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MBMS investigation of a laminar tetrahydrofuran flame

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Cyclic ethers, like tetrahydrofuran (THF), are formed during the autoignition of alkanes and subsequently influence their combustion chemistry. To learn more about the oxidation chemistry of these ether intermediates, a fuel-rich THF flame ($\phi = 1.75$) has been studied using the versatile technique of flame-sampling Molecular Beam Mass Spectrometry (MBMS) in combination with single-photon ionization. Several cyclic intermediates which are potentially formed by dehydrogenation of the fuel are identified by their ionization energies. Ethylene, propene, ketene and formaldehyde are major stable decomposition products of THF and their mole fraction profiles are presented. Detected oxygenated species include ethenol, acetaldehyde and propanal. Despite the fuel-rich conditions, the concentrations of benzene and other aromatic hydrocarbons are near the detection limit.

1. Introduction

In recent years, tightened regulations for emissions from internal combustion engines have stimulated a pronounced interest in non-conventional oxygenated fuels. Ethers, like dimethyl ether (DME), methyl-*t*-butyl ether (MTBE), ethyl-*t*-butyl ether (ETBE) and other representatives of this chemical class are used as anti-knock agents, octane boosters or ignition improvers, and their oxidation chemistry has been studied intensively, e.g. [1-8]. The production of liquid fuels from renewable sources, like biomass, could help balance the emission of carbon dioxide, a major green house gas, and diminish the dependency on fossil fuel resources. Biomass contains a variety of substituted five- and six-membered cyclic ethers and strategies are being developed to transform biomass into suitable transportation fuels or fuel additives that retain these structures. For example, in reference [9] the authors report the conversion of fructose to dimethylfuran, and in reference [10] a way to produce α-methyltetrafuran from cellulosic biomass is described.

In addition, cyclic ethers are formed during the autoignition of alkanes and alkenes by isomerisation of alkylhydroperoxide radicals [11,12]. These ethers influence the ignition properties of the hydrocarbon fuels and consequently their combustion chemistry.

Tetrahydrofuran (THF) is a simple, cyclic ether and therefore well suited as a model fuel to learn more about their combustion chemistry. The oxidation and ignition of THF have been studied previously by Dagaut et al. in shock tubes and jet-stirred reactors [13]. On the basis of these experimental data a chemical reaction mechanism has been developed. Two older studies focus on the gas-phase oxidation at low temperatures [14] and the pyrolysis of THF behind reflected shock waves [15]. Mole-fraction profiles from laminar flames provide a stringent test for reaction models, but to our knowledge laminar flame data on THF combustion have not been published prior to this study.

Flame-sampling molecular beam mass spectrometry allows the simultaneous measurement of the concentration profiles of most flame species. Here, it is combined with single-photon ionization by VUV light from a synchrotron source. The high energy resolution and precise tunability of the radiation enable the detection of individual isomers. This technique has been applied in several flame studies [1,16,17] and is especially well-suited to follow the first reaction steps in the breakdown of the fuel molecules.

2. Experiment

Detailed descriptions of the experimental set-up and data reduction strategies can be found e.g. in [17,18]. In brief, a flat THF/O_2/Ar flame is stabilized on a sintered stainless-steel McKenna burner (Holthuis and Assoc.). The stoichiometry of the flame is ϕ=1.75; the individual gas flow rates are 0.72 slm THF, 2.28 slm O_2, 1.00 slm Ar and the total mass flow is 0.00434 g s^{-1} m^{-2}. The flame is sampled through an orifice in a quartz cone. A rapid reduction in pressure impedes further reactions in the gas sample and results in the formation of a molecular beam. The beam is skimmed and crosses the VUV-photon beam in the ionization volume of a linear time-of-flight mass spectrometer (ToF-MS). Following a two-stage ion extraction, the photoions are separated in the flight tube and detected with a multichannel plate. A multiscaler records the ToF mass spectra. The mass resolution of the instrument is $m/\Delta m \approx 500$. Spatial profiles can be obtained by changing the distance between the sampling cone and the burner. A scan of the photon energy at a fixed burner position results in photoionization efficiency spectra (PIE spectra). In these measurements the energy resolution can be as good as $E/\Delta E \approx 400$.

3. Species identification and burner profiles

The quantitative spatial profiles of the major species and several stable and radical intermediates are determined.

The mole fraction profiles of the major species are shown in Figure 1. As expected for the fuel-rich flame conditions, the mole fraction of carbon monoxide is much higher than the mole fraction of carbon dioxide and considerable amounts of hydrogen are detected.

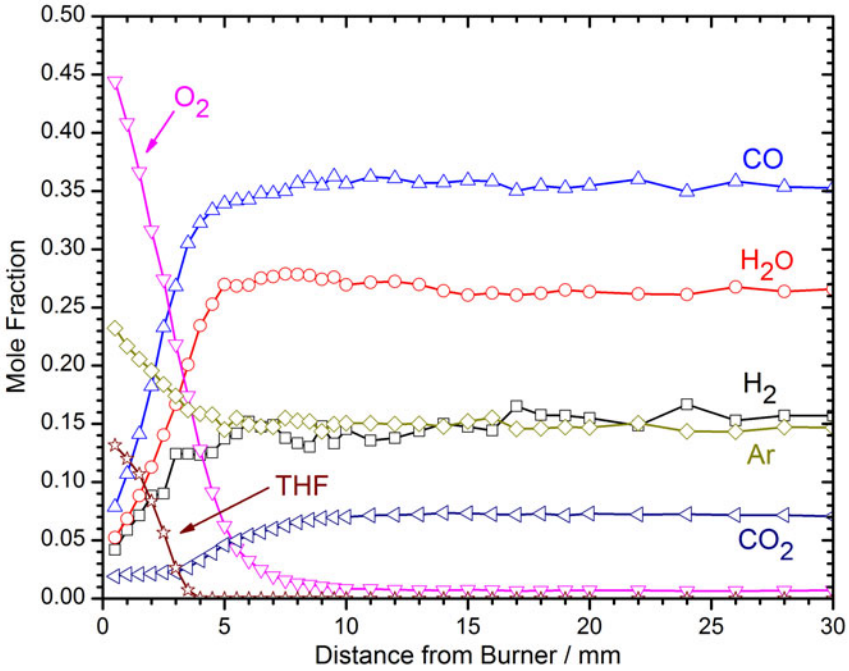

Figure 1: Major species mole fraction profiles in a fuel-rich THF flame.

3.1 First reaction steps

The earlier shock tube studies identified two main decomposition paths for THF. The main pyrolysis products were ethene, carbon monoxide and methane in one channel and propene and formaldehyde in the other channel [15]. In the jet-stirred reactor study [2] the fuel was mainly consumed through hydrogen abstractions by OH, HO_2, H, O and CH_3 radicals and subsequent decomposition of the initially formed C_4H_7O radicals to yield allyl radicals and formaldehyde or ethene, carbon monoxide and methyl radicals. These primary intermediates were oxidized further.

In fuel-rich laminar flames the first step in the destruction of the fuel is usually hydrogen abstraction. For THF, the abstracted H can be at the α- or β-carbon atom (relative to the O atom), so that initially two different C_4H_7O radicals may be formed. Neither radical was detected in this MBMS experiment, either because they are consumed so fast that their concentrations are too low or because the radical stabilizes to C_4H_8O or C_4H_6O during the sampling process. Nevertheless, the first stable intermediates with the chemical composition C_4H_6O and C_4H_4O can be identified by their ionization potentials and photoionization efficiency spectra (PIE spectra). Figure 2 shows a comparison of the flame-sampled PIE curves for mass 68 and 70 with cold-flow PIE curves of furan, 2,3-dihydrofuran and 2,5-dihydrofuran.

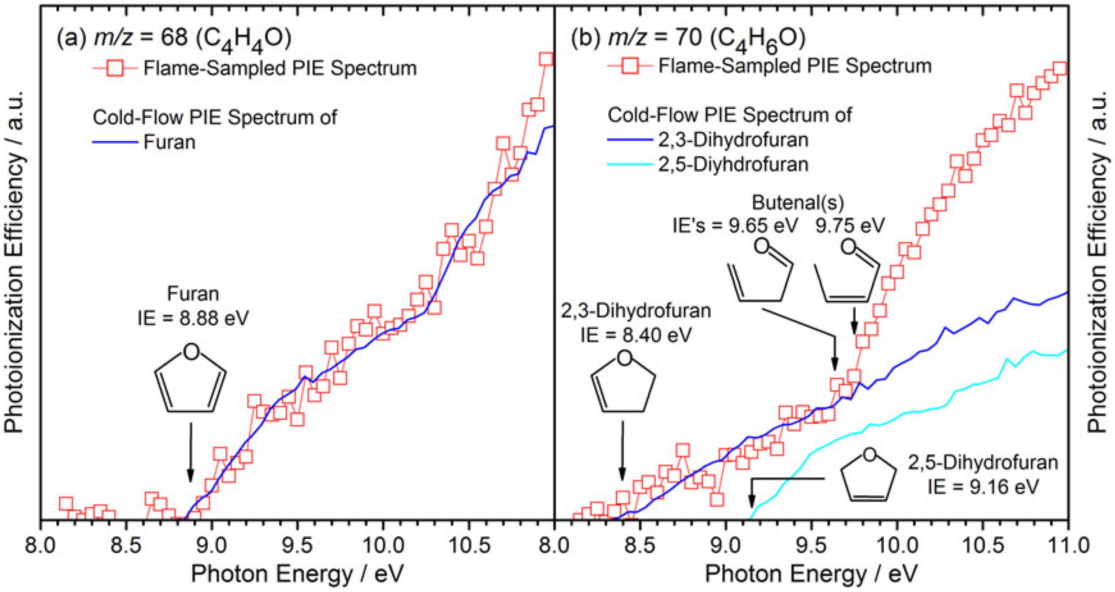

Figure 2: (a) PIE curves of furan sampled from the flame and a cold-flow. (b) Comparison of the PIE spectrum at m/z = 70 measured in the flame with the cold-flow PIE curves of 2,3-dihydrofuran and 2,5-dihydrofuran.

Below 9.7 eV the PIE spectrum in the flame at m/z = 70 is matched very well by the PIE curve of 2,3-dihydrofuran. A second onset or a deviation from the 2,3-dihydrofuran curve at 9.16 eV, which would indicate the presence of 2,5-dihydrofuran is clearly missing. Thus, it can be inferred that either 2,5-dihydrofuran is not formed in this THF flame or it isomerizes rapidly to 2,3-dihydrofuran. However, a change in the slope of the PIE spectrum at (9.70 ± 0.05) eV is observed. As indicated in Figure 2 (b), this onset could correspond to the ionization potentials of 2-butenal (9.75 eV) or 3-butenal (9.65 eV) [19]. It is conceivable that 3-butenal can be formed directly by ring-opening of the 2,3-dihydrofuran. For this reason this species is the most likely assignment in this flame, but isomerization to the resonantly stabilized 2-butenal maybe fast, so 2-butenal could be present in this flame as well. The identification of the 2,3-dihydrofuran and the absence of the 2,5-dihydrofuran imply that the first hydrogen is abstracted from the carbon atom next to ether function forming the resonantly stabilized α-C_4H_7O radical. Nevertheless, the β-C_4H_7O radical may be formed as well but it might decompose too fast to form 2,5-dihydrofuran. Furan is identified by the excellent match of the PIE curve at m/z = 68 with the cold-flow spectrum of furan.

The mole-fraction profiles of these cyclic ethers and the open-chain isomer are shown in Figure 3. The ionization cross sections of 2- and 3-butenal are unknown and the shown profile is based on an estimate, which is believed to be accurate within a factor of two. All profiles peak close to the burner before the fuel is completely consumed. The fact that the furan profile has its maximum at a larger distance than the 2,3-dihydrofuran suggests that it is formed by further dehydrogenation of the latter.

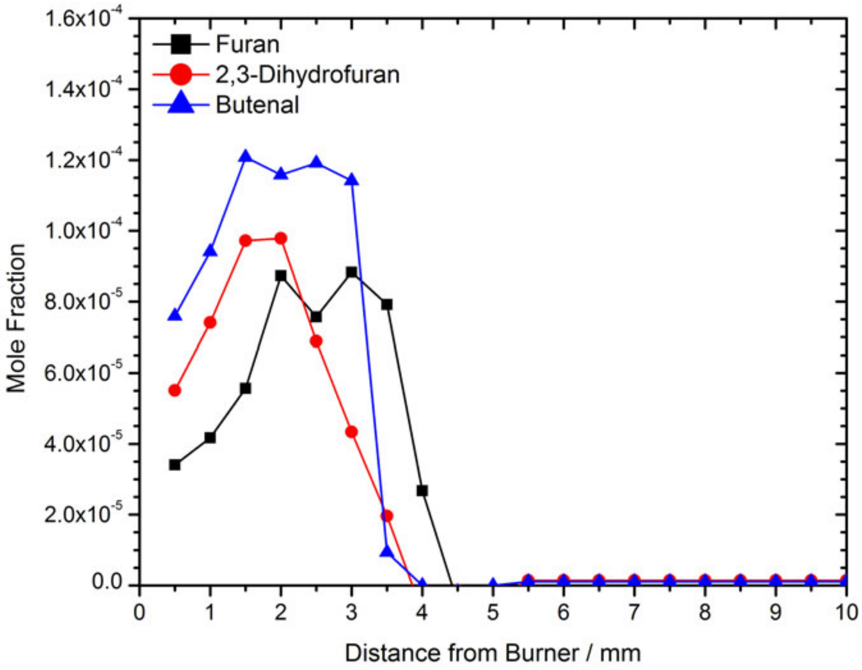

Figure 3: Mole fraction profiles of furan, 2,3-dihydrofuran and butenal.

3.2 Further combustion intermediates

In a previous study [2] ethene, carbon monoxide and methyl radicals were identified as the products of one main decomposition pathway of THF and allyl radicals and formaldehyde as the products of a second reaction path. Hydrogen abstraction at the α-carbon atom followed by β-scission of the C_4H_7O radical yields mainly ethene and vinyloxy radicals (C_2H_3O). The vinyloxy radicals cannot be detected with sufficient accuracy in this experiment because their signal in the mass spectra is obscured by a fragment from the fuel and ^{13}C contributions. Dehydrogenation of C_2H_3O radicals yields ketene, which can be detected convoluted with propene on m/z = 42. The mole fraction profiles of ethene and ketene/propene are shown in Figure 4 (a). The profile of ketene cannot be separated from the mole fraction profile of propene because the nominal masses, ionization potentials and the PIE spectra of both species are nearly the same. In addition the ionization cross section of ketene is unknown. For this reason, the ionization cross section of propene was used to calculate an approximate mole fraction.

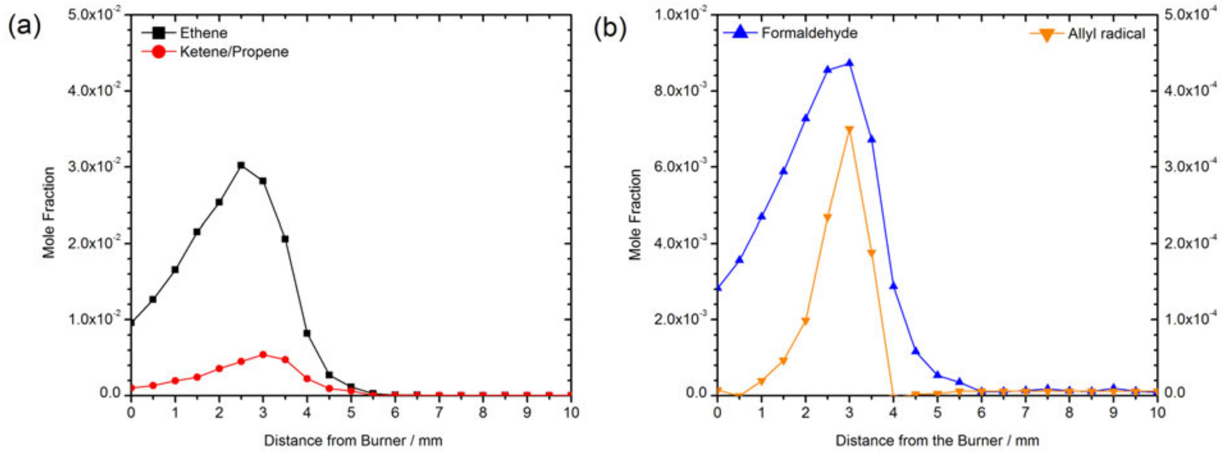

Figure 4: Mole fraction profiles of the major products produced from THF by H-abstraction followed by b-scission.

A β-scission of the β-C_4H_7O radical will yield mainly allyl radicals and formaldehyde. Both species can be detected quantitatively in this flame. The ally radical can react further to yield allene and propyne or it could stabilize to propene. Figure 4 (b) shows the mole fraction profiles of formaldehyde and the allyl radical. In subsequent reaction steps allene and propyne can form propargyl radicals. Both allyl and propargyl radicals are known benzene precursors [20], however, the mole fraction of benzene is close to the detection limit.

During the combustion process several aldehydes are formed in high concentrations. Formaldehyde, acetaldehyde and propanal emissions are listed among the 18 core hazardous air pollutants (HAPs) [21] and may limit the versatility of THF as a liquid fuel or fuel additive. The measured mole fraction profiles of these aldehydes are reported in Figure 5.

It is apparent that the mole fractions are low in the exhaust gas, so that ensuring a complete oxidation, can prevent aldehyde emissions.

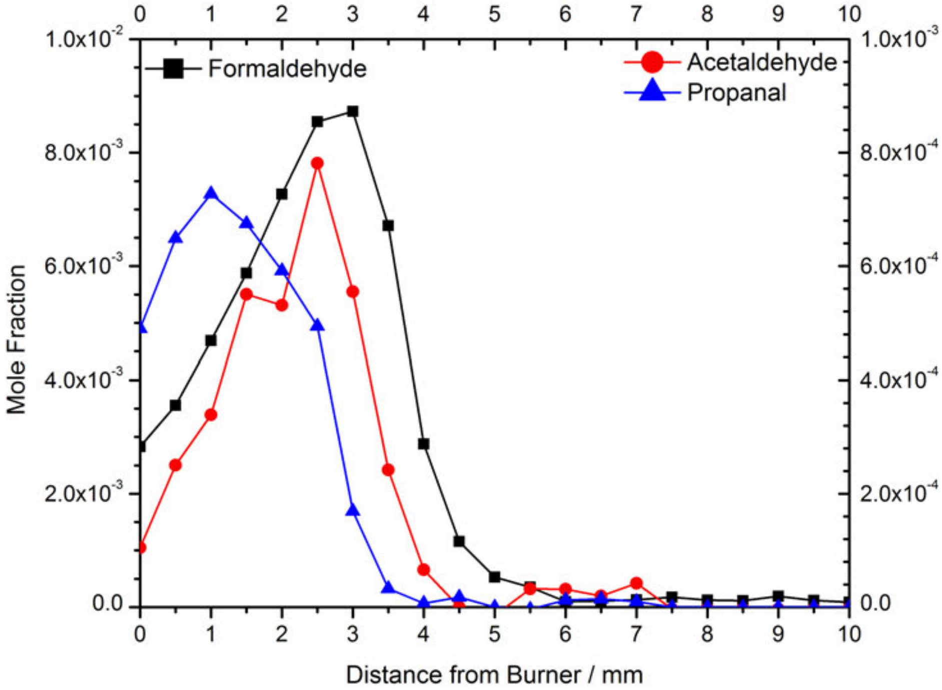

Figure 5: Mole fraction profiles of propanal, acetaldehyde and formaldehyde.

4. Conclusions and Outlook

In this work the combustion chemistry in a fuel-rich, laminar THF flame has been investigated with molecular beam mass spectrometry and the mole fraction profiles of several major reaction intermediates are reported. It is shown that the hydrogen abstraction at the α-carbon atom leads to cyclic ether intermediates as well as open-chain oxygenates. Surprisingly, only 2,3-dihydrofuran and a linear isomer are detected, while no evidence of the 2,5-dihydrofuran is found. Potential fuel destruction pathways are discussed and ethene, ketene and formaldehyde are identified as major reaction intermediates. These species can be formed plausibly by dehydrogenation of the fuel and β-scission of the resulting α- and β-C_4H_7O radicals. An assessment of the relative importance of individual reaction pathways necessitates detailed modeling studies.

Acknowledgments

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