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Understanding the reaction pathways in premixed flames fueled by blends of 1,3-butadiene and *n*-butanol

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Abstract

The oxidation of 1,3-butadiene/*n*-butanol flames was studied in a combined experimental and modeling work. The goal is to provide a detailed combustion chemistry model that allows for identification of the important pathways for butadiene and butanol oxidation as well as the formation of soot precursors and aromatics. Therefore, the chemical composition has been investigated for three low-pressure (20–30 Torr) premixed flames, with different shares of butanol ranging between 25% and 75% compared to butadiene in 50% argon. Mole fraction profiles of reactants, products, and intermediates including C_3H_x and C_4H_x radicals as well as mono-aromatics such as benzyl radicals, were measured quantitatively as a function of height above burner surface employing flame-sampled molecular-beam mass spectrometry (MBMS) utilizing photoionization with tunable vacuum-ultraviolet synchrotron radiation. The comparison of measured species profiles with modeling results provides a comprehensive view of the reaction model's quality and predictive capability with respect to the combustion chemistry of 1,3-butadiene and *n*-butanol under the current low-pressure, high-temperature conditions. In general, a good agreement was found between experimental and modeled results. Reaction flux and sensitivity analysis were used to get more insights into the combustion of the fuels.

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1. Introduction

Over the last few years, global concerns over energy security and environmental degradation have resulted in a vital interest in the potential utilization of non-petroleum-based, *i.e.* bio-derived, fuels [1–4]. Especially the combustion characteristic

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of *n*-butanol has recently received a lot of attention in the combustion community and much experimental and modeling work has been done. As all the earlier insights cannot be reviewed here, the reader is referred to the comprehensive review by Sarathy et al. [5]. In summary, it is fair to say that our understanding of the combustion chemistry of *n*-butanol has advanced significantly over the last years and combustion chemistry models with predominant predictive capabilities can be generated [6–11].

With this major accomplishment in mind and realizing that *n*-butanol is likely not to be used as a single-component fuel but rather will be entered into the market as a blend with traditional petroleum-based fuels, it is now time to move our research focus on understanding the combustion chemistry in flames fueled by hydrocarbon/*n*-butanol blends. To this end, we have experimentally and theoretically studied the reaction pathways in flames fueled by blends of 1,3-butadiene and *n*-butanol. The goal of this study is to provide mechanistic insights into how the addition of *n*-butanol affects the small molecule species pool.

1,3-Butadiene is an interesting choice for the hydrocarbon component because (a) as a small di-ene, it can be regarded as a representative for this class of compounds in more realistic fuels, and (b) its consumption pathways are expected to lead to intermediates that differ from the ones formed in *n*-butanol oxidation steps [7,12]. For example, the *i*-C₄H₅ and C₃H₃ radicals, which are likely key intermediates in the formation of the so-called “first aromatic ring” [13], are more readily formed in 1,3-butadiene than in *n*-butanol combustion processes. Generally speaking, none of the commonly considered precursor species, like C₃H₃, C₃H₅, *i*-C₄H₅, or C₅H₅, can be efficiently formed through *n*-butanol oxidation steps [6], and therefore it is not surprising that the addition of *n*-butanol to hydrocarbon flames can lead to a reduced concentration of soot and its precursors [14–17]. Such a trend is also observed in this study and the emphasis of this paper will be on how the small molecule chemistry changes based on the fuel blend composition and on the chemical insights gained from detailed kinetic modeling.

2. Experimental procedures

In this paper, we report new experimental data in the form of isomer-resolved species mole fraction profiles of premixed flames fueled by three different 1,3-butadiene/*n*-butanol blends. The flames, which were stabilized at a low pressure on a flat-flame McKenna burner, were analyzed using flame-sampling mass spectrometry with single-photon ionization. This part of the work was performed at the Chemical Dynamics Beamline

of the Advanced Light Source of the Lawrence Berkeley National Laboratory [18].

The experimental set-up consists of the McKenna burner located in a low-pressure flame chamber, a quartz probe to sample gases from within the flames, a differentially pumped vacuum system, and a reflectron time-of-flight (TOF) mass spectrometer (MS). Compared to the previously used linear TOF MS [18], the improved mass resolution ($m/\Delta m \sim 3500$) now permits the separation of flame components based on their elemental composition. An example of the new flight-time resolution is shown in Fig. 1 for $m/z = 84$ of Flame 2 (see Table 1 and next paragraph for flame conditions). Based on our calibration, the three peaks indicate contributions of C₄H₄O₂, C₅H₈O, and C₆H₁₂ isomers. It is immediately obvious that such a resolving capability is especially helpful when analyzing complex mixtures of oxygenated and hydrocarbon species as they can be expected in a mixture of 1,3-butadiene and *n*-butanol flames.

The detailed flame conditions are summarized in Table 1. The gas flows of Ar, O₂, and 1,3-butadiene were controlled with calibrated mass flow controllers and the flow of the *n*-butanol was metered by a syringe pump, evaporated, and added quantitatively into the gas stream. The C/O ratio was kept constant for all three flames (C/O = 0.5), thus resulting in slightly different stoichiometries.

Details of the experimental and data reduction procedures are sufficiently described in the literature [18–22] and are not repeated here. In short, we used a quartz probe and a differentially pumped vacuum system to sample gases from within the three different flames and then used a quasi-continuous beam of synchrotron-generated vacuum-ultraviolet (VUV) photons in the energy range of 8–17 eV as means to effectively ionize the sampled flame constituents. In a first step, we scanned the photon energy at a fixed burner position, which allowed us to record so-called photoionization efficiency (PIE) curves which were used to identify most of the compounds based on their characteristic ionization energies and PIE curves. While this is a very powerful technique, we have to keep in mind that especially for larger m/z ratios, this approach can become very complicated when potentially more isomers need to be separated and their ionization energies and PIE curves are unknown [19,23–25].

Once the main components were all identified, we recorded mass spectra as a function of distance from the burner surface at fifteen different photon energies in order to provide the most reliable isomer-resolved mole fraction profiles possible. Mole fraction profiles of about 80 hydrocarbon and/or oxygenated species were determined for each flame. It is beyond the scope of this paper to discuss all profiles in detail and only a few will

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