Combustion and Flame 159 (2012) 2254–2279

Contents lists available at SciVerse ScienceDirect

Combustion and Flame

journal homepage: www.elsevier.com/locate/combustflame

Fuel-nitrogen conversion in the combustion of small amines using dimethylamine and ethylamine as biomass-related model fuels

Arnas Lucassen [a], Kuiwen Zhang [a,b], Julia Warkentin [a], Kai Moshammer [a], Peter Glarborg [c,*], Paul Marshall [d], Katharina Kohse-Höinghaus [a,*]

[a] Department of Chemistry, Bielefeld University, Universitätsstraße 25, D-33615 Bielefeld, Germany
[b] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China
[c] Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads, 2800 Kgs. Lyngby, Denmark
[d] Department of Chemistry and Center for Advanced Scientific Computing and Modeling, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203-5017, USA

ARTICLE INFO

Article history:
Received 12 December 2011
Received in revised form 1 February 2012
Accepted 23 February 2012
Available online 21 March 2012

Keywords:
Molecular-beam mass spectrometry
Dimethylamine
Ethylamine
Biofuels
Premixed laminar flame

ABSTRACT

Laminar premixed flames of the two smallest isomeric amines, dimethylamine and ethylamine, were investigated under one-dimensional low-pressure (40 mbar) conditions with the aim to elucidate pathways that may contribute to fuel-nitrogen conversion in the combustion of biomass. For this, identical flames of both fuels diluted with 25% Ar were studied for three different stoichiometries (Φ = 0.8, 1.0, and 1.3) using *in situ* molecular-beam mass spectrometry (MBMS). Quantitative mole fractions of reactants, products and numerous stable and reactive intermediates were determined by electron ionization (EI) MBMS with high mass resolution to separate overlapping features from species with different heavy elements by exact mass. Species assignment was assisted by using single-photon vacuum-ultraviolet (VUV) photoionization (PI) MBMS. The results indicate formation of a number of nitrogenated intermediates, including toxic species such as HCN, in appreciable concentrations. Such intermediate species mole fractions may depend not only on stoichiometry, but also on fuel structure.

We attempted to analyze the major pathways in the two flames with a detailed combustion model developed for this purpose. For this, thermochemical values for a number of intermediates had to be determined from quantum chemistry calculations. Also, specific sets of reactions were incorporated for the two fuels. While many trends seen in the experiments can be successfully reproduced by the simulations, additional efforts may be needed to reliably describe the fuel-nitrogen chemistry in the combustion of biomass-related model fuels with amine functions.

1. Introduction

Fuel-nitrogen conversion chemistry, especially prediction of the formation of nitrogen oxides, NO_x, from combustion processes, remains an active subject of research since the first review by Miller and Bowman, more than two decades ago [1]. Several reasons contribute to this interest. First, detailed reaction schemes which keep track of the formation and destruction of small nitrogenated compounds in combustion, including e.g. NO, HCN, NH_3, HNO, and HNCO, and the dominant reactions that influence their interconversion have been investigated and discussed for a wide range of conditions [2–4]. Second, the introduction of alternative transportation fuels such as biodiesel has led to the re-evaluation of NO_x formation [5], given that different fuel structures entail a different reactive species mix. Third, from the nitrogen content in solid biomass and in related matter, including agricultural waste, a diverse spectrum of volatile and heterogeneously fixed nitrogen-containing compounds can be expected, complicating the prediction of fuel-bound nitrogen conversion [6–9]. Finally, nitrogen conversion is being investigated regarding novel combustion strategies for power generation such as oxy-fuel combustion of coal and/or biomass [10–12], also requiring re-evaluation of the pathways towards small nitrogen compounds.

It is interesting to note in this context that detailed studies of flames burning nitrogenated compounds are still quite scarce, especially under conditions where intermediate species concentration measurements and development of the respective combustion mechanisms are possible. Flames of or doped with ammonia have been investigated, with one recent study involving CH_4/NH_3 fuel mixtures and the analysis of their combustion with a flame model using a joint hydrocarbon/ammonia mechanism [13]. Several flames of heterocyclic compounds have also been studied, in part only providing species identification, however [14–16]. For fuels which feature an amine group, generally applicable detailed

* Corresponding authors. Fax: +49 521 106 6027 (K. Kohse-Höinghaus).
E-mail addresses: PGL@kt.dtu.dk (P. Glarborg), kkh@uni-bielefeld.de (K. Kohse-Höinghaus).

0010-2180/$ - see front matter © 2012 The Combustion Institute. Published by Elsevier Inc. All rights reserved.
doi:10.1016/j.combustflame.2012.02.024

combustion mechanisms will need to be developed. Recent investigation of the combustion chemistry of morpholine as a potential model biofuel which presents a secondary amine and an ether function has reported a complex intermediate species pool, quantified from a combination of photoionization (PI) and electron ionization (EI) molecular beam mass spectrometry (MBMS) [17]. Modeling of this rich chemistry showed remarkable agreement for some of the small nitrogen compounds, but was not yet satisfactory to predict some steps in the early fuel decomposition leading to NH_2 and NH_3. Evidence from cavity ringdown spectroscopy (CRDS) experiments in this flame also showed early NH_2 formation [18], and more information would be desirable on the thermochemistry and kinetics of potential further ammonia-related pathways.

Regarding the complexity of the combustion chemistry of the cyclic amine morpholine, a reasonable strategy pursued here is to analyze flames of smaller amine fuels in more detail. Ethylamine (EA) and dimethylamine (DMA) are the simplest isomeric amines. Thus they are especially well suited for an investigation of the structure dependence of the combustion reactions of amines. These two amines are base structures for various substances used for instance for crop and wood protection, paints and finishes [19] as well as in amine-based fuel additives. Furthermore, dimethylamino groups are a common structural feature of hypergolic fuels [20]. Small amines also play an important role during the treatment of fish waste and its energetic use [21–23]. Only few early investigations of the combustion of these compounds are available, however [24,25]. Further work has focused on the oxidation behavior and the influence of amines on hydrocarbon combustion [26–30]. Sources of aliphatic amines from agricultural and industrial processes and from fish and meat production have been reviewed recently regarding their environmental impact [31,32], with EA and DMA belonging to the most abundant amines found in the atmosphere. Dimethylamine has also received attention as a precursor to carcinogenic substances in water treatment and the atmosphere [31–33].

In the present paper we therefore provide the first comprehensive analysis of laminar premixed, identical-condition flames of ethylamine and dimethylamine, with equivalence ratios Φ spanning a reasonable range from fuel-lean to slightly rich (i.e. $\Phi = 0.8$, 1.0, and 1.3). The information from the comparison of species concentration profiles between these isomeric flames is believed to contribute valuable insight also for the combustion of more complex fuel structures involving amine groups. Also, the combustion of these isomeric amines can be compared from structural analogies to those of the corresponding oxygenated compounds, dimethylether and ethanol [34–36], under similar conditions.

2. Experiment

The experimental setups and procedures used here are quite comparable to those that have been recently employed in an investigation of the combustion of morpholine [17]. Therefore, only a very brief description is provided here. Three pairs of laminar, premixed flat flames of ethylamine and dimethylamine were investigated at 40 mbar and 25 vol.% argon dilution, a lean flame pair with $\Phi = 0.8$ (abbreviated EA08 and DMA08, respectively), a stoichiometric one with $\Phi = 1.0$ (EA10 and DMA10), and a slightly rich flame pair with $\Phi = 1.3$ (EA13 and DMA13). The flames were stabilized on water-cooled flat flame burners with 6.34 cm and 6.0 cm diameter, respectively, for the EI-MBMS and PI-MBMS setups described below. Gas flows were metered using calibrated mass flow controllers. Flame conditions are given in Table 1. The flow rates were chosen so that the cold gas velocity was the same in both experiments.

Two MBMS instruments were used for the *in situ* analysis of the local flame composition. Typical results discussed here report species mole fraction profiles as a function of flame position h, i.e. height above the burner surface. They were mostly obtained with the MBMS setup located in Bielefeld using electron ionization. Identification of species by exact mass was possible due to the high mass resolution ($m/\Delta m = 4000$) of the reflectron time-of-flight (TOF) mass analyzer which allowed the separation of elemental compositions. Ionization relied on a pulsed electron beam of $\sim 10^9$ electrons/pulse with an energy distribution of 1 eV (FWHM) which permitted to detect all species in the same mass spectrum. Different energies (10.5 eV, 12.0 eV, 15 eV, and 17.5 eV) were employed to analyze the flame and to detect and minimize potential fragmentation.

In addition, isomer separation was possible in some cases with the MBMS instrument based at the Advanced Light Source in Berkeley which used single-photon photoionization with continuous, high-intensity ($\sim 10^{13}$ photons/s) synchrotron-generated vacuum ultraviolet radiation. Its competitive energy resolution ($\Delta E = 0.05$ eV) permitted the identification of flame species via their ionization thresholds, whereas the mass resolution of its linear TOF was limited to $m/\Delta m = 400$.

Gas samples were taken from the flame with quartz nozzles; they featured orifice diameters at the tip of 0.5 mm in the EI-MBMS and 0.4 mm in the PI-MBMS experiment, and an angle of 25° (EI-MBMS) or 40° (PI-MBMS), respectively. A molecular beam was formed with two differential pumping stages; the pressure was kept at $\sim 10^{-4}$ mbar in the first stage and at $\sim 10^{-6}$ mbar in the ionization region behind a skimmer. Ions were detected using a multichannel plate and were integrated with a multichannel scaler with a sensitivity of $\sim 10^{-5}$, and mass spectra were collected for typically 10^5 ionization pulses as a function of position in the flame or of ionization energy at given position. Spectra were corrected for fragmentation and isotopic contributions of ^{13}C and ^{18}O.

The major species mole fractions were determined with calibration mixtures of known gas composition, and by taking the elemental balances of carbon, hydrogen, oxygen, and nitrogen into consideration. In this evaluation, the gas composition at the burner surface was assumed to be represented by EA or DMA, O_2, and Ar. The burnt gases at the farthest distance from the burner were assumed to consist of Ar and the products CO, CO_2, H_2, H_2O, N_2,

Table 1
Flame conditions. The flows are reported for the 63.4 mm burner used in the EI-MBMS experiment, pressure is 40 mbar, and cold gas velocity is given at 313 K. The flow rates for the 60 mm burner (divide values in table by 1.12 for conversion) were chosen to match cold gas velocity in both experiments.

Flame	Ethylamine (EA)			Dimethylamine (DMA)		
	EA08	EA10	EA13	DMA08	DMA10	DMA13
Stoichiometry	0.8	1.0	1.3	0.8	1.0	1.3
Flow Ar (slm)	0.56	0.56	0.56	0.56	0.56	0.56
Flow O_2 (slm)	1.38	1.32	1.24	1.38	1.32	1.24
Flow fuel (slm)	0.29	0.35	0.43	0.29	0.35	0.43
Velocity (cm/s)	34	34	34	34	34	34
Mass flow (10^{-3} g/s cm^2)	1.88	1.89	1.92	1.88	1.89	1.92