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Development of the Basis Naphthene Oxidation Kinetic Model for Simulation of the Practical Fuel Combustion

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Abstract

A reaction mechanism of cyclohexane (cyC_6H_{12}) and n-propylcyclohexane (cyC_9H_{18}) is developed to study its oxidation at both low and high temperatures, including PAH precursors routes. The cyclohexane oxidation kinetic mechanism is a significant update of the model developed earlier in DLR. The new model is based on the most recent C_0-C_3 chemistry studied by and includes the PAH sub-model up to 5-ringed molecules. Improvements have been done through the rivaling the main reaction classes, uncertainty boundaries of the rate coefficients and an inclusion of two additive low-temperature reaction pathways: cyclohexenyl peroxy formation and isomerization of hydroperoxy peroxy radical. The mechanism was successfully validated on the ignition delay data from rapid compression machines (RCM) and shock tube experiments, as well as laminar flame speed data. This reaction model was then further extended to the n-propylcyclohexane oxidation model. The comparison low-temperature oxidation of both fuels has been performed. It is shown, that unlike cyC_6H_{12} the ignition of n-propylcyclohexane demonstrates negative temperature coefficient (NTC) behavior.

Keywords: surrogate, reaction model, cyclohexane, n-propylcyclohexane

1. Introduction

Practical fuels such as kerosene are complex mixtures of several hundred individual species, which can be divided into four hydrocarbon families (n-/i-paraffins, naphthenes (cyclo-paraffins) and aromatics). The physical characteristics of kerosene (density, fuel energy content, boiling/freezing range, flash point, thermal conductivity, surface tension, viscosity, etc.) are of relevance when analyzing the different physical processes involved in fuel storage, fuel delivery to the combustor, engine performance and emissions. The main chemical properties related to the chemical composition are C/H ratio, concentration histories, flame speeds, ignition delays, and sooting tendency. The chemical and the physical characteristics of the fuel correlate strongly with each other and they are normally specified with Standard Specification for Aviation Turbine Fuel.

The central point of the fuel modeling is to mimic chemical, physical, and combustion properties of the fuel blends. In order to achieve these goals the advanced methodology for Fuel Model Design (FMD) is fixed on the establishment of Input Formula of Surrogate (IFS): determining a limited number of hydrocarbons from each family to be included in the surrogate model and the amount of each selected hydrocarbons in the blend, based on fulfilment of a pre-defined set of requirements for chemical and physical properties of fuel. The IFS has to reflect the relationships between different hydrocarbon families in the real fuel and the joint requirements for chemical and physical properties, which are ultimately important for the combustor hardware [1, 2].

On Fig.1 features of different surrogate blends to reflect boiling and evaporation properties are shown are their relevant can be found in Table 1. As it can be seen, the blends which content cyclo-paraffins are most closed one to the identified boiling diagram of kerosene, which declares the importance of the presence of cycloalkanes in surrogate formula.

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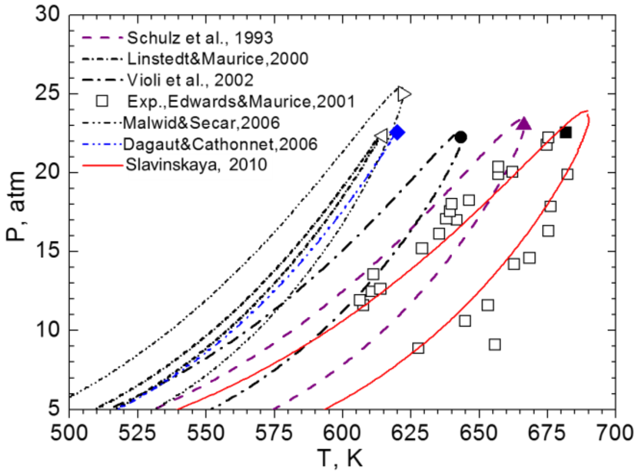

Fig.1. Calculated phase diagrams for suggested in [1, 3, 4, 5, 6, 2] fuel surrogates compared to experimental data [7] (from [2]).

Table 1. Compositions, Input Formulas of Surrogate, of the tested mixtures, Fig.1.

Ref.	Input Formulas of Surrogate
Dagaut&Cathonnet [1]	n-Decane 74%, n-Propylbenzene 15%, n-Propylcyclohexane 11%
Slavinskaya&Zizin [2]	Iso-octane 14%, n-Dodecane 22%, 1-methylnaphtalene 28% n-Hexadecane24%
Lindstedt&Maurice [3]	n-Decane 89%, Toluene 11%
Violi et al., mix #2, [4]	Xylenes 8.5%, Tetraline 8%, n-Octane 3.5%, Decalin 35%, n-Dodecane 40%, n-Hexadecane 5%
Mawid&Sekar [5]	MCH 5%, Toluene 20%, n-Decane 25%, Iso-octane 5%, n-Dodecane 25%, n-Tetradecane 20%
Schulz [6]	Iso-octane 5.0%, MCH 5.0%, m-Xylene 5.0%, Cyclo-octane 5.0%, Decane 15.0%, Butyl benzene 5.0%, 1,2,4,5-tetramethyl benzene 5.0%, Tetralin 5.0%, Dodecane 20.0%, 1-methyl naphthalene 5.0%, Tetradecane 15.0%, n-Hexadecane 10.0%

Cycloalkanes (naphthenes) are an important chemical class of hydrocarbons found in diesel (up to 35%), kerosene (~20%) and gasoline (~10%), which affects the ignition quality of the fuel. Also 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. Therefore, kinetic investigation of cyclohexane (cyC_6H_{12}) as the simplest naphthene molecule, and n-propylcyclohexane (cyC_9H_{18}) as the most convenient substituted naphthenes in the composition of commercial fuels (especially in jet surrogates), have a great importance in the way predicting the oxidation behavior of conventional fuels and pollution formation. In the present paper, the updated and further developed kinetic sub-mechanism for low-temperature oxidation of cyC_6H_{12} and cyC_9H_{18} are presented. The uncertainty of the key reaction types for both high- and low-temperature scheme have been evaluated. The required thermochemical properties specifically for low-temperature species, which have more complex structures, are revised and evaluated by applying Benson's additivity method with new available updates of Benson's groups [8] and ring corrections. The second focused center of this paper is the analysis of the main reaction pathes to the poly-aromatic molecule (PAH) formation. The performed analyses and modifications have been carried out on the basis of the experimental data modeling. For simulations of ignition delay time, the measurements performed in the rapid compression machine (RCM) [9, 10] and in the shock tubes (ST)

[11, 12] have been used. The flame speed data from [13, 14, 15] and concentration profiles from [16, 17] have been also subjected to study.

Despite of numerous investigations up to now the published reaction models for cyC_6H_{12} demonstrate significant discrepancies in the kinetic parameters and results. The uncertainty of reaction rate coefficients for some reaction classes are extremely high and can reach more than 1000. Experimental ignition delay data report contradictive information: NTC region observed for the cyC_6H_{12} ignition in the RCM was not detected in the ST experiments.

The n-propylcyclohexane oxidation chemistry is sufficiently less investigated and based on the cyC_6H_{12} model, consequently takes on every problems of the cyC_6H_{12} modeling . Only few studies were published [18, 19, 20] concerning mostly high-temperature oxidation of the cyC_9H_{18}.

2. Kinetic Model

The cyclohexane oxidation model Abbasi et al. [23] were extended with two additive pathways: isomerization of $cyOOC_6H_{10}OOH$ through the internal hydrogen transfer yielding more stable $cyC_6H_9(OOH)_2$ and the secondary low- temperature cyclohexene, cyC_6H_{10}, oxidation. The possible isomers of $cyC_6H_9(OOH)_2$ were grouped in a single lumped component, which dissociates into cyclic ketohydroperoxide and OH. This step was included in the scheme to increase the concentrations of less reactive HO_2 and cyclohexanone radicals in the intermediate temperature zone. Cyclohexenyl, cyC_6H_9, produced from cyclohexene due to the cascading cyclohexane dehydrogenation, prolongs now the low-temperature cyclohexene oxidation after oxygen addition. This path is competitive with the low-temperature hexyl oxidation. It was assumed, that the sub-model for n-propylcyclohexane, on the strength of its molecular structure, is a combination of the main reaction paths of the cyclohexane and acyclic alkanes oxidation (nC_3H_7), and has two regimes of oxidation, high- and low-temperature.

The n-propylcyclohexane high temperature oxidation proceeds through: unimolecular fuel decomposition; H-atom abstraction leading to cycloalkyl radicals, $cyC_9H_{17}A$, $cyC_9H_{17}B$, $cyC_9H_{17}E$; β-scission decomposition; cascading dehydrogenation leading to benzene and smaller radicals; isomerization and decomposition of linear radicals after the ring-opening step. Three isomers of the cycloalkyl radicals have been included in the scheme, $cyC_9H_{17}A$, $cyC_9H_{17}B$, and $cyC_9H_{17}E$. The related rate constants were evaluated as analogous to those for the cyclohexane and propyl reactions.

For the low-temperature oxidation of n-propylcyclohexane due to the high uncertainties in reaction paths, reaction rate coefficients and reduced number of experimental data, only 7 main reaction paths have been adopted. This our decision follows from the available information related to the low-temperature reactions of the cycloalkanes. Table 1 collects the main evaluations performed for the rate coefficients. As it can be understand, the number of performed investigations is very limited.

On the Fig. 2 the included in the scheme isomers, and steps of low-temperature n-propylcyclohexan are demonstrated. These steps proceed through the largely accepted and employed kinetic schemes of low-temperature alkane oxidation [24, 25]:

1) addition reaction with O_2;
2) isomerization of cyclic peroxy cyROO• to cyQOOH• hydroperoxy radical;
3) decomposition of cyQOOH• to cycloolifene and HO_2;
4) decomposition of cycloolifene;
5) O2 addition to cyQOOH• with formation of O_2QOOH• ;
6) decomposition of O_2QOOH• to cyclic ketohydroperoxides;
7) Decomposition of ketohydroperoxides.

This was due to two main reasons: large number of isomers and high un certainty of reaction rates, Fig.2.

The reaction rates of peroxy radicals, ROO and OOQOOH, following from analogues with acyclic alkanes.

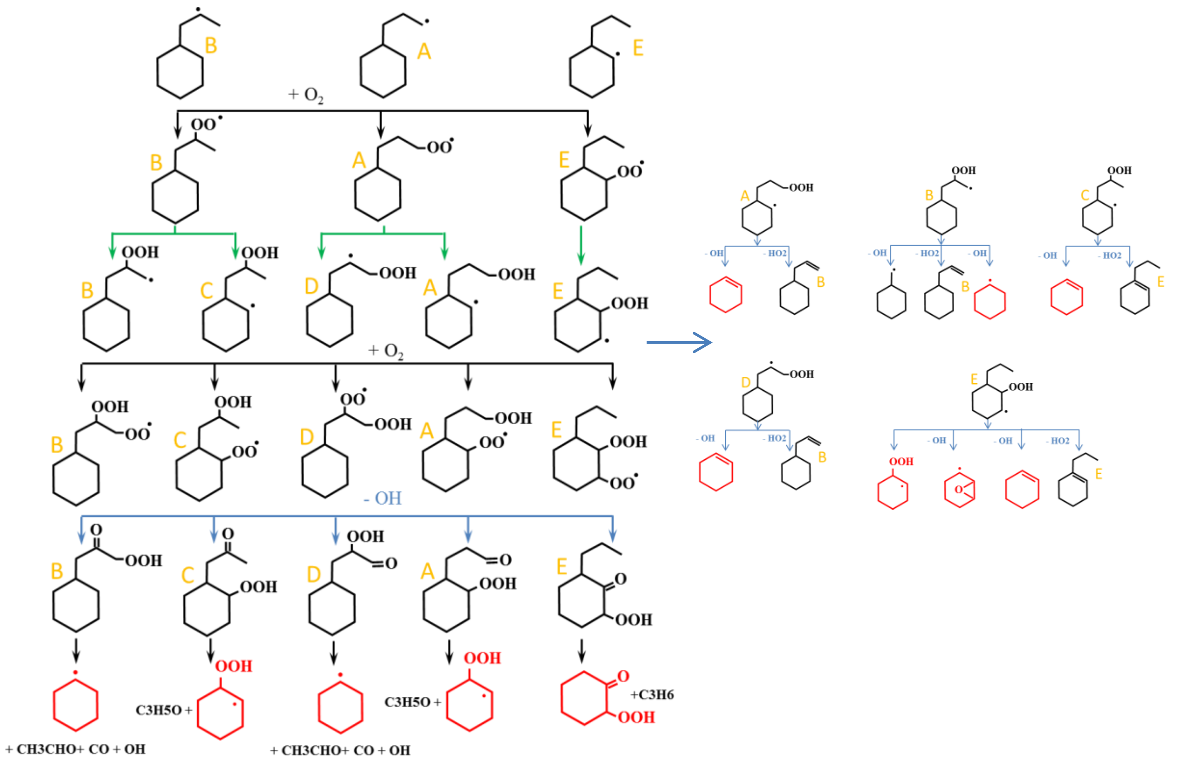

Fig.2. Principal scheme of the low temperature oxidation of cyC_9H_{18}.

3. Results and discussion

The behaviour of the low-temperature cyclohexane and n-propylcyclohexane oxidation models were validated on ignition delay times over the wide temperature range of 600-1700K at various equivalence ratios and pressure ranges, from rapid compression machines (RCM) [20] and shock tubes experiments (ST) [26] [19, 12].

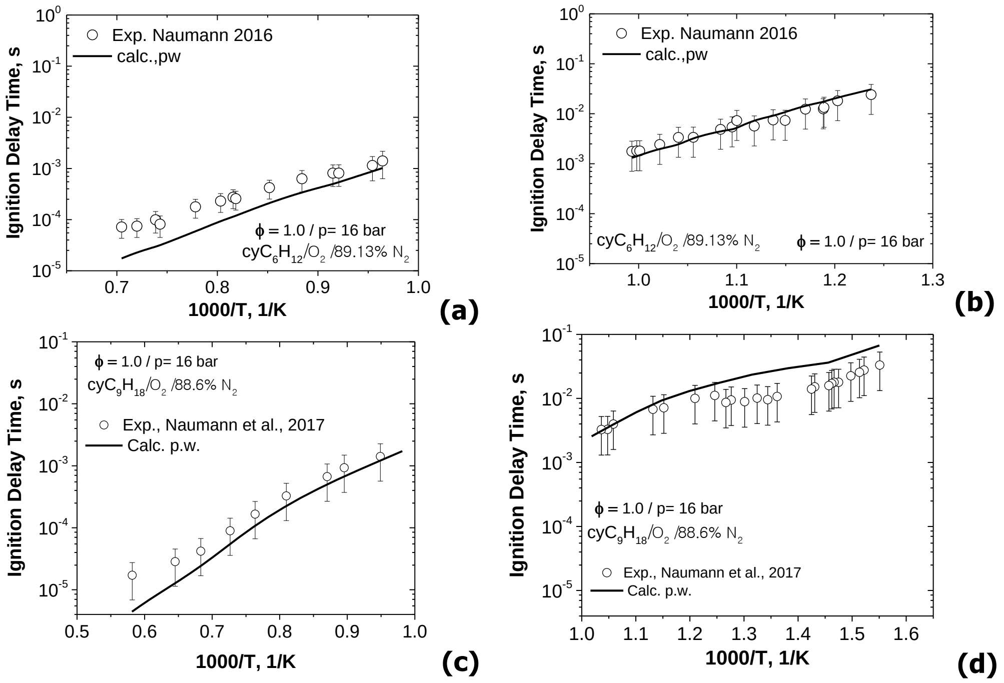

Fig.3. Comparison of simulated ignition delay times with the ST experiment [12] for stoichiometric cyclohexane/air mixtures: a),b) cycloxehane; c),d) n-propylcyclohexane.

Fig. 3 demonstrates the comparison of the simulated ignition delay times and observed in shock tube [12] under approximatively identical conditions for cyclohexane, Fig. 3a,b, and n-propylcyclohexane, Fig. 3c,d. The simulations and experimental agree well and clearly indicate, that the cyclohexane ignition delay time shape does not have the negative temperature coefficient, Fig. 3b, while n-propylcyclohexane does, Fig. 3d.

The behavior of the OH and temperature profiles of both fuels have been analyzed and presented in Fig. 4 It can be clearly see, that unlike cyC_6H_{12}, cyC_9H_{18} has peaks on the OH profile, which corresponds cool flame and the two stage ignition (Fig.4).

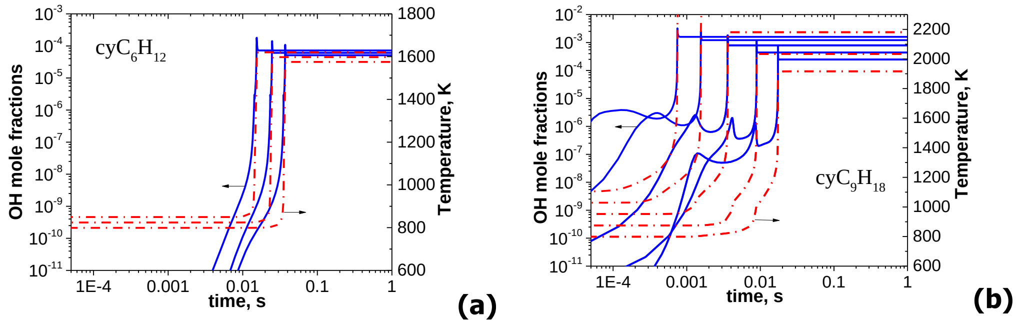

Fig.4. OH concentrations and T versus time, for T5=800-1100K, P5=16bar:a) cycloxehane; b) n-propylcyclohexane.

This explains the reason, why the low-temperature oxidation of cyC_6H_{12} unlike cyC_9H_{18} does not demonstrate NTC. Instead that, it has the gradient change, an acceleration, in the ignition delay time behavior. Also it can explain why the kinetical models, optimized on the RCM data, do not reproduce more precise experimental data from ST, Fig. 5-7.

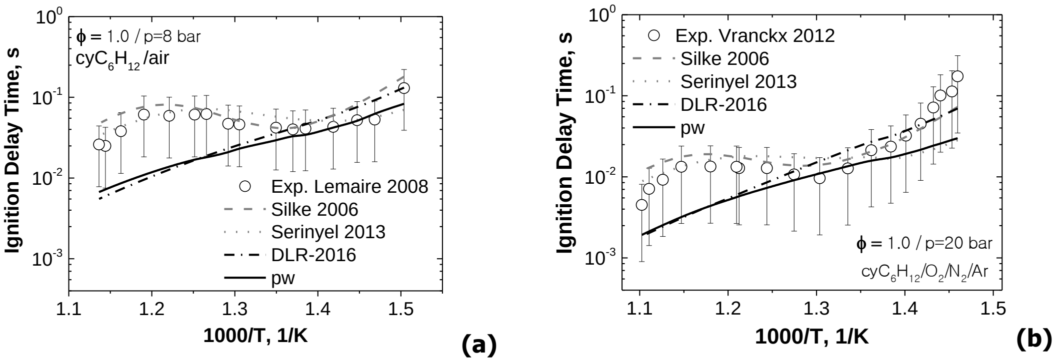

Fig.5. Cyclohexane ignition delay time from RCM experiments: a) p=8bar [9] b) p=20bar [10], versus simulations [27, 13], present work (pw)

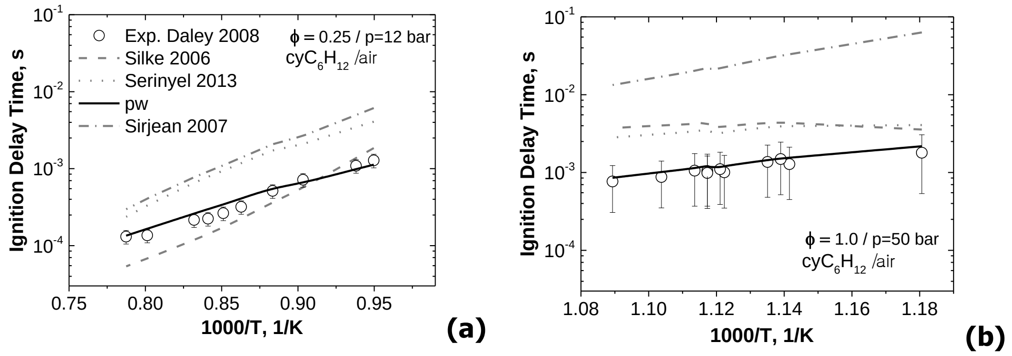

Fig.6. Comparison of ST autoignition data [11] with simulations [28, 27, 13] ,pw at: a) φ=0.25 , p=12bar; b) φ=1.0, p=50bar

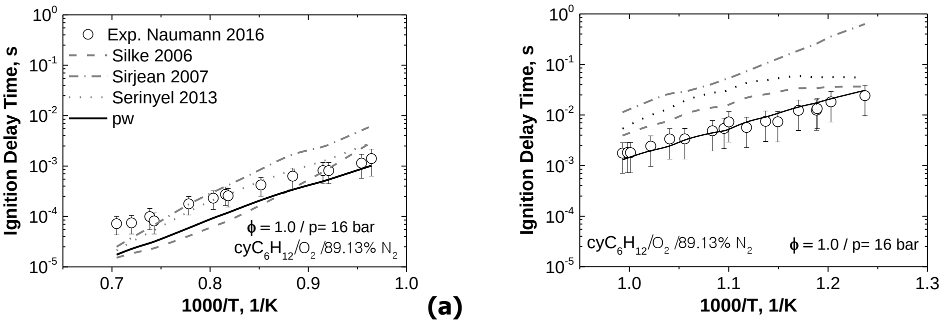

Fig.7. Comparison of ST autoignition data [12] with simulations [28, 27, 13], pw at: a)T=800-1010K b)T=1030-1420K.

The current mechanism has been also validated on the flame speed data from [13, 14, 15, 29]. The model demonstrates a good facilities to reflect the heat release in the system, describes datasets at atmospheric pressure and different preheated temperatures with a good agreement, Fig.8.

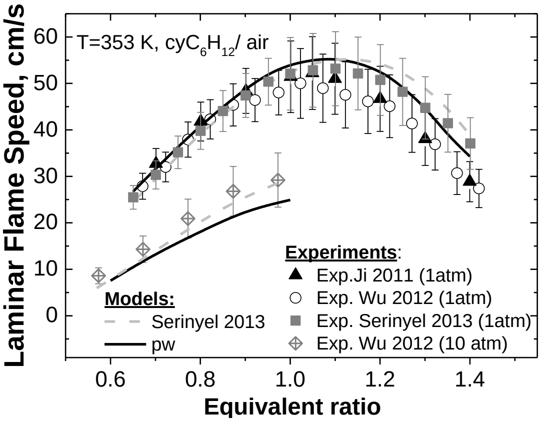

Fig.8. Laminar flame speed data [13, 14, 15] compared with simulations [13],pw.

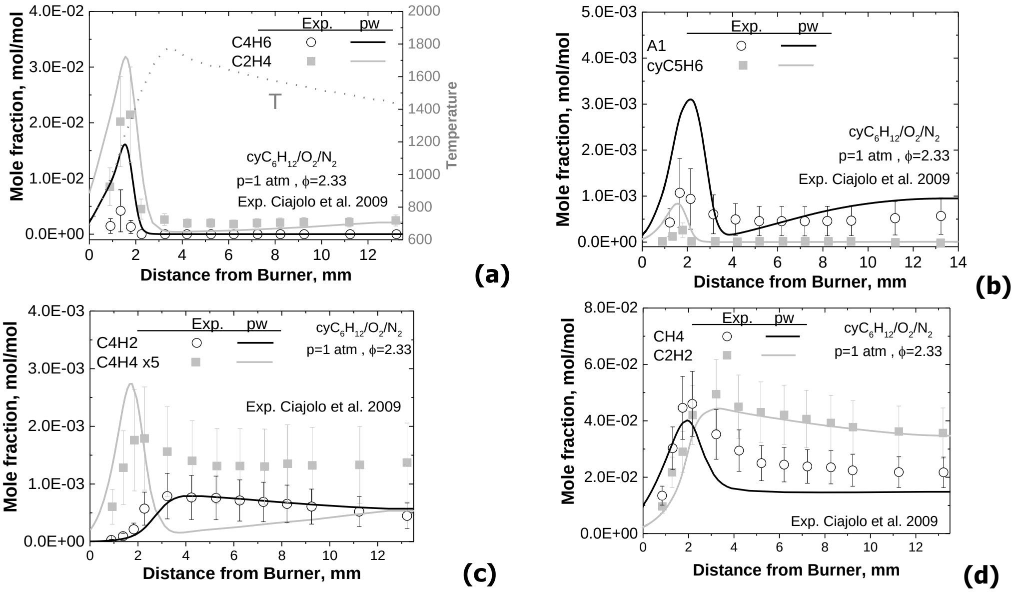

Fig.9. Species concentration profiles reported by [17] and the simulation results [pw].

Fig.9 shows simulations of the stabilized flames studied Ciajolo et al. [17]. The concentration profiles of important precursors of the PAH were successfully predicted with the present model.

The sensitivity and rate of production analysis have been carried out at three different temperatures along the given temperature profiles. It can be pointed out that, for T<1600K the cascading dehydrogenation is the main reaction path to the benzene formation. The secondary ways lead to the substituted mono-aromatics after fuel decomposition to allene and acetylene. At T>1600K, at the end of main reaction zone, the propargyl recombination controls the process of benzene formation, Fig.10.

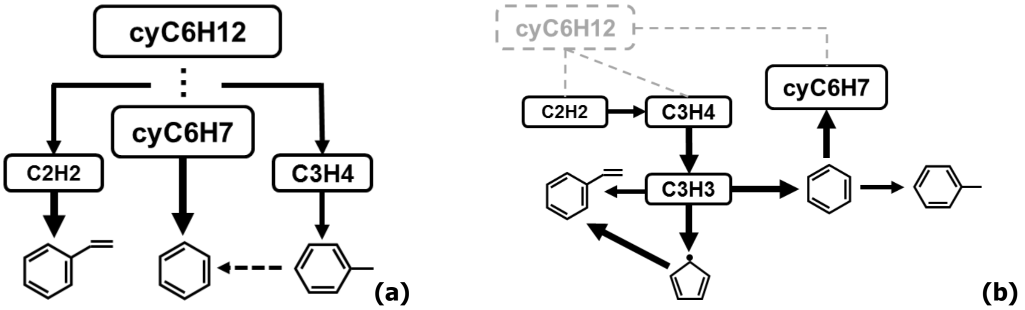

Fig.10. Schematics of reaction path analysis performed for studied flames at a) temperature flame <1600K and b) temperature flame >1600K

4. Conclusions

The semi-detailed kinetic reaction mechanism for low and high temperature cyclohexane and n-proyplcyclohexane oxidation with PAH formation is developed. Two low-temperature reaction paths were newly included in the model: cyclohexenyl peroxy formation and isomerization of hydroperoxy peroxy radical. Special care has been taken to revise of rate parameters specific to cyclic alkanes and to evaluation of uncertainty intervals for the rate coefficients of most important reactions. The developed model satisfactorily reproduces the experimental data for ignition delay times, laminar flame speeds and concentration profiles measured in laminar flames. That makes it the particularly valuable for an explanation of the cyclohexane kinetics.

The ignition simulations, thermochemistry, flow-rate and sensitivity analyses showed that, the conversion of the high-temperature oxidation to the low-temperature paths eithout NTC region for cyC_6H_{12}. Instead two stage ignition regime, the region of the gradient change (RGC) in the ignition behavior is occurred at 800<T<1100 K as a response to an increase of overall reactivity initiated by dominance of the chain branching peroxy- and hydroperoxy-radical reactions. Our numerical simulations are in accordance with the shock tube observations and support this conclusion. Unlike cyC_6H_{12}, the ignition of n-propyl cyclohexane demonstrate two-stage ignition due to high reactivity of the substituted group.

The reaction model showed a satisfactory accordance with experimental data for ignition delay times from RCM and ST experiments. Further investigation of this matter would be very useful for the development of kinetic mechanisms for larger substituted naphthenes.

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References

[1] P. Dagaut and M. Cathonnet, "The ignition, oxidation, and combustion of kerosene: A review of experimental and kinetic modeling," *Progress in Energy and Combustion Science,* vol. 32, p. 48–92, 2006.

[2] N. A. Slavinskaya and A. Zizin, "On surrogate fuel formulation," *J. Eng. Gas Turbines Power,* vol. 132, no. 11, p. 111501, 2010.

[3] P. Lindstedt and L. Maurice, "Detailed chemical–kinetic model for aviation fuels," *Journal of Propulsion and Power,* vol. 16, p. 187–195, 2000.

[4] A. Violi, S. Yan, E. Eddings, A. Sarofim, S. Granata, T. Favarelli and E. Ranzi, "Experimental formulation and kinetic model for JP-8 surrogate mixture," *Combustion Science and Technology,* vol. 174, no. 11,12, p. 399–417, 2002.

[5] M. Mawid and B. Sekar, "Development of a Detailed JP-8/Jet-A Chemical Kinetic Mechanism for High Pressure Conditions in Gas Turbine Combustors," in *Proceedings of the ASME Turbo Expo, GT2006-90478*, 2006.

[6] W. D. Schulz, "Oxidation Products of a Surrogate JP-8 Fuel," *Journal of Propulsion and Power,ACS Petroleum Chemistry Division Preprints,* vol. 37, no. 2, p. 383–392, 1991.

[7] T. Edwards and L. Maurice, "Surrogate mixtures to represent complex aviation and rocket fuels," *Journal of Propulsion and Power,* vol. 17, no. 2, p. 461–466, 2001.

[8] S. Benson, Thermochemical Kinetics, 2nd ed., New Yorck, USA: John Wiley & Sons Ltd., 1976.

[9] O. Lemaire, M. Ribaucour, M. Carlier and R. Minetti, "The Production of Benzene in the Low-Temperature Oxidation of Cyclohexane, Cyclohexene, and Cyclohexa-1,3-diene," *Combust and Flame,* pp. 1971-1980, 2001.

[10] S. Vranckx, C. Lee, H. Chakravarty and R. Fernandes, "A rapid Compression Machine Study of the Low Temperature Combustion of Cyclohexane at Elevated Pressures," pp. 377-384, 2012.

[11] S. Daley, A. Berkowitz and M. Oehlschlaeger, "A Shock Tube Study of Cyclopentane and Cyclohexane Ignition at Elevated Pressures," *International Journal of Chemical Kinetics,* p. 624–634, 2008.

[12] C. Naumann and e. al., "InnoTreib - Innovative Treibstoffe der Zukunft," Bundesministerium für Wirtschaft und Energie (BMWi), Interim reports AP 4.2 and AP 6 from 05.08.2016, 2016.

[13] Z. Serinyel, O. Herbinet, O. Frottier, P. Dirrenberger, V. Warth, P. Glaude and F. Battin-Leclerc, "An experimental and modeling study of the low- and high-temperature oxidation of cyclohexane," *Combustion and Flame,* pp. 2319-2332, 2013.

[14] C. Ji, E. Dames, B. Sirjean, H. Wang and F. Egolfopoulos, "An experimental and modeling study of the propagation of cyclohexane and mono-alkylated cyclohexane flames," *Proceedings of the Combustion Institute,* pp. 971-978, 2011.

[15] F. Wu, A. Kelley and C. Law, "Laminar flame speeds of cyclohexane and mono-alkylated cyclohexanes at elevated pressures," *Combust and Flame,* pp. 1417-1425, 2012.

[16] M. E. Law, P. R. Westmoreland, T. A. Cool, J. Wang, N. Hansen and T. Kasper, "Benzene precursors and Formation Routes in a Stoichiometric Cyclohexane Flame," *Proceedings of the Combustion Institute,* pp. 565-573, 2007.

[17] A. Ciajolo, A. Tergrossi, M. Mallardo, T. Faravelli and E. Ranzi, "Experimental and Kinetic Modeling Study of Sooting Atmospheric-Pressure Cyclohexane Flame," *Proceedings of the Combustion Institute,* pp. 585-591, 2009.

[18] A. Ristori, P. Dagaut, A. El Bakali and M. Cathonnet, "The Oxidation of N-Propylcyclohexane: Experimental Results and Kinetic Modeling," *Combustion Science and Technology,* pp. 197-228, 2001.

[19] Z. Tian, Y. Zhang, F. Yang, L. Pan, X. Jiang and Z. Huang, "Comparative Study of Experimental and Modeling Autoignition of Cyclohexane, Ethylcyclohexane, and n-Propylcyclohexane," *Energy&Fuels,* pp. 7159-7167, 2014.

[20] M. Crochet, R. Minetti, M. Ribaucour and V. G., "A detailed experimental study of n-propylcyclohexane autoignition in lean conditions," *Combustion and Flame,* vol. 157, p. 2078–2085, 2010.

[21] N. A. Slavinskaya, M. Abbasi, J. H. Starcke, R. Whitside, A. Mirzayeva, U. Riedel, W. Li, J. Oreluk, A. Hegde, A. Packard, M. Frenklach, G. Gerasimov and O. Shatalov, "Development of an UQ-Predictive Chemical Reaction Model for Syngas Combustion," *Energy&Fuels,* vol. 3, pp. 2274-2297, 2016.

[22] Slavinskaya, N.A.; Chernov, V.; Whitside, R.;Starke, J.H.; Mirzayeva, A.; Abassi, M.; Auyelkhankyzy, M., "A modeling study of acetylene oxidation and pyrolisys," *Combustion and Flame,* submitted.

[23] M. Abbasi, N. A. Slavinskaya and U. Riedel, "Kinetic Modeling of Cyclohexane Oxidation Including PAH Formation," Grapevine, Texas, USA, 2017.

[24] C. K. Westbrook, J. Warnatz and W. Pitz, "A detailed chemical kinetic reaction mechanism for the oxidation of iso-octane and n-heptane over an extended temperature range and its application to analysis of engine knock," *Proc. Combust. Inst.,* pp. 893-901, 1989.

[25] H. Curran, P. Gaffuri, W. Pitz and C. Westbrook, "A Comprehensive Modeling Study of iso-Octane Oxidation," *Combustion and Flame,* pp. 253-280, 2002.

[26] T. Dubois, N. Chaumeix and C. Paillard, "Experimental and Modeling Study of n-Propylcyclohexane Oxidation under Engine-relevant Conditions," *Energy&Fuels,* vol. 23, pp. 2453-2466, 2009.

[27] E. J. Silke, W. J. Pitz, C. K. Westbrook and M. Ribaucour, "Detailed Chemical Kinetic Modeling of Cyclohexane Oxidation," *J. Phys. Chem. A,* pp. 3761-3775, 2007.

[28] B. Sirjean, F. Buda, H. Hakka, P. Glaude, R. Fournet, V. Warth, F. Battin-Leclerc and M. R. Lopez, "The Autoignition of Cyclopentane and Cyclohexane in a Shock Tube," *Proceedings of the Combustion Institute,* pp. 277-284, 2007.

[29] S. Richter, M. B. Raida, C. Naumann and U. Riedel, "Measurement of the Laminar Burning Velocity of Neat Jet Fuel Components," *Proceedings of the World Congress on Momentum, Heat and Mass Transfer (MHMT'16), Paper No. CSP 115,* 2016.