

Kinetic Modeling of Cyclohexane Oxidation with PAH Formation

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Abstract

A skeletal reaction mechanism for low and high temperature cyclohexane oxidation with PAH formation is developed. This mechanism is the extension of the earlier elaborated reaction model for practical fuels with cycloalkane sub model. The important feature of this mechanism is its ability to describe the formation of benzene and PAH growth. The ignition delay data measured in rapid compressor machine and shock tube experiments are well reproduced by the model. Experimentally quantified benzene profile from RCM is in good agreement with model simulations. The modelling results showed dusting temperature dependence of dominating reaction routes leading to aromatics. It is shown that both reaction paths to benzene, via the dehydrogenation of cyclohexane and via recombination of small radicals are equally important for temperatures lower 1500K. Only at high temperature, $T > 1500$ K, the cyclohexane dehydrogenation is the uniquely dominant way to benzene. The formation of large aromatic molecules can proceed from small radicals, parallel with the dehydrogenation of cyclohexane.

Introduction

Cycloalkanes (naphthenes) are an important chemical class of hydrocarbons found in diesel (up to 35%), kerosene (~20%) and gasoline (~10%), which affect the ignition quality of the fuel. Cycloalkanes can raise soot emission levels because they are known to dehydrogenate and produce aromatics which can initiate the chain reaction for the production of polycyclic aromatics to soot formation and growth. In spite of its practical relevance, the chemical kinetics of naphthene pyrolysis and oxidation is not yet thoroughly investigated. Only the combustion of cyclohexane (CHX, $\text{cy-C}_6\text{H}_{12}$), the simplest of cycloalkanes, has been investigated in more detail compared to other cycloalkanes [1-7, 12-17, 20-25].

Generally our aim is to develop a short reaction model for propylcyclohexane combustion to be included in our reference fuel model [18]. We start the model elaboration with chemical kinetic mechanism of $\text{cy-C}_6\text{H}_{12}$ to develop the base reaction model for cycloalkanes. As the size of reaction models for practical fuels is critical problem, special attention was devoted to the elaboration of the base skeletal model of CHX combustion with the PAH formation.

The presented $\text{cy-C}_6\text{H}_{12}$ reaction mechanism is based on a detailed literature analysis [1-17, 19-25]. The cyclohexane oxidation at high temperatures goes through several distinct reaction pathways: unimolecular decomposition of cyclohexane leading to linear products, and H-atom abstraction leading both to dehydrogenation and formation of benzene and to β -scission reactions that break the cyclic ring. At lower temperatures, addition of molecular oxygen to cyclohexyl radicals followed by internal H-atom transfer reactions and other pathways leads to reaction branching and a negative temperature coefficient (NTC) region similar to those observed in many *n*-alkane and *iso*-alkane hydrocarbon fuels. Hence, the knowledge about the kinetic of CHX combustion is still poor compared to that about paraffins

and thus less certain. The published primary reaction classes and their reference kinetic parameters show significant discrepancies. Nevertheless, recently published measurements [4-6, 21-25] can be used for a further reaction mechanism validation and for the direct fitting of kinetic parameters to global experimental data. In this paper, we present the skeletal $\text{cy-C}_6\text{H}_{12}$ reaction mechanism obtained for modelling of the low and intermediate temperature ignition of cyclohexane and on polycyclic aromatics and soot production in laminar cyclohexane flame. The prediction of this chemistry is critical for correct simulation of ignition in HCCI and diesel engines.

Previous Cyclohexane Studies

One of the first studies of low temperature of $\text{cy-C}_6\text{H}_{12}$ oxidation was performed by Zeelenberg and Bruijn [1] which analysed the primary products of the slow oxidation of cyclohexane during the induction period at low temperature and low pressure. Tsang [2] studied the pyrolysis of cyclohexane in a shock tube. The principal products identified were ethylene, 1,3-butadiene, and 1-hexene. A further investigation of the low temperature oxidation with extensive analyses of various reaction paths was undertaken by Klai and Baronnet [3]. They described in their reaction scheme the chain propagation including the four possible isomers of hydroperoxycyclohexyl ($\text{cy-C}_6\text{H}_{10}\text{OOH}\cdot$) radical formed by isomerisation of cyclohexylperoxy ($\text{cy-C}_6\text{H}_{11}\text{OO}\cdot$) through 4-, 5-, 6-, and 7 - centres transition states. Decomposition of the 4 obtained hydroperoxycyclohexyl radicals yields cyclohexene, cyclohexanone, and three bicyclic ethers: 1,2-, 1,3- and 1,4- epoxycyclohexanes, with an additional ring including 3, 4, and 5 members respectively. The reaction rates were evaluated with thermochemical methods [23] and modified taking into account experimental data measured in [3] for low pressure. In the investigation [4-7] the reaction schemes of high temperature oxidation were studied. In [4, 5] detailed

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reaction mechanisms for cyclohexane oxidation have been evaluated by comparison of computed and experimental species mole fraction profiles measured in a jet-stirred reactor. The major part of the reaction rates of the cyclohexane sub mechanism was estimated based on literature data and analogy with small hydrocarbons or acyclic alkanes. Some reaction rates were evaluated from global fitting of experimental data from these authors. The mechanism proposed in [6] for the oxidation of cyclohexene at high temperature was build in a hierarchical and systematic way based on reaction types used as generic rules; cyclohexene and each radical are submitted to the different types of possible reactions. These reaction types are those considered in the high-temperature oxidation of alkanes and alkenes and the radical generation uses the same a priori simplifications based on the relative reactivity of the species. Literature data, thermochemical kinetic methods [26], analogy with small and linear alkenes and ignition delay experimental results [6] were used to determinate the reaction rates.

To model a stoichiometric premixed cyclohexane flame [23] ($p = 30$ Torr) a reaction model was generated in [7] which applies generic rates to some reactions in the same class while other reaction rates follow mostly from [8-11]. The generic rates were assigned to reaction classes of hydrogen abstraction, β scission and isomerisation. The procedure has been successfully applied to higher paraffins (n-hexane, n-heptane, iso-octane, n-decane, n-dodecane, and n-hexadecane), also satisfactory results were obtained for describing the combustion chemistry of cyclohexane. Benzene formation routes through cascading dehydrogenation and via combination C_2 - C_4 hydrocarbon fragments were carefully investigated.

Reaction mechanisms which combine high and low temperature oxidation of $cy-C_6H_{12}$ were developed in [12-15]. In [12] the lumped mechanism of the pyrolysis and oxidation of cyclohexane was prepared. The possible primary elementary reactions of high temperature oxidation are schematically reported together with kinetic parameters directly evaluated on the basis of kinetic parameters of the primary pyrolysis and oxidation reactions of linear and branched alkanes. The kinetic parameters of oxygen addition to cyclohexyl radical ($cy-C_6H_{11}\bullet$), successive isomerisation of peroxy radicals through double rings in the transition state and reactions of intermediate radicals were all evaluated on the basis of the similar reactions of alkyl and alkylperoxy radicals by modifying the corresponding reference rate constants. The modelling results are compared with different sets of measurements. The results of validation confirm the reliability of the overall kinetic model, as well as the validity of the lumped approach. In [13, 14] the mechanism construction was carried on the base of the determination of specific rate constants for reactions of other cyclic compounds, such as branched cyclic alkanes. The paper [13] presents a modelling study of the oxidation of cyclohexane from low to intermediate temperature (650-1050 K) including

the negative temperature coefficient (NTC) zone. A detailed kinetic mechanism has been developed using computer-aided generation and taking into account all the possible elementary steps for every isomer of peroxy and hydroperoxy radicals: the model includes 4 isomers for $cy-C_6H_{10}OOH\bullet$ and for $cy-OOC_6H_{10}OOH\bullet$. Hydroperoxycyclohexyl radicals decompose to 1,2- and 1,4-epoxycyclohexane (cyclic ether with 3 and 4 ring size) and other different acyclic molecules. For cyclohexanol production the authors of [13] proposed a disproportionation reaction of two hydroperoxyalkyl radicals thus omitting the decomposition of $cy-C_6H_{10}OOH\bullet$. The $cy-OOC_6H_{10}OOH\bullet$ radicals decompose to conventional keto hydroperoxide. For the H-abstraction reactions of $cy-C_6H_{12}$ and for reactions with oxygen the literature data for cyclohexane and analogy with n-butane reactions were used. Special care has been taken to evaluate the rate constants for the hydroperoxy radical isomerization and the formation of cyclic ethers as the ring strengths of the respective transition states are very different from those involved in reactions of linear or branched peroxy radicals. The corresponding activation energies have been evaluated from theoretical density function theory and from thermochemical calculations. A comprehensive mechanism of the oxidation of the radicals obtained by opening of the ring has also been included. This mechanism is able to reproduce satisfactorily experimental results obtained in a rapid compression machine, for temperatures ranging from 650 to 900K and in a jet stirred reactor from 750 to 1050 K.

A detailed chemical kinetic mechanism [14] has been developed and used to study the oxidation of cyclohexane also at both low and high temperatures. The rates for initiation reactions are mostly analogous to the rate constant employed in the literature for acyclic molecules. But for the reaction of unimolecular fuel decomposition, H-atom abstraction by HO_2 (assumed also for abstraction by CH_3O_2 and $cy-C_6H_{10}OO\bullet$), for ring opening reaction and alkyl radical isomerisation the cyclohexane specific rates from literature were adopted. The principal scheme of low temperature sub mechanism includes 3 isomers of peroxy cyclohexyl radical (with 5, 6, and 7 centres in transition state), and correspond three isomers of $cy-OOC_6H_{10}OOH\bullet$. Three cyclic ethers with 3, 4 and 5 ring size are formed from the $cy-C_6H_{10}OOH\bullet$ radicals. The decomposition pathways of each $cy-C_6H_{10}OOH\bullet$ radical to form a multitude of other products are carefully considered in the model [14]. For $OOC_6H_{10}OOH\bullet$ decomposition along with ketoperoxyde production the "alternative" reaction paths were developed, which lead to different products. The "alternative" decomposition goes through possible a isomerisation of $OOC_6H_{10}OOH\bullet$ to 5-, 6- or 7- membered transitions states. Special attention was devoted to the determination of similarities and differences in the correction terms between cyclic and acyclic isomerisation reactions in order to establish a formula for future mechanism development in other

cyclic hydrocarbon species. For reactions of cyclohexyl formation and isomerisation the modified recommendations [11, 19] for acyclic molecules were used. These modifications follow from the comparison of experimental data obtained for the cyclohexane reaction rates in [16, 17] accounting for the recommendations in [19]. The modified *ab initio* calculations [15] were employed for the direct elimination of olefin from cyclohexylperoxy radical and for the formation of cyclic ethers from hydroxyperoxy radicals. For other reactions of low temperature oxidation, the recommendations [11, 19, and 20] for n-alkanes were adopted. The mechanism has been validated on the data obtained in both, rapid compressor machines and jet stirred reactors. The agreement between experimental data and simulations shows the validity of the chosen approaches.

The main features of cyclohexane oxidation reaction scheme based on the performed literature analysis are briefly explained as follows. At high temperatures the oxidation proceeds through

- unimolecular fuel decomposition,
- an H-abstraction leading to the cycloalkyl radical, $\text{cy-C}_6\text{H}_{11}\cdot$,
- $\text{cy-C}_6\text{H}_{11}\cdot$ decomposition with producing olefins, di-olefins (cascading dehydrogenation leading to benzene) and smaller radicals,
- isomerisation of linear hexenyl radicals after the ring-opening step.

In general it is assumed that for these reaction classes the rate constants are similar to those of normal alkanes. Only a few specific cyclohexane reaction rates (H-atom abstraction via HO_2 , ring opening reaction and alkyl radical isomerisation) were established experimental or theoretically [16, 17, 27]. The obtained values are used with different modifications.

The low temperature cyclohexane oxidation can be predicted with the general scheme for the low temperature oxidation of alkanes [11,19], however the formation of intermediate species and transition states with 2 rings marks an important difference with respect to linear hydrocarbon reactions. So, $\text{cy-C}_6\text{H}_{11}\cdot$ reacts with O_2 to form only one type of a cycloperoxy ($\text{cy-C}_6\text{H}_{11}\text{OO}\cdot$) radical leading to chain branching pathways, through

- isomerisation of $\text{cy-C}_6\text{H}_{11}\text{OO}\cdot$ through 4-, 5-, 6-, and 7- centres transition states (transition states with 2 rings) to forth hydroperoxyalkyl radicals,
- isomerisation/decomposition of $\text{cy-C}_6\text{H}_{10}\text{OOH}\cdot$ radicals to linear hex-5-enal, cyclohexene, cyclohexanone, and three bicyclic ethers,
- O_2 addition to $\text{cy-C}_6\text{H}_{10}\text{OOH}\cdot$ with formation $\text{O}_2\text{QOOH}\cdot$ radicals,
- isomerisation/decomposition of $\text{O}_2\text{QOOH}\cdot$ to cyclic ketohydroperoxides, hydroxyl radical and different sets of products,
- disproportionation reactions between radicals important and low temperature.

For low temperature reactions also analogy rules and thermochemical calculations [19, 26] are applied.

However, the ring strengths of the respective transition states are very different from those involved in the reaction of linear or branched peroxy radicals. Special care has been taken [13, 15] to evaluate the rate constants for the isomerization and the formation of cyclic ethers involving the formation of bicyclic species. The benzene formation routes are described by investigators with cascading dehydrogenation of CHX. The formation of larger PAHs is not presented in known studies. The described investigation [7] carefully analyzes the formation of small PAH precursors at low pressure laminar flame.

Skeletal Kinetic Model of Cyclohexane Oxidation

The mechanism proposed for the oxidation of cyclohexene at high and low temperature is an extension of the reference fuel model [18] towards reactions of

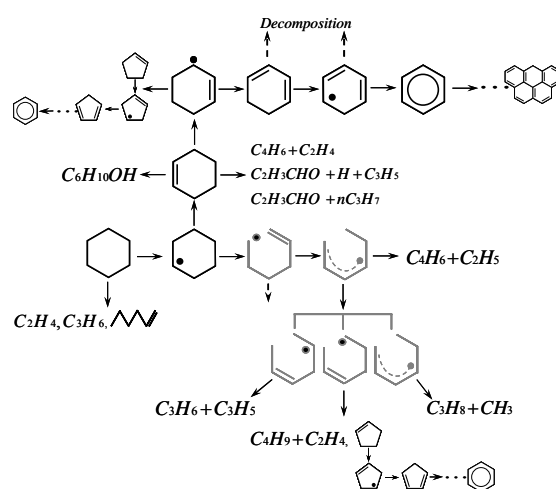


Figure1. Principal scheme of skeletal reaction model for high temperature $\text{cy-C}_6\text{H}_{12}$ oxidation.

$\text{cy-C}_6\text{H}_{12}$. This model [18] was built in a hierarchical and systematic way based on well referred chemical-kinetic data (“first principal” approach).

Sub-mechanisms for $\text{C}_1 - \text{C}_2$ chemistry, toluene, n-heptane, iso-octane, n-decane and PAH formation up to 5 aromatic ring molecules [28] are integrated in self-consistent reaction scheme. This scheme includes the reactions of such unsaturated species, as C_3H_2 , C_3H_3 , C_3H_4 (allene), C_3H_5 , C_3H_6 , C_4H_2 , C_4H_4 , iC_4H_5 , C_4H_6 (1,3-butadiene) as well as cC_5H_6 (cyclopentadiene), which are important both for the aromatic formation and the cyclohexane pyrolysis and oxidation. The model describes further growth of benzene to naphthalene, phenantrene, pyrene, benzo(a, ghi)perene and crysene and it was validated on PAH and soot production data measured in methane, ethylene, propene, toluene and n-heptane flames.

The cyclohexane submodel was first developed with all principal reactions and isomers analysed in [1-7, 12-15]. The used reaction rates were evaluated on the base of recommendations [2, 5, 19] and on specific cyclohexane reaction rates [13, 15 – 17, 22, 27]. Note, that the number of investigations specifically dedicated to

cyclohexane reactions is very limited and some discrepancies in the evaluations can be detected. Sensitivity and rate of production analyses [18] and chemical lumping were applied in order to simplify the cyclohexane oxidation scheme to skeletal one without losing its predictive capabilities. The principal schemes of the such developed high and low temperature sub-mechanisms are presented in Fig.1 and Fig.2. The grey colour on the Fig.1 was used to show the lumped radicals.

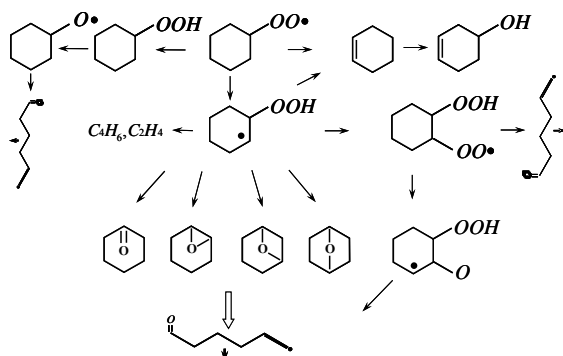


Figure 2. Principal scheme of skeletal reaction model for low temperature cy-C₆H₁₂ oxidation.

The reaction rates for fuel decomposition leading to either three ethene molecules, or two propene molecules were assumed to be the same as it was evaluated by Tsang [2] for the propene eliminating from 1-hexene. The reaction of H atom elimination from CHX is described in reverse direction, so that its rate is considered as "radical-radical" recombination. For the cy-C₆H₁₂ isomerisation to linear aC₆H₁₂, the reaction rate from [29] was used. Reaction rates for radical decomposition, H atom abstraction and isomerisation applied in the model follow mostly from [5]. Special attention was taken for the development of reaction paths leading to the formation of C₃H₅ and cC₅H₆, which are parent molecules for two stabilized radicals, propargyl and cyclopentadiene, key species for benzene formation in acyclic alkanes. These molecules are produced through reaction sequences which have a large number of cyclo – intermediates. In order to reduce the size of the reaction model these sequences were lumped to several reactions, Fig.1, with rates evaluated from reaction path analysis. Basically, the limiting step in these sequences was adopted for lumped reactions.

The principal scheme of the skeletal low temperature sub model is shown on the Fig.2. This scheme is based on the general scheme for low temperature oxidation of alkanes and on the principals of the low temperature sub model reduction, which have been successfully applied for n-heptane, iso-octane and n-decane oxidation schemes.

The initial step is an addition of molecular oxygen to the cyclohexyl radical with the rate constant evaluated on the measured data for neopentane [30]. The applied value is $7.0 \times 10^{17} T^{-2.5}$, cm³, mol, sec. Isomerisation of cy-C₆H₁₁OO• through 4-, 5-, 6-, and 7- centres

transition states was lumped to the one hydroperoxy radical, cy-C₆H₁₀OOH•, employed rate constants for non-cyclic alkylperoxy from [19]. The decomposition of QO₂H• radical by O-O scission leads to cyclohexanone and three epoxycyclohexanes. For these reactions the rate constants computed in [13, 15] were employed. The cy-C₆H₁₀OOH• radical can decompose to yield a conjugate olefin with elimination of HO₂, rate constant calculated in [15], and through the ring opening and subsequent C-C scission to a multitude of intermediate and stable products. Recommendations of [13, 19, 27, 29] were applied for these reaction rates. Cyclohexanone and three epoxycyclohexanes react with OH, O, HO₂ and CH₃ to form radicals with further decompose through ring opening step (rate constant from [27, 29]). Only one isomer of O₂QOOH was included in the short scheme of the low temperature oxidation, Fig.2, which can decompose to a set of products [19]. The formation of RO and RO₂H as important molecules at low temperature was included in scheme. The reactions of disproportionation and dissociation of RO and RO₂H follow from [13, 19].

Results and discussion

The experimental data for ignition delay times of [21 and 22] were used for the model validation, Fig.3 and 4. Data of Lemaire *et al.* [21] measured in rapid compressor machine we have simulated an average pressure of 0.8 MPa and 14 MPa, a diluent composition of N₂ only and compressed temperatures within the range of 650-900 K as the initial conditions for constant volume calculations. The ignition delay time in the model calculations is defined as the time from the end of compression to the maximum rate of pressure rise due to ignition.

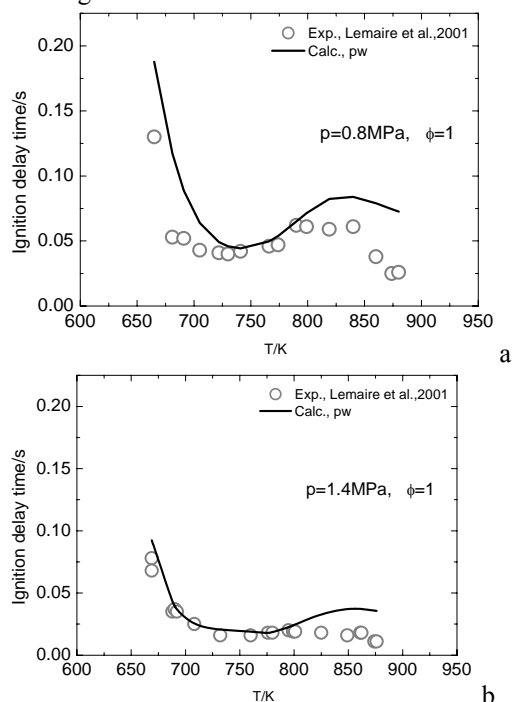


Figure 3. Experimental [21] (points) and calculated (lines) ignition delay times for a) p=0.8MPa and b) p=1.4MPa.

Data of Sirjean et al.[22] for ignition delay times of cyclohexane–oxygen–argon have been measured in a shock tube, for temperatures 1230 - 1840 K and pressures range 0.73 – 0.95 MPa.

The results shown in Figures 3 and 4 illustrate the model predicted ignition delay times for both low and high temperature ignitions. The model reproduced two stage ignition for both pressures investigated.

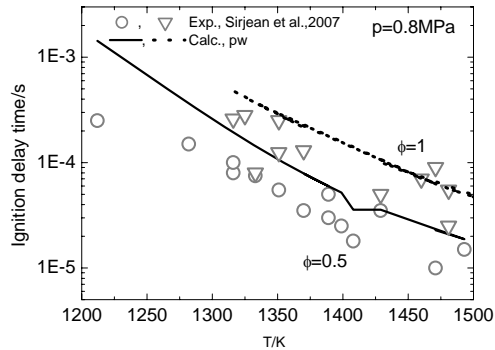


Figure 4. Experimental [22] (points) and calculated (lines) ignition delay times for $p=0.8\text{MPa}$ and $\Phi=0.5$ and 1.

The measured in the RCM [21] and predicted benzene concentration history is shown in Figure 5. Results are shown as percent carbon in the fuel. Our model predicts the formation of benzene products in agreement with the observations. However, benzene is over predicted when compared to the experimentally measured quantity. For the intermediate species, the model under predicts most of the species recorded experimentally. Results for intermediate species are not shown here to save the place for reaction path analysis performed for the benzene and PAH formation.

For the PAH reaction path analysis we used two simulations of experimental data [21 and 22] calculated at $p = 0.8\text{ MPa}$ and initial temperatures $T_0 = 790\text{ K}$ and $T_0 = 1212\text{ K}$.

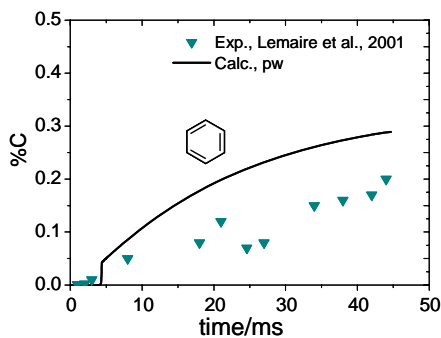


Figure 5. Experimental [21] (points) and calculated (lines) concentration profile of benzene. RCM experiment at $p=0.8\text{MPa}$ and $\Phi=1$, $T_0=727\text{ K}$.

The modelling results showed a strong temperature dependence of dominating reaction routes leading to aromatics. Three regimes of the aromatic formation can be distinguished: the low temperature regime, transient one and high temperature regime, Fig.6-8. At low

temperature regime $700\text{K} < T < 1200\text{ K}$, Fig.6, the PAH formation goes through two parallel channels: formation of benzene via direct dehydrogenation of the cyclohexane (right side

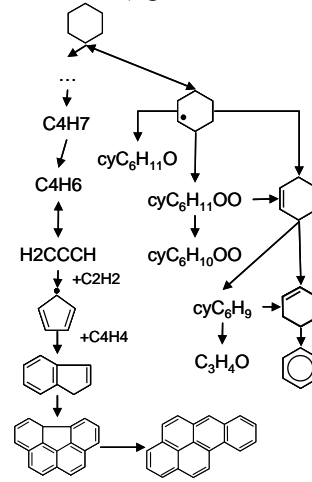


Figure 6. Low temperature regime of PAH formation. Simulation for $p=0.8\text{MPa}$, $T_0=790\text{ K}$, current $T=980\text{K}$.

of diagram on Fig.6) and its further growth to large aromatic molecules, and formation of indene from cyclopentadienyl (C_5H_5) and its further growth (left side of diagram on Fig.6). C_5H_5 is produced from propargyl and acetylene by the fuel decomposition. Dominant way for the benzene production is the

dehydrogenation of cyclohexane. But the formation of large aromatic molecules via C_5H_5 is more important.

For temperature $1200 - 1500\text{ K}$, Fig.7, the first aromatic rings can be produced via three equally important reaction types: the fuel dehydrogenation, the propargyl recombination, and the formation of the one- or two-ring aromatics from cyclopentadiene radical and small molecules.

The large PAH molecule are produced through HACA mechanism, reaction between aromatic molecules/radicals and small molecules, and reactions between aromatic molecules and aromatic radicals.

At high temperatures, $T > 1500\text{ K}$, the fuel dehydrogenation dominates the formation of benzene. Acetylene and propargyl play only a marginal role under these conditions.

On the base of modelling one can say, that dominant way to benzene is strongly depended from process conditions. Only at high temperature, $T > 1500\text{ K}$, the cyclohexane dehydrogenation is uniquely dominant way to benzene. By lower temperature parallel channels of benzene and PAH formation through small radicals are

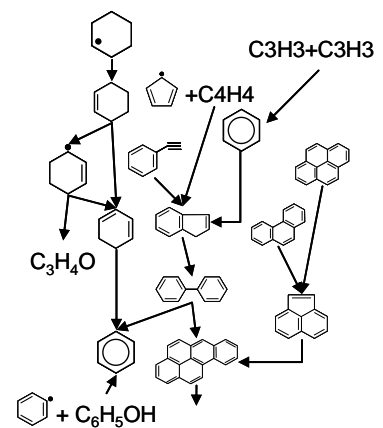


Figure 7. Transient temperature regime of PAH formation. Simulation for $p=0.8\text{MPa}$, $T_0=790\text{ K}$, current $T=1300\text{K}$.

also important and, further more, for temperatures lower than 1200 K can be dominated.

Conclusions

A skeletal reaction mechanism for low and high temperature cyclohexane oxidation with PAH formation is reported. This mechanism was based on our previous modeling of hydrocarbon oxidation, in particular of toluene, n-heptane, iso-octane and n-decane and is the extension of the reaction model for practical fuels with cycloalkane sub model.

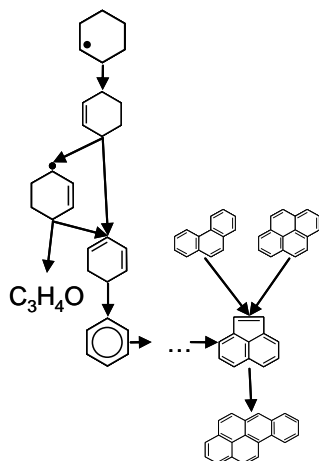


Figure 8. High temperature regime of PAH formation.

Simulation for $p=0.8\text{MPa}$, $T_0=1212\text{K}$, current $T=1600\text{K}$. Experimentally quantified benzene profile from RCM is in good agreement with model simulations. This would indicate that most of the chemical pathways leading to its formation are well understood. At the same time, some underprediction by modelling of intermediate species profiles requires the further model improving.

An important feature of this mechanism is its ability to predict the formation of benzene and PAH growth. It is shown that both reaction paths to benzene, via the dehydrogenation of cyclohexane and via recombination of small radicals are equally important for temperatures lower 1500K. Only at high temperature, $T > 1500\text{K}$, the cyclohexane dehydrogenation is the uniquely dominant way to benzene. The formation of large aromatic molecules can proceed from small radicals, parallel with the dehydrogenation of cyclohexane.

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