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Experimental and modelling study of speciation and benzene formation pathways in premixed 1-hexene flames

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This work contains supplementary material.

Abstract

An existing detailed and broadly validated kinetic scheme is augmented to capture the flame chemistry of 1-hexene under stoichiometric and fuel rich conditions including benzene formation pathways. In addition, the speciation in a premixed stoichiometric 1-hexene flame (flat-flame McKenna-type burner) has been studied under a reduced pressure of 20-30 mbar applying flame-sampling molecular-beam time-of-flight mass spectrometry and photoionization by tunable vacuum-ultraviolet synchrotron radiation. Mole fraction profiles of 40 different species have been measured and validated against the new detailed chemical reaction model consisting of 275 species and 3047 reversible elementary reactions. A good agreement of modelling results with the experimentally observed mole fraction profiles has been found under both stoichiometric and fuel rich conditions providing a sound basis for analyzing benzene formation pathways during 1-hexene combustion. The analysis clearly shows that benzene formation via the fulvene intermediate is a very important pathway for 1-hexene, which is different to previous findings based on the same kinetic model for fuel rich C_2-C_4 flames.

Keywords: 1-hexene flames, benzene formation pathways, molecular beam sampling, soft single photon, near threshold ionization, kinetic modelling.

1.0 Introduction

In today's world, the demand for more efficient and cleaner combustors is still increasing day by day. That's why combustion modeling remains an interesting subject which helps us to fulfill this demand. A very general and fundamental approach is to model the oxidation of a fuel by formulating a reaction mechanism which contains all the necessary kinetic information about the important chemical reactions involved, starting with the fuel molecule, including the broad variety of intermediate species and ending up with the final products, which can contain, especially under fuel rich conditions, also particulate matter like soot [1-4]. The mechanisms are usually provided together with thermodynamic data of the included species for calculating the rate coefficients of backward reactions (which is only valid in case the condition of detailed balance is fulfilled [5]) and transport data for the numeric simulation of diffusion, e.g. in flames [2]. Such mechanisms can be used in engineering applications for identifying favorable operating conditions for commercial combustors with regard to efficiency and emissions, but they are also used in fundamental research for establishing reliable oxidation schemes of hydrocarbons [1-8]. These models can provide a detailed chemical picture about the formation pathways of polyaromatic hydrocarbons and soot particles when successfully validated against experimental species concentration profiles [3,4,8-12]. Understanding the mechanism of the latter process is of paramount importance because of the commercial and climatic relevance of soot and its negative effect on human health. In this context the formation of benzene, the first aromatic ring, is considered to be the crucial initial step [3,4,12-18].

In the present work an existing kinetic hydrocarbon oxidation model is augmented to simulate the oxidation of 1-hexene in laminar premixed flames. The experimental data set covers the speciation in two fuel rich [19, 20] and one stoichiometric 1-hexene flame. The latter experiment is new and a result of the present joint experimental and modelling study.

There are several aspects that motivated this work. Totally independent of the value of the new reference data for the improvement of our kinetic model we can state that 1-hexene is an important decomposition intermediate in the pyrolysis and combustion of large alkanes like n-heptane and n-decane [21]. Among the three linear hexene isomers, 1-hexene is the most reactive one [21]. 1-hexene is also one of the important decomposition products of cycloalkanes and the first product formed in the combustion of cyclohexane [22]. Furthermore, biofuels contain a large amount of unsaturated fatty esters. The reactivity and number of double bonds affect the Cetane number of biofuels [23].

Besides these practical considerations, there are several points that make the speciation in 1-hexene flames an ideal experimental target for testing the comprehensiveness of our kinetic model and our long term compilation strategy. Firstly, the model has been so far only used to explore the flame chemistry of small, gaseous unsaturated C_2 to C_4 fuels [4,24,25] or the larger aliphatic n-heptane [26] and the aromatic toluene [27]. Thus, the 1-hexene data obviously fill a gap in the chemical diversity of our fuel target pool. Secondly, we claimed in a recent study on NCN formation in premixed methane and acetylene flames [28] that the rather well performance of our kinetic model and its applicability to both flames without alterations is due to its well performance in predicting H atom concentrations. However, H atom profiles have so far not been used as a validation target because they are often not provided in studies on flame chemistry [8-11, 24-26 and literature cited therein]. Therefore, the availability of both H atom and OH radical concentration profiles, the reactant and product of the most sensitive chain branching reaction in combustion chemistry, represents a critical test of our previous claim. Thirdly, we aim at assessing the benzene formation pathways in fuel rich 1-hexene flames based on a mass flow analysis using a comprehensive kinetic model, which is validated for as many fuels, reactors, combustion parameters (temperature, pressure, mixture strength), global (flame speed, ignition delay times) and local (speciation as function of time or position) indicators of chemical reactivity as possible. The joint experimental and theoretical facilities used here to address the latter issue have been developed in a long-term effort with the focus exactly directed to address this problem [8-12, 19].

2.0 Experimental

The validation targets for the kinetic model are mole fraction profiles of premixed laminar low-pressure $C_6H_{12}/O_2/Ar$ flames for equivalence ratios of 1.0, 1.7 and 2.0. The flame conditions of the three flames are given in Table 1.

-Place Table 1 approximately here-

The flames were stabilized on a flat-flame McKenna-type burner, with the gas flows being controlled with calibrated mass flow controllers and the flow of 1-hexene being metered by a syringe pump, evaporated, and added quantitatively added into the oxidizer stream.

Quantitative mole fraction profiles of more than 40 species from within each flame were measured using flame-sampling molecular-beam mass spectrometry with isomer-resolving capabilities. The details of the apparatus and procedures have been published elsewhere and are not repeated here [29-31]. Only a few important aspects are highlighted, which are important for the purpose of validating the newly developed mechanism.

As pointed out in similar previous studies, we expect the accuracies of the mole fraction profiles to be within 20 % for the major species, but somewhat larger for the intermediates [12,19,30]. The relative comparisons of the mole fractions, profile shapes, and positions between the three flames of this study should have smaller uncertainties because the experimental and analysis procedures have been the same for all three flames. The sources for the uncertainties of the individual mole fraction profiles include errors in the mass discrimination factors, the respective photoionization cross section used in the analysis, and the degree to which the target signal can be separated from overlaps caused by dissociative ionization of higher-mass species. This level of the experimental uncertainty is normally considered sufficient, because current combustion chemistry models rarely contain rate coefficients better than a factor of two in accuracy. Furthermore, it is expected that the experimental spatial location has an absolute accuracy of ±0.5 mm.

The flame temperatures were measured using OH laser-induced fluorescence (LIF) according to the procedure described in Ref. [12] and after smoothing, the profiles were used as input for the model calculations. Again, the levels of accuracy (~150 K in the postflame zone and somewhat larger in the preheat zone) are expected to be sufficient for the modeling purposes. As a matter of fact, Dooley *et al*. have shown that even worst-case disturbances to the measured temperature profile are likely to not alter any mechanistic conclusions drawn from modeling results [32].

3.0 Chemical kinetic model

The development of the sub-mechanism for 1-hexene oxidation follows the general concept introduced for the augmentation of the C1-C4 core chemistry for n-heptane degradation [26]. The sub-mechanism is divided into 25 reaction classes following the approach of Curran et al. [7], also introduced for n-heptane oxidation. Additional rules, proposed by Ranzi and co-workers [21], have been applied for deriving kinetic data for reactions involving double bonds and dienes. The current baseline mechanism builds on the model of Hoyermann et al. [8], which was developed with a special focus on tracing benzene formation pathways in acetylene, propene, and mixed propene flames. This modelling study and the experimental studies of the Kohse-Höinghaus group [9-11] were the first works, in which the focus was directed on flame pairs and multi-fuel kinetic models in order to make the benzene formation pathway analysis more reliable (see e.g. the discussion in [33] on page 378). Important updates of the mechanism include toluene oxidation [27], and recently the flame chemistry of butane and butene isomers [24,25]. In the present study some modifications of the kinetic data were required in order to capture the oxidation of 1-hexene with regard to reactions of C_3H_4 and C_6H_6 species. Because fulvene was observed in the 1-hexene flames and was not initially present in the model, reactions involving this species have been added to the current mechanism using kinetic data provided by [15,16,18].

All flame calculations have been performed with the premixed burner stabilized flame module of the current version of the LOGESoft package [34]. The thermodynamic properties of several new species in the 1-hexene sub-mechanism were evaluated implementing Benson's group additivity method [35]. The Goos, Burcat, Rusic data base was used for thermodynamic data of fulvene [36].

The complete model is composed of 275 species and 3047 reversible elementary reactions and is presented in the supplementary material. It should be mentioned that the model also captures the ignition timing of 1-hexene in shock tube experiments (see supplement) and predicts a laminar flame speed of 43 cm/s for phi=1.0 at standard conditions.

4.0 Results and discussion

First, the main degradation pathways of 1-hexene as revealed by a C-atom mass flow analysis for stoichiometric and fuel rich conditions are discussed. Then a comparison of experimental and modelling results is presented covering reactants, main products, and a series of important intermediates for both the overall combustion process and the formation of benzene. Finally, the formation pathways of benzene are analyzed and the results compared to previous work.

4.1 Degradation of 1-hexene

Common degradation pathways of 1-hexene, which operate for all equivalence ratios, proceed *via* the n-propyl (n-C_3H_7) and the allyl (C_3H_5) radicals. These radicals are formed mainly through a unimolecular C-C-scission of 1-hexene under fuel rich conditions. For the stoichiometric flame n-propyl is formed in addition through bimolecular reactions of H and OH with the fuel molecule. These reactions represent global steps *via* short lived radicals. They were implemented in the kinetic model in analogy to our findings for 1-butene, 2-butene oxidation in fuel rich flames [24] and improved the overall model performance. We note that at high flame temperatures these reactions open additional fast channels to smaller degradation products, whose exact formation mechanisms are often very difficult to isolate in kinetic experiments or to assess in theoretical studies (see also discussion in [24]). These C_3 species further react to C_2 species; especially to ethylene (C_2H_4) which forms via the vinyl radical by dehydrogenation acetylene (C_2H_2). The latter species is important for benzene formation, either directly through the reactions with n-C_4H_5 [6] and i-C_4H_5 [12,37] or *via* the build-up of the propargyl radical [8]. The main degradation pathway of C_2H_2 is the formation of the ketenyl radical (HCCO) in the reaction with O atoms. Ketenyl mainly decomposes to

CH and CO and the oxidation of CO leads finally to the main reaction product CO_2. In the supplementary material detailed mass flow analysis are presented for Φ=1.0 and Φ=2.0 illustrating the high mass flows through C_2H_4, C_2H_3 and C_2H_2 and HCCO. The compilation (based on kinetic data from extensive studies by Miller, Temps, Wagner, and co-workers [see e.g. 15,16,38]) and the validation of the sub-mechanism involving these C_2 species and their chemical coupling to C_3 species via reactions of acetylene with CH, $^3CH_2$ and $^1CH_2$ is the chemical core of our flame model and also of paramount importance for the prediction flame speeds as extensively discussed in [8,26]. The kinetic data of this sub-mechanism remained largely unchanged. Due to the complexity of a C_6 fuel there exist many minor fuel degradation pathways via C_4 and C_5 species. These pathways are illustrated in the detailed flow analysis in the supplementary material. A detailed discussion of this chemistry is not presented here with regard to focus on benzene formation. However, one minor pathway of 1-hexene degradation has to be mentioned. In the kinetic model the formation of cyclohexane and its dehydrogenation to benzene is implemented [27,39-41] and the importance for benzene formation is discussed below.

4.2 Species profiles

In this section the mole fraction profiles of reactants, final product and selected intermediates are discussed. Predominantly those Intermediates are shown which are of relevance for benzene formation (e.g. C_3H_3) or for overall reactivity (H atoms, OH radical).

Major species and temperature profile

Figure 1 shows the mole fractions of the stable main products in 1-hexene/O_2/Ar Φ=1.0, 1.7 and 2.0 flames. In general, the model shows for 1-hexene, O_2, CO, CO_2, O_2, H_2O, H_2 and Ar very good agreement with the experiments. The CO profile at Φ=1.0 is slightly underpredicted (although within error range), at other equivalence ratios it is very well predicted. For Φ=1.7, the experimental values of 1-hexene decomposition at the burner surface are lower than in the simulation, but this region is in general difficult to model [25].

Experimental temperature profiles are used for the simulation. They are given in lower panel Figure 1.

H atoms, hydroxyl , methyl, and methane

Figure 2 shows the profiles of the small transient species, which propagate the combustion process, namely the H atom and the OH radical and the CH_3 radical together with the stable CH_4. H atom and OH radical profiles have not been used for model validation in previous work on flame chemistry. The comparison in Figure 2 shows that for the stoichiometric case both H and OH profiles are captured very well by the simulation, whereas under fuel rich conditions, especially for Φ=2.0 the agreement becomes less convincing. However, the overprediction of about a factor of 2 seems acceptable since no efforts have been made to alter kinetic data for improving H atom predictions. The reason is the high sensitivity on other experimental targets of the reactions, which control H and OH profiles. We note that the inclusion of soot formation did only marginally affect the predicted H atom concentration. Also the OH mole fraction profiles are overpredicted but here the experimental data is taken at the detection limit. CH_3 profiles are nicely captured by the model for all flames, CH_4 is slightly underpredicted. As mentioned above, the reactions controlling these species are the central part of our flame model, which was not altered in this work. Accepting slightly larger errors for these species than in single fuel kinetic models is the price or the consequence of our modelling approach. Nevertheless, we aim at improving the predictions of these species in future work. The validation will then be against the complete target set of our fuel pool.

C_2 and C_3 species relevant for benzene formation

As outlined above, the main degradation pathways lead to the accumulation of C_2H_4 and C_2H_2 and these species can further react to C_3 species. Additionally, C_3H_5 is formed promptly via the decomposition of 1-hexene, especially under fuel rich conditions. This means that the propargyl radical (C_3H_3) is formed from two pathways, which operate on different chemical time scales, namely the build-up from acetylene and dehydrogenation of allyl [8]. The early formation of allyl is specific for the 1-hexene flame. Since several assumed benzene pathways proceed via allyl, we find a fuel specific chemical environment for benzene formation. However, before we draw conclusions on this part of the 1-hexene flame chemistry it must be shown that the mole fraction profiles of abovementioned intermediates are captured by the model. This validation is shown in Figure 3. In general, a good agreement between experiment and model predictions is found for all equivalence ratios. The minor deviations are within the experimental error. For some species like C_3H_6, the peak position is not exactly met by the simulation, which may leave room for future model improvement but might also be an effect of the molecular beam sampling technique.

4.3 Benzene formation pathways

In the section above it was shown that the chemical model captures benzene precursor mole fraction profiles providing a sound basis for analyzing benzene formation pathways. The first important observation is that the benzene profile is not captured (lower panel of Figure 4) with the benzene build chemistry of the old mechanism [8], which was validated for a number of C_2-C_4 flames [8,24,25]. However, the sizeable concentrations of fulvene in the $\Phi=2.0$ flame indicate that benzene formation via this intermediate plays an important role. Therefore we implemented benzene formation pathways via fulvene [15,16,18] in our model. With this change both fulvene and benzene mole fraction profiles could be successfully modelled (see upper panels of Figure 4). The mass flow analysis shows that benzene formation is dominated by the fulvene pathway (~69%), followed by propargyl recombination (~12%) and the minor pathways of dehydrogenation of cyclohexane (~8%) and the *n*-C_4H_5 + C_2H_2 (~3.5%) reaction. This analysis shows that the simultaneous measurement of fulvene and benzene concentrations was the key for deriving the contributions for the individual pathways. The findings indicate that benzene formation *via* fulvene may also apply for other flames, which can be tested by the experimental approach applied in this work.

5. Conclusions

We have shown that an existing kinetic model can be augmented for simulating the 1-hexene flame chemistry including benzene formation. New experimental data on speciation in a stoichiometric premixed 1-hexene flame were provided employing flame-sampling molecular-beam time-of-flight mass spectrometry and photoionization by tunable vacuum-ultraviolet synchrotron radiation. The model shows for a large range of species and flame stoichiometries good agreement with experimental data. For the stoichiometric case H atom and OH radical profiles were well captured, for the fuel rich case a slight underprediction up to a factor of 2 was found. The main conclusion is that 1-hexene shows specific benzene formation pathways, dominated by the route *via* fulvene. This specialty of 1-hexene is shared with its isomer, cyclohexane, which also shows a specific benzene formation pathway *via* successive H atom abstraction. This hydrogenation pathway contributes to 8% of benzene formation in the 1-hexene flames. The direct dehydrogenation of 1-hexene does not contribute to benzene formation. The reason for this interesting behavior is probably the different unimolecular chemistry: A prompt formation of C_3 species (allyl) by C-C fission in case of 1-hexene and a hindered unimolecular decomposition in case of cyclohexane due to the stability of the 6-ring.

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References

[1] J. Warnatz, in: W. C. Gardiner Jr.(Ed.), Combustion Chemistry, Springer, New York, 1984.

[2] J. Warnatz, U. Maas and R. W. Dibble, Combustion, Springer, Heidelberg, 1997.

[3] M. Frenklach, J. Warnatz, Combust. Sci. Technol. 51 (4–6) (1987) 265–283.

[4] H. Wang, Proc. Combust. Inst. 33 (2011) 41-67.

[5] J. A. Miller, S. J. Klippenstein, S. H. Robertson, M. J. Pilling, N. J. B. Green. Phys. Chem. Chem. Phys. 11 (2009) 1128–1137.

[6] H. Wang and M. Frenklach, Combust. Flame 110 (1997) 173-221.

[7] H. J. Curran, P. Gaffuri, W. J. Pitz and C. K. Westbrook, Combust. Flame 114 (1998) 149-177.

[8] K. Hoyermann, F. Mauss, T. Zeuch. Phys. Chem. Chem. Phys. 6 (14) (2004) 3824-3835.

[9] B. Atakan, A. T. Hartlieb, J. Brand, K. Kohse-Höinghaus, Proc. Combust. Inst. 27 (1998) 435-444.

[10] A. Lamprecht, B. Atakan, K. Kohse-Höinghaus, Combust. Flame 122 (2000) 483-491.

[11] B. Atakan, A. Lamprecht, K. Kohse-Höinghaus, Combust. Flame, 133 (2003) 431-440.

[12] N. Hansen, J.A. Miller, T. Kasper, K. Kohse-Höinghaus, P.R. Westmoreland, J. Wang, T.A. Cool, Proc. Combust. Inst. 32 (1) (2009) 623–630.

[13] P.R. Westmoreland, A.M. Dean, J.B. Howard, J.P. Longwell, J. Phys. Chem. 93 (25) (1989) 8171–8180.

[14] J.A. Cole, J.D. Bittner, J.P. Longwell, J.B. Howard, Combust. Flame 56 (1) (1984) 51–70.

[15] J.A. Miller, C.F. Melius, Combust. Flame 91 (1) (1992) 21–39.

[16] C.J. Pope, J.A. Miller, Proc. Combust. Inst. 28 (2) (2000) 1519–1527.

[17] J.A. Miller, S.J. Klippenstein, J. Phys. Chem. A 107 (39) (2003) 7783–7799.

[18] N.M. Marinov, M.J. Castaldi, C.F. Melius, W. Tsang, Combust. Sci. Technol. 128 (1997) 295–342.

[19] N. Hansen, T. Kasper, B. Yang, T.A. Cool, W. Li, P.R. Westmoreland, P. Oßwald, K. Kohse-Höinghaus, Proc. Combust. Inst. 33 (1) (2011) 585–592.

[20] N. Hansen, W. Li, M. E. Law, T. Kasper, P. R. Westmoreland, B. Yang, T. A. Cool and A. Lucassen. Phys. Chem. Chem. Phys. (2010) 12(38) 12112-12122.

[21] M. Mehl, G. Vanhove, W. J. Pitz, E. Ranzi, Combust. Flame 155 (2008) 756-772.

[22] J. H. Kiefer, K. S. Gupte, L. B. Harding, S. J. Klippenstein, J. Phys. Chem. A 113 (2009) 13570-13583.

[23] M. Mehl, T. Faravelli, F. Giavazzi, E. Ranzi, P. Scorletti, A. Tardani, D. Terna, Energy Fuels 20 (6) (2006) 2391–2398.

[24] P. Oßwald, K. Kohse-Höinghaus, U. Struckmeier, T. Zeuch, L. Seidel, L. Leon, F. Mauß, Z. Phys. Chem. 225 (9-10) (2011) 1029–1054.

[25] M. Schenk, L. Leon, K. Moshammer, P. Oßwald, T. Zeuch, L. Seidel, F. Mauß, K. Kohse-Höinghaus, Combust. Flame 160 (2013) 487-503.

[26] S.S. Ahmed, F. Mauss., G. Moréac, T. Zeuch, Phys. Chem. Chem. Phys. 9 (2007) 1107–1126.

[27] S.S. Ahmed, F. Mauß, T. Zeuch, Z. Phys. Chem. 223 (2009) 551–563.

[28] E. Goos, C. Sickfeld, F. Mauß, L. Seidel, B. Ruscic, A. Burcat, T. Zeuch, Proc. Combust. Inst. 34 (2013) 657–666.

[29] T. A. Cool, A. McIlroy, F. Qi, P.R. Westmoreland, L. Poisson, D.S. Peterka, M. Ahmed, Rev. Sci. Instrum. 76 (2005) 094102.

[30] N. Hansen, T. A. Cool, P.R. Westmoreland, K. Kohse-Höinghaus, Progr. Energy Combust. Sci. 35 (2009) 168-191.

[31] P. Osswald, U. Struckmeier, T. Kasper, K. Kohse-Höinghaus, J. Wang, T.A. Cool, N. Hansen, P.R. Westmoreland, J. Phys. Chem. A, 111 (2007) 4093-4103.

[32] S. Dooley, F.L. Dryer, B. Yang, J. Wang, T.A. Cool, T. Kasper, N. Hansen, Combust. Flame 158 (4) (2011) 732-741.

[33] H.R. Zhang, E.G. Eddings, A.F. Sarofim, C.K. Westbrook, Proc. Combust. Inst. 32 (2009) 377–385.

[34] LOGEsoft: http://loge.se/Products/LOGE_Products.html

[35] S.W. Benson Thermochemical Kinetics. John Wiley and Sons, Inc., New York, 1976.

[36] E. Goos, A. Burcat, B. Ruscic, “Extended Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with updates from Active Thermochemical Tables”; available at ftp://ftp.technion.ac.il/pub/supported/aetdd/thermodynamics/

[37] N. Hansen, S. J. Klippenstein, C. A. Taatjes, et al. J. Phys. Chem. A 110 (10) (2006) 3670-3678.

[38] T. Böhland, K. Héberger, F. Temps, H. Gg. Wagner, Ber. Bunsen-Ges. Phys. Chem. 93 (1989) 80-87.

[39] W. Tsang, International Journal of Chemical Kinetics 10 (1978) 1119–1138.

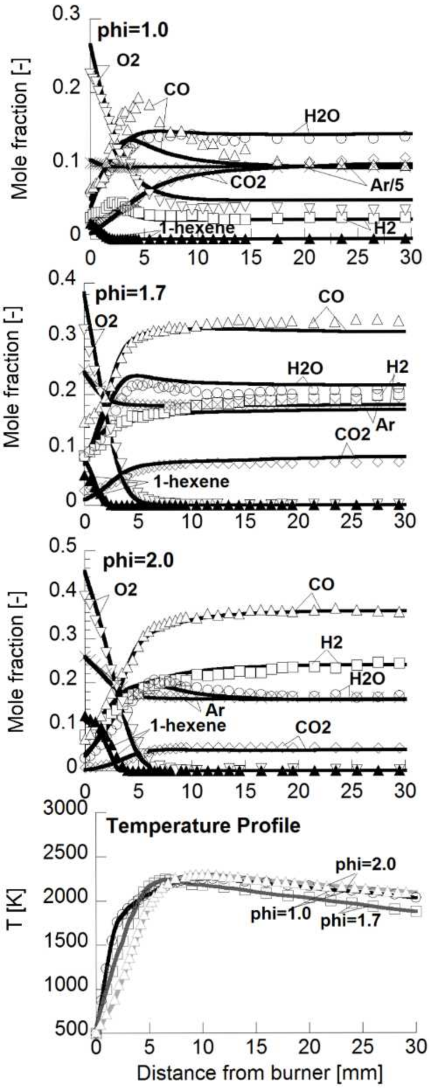
[40] D. Voisin, A. Marchal, M. Reuillon, J.-C. Boettner, M. Cathonnet, Combust. Sci. Tech 138 (1-6) (1998) 137–158.

[41] H. R. Zhang, L. K. Huynh, N. Kungwan, Z. Yang, S. Zhang, J. Phys. Chem. A 111 (2007) 4102–4115.

Table 1: Flame Conditions

	Φ	1-hexene	O_2	Ar	Pressure (Torr)	cold gas velocity (cm s^{-1})
Flame 1	1.0	4.0	36.0	60.0	15	128.1
Flame 2[a)]	1.7	11.1	58.9	30.0	30	49.2
Flame 3[b)]	2.0	12.7	57.3	30.0	30	49.2

a) Ref. [19] b) Ref. [20]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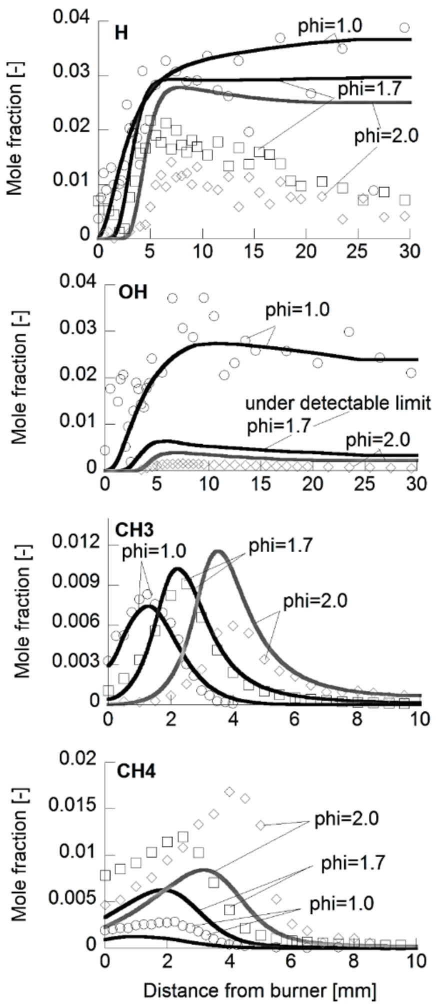
CO
H2O
CO2
Ar/5
1-hexene
H2
phi=1.7
O2
CO
H2O
H2
CO2
Ar
1-hexene
phi=2.0
O2
CO
H2
H2O
Ar
1-hexene
CO2
Mole fraction [-]
0
0.1
0.2
0.3
0.4
0.5
Temperature Profile
phi=2.0
phi=1.0
phi=1.7
T [K]
500
1000
1500
2000
2500
3000
0
5
10
15
20
25
30
Distance from burner [mm]

Figure 1


H
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phi=1.7
phi=2.0
Mole fraction [-]
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0.03
0.02
0.01
0
0
5
10
15
20
25
30
OH
phi=1.0
under detectable limit
phi=1.7
phi=2.0
Mole fraction [-]
0.04
0.03
0.02
0.01
0
0
5
10
15
20
25
30
CH3
phi=1.0
phi=1.7
phi=2.0
Mole fraction [-]
0.012
0.009
0.006
0.003
0
0
2
4
6
8
10
CH4
phi=2.0
phi=1.7
phi=1.0
Mole fraction [-]
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0.015
0.01
0.005
0
0
2
4
6
8
10
Distance from burner [mm]

Figure 2

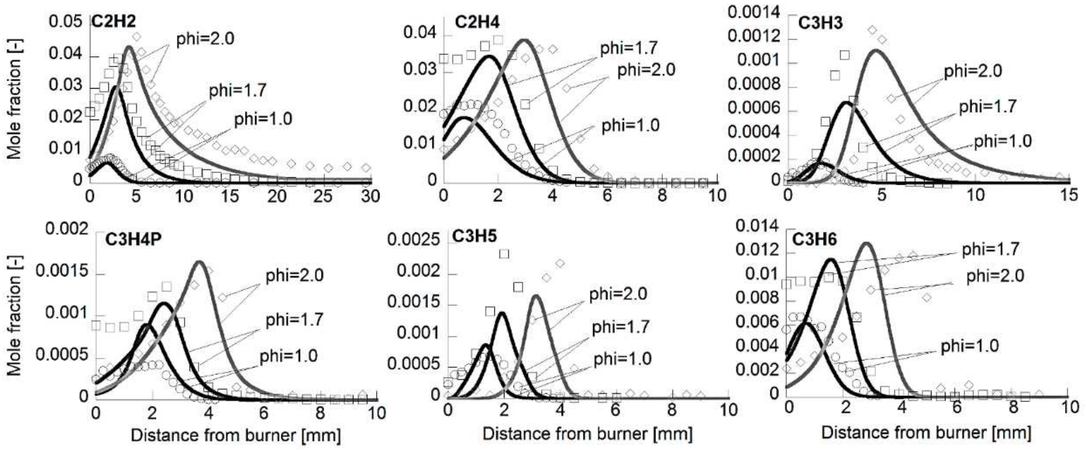
C2H2
phi=2.0
phi=1.7
phi=1.0
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
25
30
Mole fraction [-]
C2H4
phi=1.7
phi=2.0
phi=1.0
0.04
0.03
0.02
0.01
0
0
2
4
6
8
10
C3H3
phi=2.0
phi=1.7
phi=1.0
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
0
5
10
15
C3H4P
phi=2.0
phi=1.7
phi=1.0
0.002
0.0015
0.001
0.0005
0
0
2
4
6
8
10
Mole fraction [-]
Distance from burner [mm]
C3H5
phi=2.0
phi=1.7
phi=1.0
0.0025
0.002
0.0015
0.001
0.0005
0
0
2
4
6
8
10
Distance from burner [mm]
C3H6
phi=1.7
phi=2.0
phi=1.0
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
2
4
6
8
10
Distance from burner [mm]

Figure 3

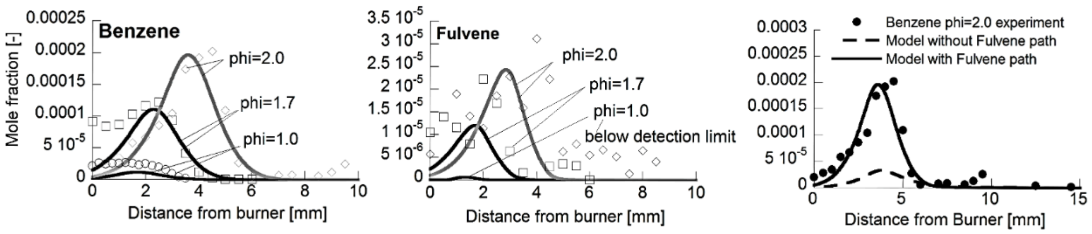
Benzene
Mole fraction [-]
0.00025
0.0002
0.00015
0.0001
5 10-5
0
phi=2.0
phi=1.7
phi=1.0
0
2
4
6
8
10
Distance from burner [mm]
Fulvene
3.5 10-5
3 10-5
2.5 10-5
2 10-5
1.5 10-5
1 10-5
5 10-6
0
phi=2.0
phi=1.7
phi=1.0
below detection limit
0
2
4
6
8
10
Distance from burner [mm]
Benzene phi=2.0 experiment
Model without Fulvene path
Model with Fulvene path
0.0003
0.00025
0.0002
0.00015
0.0001
5 10-5
0
0
5
10
15
Distance from Burner [mm]

Figure 4

List of captions

Fig. 1: Measured major species (dots) and model prediction (lines) for the 3 flames and the measured temperature profile and model input.

Fig. 2: Measurement for OH, H, CH3 and CH4.Lines: model prediction.

Fig. 3: Measurement for C2H2, C2H4, C3H5, C3H4P, C2H5 and C3H6. Lines: model prediction

Fig. 4: Measurement for benzene, fulvene and influence of fulvene chemistry on the benzene formation. Lines: model prediction

Supplemental Material

- Hexene_supp_validation.pdf – A .pdf document with additional plots showing the validation of all measured species, ignition delay time and a flux diagram for each flame.
- Expt_temp_profile_hexene_phi1.0.txt – Experimental temperature profile
- Expt_temp_profile_hexene_phi1.7.txt – Experimental temperature profile
- Expt_temp_profile_hexene_phi1.7.txt - Experimental temperature profile
- Expt_hexene_flame_phi1.0.txt – Measured data for phi=1.0
- Expt_hexene_flame_phi1.7.txt – Measured data for phi=1.7
- Expt_hexene_flame_phi2.0.txt – Measured data for phi=2.0
- 1-Hexene_mechanism.txt – The reaction scheme in standard format
- 1-Hexene_therm.txt – The thermodynamic datat
- 1-Hexene_tran.txt – The transport data