Pyrolysis and oxidation of ethylamine, dimethylamine and diethylamine: Theoretical and kinetic modeling study

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Introduction: Aliphatic amines are an important class of nitrogen-containing compounds present in renewable fuels such as bio-oils. Conversion of this fuel-bound nitrogen can lead to the formation of HCN and NH_3. Gaining insight into the decomposition of these nitrogen-containing compounds is essential in order to minimize the emissions of these pollutants.

Aim: The aim of this work is to improve understanding of the pyrolysis and oxidation chemistry of small aliphatic amines by combining quantum chemical calculations, chemical kinetic modelling and experimental validation. The influence of the degree of substitution on the nitrogen atom and the alkyl chain length on the reactivity and product distribution is studied via three model compounds: ethylamine, dimethylamine and diethylamine.

Methods: A new kinetic model is constructed with the automatic kinetic model builder Genesys to describe the pyrolysis and oxidation of ethylamine, dimethylamine and diethylamine. Quantum chemical calculations at the CBS-QB3 level of theory are used to determine accurate thermodynamic and high-pressure limit reaction rate coefficients for fuel specific reactions. Three different experimental datasets available in literature are used to validate the developed kinetic model. These include species profiles obtained from shock tube studies, jet-stirred reactor experiments and laminar premixed flames. These datasets cover a wide range of experimental conditions ($T = 500 – 2000$ K, $p = 4 – 170$ kPa, $\tau = 2\ 10^{-3} – 2$ s).

Results: The dominant decomposition pathway under all the studied conditions is a set of hydrogen abstractions from the C_α and N positions followed by β-scission of the fuel radicals. These positions correspond to the weakest C-H bond dissociation energies, as shown in Figure 1.

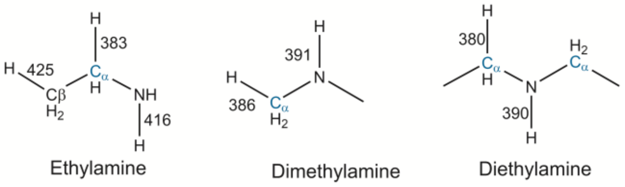

Figure 1: Bond dissociation energies [kJ mol^{-1}] calculated at the CBS-QB3 level of theory.

The proposed elementary step model succeeds in capturing the experimental trends of the species profiles. As an example, Figure 2 depicts the experimental and simulated profiles of the NH_2 radical during the shock tube pyrolysis of EA.[1] In pyrolysis, HCN is the main nitrogen-containing product, while in oxidation, HCN is completely converted to N_2 and NO at temperatures above 1100 K.

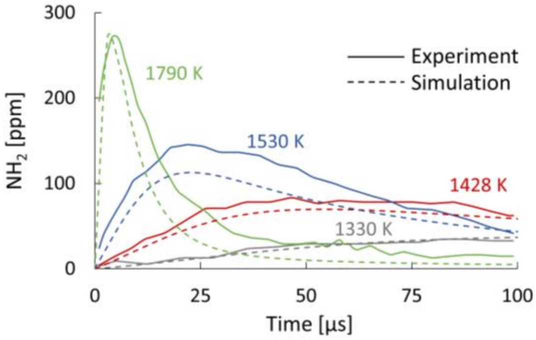

Figure 2: Comparison between experimental and model predictions of the NH_2 profiles during the shock tube pyrolysis of ethylamine.

Conclusion: A newly developed elementary step model can successfully predict the experimental trends of the species profiles during the pyrolysis and oxidation of the ethylamine, dimethylamine and diethylamine. Hydrogen abstractions from the C_α and N positions followed by β–scission of the fuel radicals are the dominant decomposition pathways of the amine species. The higher number of C_α-H bonds of the secondary amines (dimethylamine, diethylamine) explains the increased reactivity compared to the primary amine ethylamine.

References:

1. Li S., Davidson D.F., Hanson R.K. Shock tube study of ethylamine pyrolysis and oxidation. *Combustion and Flame* 2014; 161; 2512 – 2518.