

The chemical structure of low-pressure premixed flames fired by *iso*-butanol/1,3-butadiene mixtures

M. Braun-Unkhoff^{1,*}, T. Kathrotia², and N. Hansen³

¹Institute of Combustion Technology, German Aerospace Center (DLR), Stuttgart, Germany

²Institute of Combustion Technology for Aerospace Engineering, Stuttgart University,

³Sandia National Laboratories, Combustion Research Facility, USA

Abstract

The objective of the present work is to develop a detailed combustion chemistry model for a combined *iso*-butanol/1,3-butadiene flame, which allows to identify the important pathways for butadiene and *iso*-butanol oxidation as well as for formation of aromatic species and their precursors. In particular, the importance of vinyl addition to 1,3-C₄H₆ and/or C₄H₄ to benzene formation is studied. To this end, detailed kinetic modeling results are compared against flame-sampling molecular-beam mass spectrometry data of three fuel-rich laminar premixed flames. The experimental data are obtained by utilizing photoionization by tunable vacuum-ultraviolet synchrotron radiation allowing the identification and separation of combustion species by their characteristic ionization energies. The chemical kinetic model based on the reaction set that was used previously [Hansen *et al.*, *Proc. Combust. Inst.*, **2015**, 35(1), 771-778] was now extended by an *iso*-butanol sub-model to describe *iso*-butanol oxidation. The predicted mole fraction profiles for important species in the mass range from $m/z=2$ (H₂) to $m/z=78$ (benzene) are in reasonable agreement with the experimentally observed profiles thus allowing for an assessment of the importance of various fuel consumption and benzene formation pathways by using reaction flux and sensitivity analyses.

Introduction

This work is part of our efforts to understand the influence of alcohol addition on the flame chemistry of hydrocarbon flames [1]. It is politically motivated by the fact that global warming due to CO₂ emissions, resulting from the combustion of fossil fuels, and rapidly depleting limited resources have triggered the search for new preferably non-fossil based fuels. Many nations currently transition away from petroleum-based fuel sources and promote at the same time the utilization of biomass-derived fuels. However, these bio-fuels are likely to enter the market first as mixtures with conventional hydrocarbon fuels. Indeed, several countries already mandate to mix fossil with biogenic fuels, such as bio-ethanol or bio-diesel, in order to meet self-imposed goals on greenhouse gas emissions.

Scientifically, this work is motivated by the need to develop a detailed combustion chemistry model for combined hydrocarbon/alcohol flames, which allows for identifying the important pathways for hydrocarbon and alcohol oxidation. It is conceivable that the interactions of the reactive intermediates from both components in such fuel blends may have consequences for the overall combustion emission. A particular emphasis of this paper is on the formation of aromatic species and other regulated oxygenated air pollutants such as aldehydes.

For several reasons, especially the butanol isomers (*n*-, 2-, and *iso*-butanol) are of great interest as fuel additives to gasoline. That is, the butanols are sustainably producible and their use promises a less sooting behavior than hydrocarbons [2]. Also, they are characterized by high octane numbers. Therefore, the combustion characteristics of butanol isomers have recently gained much interest and a recent

comprehensive review [2] provides a broad overview on the combustion chemistry of butanol.

Recently, we reported an investigation concerning reaction pathways in premixed low-pressures *n*-butanol/1,3-butadiene flames [1]. We have now extended this work to study how the isomeric alcohol *iso*-butanol influences the chemistry in the same 1,3-butadiene flames. In this study, we compare detailed kinetic modeling results against the experimentally determined chemical structure of a simple model flame fueled by a mixture of 1,3-butadiene and *iso*-butanol.

1,3-Butadiene is an interesting choice for a hydrocarbon fuel because the addition of 1,3-butadiene to single-ring aromatics (benzene) are considered as major steps in PAH formation and growth reactions [3,4].

The experiments used to study the composition of the flames and the development of the chemically detailed model are described in the next sections.

Experimental

Three premixed, laminar low-pressure flames fueled by mixtures of 1,3-butadiene and *iso*-butanol were stabilized on a 6 cm-diameter stainless steel McKenna-type burner at 30 Torr. The cold-gas mixtures were the following:

- Flame 1, $\phi = 1.45$: 7.7% 1,3-butadiene, 2.6% *iso*-butanol, 39.7% oxygen, and 50.0% argon;
- Flame 2, $\phi = 1.53$: 5.3% 1,3-butadiene, 5.3% *iso*-butanol, 39.5% oxygen, and 50% argon;
- Flame 3, $\phi = 1.62$: 2.7% 1,3-butadiene, 8.1% *iso*-butanol, 39.2% oxygen, and 50% argon.

For all three flames, the C/O ratio was 0.5. The flows were controlled with calibrated mass flow controllers, and the *iso*-butanol flow was metered by a syringe pump, evaporated, and quantitatively added

*) corresponding author: marina.braun-unkhoff@dlr.de
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into the gas stream. The cold-gas velocity was 65.1 cm s^{-1} at 300 K. The chemical structures of these three flames were then analyzed using flame-sampling molecular-beam mass spectrometry.

To this end, the flames were probed by a quartz nozzle; the sampled gases expanded into the ionization chamber of a mass spectrometer, where the molecular beam was intersected by monochromated VUV synchrotron light. The photoionization by tunable synchrotron-generated vacuum-ultraviolet (VUV) radiation allows for isomer-selected species identification and quantification. The experiments were carried out at the Chemical Dynamics Beamline of the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory and a detailed description of the technique, the custom-built mass spectrometer, and the data analysis procedures have been published elsewhere [5-7].

Recently, the mass spectrometer has been upgraded to a reflectron system achieving a mass resolution of $m/\Delta m \sim 3000$ allowing for the separation of oxygenated from hydrocarbon species in the interesting mass range of $m/z = 1-78$. In the course of this study, we have determined mole fractions as function of distance to the burner surface of about 60 different species (reactants, products, and intermediates) for each flame.

In order to assess the quality of the model's predictions, it is important to understand the uncertainties of the profiles. It is estimated that the accuracy of the major species profiles is within 20% and for intermediates, especially the ones with unknown photoionization cross sections, up to a factor of two. A more detailed discussion can be found in Ref. [8].

The flame temperatures, which are important input parameters for the model calculations, are taken from the equivalent 1,3-butadiene/*n*-butanol flame (Flame 3) or measured with laser-induced fluorescence (LIF) using the frequency-doubled output of an optical parametric oscillator (Continuum Sunlite EX OPO) near 306 nm to excite the OH $A-X$ (0,0) transition (Flames 1 and 2). We estimate the accuracy of the temperature measurements to be $\pm 150\text{K}$ in the postflame and reaction zones and somewhat larger in the preheat zone.

In the current work, no shift of the temperature profile commonly done to account for probe perturbations was done, although a shift would have led to a better agreement between modeled and measured peak positions of various combustion intermediates, e.g. for Flame 3 by 0.6 mm.

Modeling

The chemical kinetic model presented in this work comprises 1123 reactions, with 237 species involved. In the past, the DLR reaction model was used to describe the oxidation of low-pressure propene and cyclopentene flames [9,10] including soot precursors and aromatics. Recently, the DLR

reaction model was shown to describe sufficiently the oxidation of 1,3-butadiene mixtures blended with *n*-butanol [1], and also the oxidation of low-pressure oxygen-argon flames, with the fuels 1,3-butadiene [11] and *n*-butanol [12], respectively. This reaction model was further enlarged by incorporating a sub-model gathered from Sarathy *et al.* [13] for describing the oxidation of *iso*-butanol, with 21 species and 95 elementary reactions.

Computer simulations were performed with the SANDIA code PREMIX [14] including thermal diffusion. For the species involved, transport data were taken from the CHEMKIN transport database [15], thermodynamical data from [16] or evaluated with group additives rules [17].

Results and Discussion

The predictive capability of the reaction model with respect to species profiles measured within the combustion of three low-pressure premixed flames of blends of 1,3-butadiene and *iso*-butanol, diluted with argon, is presented below. As the fuel inlets range from 3:1, 1:1 and 1:3 in the ratio of 1,3- C_4H_6 /*iso*- $\text{C}_4\text{H}_9\text{OH}$, the influence of the alcoholic compound on the amount of soot precursors (propargyl, C_3H_3) and aromatics (benzene, A1) might become obvious.

The comparison between measured and predicted mole fraction profiles is given for major species including temperature (Figs. 1-2) and selected intermediates including radicals (Figs. 3-7). Note that besides the maximum mole fraction, the profile shapes and peak positions are also valuable for testing the quality of the reaction model. Such a comparison between measured and modeling results provides a comprehensive view of the predictive capabilities of the reaction model.

As will be discussed, most predicted mole fraction profiles are in good agreement with the experimentally obtained profiles. Also, reaction flux and sensitivity analyses were performed to investigate the importance of consumption pathways of the educts (see Figs. 8-9).

Reactants and major products

The comparison between predicted and measured species profiles is shown in Fig. 1 for hydrogen (H_2), water (H_2O), carbon monoxide (CO), and carbon dioxide (CO_2) as the major products. Included are also the profiles for oxygen (O_2) and argon (Ar); the measured temperature profiles used for modeling are given in Fig. 2, together with the concentration profiles of 1,3-butadiene and *iso*-butanol.

Similar levels of agreement were found for all three flames. The consumption of 1,3 butadiene is predicted faster than the one of *iso*-butanol whereas from the measurements, a similar rate of consumption is observed (Fig. 2, medium). Larger discrepancies occur near the surface of the burner, where probe perturbation and uncertainties of the

temperature profiles are known to have some effects [8]. Readers are here reminded that no shift of the temperature profile was done in simulated input temperatures. Clearly, the reaction model used matches the major species profiles, within the expected uncertainties.

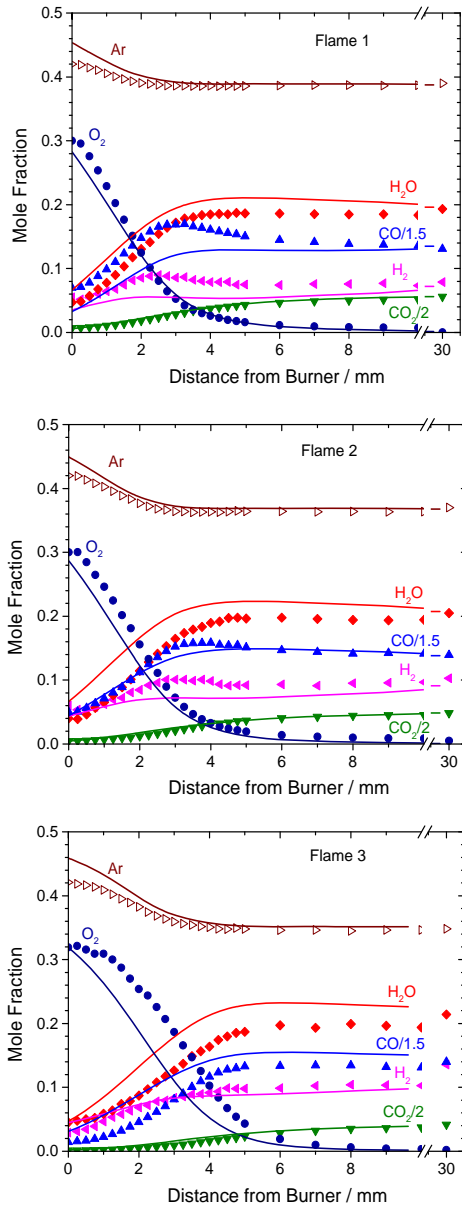


Fig. 1: Experimental (symbols) and predicted (lines) major species profiles for Flames 1-3.

C₁ and C₂ hydrocarbons

Predicted and experimentally observed methyl (CH₃, circles) and methane (CH₄, triangles) profiles are displayed in Fig. 3. Good agreement between experimentally observed and predicted profiles is obvious, with respect to shape, position, and concentration. Methane has a higher peak concentration than methyl; and, also, it is formed earlier, at lower distance from the burner surface, as expected and similar to the findings for

1,3-butadiene/*n*-butanol flame [1]. The smaller the ratio of 1,3-C₄H₆/*iso*-C₄H₉OH, the higher the ratio of CH₄/CH₃.

The reaction model's performance concerning C₂ hydrocarbons, acetylene (C₂H₂), vinyl radicals (C₂H₃), and ethylene (C₂H₄), is shown in Fig. 4. The model succeeds in predicting the profile shapes, peak positions, and tendency in size of peaks. However, the measured concentration profiles of acetylene (C₂H₂) are underpredicted for the three flames studied. It must be stated that a better match of the acetylene profiles was found in the case of 1,3-butadiene/*n*-butanol flames [1]. More work is needed to resolve this finding. For ethylene, a good agreement between measured and calculated profiles is seen. The measured C₂H₃-profiles are well predicted, in particular for Flames 1 and 2.

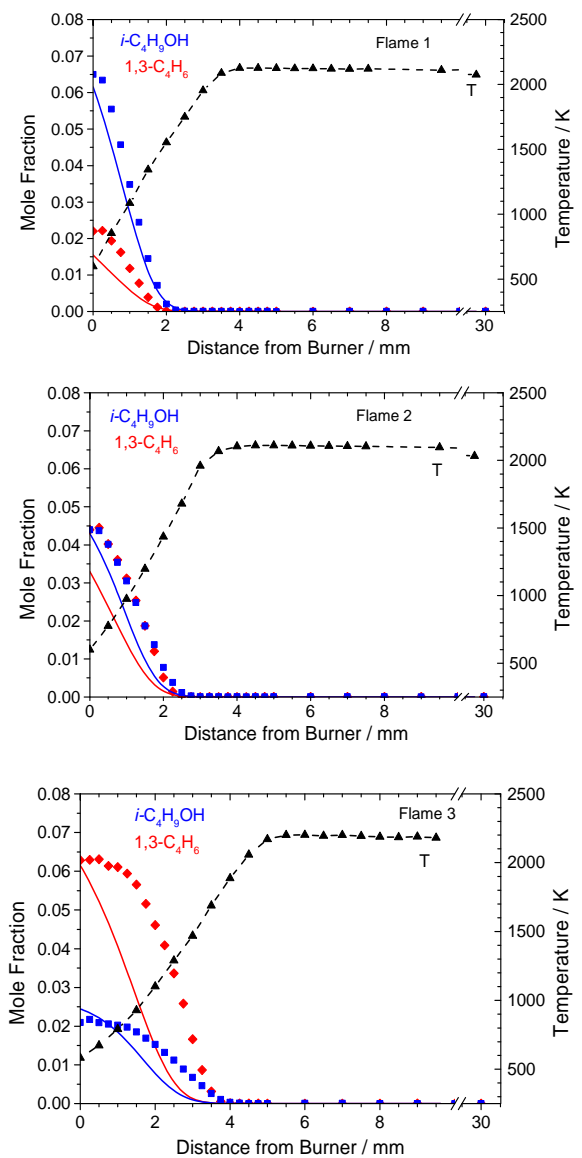


Fig. 2: Experimental (symbols) and predicted (lines) species profiles of fuel components and temperature for Flames 1-3.

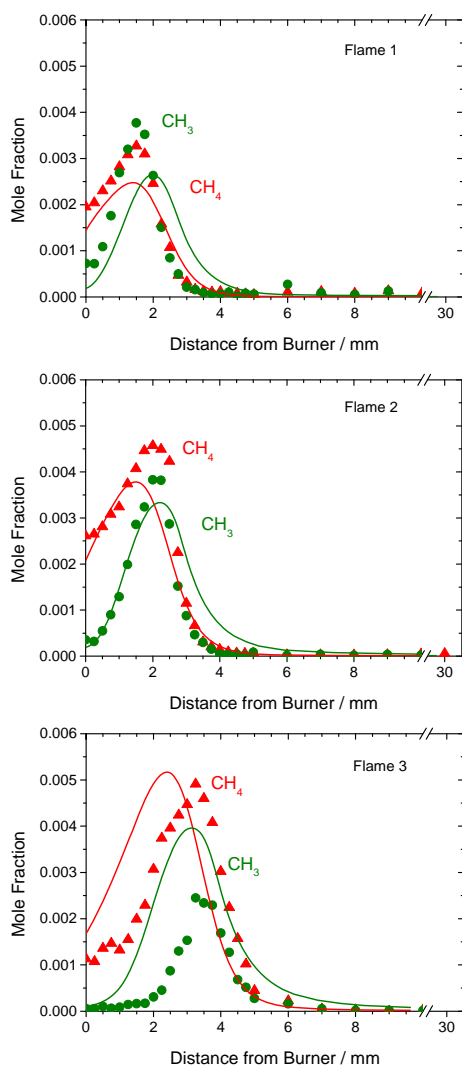


Fig. 3: Experimental (symbols) and predicted (lines) mole fraction profiles of CH_3 and CH_4 for Flames 1-3.

C_3 hydrocarbons and benzene

Propargyl (C_3H_3) and allyl (C_3H_5) radicals are of major interest because they are considered to be important for benzene formation, and thus, as early soot precursors. Therefore, their comparison between measured and predicted mole fraction profiles is shown in Fig. 5. Three observations shall be pointed out. First, measured profiles of propargyl are very well matched by the reaction model. Secondly, measured allyl radicals are underpredicted by up to a factor of three. Third, more propargyl radicals than allyl radicals are predicted, in contradiction to the experimental findings. This is a different pattern when compared to the results obtained previously for the 1,3-butadiene/*n*-butanol flame [1]. This argues for a more detailed study in the future.

The observed ratios of the peak mole fractions of benzene to propargyl (Fig. 6) are following the results obtained for the 1,3-butadiene/*n*-butanol flames [1]. The smaller the ratio of 1,3- C_4H_6 /*iso*- $\text{C}_4\text{H}_9\text{OH}$, the lower the concentrations of propargyl (Fig. 5) and of benzene, as well.

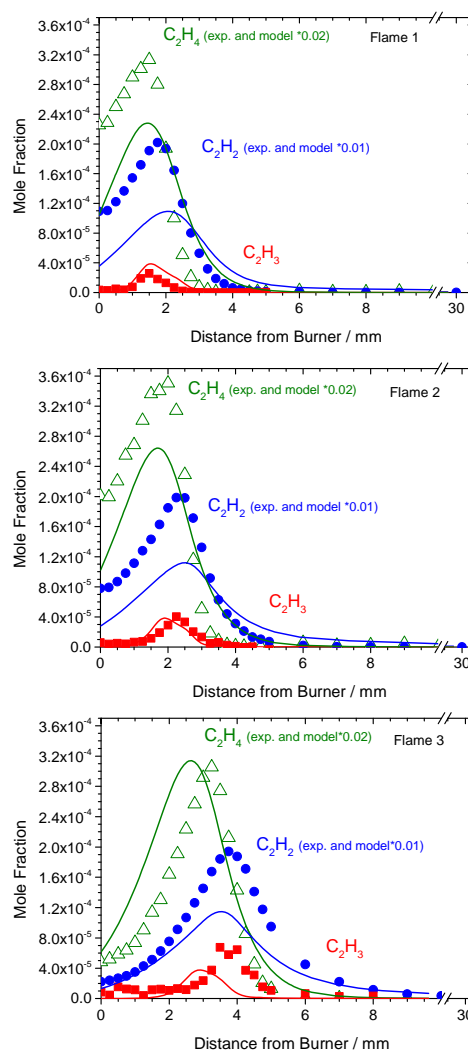


Fig. 4: Experimental (symbols) and predicted (lines) mole fraction profiles of C_2H_2 , C_2H_3 , and C_2H_4 for Flames 1-3.

Small aldehydes

Experimental and calculated mole fraction profiles of small aldehydes (CH_2O , CH_3CHO) as major oxygen-containing intermediates are plotted in Fig. 7. In general, a good agreement is seen with respect to height and shape - in particular for acetaldehyde (CH_3CHO).

Reaction-flux and sensitivity analysis

Reaction-flux and sensitivity analysis were done to identify the dominant mechanistic pathways for the consumption of the fuel as well as of major intermediates and their formation to see where more accurate rate constant calculations might be required.

According to Fig. 8, the reactions identified as the most important ones concerning the concentrations of propargyl and benzene, occur via C_3H_3 and C_3H_4 species or C_4H_5 radicals. Benzene itself is mostly built up via recombination of phenyl and H atoms as well as of propargyl radicals, besides reaction of C_4H_5 and C_2H_2 .

The sensitivity analysis (Fig. 9) with respect to propargyl and benzene (Flame 2) reveals that the overall performance of the current detailed reaction depends mainly on the rates of H-abstraction reactions, besides the well-known reactions of the HCO and H/O-system. The importance of C_4H_5 and C_3H_3 radical reactions for benzene is confirmed.

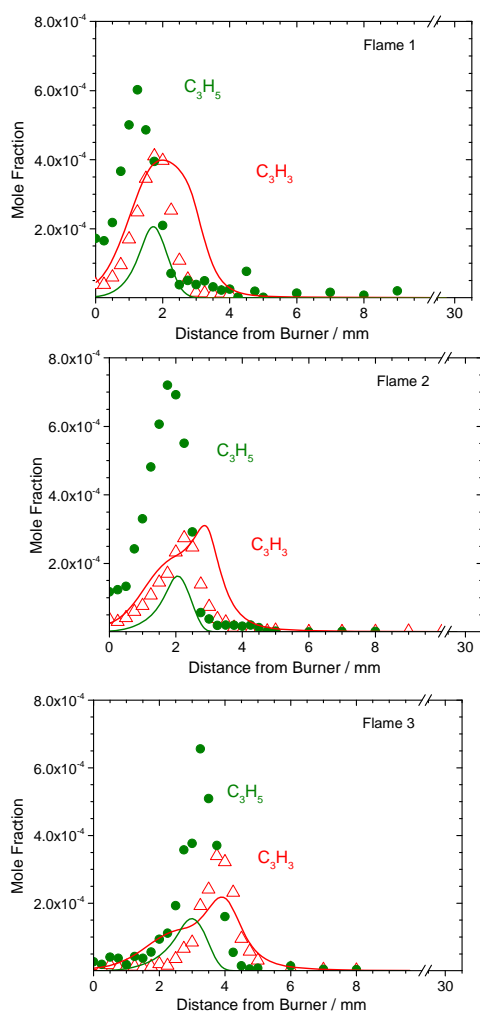


Fig. 5: Experimental (symbols) and predicted (lines) mole fraction profiles of the commonly considered benzene precursors propargyl (C_3H_3) and allyl (C_3H_5).

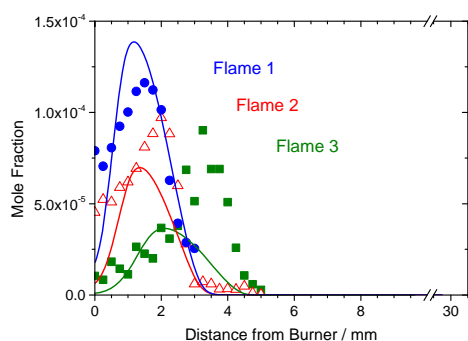


Fig. 6: Experimental (symbols) and predicted (lines) mole fraction profiles of benzene for Flames 1-3.

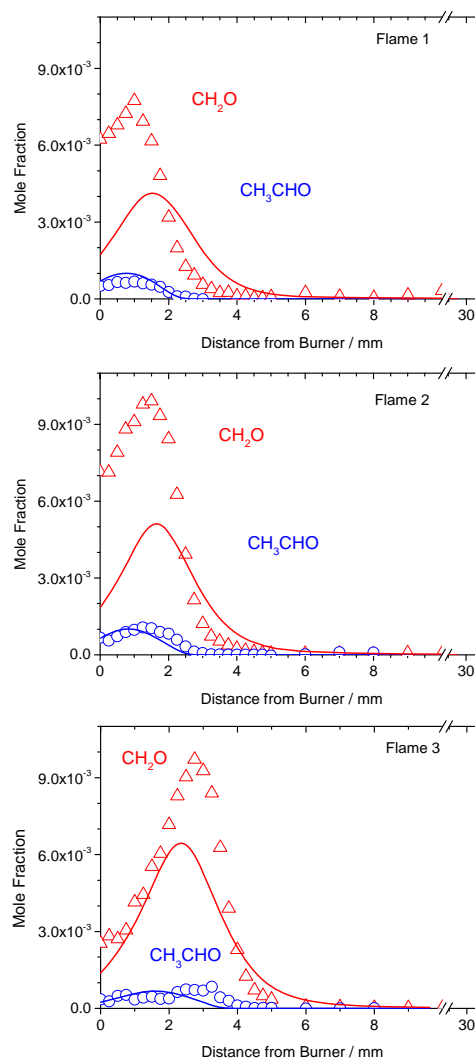


Fig. 7: Experimental (symbols) and predicted (lines) mole fraction profiles of, formaldehyde (CH_2O), and acetaldehyde (CH_3CHO).

Conclusions

A detailed in-house combustion chemistry model shown recently to describe the oxidation of 1,3-butadiene/*n*-butanol, propene, and cyclopentene flames was developed further for a combined 1,3-butadiene/*iso*-butanol flame, which allows identifying the important pathways for butadiene and butanol oxidation as well as for formation of benzene and its precursors. An *iso*-butanol sub-model was added gathered from Sarathy *et al.*[13].

Therefore, the structure of three *iso*-butanol/1,3-butadiene flames experimentally obtained from flame-sampled molecular-beam mass spectrometry data was compared with flame model predictions. Overall, the predicted mole fraction profiles are mostly in good agreement with the measured profiles. However, for some species the discrepancies between experimental and modeled data appear to be larger than the expected errors and a future refinement of the model is warranted.

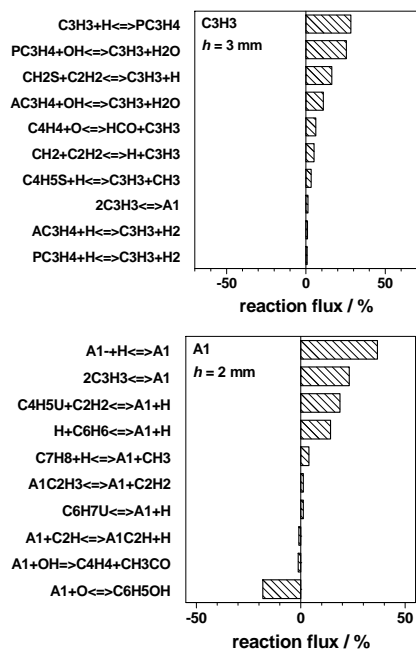


Fig. 8: Reaction flux analysis, Flame 2: Propargyl (C_3H_3) and benzene (A1).

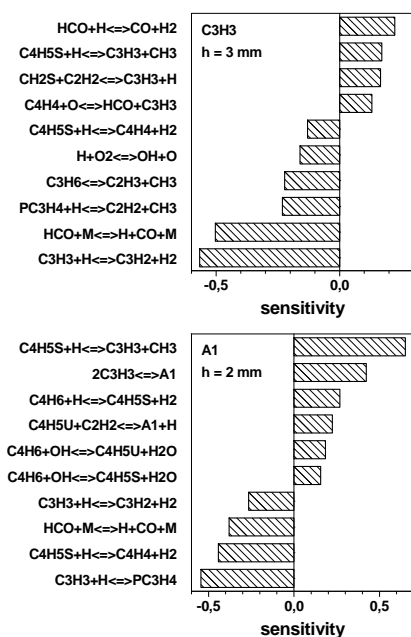


Fig. 9: Sensitivity analysis, Flame 2: Propargyl (C_3H_3) and benzene (A1).

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