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## A MODELING STUDY OF ALLENE OXIDATION AND PYROLYSIS

**Abstract.** The present work is an extension and upgrade of the earlier published detailed DLR reaction mechanism for the allene oxidation chemistry. Experimental data for ignition delay times obtained in shock tubes (ST), laminar flame speed data and species concentrations measured in laminar flames were used for the model revision and refinement. Threeoxygenated components  $C_3H_3OO$ ,  $C_3H_2OOH$ ,  $H_2CCHCO$  and their reactions, related to the lower temperature oxidation reactions, were newly included in the model. The thermodynamical properties of these species and reaction rate coefficients for  $H_2CCCH+O_2 \rightleftharpoons C_3H_3OO$ ,  $C_3H_3OO \rightleftharpoons C_3H_2OOH$  and  $C_3H_2+HO_2 \rightleftharpoons C_3H_2OOH$  were estimated using group additivity methods. The rate coefficients for most important reactions were revised on the basis of literature data; their uncertainty factors were estimated using statistical method. The developed mechanism was validated on the literature experimental data over parameters ranges of initial pressure 0.03-10 atm, the temperature 300-2500 K, the equivalence ratio 0.7-1.7 for allene and its mixtures, such as allene/propyne, allene/metane, allene/acetylene. The obtained model reflects well experimental data, but there is some inconsistency between experimental data for ignition delay times. However, the performed improvements in the  $C_3H_4$  oxidation chemistry led to progress in simulation of concentration profiles of the polyaromatic hydrocarbon (PAH) precursors.

**Keywords:** reaction mechanism, allene, oxidation, ignition, flame.

### Introduction

Better understanding of the  $C_3$  hydrocarbon oxidation is an important scientific topic, due to two reasons: they are key intermediates in the combustion of hydrocarbon fuels such as propane, n-butane, n-heptane and iso-octane [1-3], and play an active role in the propargyl formation, which is one of the most important PAH precursors.

Allene is a significant intermediate in the combustion of propene. The resonantly stabilized propargyl ( $H_2CCCH$ ) radical, which plays the major role in formation of first aromatic molecule, benzene (A1), is formed mostly in reactions of the allene decomposition and H-atom abstraction. The literature analysis showed that only several studies, numerical and experimental [2,4-8] were addressed to the  $C_3H_4$  combustion.

Fournet et al. [5] measured the ignition delay times of allene and propyne behind reflected shock waves in the temperature range of 1000-1650 K and the rather narrow pressure range of 8.5-10 atm. On this basis, their reaction mechanism for acetylene, propyne, allene and 1,3-butadiene was developed [5]. Besides their measured data [5], experiments on the species concentration profiles obtained in premixed flames with fuels such as acetylene by Bastin et al. [9], Westmoreland et al. [10], and 1,3-butadiene by Cole et al. [11] premixed flames were used for the allene sub-mechanism [5] validation.

Faravelli et al. [7] studied the oxidation of propyne and allene in a jet-stirred reactor (JSR) and proposed the chemical kinetic scheme for the  $C_3H_4$  oxidation at the intermediate- and high-temperature regions. Faravelli et al. [7] shown that the isomerization reactions proceeding via direct and H addition routes are significant in the oxidation. The developed reaction scheme has been tested on the experimental results obtained in ST experiments of Curran et al. [4], laminar flame of Miller et al. [12] and JSR [7].

Petrova et al. [8] proposed a detailed chemical-kinetic mechanism for the high-temperature combustion of allene. It was shown that the combustion properties of allene and propyne are quite similar and their ignition times measured in shock tubes are practically identical. The mechanism [8] was verified against ST experimental data [4] and laminar flame speed data of Davis et al. [6].

The most detailed study was recently published by Vourliotakis et al. [2]. They extensively studied existing uncertainties regarding the  $C_3H_4$  isomers chemistry and tested their model on the ST ignition delay data [4] and on concentration species investigated by Hansen and co-workers [13,14] in laminar flames of allene and propyne. It was concluded [2] that the dynamics of allene and propyne breakdown are more dependent on the initial stoichiometry, and less dependent on the isomeric structure.

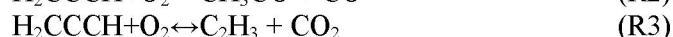
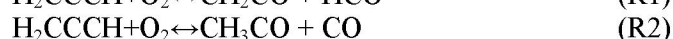
The present study is a part of the on-going work aimed at optimizing the PAH kinetic mechanism formation [15-17] and reports results of the  $C_3H_4$  sub-model upgrade at lower temperature, i.e. the second stage in the planned  $C_3$  oxidation chemistry updating. The reaction model was improved on the experimental data for ignition delay times obtained in the shock tubes, laminar flame speed data and species concentrations measured in laminar flames. Overall integrated parameter ranges were: initial pressure 0.03-10 atm, the temperature 300-2500 K, the equivalence ratio 0.7-1.7 for allene and its mixtures, such as allene/methane, and allene/acetylene.

### Kinetic Model

The detailed chemistry of  $C_3H_4$  sub-model is a part of earlier published  $C_3H_4$  sub-mechanism of Auyelkhanzy et al. [15] at high-temperature, which consists of 111 species and 926 reversible elementary reactions including the PAH chemistry up to 5-ring molecules. The  $C_3H_4$  sub-model upgrade was carried out through the model optimization based on the experimental data from [4-6,12,13,18]. The numerical calculations have been performed with Chemkin [19] and Chemical Workbench [20] software. Constant-volume, homogeneous, and adiabatic conditions behind the reflected shock wave have been used to model the shock tube experiments.

First simulations of ignition delay times revealed that the model [15] does not reproduce correctly ignition delay data for lower temperatures: in this case 1100-1350 K. It was found out that the oxidation of allene at lower temperature was inhibited with the  $H_2CCCH$  formation. This has been explained with a disbalance between the chain-branching reactions of a prompt dissociation and the chain propagation by bimolecular reactions of chemically activated species.

The chain propagation bimolecular reactions being in the model



are very important at high-temperature oxidation [18], but they did not influence the low-temperature oxidation. The reaction channels which could contribute to propargyl consumptions significantly have not found. According to the general reaction schemes [21,22] for low-temperature oxidation, we supposed to include the peroxy radical,  $C_3H_3OO$ , formation in the studied model



The following sequence converts peroxy radicals to other radicals



Four oxygenated components  $C_3H_3OO$ ,  $C_3H_2OOH$ ,  $H_2CCHCO$ , and  $C_3H_2O$  were finally included in the model. The presence of  $H_2CCHCO$  in the system has been shown in the study of Nguyen et al. [17], who investigated the  $H_2CCHCO$  radical formation by oxygen attack of  $C_3H_4$ .

The reaction rate coefficients for (R4), (R5) and (R7) have been evaluated applying group additivity methods [23]. The rate coefficient of (R6) was evaluated by analogy with similar reaction,

$\text{CH}_2\text{CHOO}=\text{CH}_2\text{CHO}+\text{O}$ , studied by Goldmith et al. [24] and finally the  $k_6$  was multiplied to 10. The modification in the DLR mechanism [15] conducted in the present work is shown in Table 1.

Table 1 - Modifications in the DLR mechanism conducted in the present work

	Reaction	$k, \text{cm}^3, \text{s}, \text{mole}, \text{K}$			Ref.
		A	n	$E_a$	
R4	$\text{H}_2\text{CCCH}+\text{O}_2\rightleftharpoons\text{C}_3\text{H}_3\text{OO}$	6.000E+12	0.00	0.00	This work
R5	$\text{C}_3\text{H}_3\text{OO}\rightleftharpoons\text{C}_3\text{H}_2\text{OOH}$	2.032e+08	1.14	17395.0	This work
R6	$\text{C}_3\text{H}_3\text{OO}\rightleftharpoons\text{H}_2\text{CCHCO}+\text{O}$	5.220E+30	-4.71	21170.0	See text
R7	$\text{C}_3\text{H}_2+\text{HO}_2\rightleftharpoons\text{C}_3\text{H}_2\text{OOH}$	1.000e+13	0.00	0.00	This work
R8	$\text{H}_2\text{CCCH}+\text{H}_2\text{O}\rightleftharpoons\text{CH}_2\text{CHCHO}+\text{H}$	6.000E+12	0.00	1042.0	[2]
R9	$\text{CH}_2\text{CHCHO}+\text{H}\rightleftharpoons\text{H}_2\text{CCHCO}+\text{H}_2$	1.150E+13	0.00	12107.3	[25]
R10	$\text{CH}_2\text{CHCHO}+\text{OH}\rightleftharpoons\text{H}_2\text{CCHCO}+\text{H}_2\text{O}$	8.000E+14	0.30	8304.0	[25]
R11	$\text{H}_2\text{CCHCO}\rightleftharpoons\text{C}_2\text{H}_3+\text{CO}$	1.000E+15	0.00	8304.0	[25]
R12	$\text{H}_2\text{CCCH}+\text{O}\rightleftharpoons\text{C}_3\text{H}_2\text{O}+\text{H}$	2.100E+14	0.00	17300.0	[2]
R13	$\text{H}_2\text{CCCH}+\text{OH}\rightleftharpoons\text{C}_3\text{H}_2\text{O}+\text{H}_2$	1.400E+14	0.00	0.00	[2]
R14	$\text{C}_3\text{H}_2\text{O}\rightleftharpoons\text{C}_2\text{H}_2+\text{CO}$	1.200E+13	0.00	0.00	[2]
R15	$\text{C}_3\text{H}_2\text{O}+\text{O}\rightleftharpoons\text{HCO}+\text{HCCO}$	8.510E+14	0.00	35722.9	[2]
R16	$\text{C}_3\text{H}_2\text{O}+\text{OH}\rightleftharpoons\text{HCO}+\text{CH}_2\text{CO}$	1.000E+13	0.00	0.00	[2]
R17	$\text{H}_2\text{CCHCO}+\text{H}\rightleftharpoons\text{C}_3\text{H}_2\text{O}+\text{H}_2$	1.000E+13	0.00	0.00	[2]
R18	$\text{H}_2\text{CCHCO}+\text{O}\rightleftharpoons\text{C}_3\text{H}_2\text{O}+\text{OH}$	6.000E+13	0.00	0.00	[2]

The rate constants are given at 1 atm ( $k(T) = AT^n \exp(-E_a/T)$ ) in  $\text{cm}^3, \text{mol}, \text{s}, \text{K}$  units.

## Results

### Ignition of $\text{C}_3\text{H}_4/\text{O}_2/\text{Ar}$ mixtures

The simulations of experimental data [4,5] identified some discrepancies between these two data sets. Despite the similar initial temperature and identical mixture compositions, the results obtained in these studies demonstrate quite different trends. The data from [5], Fig.1, shows the faster ignition than it was observed in [4] for temperature  $>1650$  K, and are slower than data [4] at temperature lower than 1350 K under similar conditions for equivalence ratio. The faster observations can be logically explained with the higher pressure. One possible explanation for the deaccelerating of the ignition delay time with the pressure growth could be an increasing of the  $\text{HO}_2$  production caused by higher pressure, i.e.  $p_5=8.5\text{-}10.0$  atm, in experiment [5], in comparison to  $p_5=2.1, 3.5$  and  $5.0$  atm in experiment [4]. However, at studied temperatures [4,5],  $T_5 = 1350\text{-}1850\text{K}$ , this effect is no longer so strong to slowdown the ignition delay time with factor of 2.5, as it follows from the experimental data comparison, Fig.1. The sensitivity analysis has been carried out by changing the rate constant of  $\text{C}_3\text{H}_4+\text{HO}_2\rightleftharpoons\text{H}_2\text{CCCH}+\text{H}_2\text{O}_2$  in ranges defined with uncertainty analysis [15]. The results of this analysis indicate the nonsignificant influence of this reaction in contribution to the changing of the ignition trends. This analysis can indicate on the possible inconsistency of these two datasets.

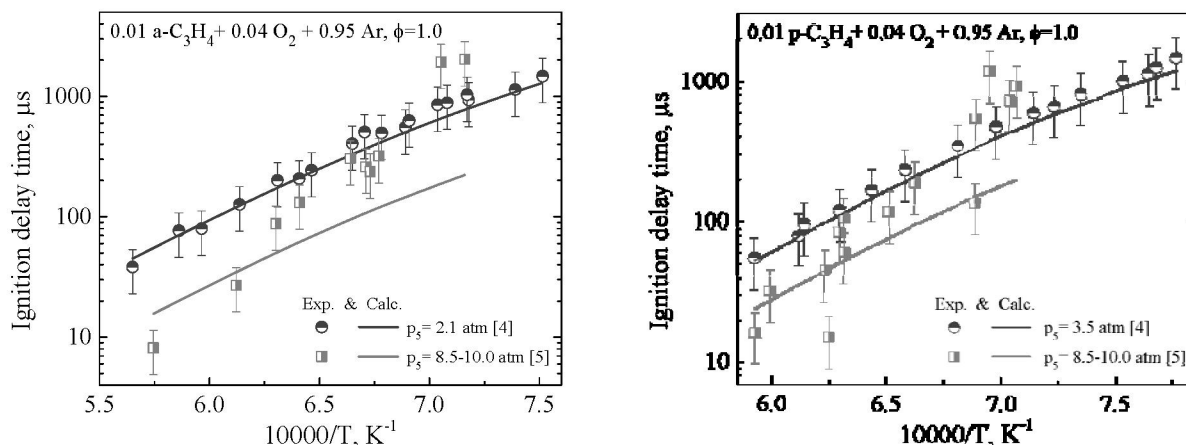


Figure1 - Comparison between computed and experimental [4,5] ignition delay times of  $\text{C}_3\text{H}_4/\text{O}_2/\text{Ar}$

The introduced reactions (R4)-(R7) improved sufficiently the simulations of data from Curran et al. [4] for  $T_5 < 1350$  K, Fig. 1, and increased the disagreement with data of Fournet et al. [5] for these temperatures: the model under-predicts measurements from [5]. Calculated values, as it was described above, were used for  $k_4$ ,  $k_5$ ,  $k_7$  without any changes. The rate constant  $k_6$  was multiplied to 10 to accelerate the ignition simulations at lower temperatures.

The obtained progress in experimental data reproduction is shown in the Fig. 2. The least square residual for ignition delay time calculated with initial model and with the present one was reduced from  $8.03E+01$  to  $2.96E+01$ .

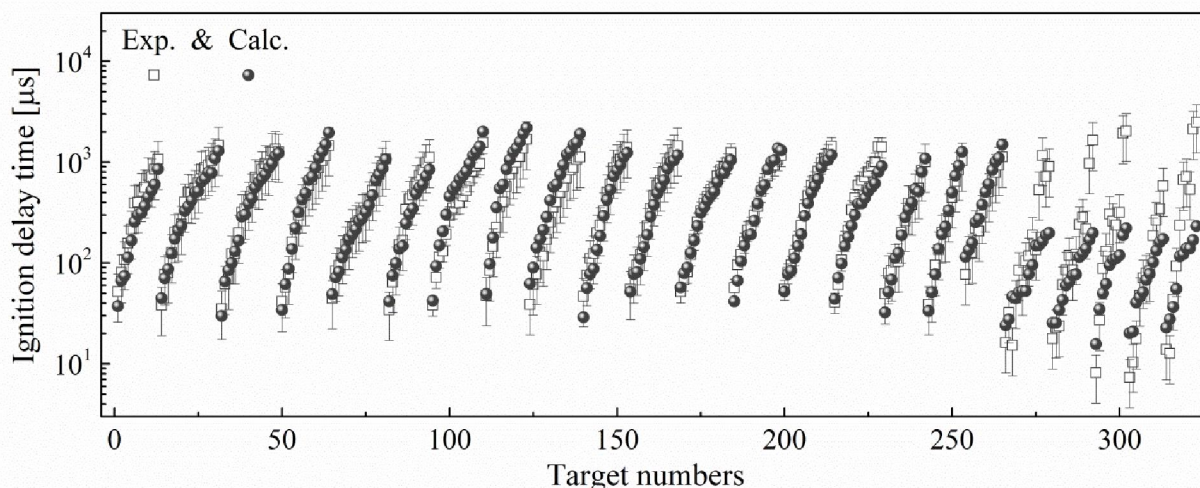


Figure 2 - Comparison between computed models and experimental ignition delay times of  $C_3H_4/O_2/Ar$  [4,5]

#### *Laminar flame speed of $C_3H_4$ /air mixtures*

The present mechanism validated on the basis of the experimental data by Davis et al. [6], which studied the oxidation of propyne/(18%  $O_2$  in  $N_2$ ) mixtures in laminar premixed flames using the counter-flow twin flame configuration. The sensitivity analysis is populated with reactions of hydrogen and  $C_1$  hydrocarbon species, and there are only a few reactions of allene and propargyl that influence laminar flame speed at all stoichiometric conditions. The addition of the reactions (R4)-(R8) to the mechanism lead to nonsignificant change in the laminar flame speed data at lean to rich equivalence ratio. This modification leads to predict the shape of the laminar flame speed curve reasonably well. The results are shown in [15].

#### *Concentration species of $C_3H_4/O_2/Ar$ mixtures*

A successful reproduce the ignition delay times of both allene and propyne mixtures and laminar flame speed data for propyne leads to main goal of this study; it is to describe the major and intermediate species formed in flames and to improve the reaction pathways of PAH formation and growth in modelling tools to predict soot precursors formation in allene flame.

The initially validated against species concentration profiles data results show in excellent agreement for major stable species, such as  $C_3H_4$ ,  $O_2$ , Ar,  $H_2$ ,  $H_2O$ , CO,  $CO_2$  in all flames. The model over-predicts the  $CH_3$  and  $CH_4$  mole fractions obtained from [13], but the experimental data observed from [12] accurately reproduced very well, Fig. 3. It can be explained, as it noted from [13], in experimental data obtained from [13] mole fractions of these components no detectable amount in the post-flame region.

Concentration profiles of  $C_2H_2$ ,  $C_2H_3$ ,  $C_2H_4$ , and  $C_2H_6$  was obtained from [18] and [13]. Mole fraction of  $C_2H_2$  obtained from [13] predicted quite accurately, but experimental data obtained from [18] is over-predicted almost 2 times. The data between each other is not consistent. Lower mole fraction for  $C_2H_3$  is observed with the present model compare the experimental data [13]. The mole fraction profiles for  $C_2H_4$  and  $C_2H_6$  obtained in both experimental data from [13,18] model reproduced in excellent agreement. Figure 4 shows the comparing of the experimental data and modeling results of  $C_2H_2$  and  $C_2H_4$ .

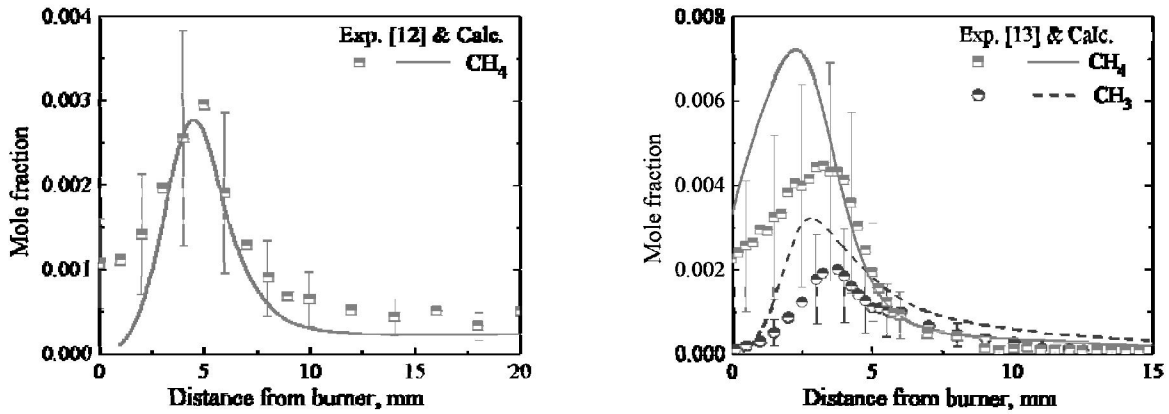


Figure 3 - Experimental (symbol) [12,13] and computed (line) mole fraction profiles of CH<sub>3</sub> and CH<sub>4</sub> in C<sub>3</sub>H<sub>4</sub>/O<sub>2</sub>/Ar flame

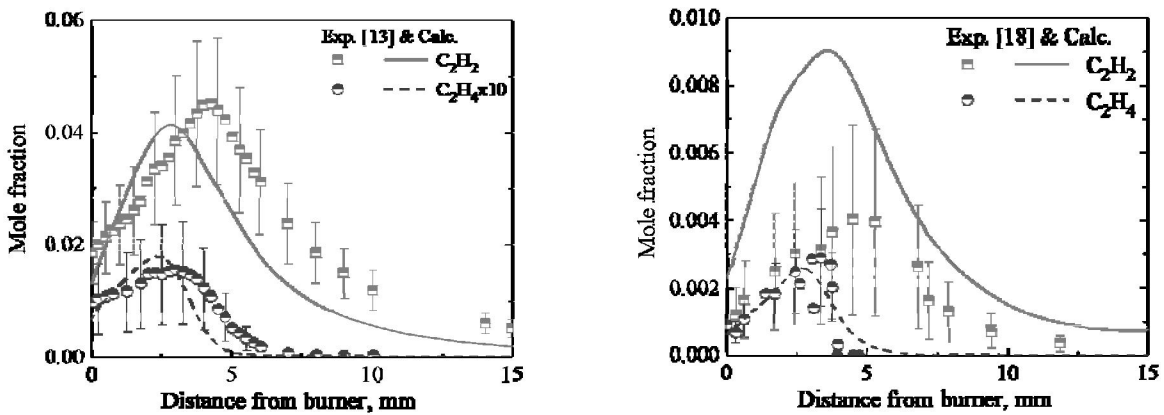


Figure 4 - Experimental (symbol) [13,18] and computed (line) mole fraction profiles of main and intermediate species in C<sub>3</sub>H<sub>4</sub>/O<sub>2</sub>/Ar flame

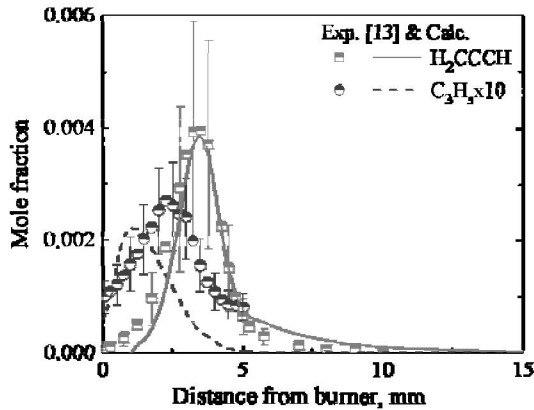


Figure 5 - Mole fraction profiles of H<sub>2</sub>CCCH and C<sub>3</sub>H<sub>5</sub> in C<sub>3</sub>H<sub>4</sub>/O<sub>2</sub>/Ar flame [13]

Nevertheless, the detection the isomeric composition for C<sub>3</sub> hydrocarbons [13] in allene flame we have only singlet propargylene (HCCCH) as C<sub>3</sub>H<sub>2</sub> and allene as C<sub>3</sub>H<sub>4</sub> in present model. The first reason is the objective of achieving simplifications and secondly is the indistinguishable behavior of the ignition of allene and propyne. Predicted and experimentally derived mole fractions profiles for radicals C<sub>3</sub>H<sub>3</sub> and C<sub>3</sub>H<sub>5</sub> are in excellent agreement, Fig. 5. The C<sub>3</sub>H<sub>2</sub> mole fractions peak at experiment is 1.00x10<sup>-4</sup>, but prediction is 2.25x10<sup>-4</sup>. The present model is over-predicted the mole fraction profiles for molecules C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> obtained from [18]. It is the next goals.

The present model reproduced lower mole fractions profiles for  $C_4H_2$  obtained [13] and [12], Fig. 6. Mole fractions profiles for  $C_4H_4$  obtained from [13] and [12] is inconsistency, for data obtained from [13] model is under-predicted, but for data from [18] model is over-predicted. Mole fraction profiles for  $C_4H_5$  obtained from [13] are  $2.00 \times 10^4$ , but prediction is 2 times high.  $C_4H_8$  mole fractions profiles obtained from [18] predicted accurately. The  $C_3H_5$  mole fractions peak at experiment is  $1.50 \times 10^4$  from [13] but prediction is  $7.50 \times 10^5$ .

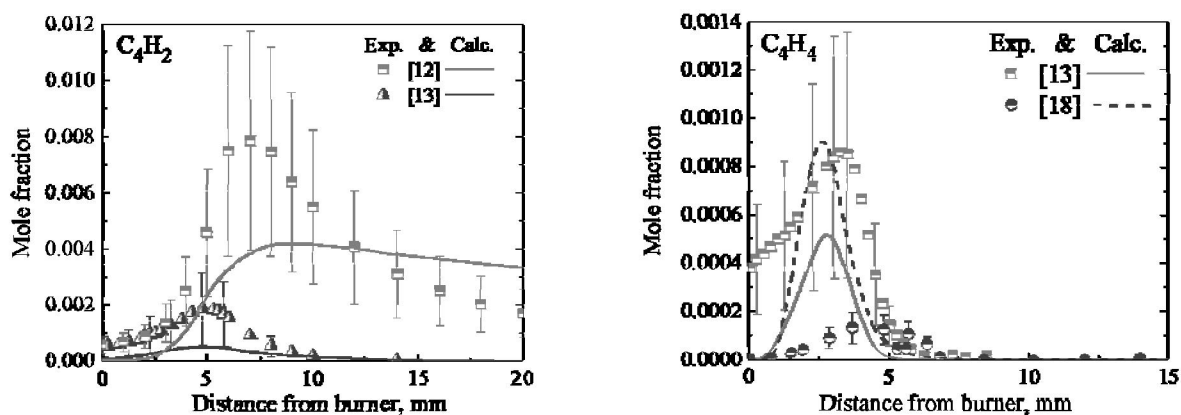


Figure 6 - Experimental (symbol) [12,13,18] and computed (line) mole fraction profiles of  $C_4H_2$  and  $C_4H_4$  in  $C_3H_4/O_2/Ar$  flame

Prediction the concentration profiles of benzene is too high for all these three flames. The prediction of benzene profiles is possible after developing the sub-models to propene and propane.

### Conclusions

A new detailed kinetic mechanism has been proposed to model the oxidation of allene and their mixtures. The mechanism for allene is derived from recent mechanisms for the oxidation of acetylene and allene and has been successfully validated using experimental results obtained in a shock tube reactor and in laminar flames. The mechanism for the mixture can qualitatively reproduce the evolution of the ignition delay times, laminar flame speed, and species concentration profiles observed. Three more of the missing reactions with propargyl radical, which is not been previously reported in the literature have been added. Addition of these reactions is given possibility reproduced the ignition delay time at lower temperatures. Unfortunately, due to non-availability the experimental data of the oxidation of allene at low-temperature  $T > 1000$  K do not impossible to validate the mechanism. The hierarchical structure of present  $C_3H_4$  sub-mechanism will be used for further developing a sub-mechanism for propene that is consistent with the available experimental combustion data for this fuel; then, finally, keeping these mechanisms fixed, find a successful mechanism for propane.

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#### АЛЛЕННІҢ ТОТЫҒУЫН ЖӘНЕ ПИРОЛИЗІН МОДЕЛЬДІК ЗЕРТТЕУ

**Аннотация.** Осы мақалада НАО-ның реакциялық механизмі негізінде алленнің тотығуының химиялық реакциялары кеңейтілді және жаңартылды. Реакциялық механизмді тексеру және оңтайландыру үшін соққы түтігінде алынған тұтану уақыты бойынша, ламинарлы жалын жылдамдығы бойынша және компоненттердің концентрацияларының профильдері бойынша алынған эксперименттік деректер қолданылды. Нәтижесінде, алленнің төмен температурада тотығуын сипаттау үшін механизмге жаңадан үш оттегімен байытылған C<sub>3</sub>H<sub>3</sub>OO, C<sub>3</sub>H<sub>2</sub>OOH, H<sub>2</sub>CCNCO компоненттері және олардың реакциялары енгізілді. Осы компоненттердің

термодинамикалық қасиеттері және  $\text{H}_2\text{CCCH}+\text{O}_2\rightleftharpoons\text{C}_3\text{H}_3\text{OO}$ ,  $\text{C}_3\text{H}_3\text{OO}\rightleftharpoons\text{C}_3\text{H}_2\text{OON}$ ,  $\text{C}_3\text{H}_2+\text{HO}_2\rightleftharpoons\text{C}_3\text{H}_2\text{OON}$  реакцияларының жылдамдығының коэффициенттері топтық қосынды әдісі арқылы бағаланды. Ең маңызды реакциялардың жылдамдық коэффициенттері әдеби деректер негізінде қайта қаралды және олардың белгісіздік факторлары статистикалық өңдеу арқылы бағаланды. Өңделген модель әдеби тәжірибелік деректер негізінде қысым 0.03-10 атм, температура 300-2500 К және эквиваленттік қатынасы 0,7-1,7 тең аллен және олардың қоспалары аллен/пропин, аллен/метан және аллен/ацетилен негізінде тексерілді. Алынған модель эксперименттік деректерді жақсы сипаттайды, бірақ тұтану уақыттары бойынша эксперименттік деректер арасында сәйкессіздік бар. Алайда,  $\text{C}_3\text{H}_4$  тотығуының химиялық реакцияларының кеңейтілуі полиароматты көмірсутектердің (ПАК) концентрацияларының профилдерін толық сипаттауға әкелді.

**Тірек сөздер:** реакциялық механизм, аллен, тотығу, тұтану, жалын

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### МОДЕЛИРОВАНИЕ ОКИСЛЕНИЯ И ПИРОЛИЗА АЛЛЕНА

**Аннотация.** Настоящая работа посвящена расширению и улучшению ранее опубликованного подробного механизма реакции DLR для химии окисления аллена. Экспериментальные данные по временам задержек воспламенения полученных в ударных трубах, данные по скоростям ламинарных пламен и профилям концентрации компонентов, полученных в ламинарных пламенах, были использованы для тестирования и оптимизации реакционного механизма. Три оксигенированные компоненты  $\text{C}_3\text{H}_3\text{OO}$ ,  $\text{C}_3\text{H}_2\text{OON}$ ,  $\text{H}_2\text{CCCHO}$  и их реакции, которые важны для низкотемпературного окисления, были впервые включены в настоящую модель. Термодинамические свойства этих компонентов и коэффициенты скорости реакции  $\text{H}_2\text{CCCH}+\text{O}_2\rightleftharpoons\text{C}_3\text{H}_3\text{OO}$ ,  $\text{C}_3\text{H}_3\text{OO}\rightleftharpoons\text{C}_3\text{H}_2\text{OON}$  и  $\text{C}_3\text{H}_2+\text{HO}_2\rightleftharpoons\text{C}_3\text{H}_2\text{OON}$  были оценены с использованием метода групповой аддитивности. Коэффициенты скорости для наиболее важных реакций были пересмотрены на основе литературных данных и их коэффициенты неопределенности оценивались с использованием статистического метода. Разработанный механизм был подтвержден литературными экспериментальными данными при давлении 0,03-10 атм, температуре 300-2500 К, и при коэффициенте эквивалентности 0,7-1,7 для аллена и его смесей, таких как аллен/пропин, аллен/метан, аллен/ацетилен. Полученная модель удовлетворительно воспроизводит экспериментальные данные, но есть некоторые несогласованность между экспериментальными данными по временам задержек воспламенения. Однако выполненные улучшения в химии окисления  $\text{C}_3\text{H}_4$  привели к прогрессу в моделировании профилей концентрации полиароматических углеводородов (ПЦАУ).

**Ключевые слова:** реакционный механизм, аллен, окисление, воспламенение, пламя.