Pyrolysis and Oxidation of Cyclo-Alkanes


Dipartimento CMIC, Politecnico di Milano, Milano - ITALY

Introduction

Detailed kinetic mechanisms of oxidation and combustion processes are useful tools for the evaluation of knocking tendency of the different fuels as well as for the prediction of pollutant formation in terms of PAH, soot and NOx. Detailed kinetic schemes for methane and natural gas combustion are reliable and widely used in the scientific community. GRI Mechanism is a well known and largely diffused example. On the contrary, the kinetic knowledge and above all the availability in the scientific literature of reliable kinetic schemes for liquid fuels is scarce. Real gasolines consist of mixtures of most of the hydrocarbon isomers in the C4-C9 fraction possibly including also different additives. RON, MON and BRON commercial indexes are widely used in order to define the knocking propensity of the gasolines in terms of a surrogate mixture of only two primary reference fuels: iso-octane and n-heptane. Oxidation and combustion of gasolines is therefore described with detailed kinetic mechanisms of these two model fuels even if kinetic schemes with a detailed description of several isomers in the paraffin fractions have been developed in the recent years. These kinetic schemes are very detailed in the initial propagation reactions taking into account all of the different isomer species but strongly sacrifice the successive steps of the huge number of intermediate species [1].

The proper characterization and description of diesel, kerosene and jet fuels is a more difficult task. In facts, these liquid fuels consist of complex mixtures of heavy hydrocarbons, including alkanes, cycloalkanes and aromatic molecules in the C10-C16 fraction.

As already discussed elsewhere, the definition of primary reaction classes with their reference kinetic parameters for normal and branched alkanes allows the automatic generation of detailed kinetic schemes. In this way, it is well evident that the description of pyrolysis and combustion of large alkane molecules such n-dodecane or iso-cetane becomes a feasible task [2].

This work presents and discusses some features of the kinetic behaviour of cycloalkane combustion, where larger uncertainties are still present.

Main classes of primary propagation reactions of cycloalkanes.

As already mentioned, the primary oxidation reactions of alkanes to form primary products and intermediate radicals have already been discussed in previous papers [3]. On very similar basis, it is possible to follow the reaction paths of cyclo-alkanes both for the high and low temperature oxidation mechanisms. At high temperatures, alkyl radicals from cyclo-hexane and methyl-cyclohexane undergo β-decomposition reactions to form not only cyclo-alkenes radicals but also hexenyl and heptenyl radicals, respectively. These radicals can subsequently isomerize to form the resonantly stabilized radicals of allyl type. Hexenyl, heptenyl and resonant radicals can then β-decompose to form smaller radicals and diolefines.

As usual for the low temperature reactions, oxygen addition on alkyl radicals is in competition with the H-abstraction reactions to form alkenes and HO2●. The formation of peroxy radicals, without activation energy, prevails at low temperatures and this is the first step towards the usual degenerate branching path involving the following successive elementary steps:
• Isomerization of peroxy radicals (ROO$^\cdot$) to form hydro-peroxy-alkyl radicals (QOOH$^\cdot$).
• O$_2$ addition on QOOH$^\cdot$ to form hydro-peroxy-alkyl-perossidic radicals (OOQOOH$^\cdot$).
• Isomerization and decomposition of OOQOOH to form OH$^\cdot$ and a ketohydroperoxide.
• Decomposition of ketohydroperoxides to form 2 radicals.

These reactions are important at low temperatures and high pressures, since they depend on O$_2$ concentration. The importance of ketohydroperoxide formation lies in its very fast unimolecular decomposition reaction ($k_{dec} \approx 10^6 \exp(-42000/RT)$ [s$^{-1}$]) with the net formation of two new radicals.

At intermediate temperatures QOOH$^\cdot$ radicals can also form HO$_2^\cdot$ and parent alkenes or OH and carbonilic compounds (through $\beta$-decomposition reactions) or finally cyclic heters (through a O-O homolysis reactions).

A peculiar aspect of isomerization and homolysis reactions of cyclo-alkyl radicals is the possible formation of double ring intermediates. In facts, isomerization reactions of alkyl and peroxy radicals involve the formation of intermediate ring structures. Therefore, their kinetic parameters are usually evaluated on the basis of the corresponding strain energy corrections and to the number of rotors blocked in the transition state. When considering cyclo-alkane (and derived) radicals, the structure of the intermediate species presents two rings, since their original cyclic structure.

Figure 1 shows one example of the isomerization reaction of the peroxy radical of cyclo-hexane. A strain energy correction in the activation energy of 2000-3000 cal/mol is applied for the 5, 6 or 7 membered double ring intermediates. This energy value is only a very first guess and it requires a better definition with accurate ‘ab initio’ calculations. No reference values are suggested in the literature. Nevertheless, the results obtained using this correction in the detailed kinetic models of both cyclo-C6 and MCH oxidation show a reasonable agreement with experimental data. From a theoretical and kinetic point of view, it is important to observe that one should expect larger corrections in the activation energy with a significant increment in the frequency factor.

**Lumped reactions and extension of the oxidation scheme.**

As already described for paraffins, also for cycloalkanes a lumped kinetic scheme is developed on the basis of a limited number of pseudo-species and pseudo-reactions.
representative of the whole reaction path. The lumped scheme is obtained by imposing the agreement with the cumulated selectivities of primary products obtained with the detailed scheme. Fig. 2 shows the typical behavior of these selectivities at 1 atm. Higher pressures favour the branching reaction paths.

In order to show the relative reactivity of cyclo-alkanes, Fig. 3 shows the concentration of OH radical vs time for the oxidation of n-pentane, n-heptane, iso-octane, cyclo-hexane and MCH. This radical is a clear index of the system reactivity during a typical two-stage ignition process, for instance in a rapid compression machine.

According to the Octane Number (ON) of the different fuels, this plot confirms the higher reactivity of n-paraffines compared to cyclo- and branched- alkanes.

Moreover this figure indicates that the knocking tendency of the different fuels is well explained in terms of the delay time of high temperature ignitions. In facts their ON are the following:

<table>
<thead>
<tr>
<th>Species</th>
<th>ON</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>0</td>
</tr>
<tr>
<td>n-pentane</td>
<td>26</td>
</tr>
<tr>
<td>MCH</td>
<td>83</td>
</tr>
<tr>
<td>cyclo-hexane</td>
<td>88</td>
</tr>
<tr>
<td>iso-octane</td>
<td>100</td>
</tr>
</tbody>
</table>

The predicted delay time of the low temperature ignition of iso-octane appears shorter than the corresponding times of the two cyclo-alkanes. These results mainly reflect the kinetic assumptions related to the isomerization reactions and it is qualitatively in line with recent experimental evidences [4].

**Comparisons with experimental data**

For sake of space limitations, the comparisons with experimental data will be very limited and only related to the low temperature mechanism. Fig. 4 shows behavior of cyclo-hexane oxidation in a stirred reactor. By varying the initial reactor temperature from 530 up to 600 K, model predictions of the temperature profiles along the time for different reactor temperatures agree with the experimental behavior moving from slow combustion to 3 cool flames [5]
Recent experimental data on MCH oxidation have been obtained in a pressurized, adiabatic plug flow reactor at Drexel University [6]. These experiments analyze the low temperature reactivity of different mixtures with the CCD (Controlled Cool Down) technique. During the experiments reactor temperature decreases with a fixed cooling speed and the combustion heat allows to describe the reactivity of the system until the NTC zone. Fig. 5 showss, in terms of a CO reactivity map, the behavior of a binary mixtures with 37% of n-dodecane and 63% of MCH. Two CCD experiments were conducted with different fuel concentration. For both the experiments, model predictions well agree with the experimental measurements in terms of initial reactivity as well as in terms of the maxima CO location. The model slightly over predicts the residual reactivity of the system at intermediate temperatures (750-800 K). A large set of comparisons between model predictions and experimental measurements in the high temperature conditions was already reported elsewhere [2]

**Conclusion and future developments**

The proposed kinetic scheme has been successfully validated in comparison with several experimental data obtained in different devices and conditions, from the high temperature to the cool flame and low temperature ignitions. Despite these encouraging comparisons further work is needed to improve and confirm the kinetic model. Particularly, the corrections for the double rings in the transition state should be accurately evaluated by new measurements and researches in order to complete the kinetic analysis of cycloalkanes oxidation.

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**References**