 129, 253–280.
- [4] Knox, J. H. In *Photochemistry and Reaction Kinetics*, Ashmore, P. G., Sugden, T. M., Dainton, F. S., Eds.; Cambridge University Press: Cambridge, 1967.
- [5] Fish, A. In *Oxidation of Organic Compounds–II*, Mayo, F. R., Ed.; *Adv. in Chem. Ser. 76*; American Chemical Society: Washington, D. C., 1968; vol. 2. 69.
- [6] Pollard, R. T. In *Comprehensive Chemical Kinetics: Gas-phase Combustion*, Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1977; vol. 17.
- [7] Cox, R. A.; Cole, J. A. *Chemical Aspects of the Autoignition of Hydrocarbon/air Mixtures*. *Combust. Flame* 1985, 60, 109–123.
- [8] Walker, R. W.; Morley, C. In *Comprehensive Chemical Kinetics: Low-temperature Combustion and Autoignition*, Pilling, M. J., Ed.; Elsevier: Amsterdam, 1997; vol. 35.