

Experimental and kinetic modeling study of the oxidation of a bio-fuel nitrogen-containing model compound

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Introduction

Over the past decades a good understanding of the oxidation of linear hydrocarbons has been obtained. However, the oxidation chemistry of hetero-atom containing compounds is less understood, which is in particular relevant to describe the thermal decomposition and combustion of complex bio-oils. Aside from oxygenates, nitrogen-containing compounds can be present in bio-oils. [1] The decomposition of these compounds results in the formation of nitrogen oxides, leading to considerable air pollution. [2, 3] In this work, the low- to intermediate temperature oxidation of diethylamine (DEA), which can be considered as one of the most simple nitrogen-containing model compounds in bio-oils, is studied both experimentally and theoretically.

Experimental results

In the present work, the oxidation of diethylamine is studied in an isothermal quartz jet-stirred reactor with online species detection by a series of 3 gas chromatographs. This setup is highly suited for kinetic model development of model compounds, because of its ability to measure detailed effluent concentration profiles. [4-6]

Oxidation of DEA is performed at three different equivalence ratios $\phi=2.0$, 1.0 and 0.5, under atmospheric pressure. The temperature is varied from 500 K to 1100 K to cover the complete conversion range. The space time is equal to 2s for a reactor volume of 81.2 cm³ and the DEA inlet mole fraction is equal to 0.01. In contrast to oxygenated species, such as diethyl ether, no low temperature reactivity is observed for DEA. A total of 25 species are detected using the online GCs. For identification of the non-calibrated nitrogen-containing product species, offline samples are submitted to the GC×GC-TOF/MS. In the intermediate temperature range, i.e. from 600 K to 800 K, large nitrogen-containing species, containing five carbon atoms and at least two nitrogen atoms, are identified. In addition to CO and CO₂, the main carbon-containing products are methane, ethane and ethylene. The main nitrogen-containing compounds are hydrogen cyanide, acetonitrile, propane nitrile, as well as N₂, NO and NO₂. The profiles of the main products are depicted in Figure 1.

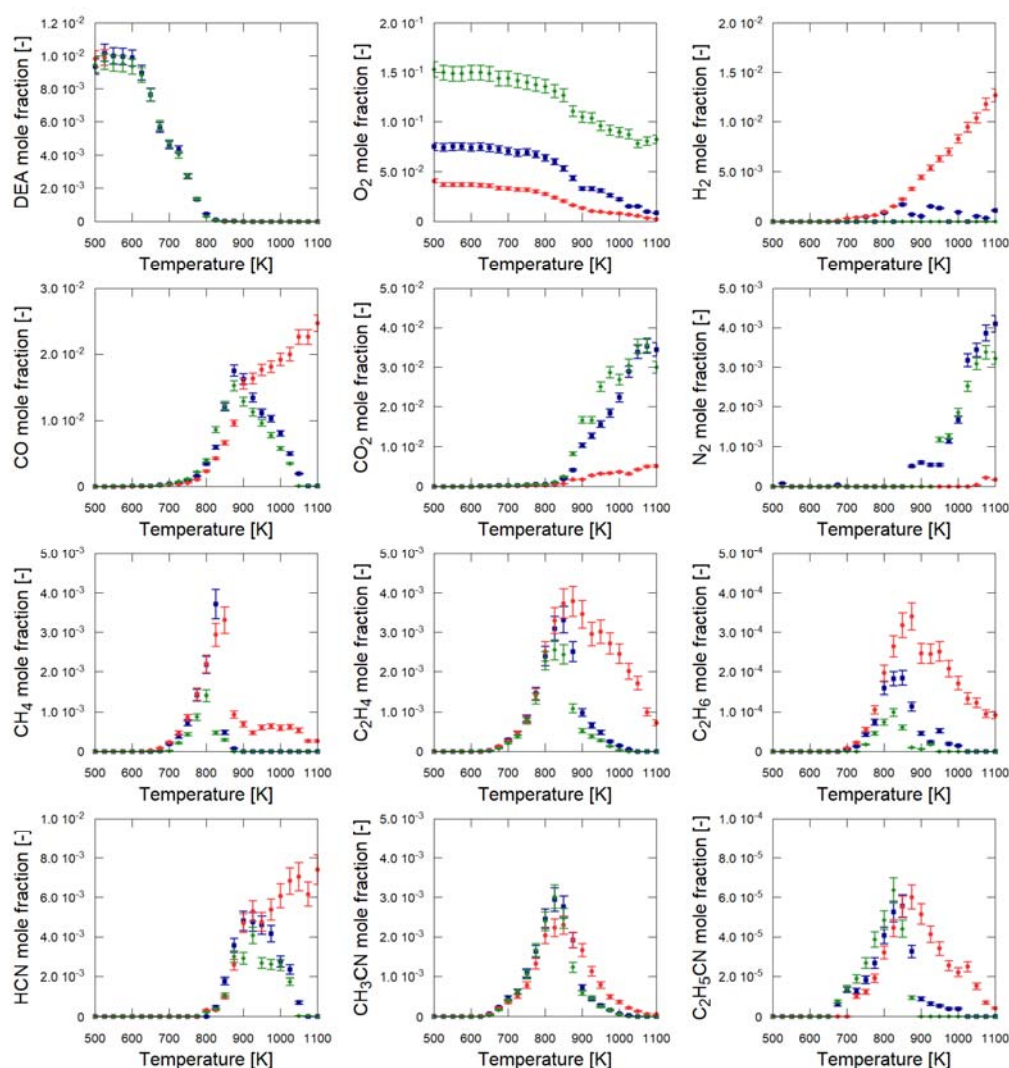


Figure 1. Experimental major product yields of DEA oxidation ($\phi=1.0$ blue ■, $\phi=2.0$ red ●, $\phi=0.5$ green ◆). Experimental conditions are $P=1.07$ bar, DEA inlet mole fraction 0.01 and space time 2.0 s for a reactor volume of 81.2 cm³. Experimental relative uncertainties are 5% for species calibrated with a known substance amount and 10% for calibration with the effective carbon number method.

Kinetic modelling

A kinetic model for the oxidation of DEA is developed with the use of an automatic kinetic model generation tool called Genesys.[7] A prerequisite for the generation of detailed kinetic models is the availability of accurate thermodynamic and kinetic data. Due to the lack of accurate experimental data for nitrogen-containing compounds, computational chemistry is the only viable alternative. Because of the complexity of the generated model, not all parameters can be obtained via computational chemistry and hence approximation methods are required. In Genesys, Benson's group additivity method [8] based on *ab initio* calculations is used to assign rate coefficients to reactions and thermodynamic parameters to species. The implemented group additivity databases are extended to enable its application to nitrogen-containing compounds.[9, 10] Both for radical and non-radical nitrogen-containing species as well as for the main elementary reaction families (hydrogen abstraction, β -scission) new group additivity schemes have been determined. In Figure

2, the methodology is depicted for determination of both the forward and reverse rate coefficient of the hydrogen abstraction from the N-H bond in DEA by a hydrogen atom making use of the calculated group additivity values.

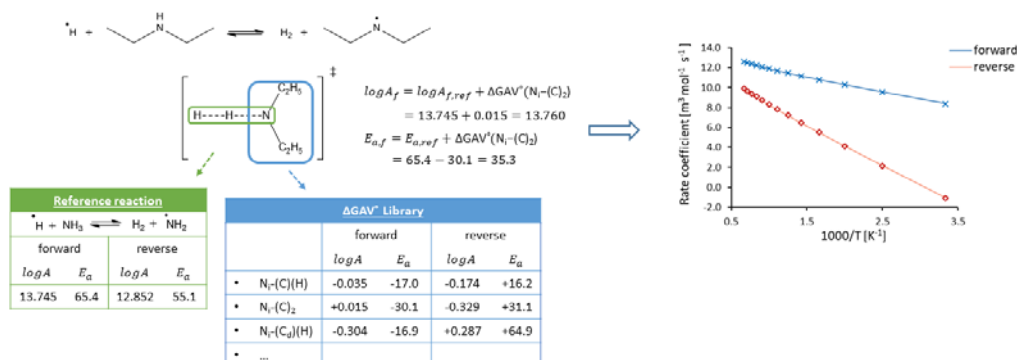


Figure 2: Methodology for determining the Arrhenius parameters of the hydrogen abstraction from the N-H bond in DEA making use of the calculated group additivity values. Arrhenius plot of both the forward (blue) and reverse (red) reaction rate coefficients: full lines indicate the *ab initio* calculated values, data points indicate the group additivity approximated values.

For the determination of both the thermodynamic and kinetic parameters from *ab initio* calculations, the following methodology is used. Electronic structure calculations are performed with Gaussian 09, as implemented on the high-performance supercomputer at Ghent University, at the CBS-QB3 level of theory. The standard enthalpy of formation, the standard entropy and the heat capacity are all calculated from the Gaussian output file. All internal modes are treated as harmonic oscillators except for low frequency hindered rotors with a hindrance potential exceeding a certain threshold value (50 kJ/mol). These are approximated as one-dimensional hindered internal rotations. The hindrance potentials are calculated at the B3LYP/6-31G(d) level of theory with relaxed surface scans in which all coordinates, except for the considered dihedral angle, are re-optimized at each scan angle. The Fourier series expression of the hindrance potential together with reduced moment of inertia calculated at the $I^{(2,3)}$ level, are used to construct the Schrödinger equation for 1-dimensional internal rotation. The eigenvalues of the solution are used to determine the partition function as a function of temperature. The thermodynamic data is calculated from the total partition function after performing a correction for the symmetry and the number of optical isomers. Conventional transition state theory is used to calculate the rate coefficients over a temperature range 300 K – 1500 K with 50 K increment. Tunneling is accounted for using the asymmetric Eckart potential. The resulting rate coefficients are regressed to a simple Arrhenius expression. The kinetic parameters for the primary DEA oxidation steps are obtained from quantum chemical calculations using this methodology, while the kinetic parameters for the other reactions are approximated with the group additivity method. The oxidation of DEA is mainly initiated by H abstraction from the α carbon atom of DEA by molecular oxygen, as this C-H bond has the lowest dissociation energy, i.e. 383 kJ/mol.

Conclusions

New experimental data on the low- and intermediate temperature oxidation of DEA is acquired in an isothermal quartz jet-stirred reactor. In order to address the lack of accurate data for nitrogen-containing compounds, new kinetic and thermodynamic data are determined starting from

quantum chemical calculations at the CBS-QB3 level of theory. Using these data, a model is developed for the oxidation of DEA with Genesys in order to study the formation of the main carbon- and nitrogen containing products with particular attention of reaction paths related to NO_x formation.

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