

BULLETIN OF NATIONAL ACADEMY OF SCIENCES  
OF THE REPUBLIC OF KAZAKHSTAN

ISSN 1991-3494

Volume 6, Number 370 (2017), 5 – 12

UDC 541.183; 547.532:542.943; 547.91:542.943

M. Auyelkhanzy<sup>1,2</sup>, M. Abbasi<sup>1</sup>, N. Slavinskaya<sup>1</sup>, Z. Mansurov<sup>2</sup>

<sup>1</sup>Institute of Combustion Technology (DLR), Stuttgart, Germany,

<sup>2</sup>Al-Farabi Kazakh National University, Almaty, Kazakhstan.

E-mail: auyelkhanzy@gmail.com

### REACTION MECHANISM FOR THE OXIDATION OF ALLENE AND PROPYNE

**Abstract.** The study of detailed chemistry of allene and propyne in hydrocarbon combustion are very important, because they are precursors of propargyl radical ( $\text{H}_2\text{CCCH}$ ). Propargyl radical plays a main role in formation of first aromatic molecules, benzene, which it is start to growth polyaromatic hydrocarbons (PAHs), and soot formation.

This paper focuses on the development a reaction kinetic sub-mechanism for the oxidation of allene and propyne which is included in the reaction data of the base of the DLR. The detailed chemistry of allene and propyne is a part of earlier published  $\text{C}_2$ -mechanism with polyaromatic hydrocarbons (PAHs) formation. The sub-mechanism of  $\text{C}_3\text{H}_4$  reaction was analyzed on the basis of published studies. Experimental data of ignition delay times and laminar flame speed have been used for validation and improvement of general oxidation reaction paths. In the results, the mechanism was adopted 6 reactions; the rate constants for 7 reactions at the high- ( $T > 1500\text{K}$ ) and low-temperatures ( $T < 1500\text{K}$ ) ignition were modified. The rate coefficients for reactions  $\text{C}_3\text{H}_4 + \text{H} = \text{H}_2\text{CCCH} + \text{H}_2$ ,  $\text{C}_3\text{H}_4 + \text{H} = \text{CH}_3 + \text{C}_2\text{H}_2$  and  $\text{C}_3\text{H}_4 + \text{HO}_2 = \text{H}_2\text{CCCH} + \text{H}_2\text{O}_2$  have evaluated with statistical treatment. Modified model shows to accurately reproduce the ignition delay times and laminar flame speed of both allene and propyne mixtures at  $p_5=2-10$  bar,  $T_5=1100-1840$  K and  $\phi=0.5-2.0$  and laminar flame speed at  $T_0=298\text{K}$ ,  $p=1$  bar,  $\phi=0.6-1.8$ .

**Keywords:** modeling, mechanism, allene, propyne, oxidation.

**Introduction.** Polycyclic aromatic hydrocarbons (PAHs) and soot particles are among the priority pollutants, as they have carcinogenic activity and are dangerous for human health. In this connection, the scientific interests to investigation the kinetic mechanism of PAHs and soot formation have not weakened in recent decades [1-3].

The study of detailed chemistry of allene and propyne in hydrocarbon combustion and pyrolysis are very important, because they are precursors of propargyl radical ( $\text{H}_2\text{CCCH}$ ). It is now well established as experimentally and as theoretically that propargyl radical is important radical, which is a critical intermediate on the formation of the first aromatic ring, PAHs, and soot formation.

This paper aim is to develop a reaction kinetic sub-mechanism for the oxidation of allene and propyne.

**$\text{C}_3\text{H}_4$ -sub model.** The detailed chemistry of allene and propyne is a part of earlier published  $\text{C}_2$  mechanism [4] which consists of 111 species and 920 reversible elementary reactions. This mechanism has been initially validated against ignition delay data [5, 6] and laminar flame speed [7] of both allene- and propyne-oxygen-argon at pressures  $p_5 = 2-10$  bar and for a wide range of stoichiometries  $\phi = 0.5-2.0$ . The characteristic data of experimental flames and their uncertainties are summarized in Table 1.

Table 1 – Evaluation of uncertainty intervals for the selected shock tube experimental data

Ref.	Driven section				$T_5$ , K		$p_5$ , bar		$\phi$	Dilution	$t_{meas}$ , $\mu$ s	Uncert., %
	L, m		Int. d, cm									
[5]	3.65	+5%	4.5	+5%	1200-1900	+5%	2.0-5.0	+5%	0.5-2.0	yes	+5%	45%
[6]	4.0	+5%	7.8	+5%	1000-1650		8.5-10.0	+5%	0.5-1.0	yes	+10%	45%

\*Initial uncertainty is 20%.

Numerical modelling was performed using the SENKIN (for simulation of ignition delay time) and PREMIX (for simulation of laminar flame speed, sensitivity analysis, rate of production analysis (ROPAD)) code from the CHEMKIN II package [8] and Chemical Workbench [9].

The initially validation against experimental data of ignition delay time and laminar flame speed shows that the mechanism is described the oxidation of allene and propyne ( $C_3H_4$ ) the range of temperature interval 1300–1500 K, but does not describe at high- ( $T > 1500K$ ) and low-temperature ( $T < 1300K$ ).

First step of the improving the sub-mechanism of  $C_3H_4$  is sensitivity analysis, which to identify the most important reactions for the development of the oxidation reaction chain. Analysis have been carried for several temperatures, as at satisfactory described ( $T_5 = 1381$  K) and as at unsatisfactory described ( $T_5 = 1893$  K,  $T_5 = 1636$  K,  $T_5 = 1226$  K). For every temperature 10 major reactions, which influence to ignition delay time are shown in Figure 1. This analysis has shown that allene/propyne decomposition reaction  $H_2CCCH + H (+M) = C_3H_4 (+M)$  (R403) is important reaction for low- and high-temperatures. Another the most important reactions for high temperature are H-consuming reactions:  $C_3H_4 + H = H_2CCCH + H_2$  (R395) and  $C_3H_4 + H = CH_3 + C_2H_2$  (R397); and to low temperatures  $C_3H_4 + HO_2 = H_2CCCH + H_2O_2$  (R396) reaction.

The theoretical and experimental rate constant of reactions (R395)-(R396), which were recommended in literature from different sources [10-20] have demonstrated that these rates are different at same flame temperatures. For instance, the rate constant of Davis et al. [10] for reaction (R395) is almost 100 times faster than the corresponding rate of Miller et al. [13]. The rate coefficients for reactions

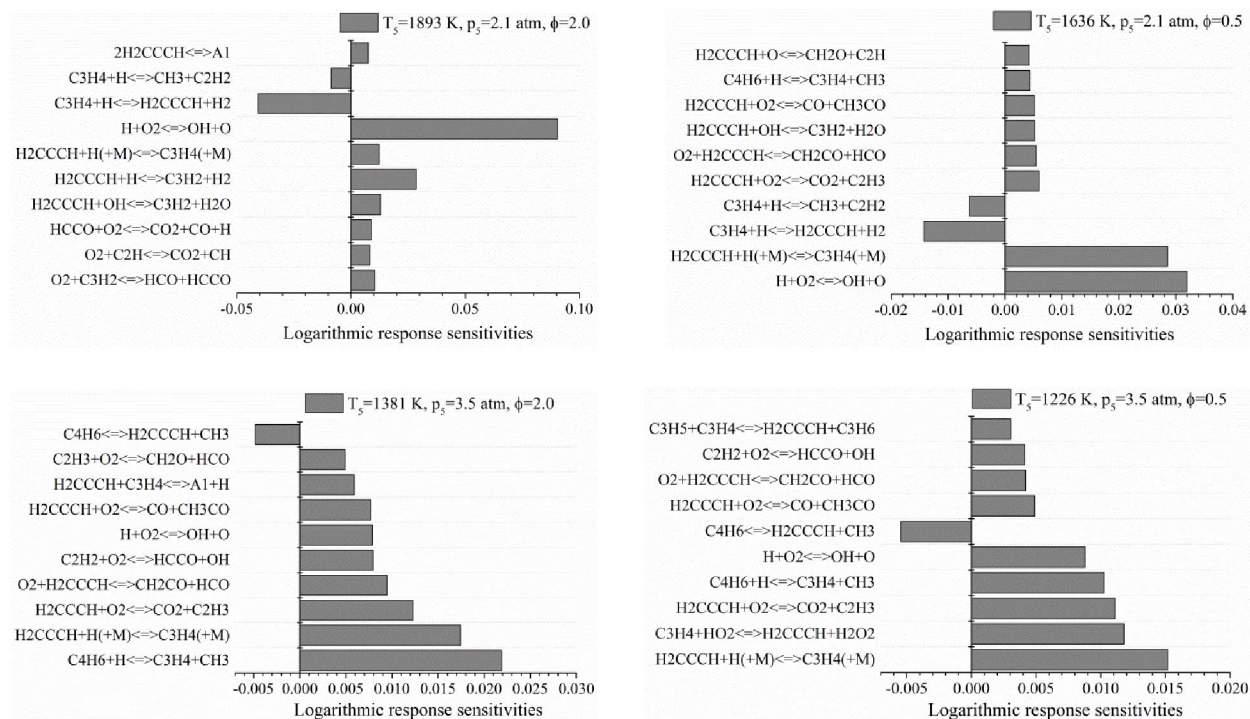


Figure 1 – Logarithmic response sensitivities computed with initial  $C_2$  mechanism for ignition delay time

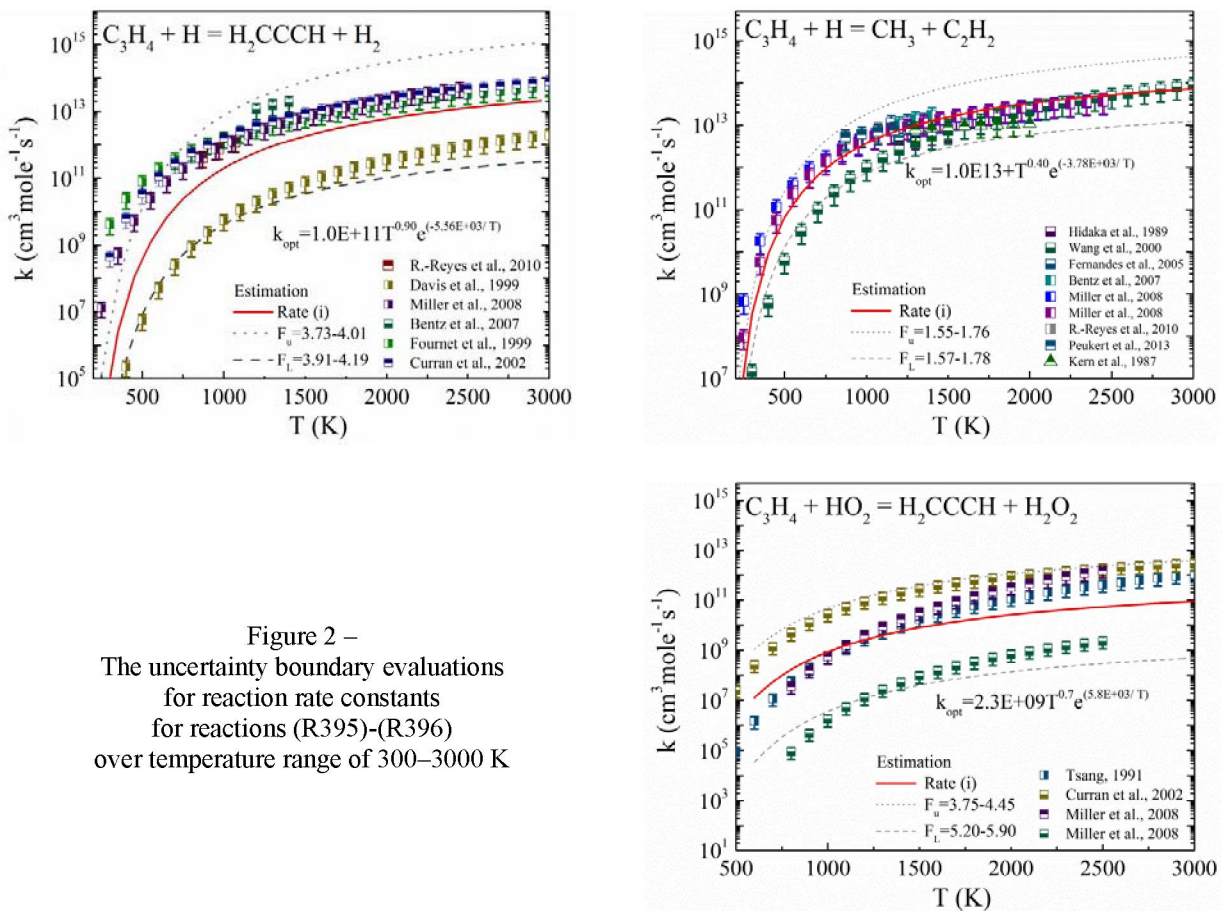
$C_3H_4 + H = H_2CCCH + H_2$  (R395),  $C_3H_4 + H = CH_3 + C_2H_2$  (R397), and  $C_3H_4 + HO_2 = H_2CCCH + H_2O_2$  (R396) have evaluated with statistical treatment (Figure 2). This allows the calculation of the uncertainty factor,  $f(T)$ , (generally not symmetric) traditionally used in chemical kinetics to determine the uncertainty level for the reaction:

$$f_u(T) = \frac{k_{upper}(T)}{k_0(T)}; \quad f_l(T) = \frac{k_0(T)}{k_{low}(T)},$$

where  $k_0$  is the nominal rate coefficient in the Arrhenius expression ( $cm^3, mol, s, K$ )

$$k(T) = AT^n \exp(-E_a/T),$$

$A, n, E_a$  – Arrhenius parameters;  $k_{low}$  and  $k_{upper}$  are lower and upper bounds, respectively.



To improve simulations of ignition delay times at high-temperature the reactions (R375), (R398)-(R402) were newly adopted.

The unimolecular decomposition reaction (R398) competing to reaction (R403) plays an important role at high temperature as well. The reactions of hydrogen abstraction (R399)-(R402) were added in the model, because they are important reactions for the chain propagation and active radical production. The reaction rate coefficients  $k_{398} - k_{400}$  were adopted from Fournet et al. [6]; the rates of reactions  $k_{401}$  and  $k_{402}$  were added from Zhang et al. [21].

The important reaction for the chain branching (R375) was studied by Klippenstein et al. [2] at  $T = 600-2000$  K and  $p = 0.001-100$  atm. The reaction rate coefficients for (R376) and (R380) were analyzed and revised. Finally, the rate coefficient values followed from [22] were prescribed to these reactions (Table 2).

Table 2 – Modifications in the DLR mechanism conducted in the present work

N	Reactions	A	n	Ea	Ref.
R375	$\text{H}_2\text{CCCH}=\text{C}_3\text{H}_2+\text{H}$	3.500E+38	-6.78	54250.0	[2]
R376	$\text{H}_2\text{CCCH}+\text{OH}=\text{HCO}+\text{C}_2\text{H}_3$	4.000E+12	0.00	0.00	[22]
R377	$\text{H}_2\text{CCCH}+\text{H}=\text{C}_3\text{H}_2+\text{H}_2$	5.000E+11	0.00	0.00	[23]
R380	$\text{H}_2\text{CCCH}+\text{O}_2=\text{CO}_2+\text{C}_2\text{H}_3$	3.010E+09	0.00	1443.0	[22]
R385	$\text{H}_2\text{CCCH}+\text{OH}=\text{C}_3\text{H}_2+\text{H}_2\text{O}$	2.000E+12	0.00	0.00	[24]
R395	$\text{C}_3\text{H}_4+\text{H}=\text{H}_2\text{CCCH}+\text{H}_2$	1.000E+12	0.90	5560.0	[Est.]
R396	$\text{C}_3\text{H}_4+\text{HO}_2=\text{H}_2\text{CCCH}+\text{H}_2\text{O}_2$	2.300E+10	0.70	5800.0	[Est.]
R397	$\text{C}_3\text{H}_4+\text{H}=\text{CH}_3+\text{C}_2\text{H}_2$	1.000E+14	0.40	3780.0	[Est.]
R398	$\text{C}_3\text{H}_4=\text{C}_2\text{H}+\text{CH}_3$	4.200E+16	0.00	50000.0	[6]
R399	$\text{C}_3\text{H}_4+\text{OH}=\text{CH}_2\text{O}+\text{C}_2\text{H}_3$	2.000E+12	0.00	100.0	[6]
R400	$\text{C}_3\text{H}_4+\text{HO}_2=\text{C}_2\text{H}_4+\text{CO}+\text{OH}$	6.000E+09	0.00	4000.0	[6]
R401	$\text{C}_3\text{H}_4+\text{OH}=\text{HCO}+\text{C}_2\text{H}_4$	1.000E+12	0.00	0.00	[21]
R402	$\text{C}_3\text{H}_4+\text{O}=\text{CH}_2\text{O}+\text{C}_2\text{H}_2$	9.000E+12	0.00	1870.0	[21]

\*Est. – Rate constants were estimated in this work. 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.

The addition of these reactions led to the improved agreement with experimental data of ignition delay time at high-temperature. However, the simulation shows that oxidation of allene at lower-temperature should be further investigated. The principal scheme of low-temperature oxidation for allene and propyne will be developed and oxygenated compounds like  $\text{C}_3\text{H}_4\text{O}$ ,  $\text{C}_3\text{H}_4\text{O}_2$ ,  $\text{C}_3\text{H}_2\text{O}$  will be added to the model.

Final simulation with  $\text{C}_3\text{H}_4$ -sub model is shown that adopted and modified reactions reproduce accurately the ignition delay time for both of allene and propyne mixture flame at high-temperature, Figure 3.

The present kinetic model predicts the shape of the laminar flame speed curve reasonably well, but it over-predicts the experimental data at lean to stoichiometric equivalence ratios ( $\phi = 0.7-1.1$ ) (Figure 4). Based on the model, the consumption of propyne and allene in laminar premixed flame is mainly due to reaction R398.

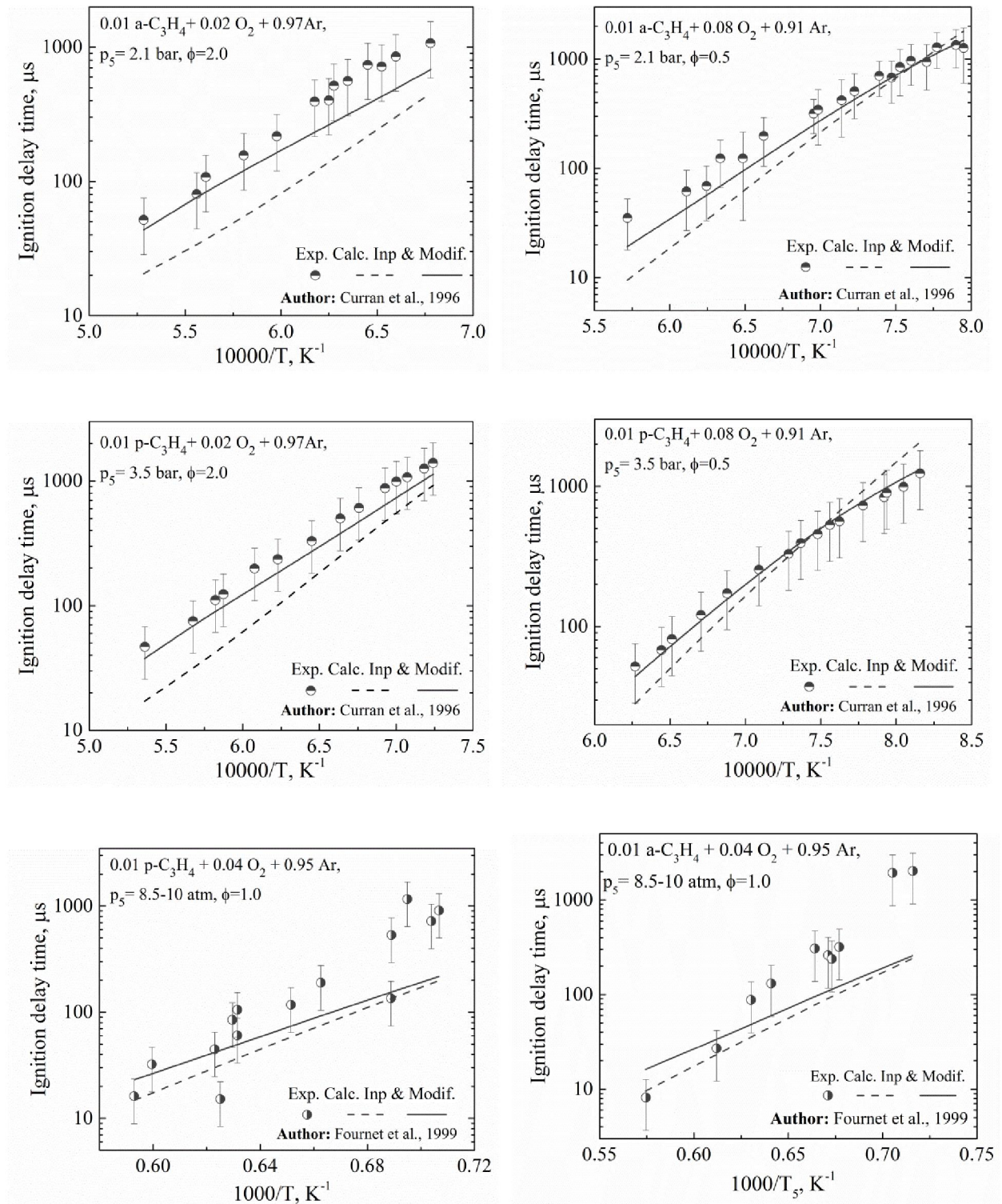


Figure 3 – Comparison between computed (dash line – initial-; solid lines – modified- mechanism) and experimental (symbols) ignition delay times of  $C_3H_4/O_2/Ar$  mixtures [5, 6]

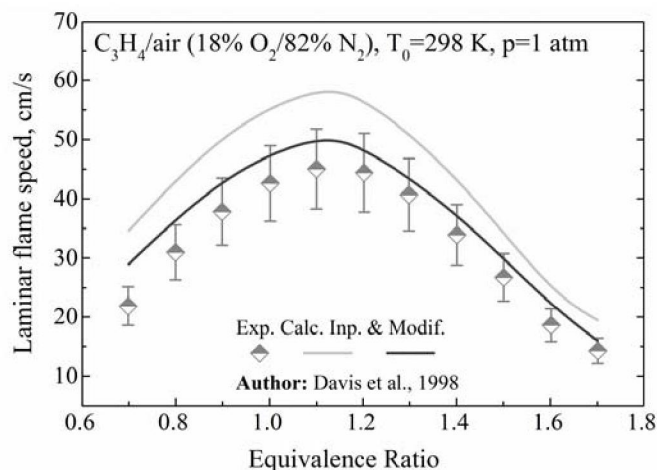


Figure 4 – Experimental (symbol) [7] and computed (line) of the laminar flame speed of  $C_3H_4$ /air flame

The complete scheme of the main reaction paths of oxidation and pyrolysis of allene and propyne at high temperature in  $C_3H_4$ -sub model are shown on the Figure 5.

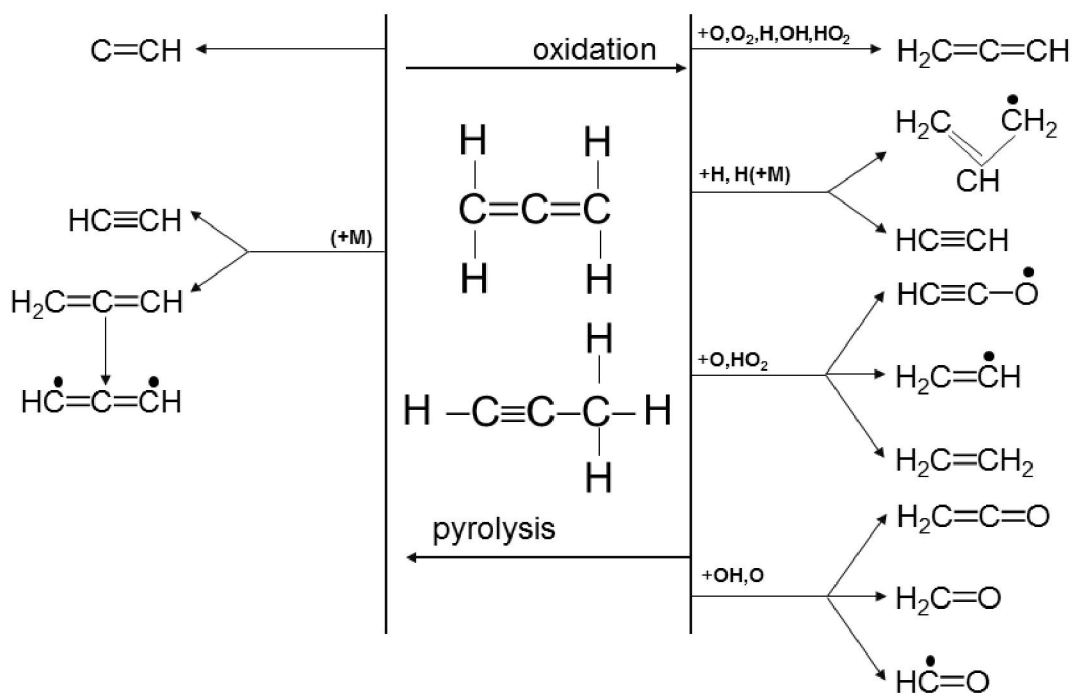


Figure 5 – The major initial stages of oxidation and pyrolysis of allene and propyne in  $C_3H_4$ -sub model

**Conclusion.** A detailed kinetic model was modified and verified against the experimental data of the shock-tube ignition delay and the laminar flame speed data available in the literature. It was shown that sub-mechanism of  $C_3H_4$  predicts the allene and propyne oxidation and pyrolysis at high-temperature data reasonably well. The sensitivity analysis shows that reaction of  $C_3H_4=C_2H+CH_3$  plays the important role in pyrolysis of allene and propyne at high temperature. A detailed kinetic  $C_3H_4$  sub-mechanism of oxidation of allene and propyne for low-temperature will be discussed later.

**Acknowledgments.** The authors are grateful to the German Academic Exchange Service (DAAD) for financial support through the Research Grants for Doctoral Candidates and Young Academic Scientists (2017–2018).

## REFERENCES

- [1] Giri B.R., Fernandes R.X., Bentz T., Hippler H., Olzmann M. (2011) High-temperature kinetics of propyne and allene: Decomposition vs. isomerization, *Proceedings of the Combustion Institute*, 33:267-272. DOI: 10.1016/j.proci.2010.05.072
- [2] Klippenstein S.J., Miller J.A., Jasper A.W. (2015) Kinetics of propargyl radical dissociation, *J. Phys. Chem. A*, 119:7780-7791. DOI: 10.1021/acs.jpca.5b01127
- [3] Vourliotakis G., Malliotakis Z., Keramiotis Ch., Skevis G., Founti M.A. (2016) Allene and propyne combustion in premixed flames: a detailed kinetic modeling study, 188: 776-792. DOI: 10.1080/00102202.2016.1138816
- [4] Slavinskaya N.A., Chernov V., Starke J.H., Mirzayeva A., Abassi M., Auyelkhankyzy M. (2017) A modeling study of acetylene oxidation and pyrolysis, *Combustion and flame*, [in press]
- [5] Curran H., Simmie J.M., Dagaut P., Voisin D., Cathonnet M. (1996) The ignition and oxidation of allene and propyne: experiments and kinetic modeling, *Twenty-Sixth Symposium (International) on Combustion/The Combustion Institute*, 26:613-620. DOI: 10.1016/S0082-0784(96)80267-0
- [6] Fournet R., Bauge J.C., Battin-Leclerc F. (1999) Experimental and modeling of oxidation of acetylene, propyne, allene and 1,3-butadiene, *Int. J. Chem. Kinet.*, 31:361-379. DOI: 10.1002/(SICI)1097-4601(1999)31:5<361::AID-KIN6>3.0.CO;2-K
- [7] Davis S.G., Law C.K., Wang H. (1998) An experimental and kinetic modeling study of propyne oxidation, *Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute*, 27:305-312. DOI: 10.1016/S0082-0784(98)80417-7
- [8] Kee R.J., Rupley F.M., Miller (1993) JA. Report NSAND89-8009B, Sandia Laboratories Report
- [9] <http://www.kinetechlab.com/products/chemical-workbench/>
- [10] Davis S.G., Law C.K., Wang H. (1999) Propene pyrolysis and oxidation kinetics in a flow reactor and laminar flames, *Combustion and flame*, 199:375-399. DOI: 10.1016/S0010-2180(99)00070-X
- [11] Curran H.J., Gaffuri P., Pitz W.J., Westbrook C.K. (2002) A comprehensive modeling study of iso-octane oxidation, *Combustion and flame*, 129:253-280. DOI: 10.1016/S0010-2180(01)00373-X
- [12] Bentz T., Giri B.R., Hippler H., Olzmann M., Striebel F., Syori M. (2007) Reaction of hydrogen atoms with propyne at high temperatures: an experimental and theoretical study, *J. Phys. Chem. A*, 111:3812-3818. DOI: 10.1021/jp070833c
- [13] Miller J.A., Senosiain P., Klippenstein S.J., Georgievskii Z. (2008) Reactions over multiple, interconnected potential wells: unimolecular and bimolecular reactions on a C<sub>3</sub>H<sub>5</sub> potential, *J Phys Chem A.*, 112:9429-38. DOI: 10.1021/jp804510k
- [14] Rosado-Reyes C.M., Manion J.A., Tsang W. (2010) Kinetics of the thermal reaction of H atoms with propyne, *J. Phys. Chem. A*, 114:5710-5717. DOI: 10.1021/jp9122858
- [15] Hidaka Y., Nakamura T., Miyauchi A., Shiraiishi T., Kawano H. (1989) Thermal decomposition of propyne and allene in shock waves, *Intern. J. Chem. Kinet.*, 21:643-666. DOI: 10.1002/kin.550210805
- [16] Tsang W. (1991) Chemical kinetic data base for combustion chemistry. Part V. Propene, *J. Phys. Chem. Ref. Data*, 20:221-273. DOI: 10.1063/1.555880
- [17] Kern R.D., Xie K. (1991) Shock tube studies of gas phase reactions preceding, *Prog. Energy Combust. Sci.*, 17:191-210. DOI: 10.1016/0360-1285(91)90010-K
- [18] Wang B., Hou H., Gu Y. (2000) Mechanism and rate constant of the reaction of atomic hydrogen with propyne, *J. Chem. Phys.*, 112:8458-8465. DOI: 10.1063/1.481484
- [19] Fernandes R.X., Giri B.R., Hippler H., Kachiani C., Striebel F. (2005) Shock wave study on the thermal unimolecular decomposition of allyl radicals, *J. Phys. Chem. A*, 109:1063-1070. DOI: 10.1021/jp047482b
- [20] Peukert S.L., Labbe N.J., Sivaramkrishnan R., Michael J.V. (2013) Direct measurements of rate constants for the reactions of CH<sub>3</sub> radicals with C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>2</sub> at high temperatures, *J. Phys. Chem. A*, 117:10228-10238. DOI: 10.1021/jp4073153
- [21] Zhang H.Z., McKimmon J.T. (1995) Elementary reaction modeling of high-temperature benzene combustion, *Combustion Science and Technology*, 107:261-300. DOI: 10.1080/00102209508907808
- [22] Manion J.A., Huie R.E., Levin R.D., Burgess D.R., Orkin V.L., Tsang W., McGivern W.S., Hudgens J.V., Knyazev V.D., Atkinson D.B., Chai E., Tereza A.M., Lin C.Y., Allison T.C., Mallard W.G., Westley F., Herron J.G., Hampson R.F., Frizzell D.H. NIST Chemical Kinetics Database, NIST Standard Reference Database 17, Version 7.0 (Web Version), Release 1.6.8, Data version 2015.12, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899-8320. <http://kinetics.nist.gov/>
- [23] Leung K.M., Lindstedt R.P. (1995) Detailed kinetic modeling of C<sub>1</sub>-C<sub>3</sub> alkane diffusion flames, *Combustion and flame*, 102:129-160. DOI: 10.1016/0010-2180(94)00254-P
- [24] Miller J.A., Melius C.F. (1992) Kinetics and thermodynamic issues in the formation of aromatic compounds in flames of aliphatic fuels, *Combustion and flame* 91:21-39. DOI: 10.1016/0010-2180(92)90124-8

М. Әуелханқызы<sup>1,2</sup>, М. Аббаси<sup>1</sup>, Н. А. Славинская<sup>1</sup>, З. А. Мансуров<sup>2</sup>

<sup>1</sup>Жану технологияларының институты, Неміс аэроғарыш орталығы (НАО), Штутгарт, Германия,

<sup>2</sup>Әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан

### АЛЛЕН ЖӘНЕ ПРОПИННІҢ ТОТЫҒУ РЕАКЦИЯСЫНЫҢ МЕХАНИЗМІ

**Аннотация.** Көмірсутектер жанғанда түзілетін аллен және пропиннің химиясын толық зерттеу өте маңызды, себебі олар пропаргил радикалының ( $H_2CCCH$ ) прекурсорлары болып табылады. Пропаргил радикал, полициклді ароматты көмірсутектердің (ПЦАК) және күйе бөлшектерінің түзілуінде бастапқы рөл атқаратын бірінші ароматты молекула – бензолдың түзілуінде өте маңызды.

Осы мақалада НАО-ның реакциялық базасы негізінде аллен мен пропиннің тотығуының суб-механизмінің кинетикалық реакциясын жасауға көңіл бөлінді. Аллен мен пропиннің химиясы бұрын жарияланған ПЦАК бар  $C_2$  механизмнің бір бөлігі болып табылады.  $C_3H_4$  суб-механизміндегі реакцияларға жарияланған зерттеу жұмыстар негізінде талдау жасалды. Тұтану уақыты және ламинарлы жалын жылдамдығының эксперименттік деректері реакция механизмін тексеру және оңтайландыру үшін пайдаланылды. Нәтижесінде, механизмге 6 реакция қосылды; төменгі ( $T < 1500K$ ) және жоғары температурада ( $T > 1500K$ ) тұтану уақытын сипаттау үшін 7 реакцияның жылдамдық константасы жанартылды.  $C_3H_4 + H = H_2CCCH + H_2$ ,  $C_3H_4 + H = CH_3 + C_2H_2$  және  $C_3H_4 + HO_2 = H_2CCCH + H_2O_2$  реакцияларының жылдамдық коэффициенттері деректерді статистикалық өңдеу арқылы бағаланды. Өңделген модел аллен және пропин қоспасы үшін  $p_5 = 2-10$  бар,  $T_5 = 1100-1840$  К,  $\phi = 0,5-2,0$  кезінде тұтану уақытын және  $T_0 = 298K$ ,  $p = 1$  бар,  $\phi = 0,6-1,8$  кезіндегі ламинарлы жалынның жылдамдығын толық сипаттайды.

**Түйін сөздер:** моделдеу, механизм, аллена, пропен, тотығу.

М. Ауелханқызы<sup>1,2</sup>, М. Аббаси<sup>1</sup>, Н.А. Славинская<sup>1</sup>, З.А. Мансуров<sup>2</sup>

<sup>1</sup>Институт Технологий горения (НАЦ), Штутгарт, Германия,

<sup>2</sup>Казахский национальный университет им. аль-Фараби, Алматы, Казахстан

### МЕХАНИЗМ РЕАКЦИЙ ОКИСЛЕНИЯ АЛЛЕНА И ПРОПИНА

**Аннотация.** Изучение детальной химии аллена и пропина при горении углеводородов очень актуально, поскольку они являются прекурсорами пропаргильного радикала ( $H_2CCCH$ ). Пропаргильный радикал играет основную роль в образовании первой ароматической молекулы, бензола, который дает старт росту полициклических ароматических углеводородов (ПЦАУ) и образованию сажи.

В настоящей работе основное внимание уделяется разработке реакционного кинетического суб-механизма для окисления аллена и пропина, входящего в реакционную базу НАЦ (DLR). Детальная химия аллена и пропина является частью ранее опубликованного механизма  $C_2$  с образованием ПЦАУ. Суб-механизм реакции  $C_3H_4$  был проанализирован на базе опубликованных исследований. Экспериментальные данные по временам задержек воспламенения и скоростям ламинарных пламен были использованы для тестирования и оптимизации реакционного механизма. В результате механизм был дополнен 6 реакциями; константы скоростей 7 реакций для низкотемпературного ( $T < 1500K$ ) и высокотемпературного ( $T > 1500K$ ) воспламенения были модифицированы. При этом коэффициенты скоростей реакций  $C_3H_4 + H = H_2CCCH + H_2$ ,  $C_3H_4 + H = CH_3 + C_2H_2$  и  $C_3H_4 + HO_2 = H_2CCCH + H_2O_2$  были оценены путем статистической обработки данных. Модифицированная модель удовлетворительно воспроизводит времена задержек воспламенения для смесей аллена и пропина при  $p_5 = 2-10$  бар,  $T_5 = 1100-1840$  К,  $\phi = 0,5-2,0$  и скорости ламинарных пламен для аллена при  $T_0 = 298K$ ,  $p = 1$  бар,  $\phi = 0,6-1,8$ .

**Ключевые слова:** моделирование, механизм, аллен, пропин, окисления.