



Shock tube study of ethylamine pyrolysis and oxidation



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ABSTRACT

Ethylamine (CH₃CH₂NH₂) pyrolysis and oxidation were studied using laser absorption behind reflected shock waves. For ethylamine pyrolysis, NH₂ time-histories were measured in 2000 ppm ethylamine/argon mixtures. For ethylamine oxidation, ignition delay times, and NH₂ and OH time-histories were measured in ethylamine/O₂/argon mixtures. Measurements covered the temperature range of 1200–1448 K, with pressures near 0.85, 1.35 and 2 atm, and fuel mixtures with equivalence ratios of 0.75, 1 and 1.25 in 0.2%, 0.8% and 4% O₂/argon. Simulations using the recent Li et al. mechanism gave significantly shorter ignition delay times and higher intermediate radical species concentrations than the experimental results. The reaction rate constants for the two major ethylamine decomposition pathways were modified in the Li et al. mechanism to improve the prediction of the time-histories of NH₂ and OH in ethylamine pyrolysis. In addition, recommendations from recent studies of ethylamine + OH reactions were implemented. With these modifications, the Modified Li et al. mechanism provides significantly improved agreement with the species time-history measurements and the ignition delay time data.

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1. Introduction

Biofuels, as additives and alternatives to petroleum-based transportation fuels, are of increasing interest. While biofuels have the advantages of fuel-resource regenerability and the potential for reducing emissions of carbon dioxide, aromatic hydrocarbons and soot, previous studies have shown that biofuels may produce increased NO_x emissions due to the wide existence of nitrogen-containing compounds in biofuels. Fuel-nitrogen chemistry thus needs to be further examined for biofuel combustion.

In previous studies, morpholine (C₄H₉NO, 1-oxa-4-azacyclohexane) was chosen as a representative candidate for a nitrogen-containing biofuel compound [1–4]. In combination with molecular-beam mass spectrometry (MBMS) [2] and cavity ring-down spectroscopy (CRDS) [3] experimental work, a combustion reaction set was developed using analogies to cyclohexane combustion [4]. The morpholine combustion reaction set developed in [4] was further improved based on the morpholine decomposition time-histories during pyrolysis experiments and ignition delay time measurements in a shock tube [5]. Because of the complexity of the fuel-nitrogen chemistry of morpholine, a 6-membered cyclic amine, more detailed analysis of the smaller aliphatic amines was still required under combustion conditions. However, only a few

early studies of the combustion of aliphatic amines, and their effects on hydrocarbon ignition as combustion inhibitors were available [6–14]. Atkinson and Pitts [11] and Slagle et al. [12] examined the kinetics of the reactions of oxygen atoms with amines, using a photoionization technique. Votsmeier et al. [14] studied monomethylamine thermal decomposition, employing NH₂ concentration time-history measurements in a shock tube. Recently, Lucassen et al. [15] studied laminar premixed flames of dimethylamine and ethylamine under one-dimensional low-pressure conditions. A detailed combustion model was developed to analyze the major pathways in those two flames [15], which successfully reproduced many trends observed in the flame experiments.

Additional efforts are needed to augment the aliphatic amines experimental database, and to provide a reliable and quantitative description of the fuel-nitrogen chemistry in the combustion of model biofuels containing amine groups. In the current study, ethylamine (EA: CH₃CH₂NH₂) pyrolysis and oxidation were investigated using shock tube/laser absorption methods. For ethylamine pyrolysis, NH₂ concentration time-histories in ethylamine/argon mixtures were measured. For ethylamine oxidation, ignition delay times and time-histories of OH and NH₂ radical were measured in ethylamine/oxygen/argon mixtures. The CHEMKIN PRO package [16] was used to simulate all the experimental data, under the standard constant energy and volume assumptions, using the Li et al. mechanism [5] as the base mechanism.

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2. Methods

2.1. Shock tube facility

Ethylamine pyrolysis and oxidation were studied behind reflected shock waves in a shock tube with a 3.7 m driver section and a 10 m driven section, both with an inner diameter of 15.24 cm. The incident shock speeds were measured using five piezoelectric pressure transducers over the last 1.5 m of the shock tube and linearly extrapolated to the endwall. The ignition pressures were monitored using a piezoelectric pressure transducer (Kistler Model 603B1) located 2 cm from the end wall; laser absorption measurements were conducted at the same axial location. The ignition delay times were determined by extrapolating, back to the baseline pressure, the steep increase in pressure concurrent with ignition. More details concerning this shock tube can be found in [17].

2.2. Laser absorption diagnostics

2.2.1. Laser absorption of NH_2

NH_2 was measured using the output of a narrow-linewidth ring dye laser near 597.4 nm. The NH_2 laser absorption diagnostic employed the overlapping $\tilde{A}_1 \leftarrow X^2B_1(090 \leftarrow 000)\Sigma^p Q_{1,N}7$ doublet lines, previously characterized in our laboratory [18–20]. Visible light near 597.4 nm was generated by pumping Rhodamine 6G dye in a Spectra Physics 380 laser cavity with the 5 W, continuous wave, output of a Coherent Verdi laser at 532 nm. Using a common-mode-rejection detection setup, a minimum NH_2 detection sensitivity of ~ 5 ppm could be achieved for most conditions studied in the current work. Details of the NH_2 laser diagnostic setup are described elsewhere [19].

2.2.2. UV laser absorption of OH

OH was measured using the frequency-doubled output near 306.7 nm of the same ring dye laser system employed for the NH_2 diagnostic. The chosen wavelength was the peak of the well-characterized $R_1(5)$ absorption line in the OH A–X(0,0) band [17]. Visible light near 613.4 nm generated in the Spectra Physics 380 laser cavity was intracavity frequency-doubled using a temperature-tuned AD*A nonlinear crystal to generate ~ 1 mW of light near 306.7 nm. Using a common-mode-rejection detection setup, a minimum OH detection sensitivity of ~ 0.5 ppm could be readily achieved. The details of the OH laser diagnostic setup are included in [17].

A schematic of the setup for the NH_2 and OH time-history measurements is given in Fig. 1.

3. Experimental results

3.1. Ethylamine pyrolysis

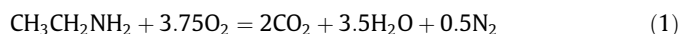
For the ethylamine pyrolysis study, NH_2 time-histories in 2000 ppm ethylamine/argon mixtures were measured. Figure 2 shows representative measured NH_2 time-histories at different temperatures and at pressures near 1.3 atm. During the ethylamine pyrolysis process, NH_2 radicals form quickly though the ethylamine decomposition reaction: $\text{CH}_3\text{CH}_2\text{NH}_2 = \text{C}_2\text{H}_5 + \text{NH}_2$, then the NH_2 radicals are consumed to form more stable species such as NH_3 . The resulting NH_2 time-histories have positive-skewed bell shapes as shown in Fig. 2. Also included in Fig. 2 are the simulation results, using the Li et al. mechanism, in dashed lines. The Li et al. mechanism clearly overpredicts the NH_2 formation rates and the peak NH_2 concentrations, and hence fails to adequately capture the measured NH_2 time-histories. To resolve these discrepancies, a sensitivity analysis of the mechanism was performed and modifications were recommended that are presented in following sections.

3.2. Ethylamine oxidation

For ethylamine oxidation, ignition delay times and time-histories of NH_2 and OH radicals were measured in ethylamine/oxygen/argon mixtures.

3.2.1. Ethylamine ignition delay times

Ignition delay times were determined by extrapolating, back to the baseline pressure, the steep increase in pressure concurrent with ignition. The current ignition delay time measurements cover the temperature range 1200–1448 K, with pressures near 0.85, 1.35 and 2 atm, and equivalence ratios of 0.75, 1 and 1.25 in 4% oxygen/argon. The stoichiometric case was defined as:



A shock tube can reproduce close, but not identical, pressures from shock experiment to shock experiment. For a uniform graphic presentation of the results, a pressure scaling of all the ignition delay time data in a narrow pressure regime is implemented. Many previous studies have shown that ignition delay times have pressure dependence close to P^{-1} . Since the actual pressures are close to the reported pressure (within 15%) for one set of data on an ignition delay time plot, this simple power law dependence was used to normalize the data in Figs. 3, 4, 12 and 13.

Figure 3 shows the measured ignition delay times at three nominal pressures, 0.85, 1.35 and 2 atm, along with the simulation results using the Li et al. mechanism. As expected, the ignition delay times are shorter at higher pressures. The Li et al. mechanism predicts shorter ignition delay times than the experimental data.

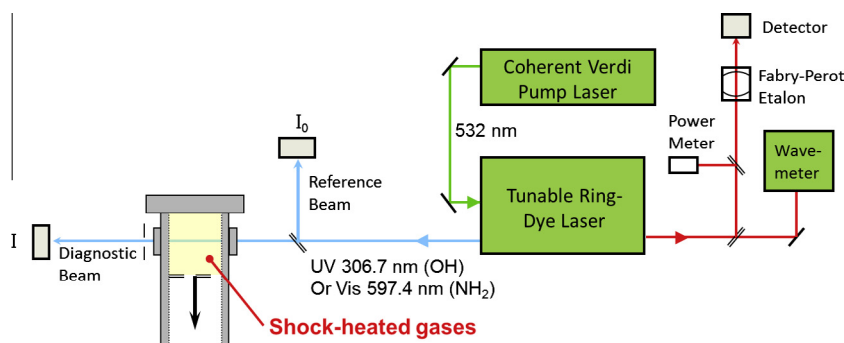


Fig. 1. Schematic of the shock tube/laser absorption diagnostic setup.

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