Performances and limitations of the detailed kinetic models of low-temperature oxidation of alkanes and alkenes

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1 Introduction

The increasing concern for environmental issues and for energy conservation has led academic and industrial researchers to devote many effort to develop more and more sophisticated detailed chemical kinetic models, based on a large number of elementary reactions, for a large and widening variety of model fuels. The purpose of this paper is to summarize the conclusions which can be derived from a review of the gas-phase detailed kinetic models which have been recently developed to model the oxidation and autoignition of alkanes and alkenes (this work in mainly based on [1]).

2 Alkanes

Alkanes are by far the best studied class of compounds for which reliable and detailed chemical kinetic models for combustion exist. That explains why the search for correlations between fuel chemical structure and octane number rating in spark-ignition engines has mostly been done for alkanes and why n-heptane was so often considered as a surrogate of diesel fuel.

The low temperature reaction channels for the oxidation of alkanes are known for many years and nowadays several models exist for the oxidation of alkanes representative of those contained in automobile fuels, especially n-heptane [2-4] and iso-octane. However while many detailed kinetic models are available for the oxidation of mixtures representative of gasolines, they are much less numerous in the case of diesel fuels because of their more complex composition and explained a lack of relevant experimental data. A comparison of the ignition delay times computed for an adiabatic static system for a range of alkanes from C_7 to C_{16} has been made by Biet et al. [5] and is shown in figure 1. The kinetic models have been automatically generated using software EXGAS [4-5]. It can been seen on figure 1 that a difference of reactivity between the compounds is mainly obtained between 750 and 950 K, i.e. in the area where the negative temperature coefficient is observed. The change in reactivity is larger when going from n-heptane to n-decane (up to a factor 4) than when going from n-decane to n-hexadecane (only up to a factor 2).

The most part of the models give good results for reproducing the available experimental results. For instance, in the case of n-heptane, data measured in a shock tube, a rapid

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compression machine and a jet stirred reactor have been satisfactorily modelled by several groups [2-4]. However when analysing major models of the literature in term of the considered types of elementary steps and of the used rate coefficients, it is striking to see the important differences existing even for simple compounds such as alkanes. The only reliable estimations of rate parameters are deduced from a few studies performed before 1995 [6]. Considering these discrepancies and the weakness of the basis on which these rate parameters have been estimated, the good results obtained by the existing models are almost surprising. Differences in the used thermochemical properties probably partly compensate for the difference in kinetic data.



Figure 1: Computed ignition delay times for a series of linear alkanes for stoichiometric alkane/air mixtures at 12 bar [2].

Elementary steps of particular importance are the reactions of oxygen molecules with alkyl radicals. The parameterizing of the rate constants as a function of temperature and pressure (P-T parameterization) of this multi-channel reaction has been proposed for ethyl and propyl radicals [7]. It would be of great interest to extent this approach to heavier radicals.

To avoid an explosion of the size of the mechanisms, the reactions of the degradation of the first oxidation products, such as hydroperoxides, alkenes, cyclic ethers and aldehydes, are in most cases written under a simplified form, e.g. use of lumped reactions [3][4]. The writing of these secondary reactions should be more carefully considered, so that more chemical information is taken into account with a reasonable size of the obtained mechanism.

3 Alkenes

The presence of a double bond in alkene molecules involves an important increase of complexity of the chemistry of low temperature oxidation. The radicals directly deriving from the reactant are no longer of a single type, as alkyl radicals from alkanes, but of at least three types, alkylic and allylic alkenyl radicals being obtained by H-abstraction and hydroxyalkyl radicals being obtained by addition of •OH radicals to the double bond. This explains the scarcity of models related to alkenes, representative of the compounds present in gasoline, even if these unsaturated compounds are the major products of the oxidation of alkanes.

Software EXGAS adapted to alkenes has been used to model ignition delay times of 1-pentene and the linear isomers of hexene and heptene [9-10]. Mehl et al. [11] have also proposed detailed kinetic

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schemes to simulate ignition delay times of the three linear isomers of hexene. All these models allow a satisfactory modelling of ignition and cool flame delay times measured in rapid compression machines. However more problems are encountered for reproducing the formation of products. As shown in figure 2 for 1-hexene, the EXGAS model reproduces within a factor 2.5 the formation of dienes, saturated cyclic ethers and C_6 aldehydes, but deviates more for the formation of unsaturated cyclic ethers and smaller aldehydes, and predicts the formation of hydroxy cyclic ethers, which has not yet been experimentally demonstrated and the ways of formation of which are not included in the models of Mehl et al. [11]. It is also worth noting that the agreement deteriorates for 2- and 3-hexene [10].



Figure 2: Comparison between the experimental (light grey) [8] and the predicted (dark grey) [10] selectivity of products during the pre-ignition period of 1-hexene in a rapid compression machine (P_c from 6.8 to 10.9 bar, $T_c=707$ K, $\phi=1$).

While new experimental measurements on the elementary steps of importance to model the oxidation of alkenes would be valuable, theoretical calculations should allow a better understanding of these reactions channels and to more accurately estimate the related rate parameters. That could be of special interest for the addition of OH• radicals to the double bond, for the reactions of the peroxy radicals deriving from allylic alkenyl radicals, for the reactions of hydroxyperoxyalkyl radicals and for the formation of the new types of cyclic ethers. Quantum mechanical calculations by Bounaceur et al. [10] have shown that *cis-trans* conformations should be taken into account and that isomerizations of alkenyl and alkenyl peroxy radicals involving a transition state including a double bond could be neglected.

The fact that the model of Mehl et al. [11] does not predict any formation of hydroxy cyclic ethers is due to the fact that they consider that hydroxyperoxyalkyl radicals can only react through the mechanism of Waddington, i.e. leading to the formation of aldehydes and •OH radicals, according to ab initio calculations of Sun et al. [12] for isobutene. It is not yet clear if the conclusions obtained for isobutene can be straightforward applied to long linear alkenes, such as hexenes or heptenes, and if the isomerisations of hydroxyperoxyalkyl radicals to give hydroxyalkylhydroperoxy radicals considered by Bounaceur et al. [10] should be neglected.

4 General comments

The models proposed for alkanes and alkenes containing from 4 to 8 carbon atoms can correctly reproduce most of the results published in the literature, apart from those obtained in very lean mixtures or with highly branched compounds. There is a lack of experimental data for very rich mixtures (equivalence ratio above 3) in well validated experimental systems.

The still existing uncertainties on the reaction channels and the rate parameters would probably lead to important deviations when trying to model the formation of minor products, such as heavy alkenes, dienes, aromatic compounds, aldehydes, ketones, alcohols and acids, which can be toxic to human health and are of great importance in air pollution, as they are involved in the formation of urban smog and acid rain. If a satisfactory prediction of the formation of these species is desired, the degree of accuracy of the models should be increased and fundamental studies on the involved elementary steps would be needed, including experimental work and theoretical calculations.

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