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Kinetics of nitrosamine and amine reactions with NO_3 radical and ozone related to aqueous particle and cloud droplet chemistry

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ABSTRACT

Aqueous phase reactivity experiments with the amines dimethylamine (DMA), diethanolamine (DEA) and pyrrolidine (PYL) and their corresponding nitrosamines nitrosodimethylamine (NDMA), nitrosodiethanolamine (NDEA) and nitrosopyrrolidine (NPYL) have been performed. NO_3 radical reaction rate coefficients for DMA, DEA and PYL were measured for the first time and are 3.7×10^5, 8.2×10^5 and 8.7×10^5 M^{-1} s^{-1}, respectively. Rate coefficients for NO_3 + NDMA, NDEA and NPYL are 1.2×10^8, 2.3×10^8 and 2.4×10^8 M^{-1} s^{-1}. Compared to OH radical rate coefficients for reactions with amines, the NO_3 radical will most likely not be an important oxidant but it is a potential nighttime oxidant for nitrosamines in cloud droplets or deliquescent particles. Ozone is unreactive towards amines and nitrosamines and upper limits of rate coefficients suggest that aqueous ozone reactions are not important in atmospheric waters.

1. Introduction

Amines can be emitted to the atmosphere from a number of different natural or anthropogenic sources such as biodegradation of organic matter, biomass burning, vegetation or animal husbandry and industrial processes (Ge et al., 2011). The motivation for the present study is the emission of amines from fossil fuel combustion power plants which are equipped with carbon capture and storage (CCS) technology utilizing amine based solvents in the CO_2 scrubbing process. When organic compounds such as amines enter the atmosphere they are usually transformed and decomposed through oxidation reactions with atmospheric radicals or ozone. These chemical transformations occur both in the gas phase as well as the condensed phase of the troposphere which includes aerosol particles, cloud, fog and rain droplets (Nielsen et al., 2012; Qiu and Zhang, 2013). Nitrosamines can potentially form from emitted amines in the gas phase or they could be directly emitted in trace amounts from the power plants exhaust. Because of their severe carcinogenicity the atmospheric fate of nitrosamines is of special concern (Hutchings et al., 2010; Nielsen et al., 2012). Given the complicated nature of the interaction of gas and condensed phase oxidations, it is necessary to assess the potential impact of amines and nitrosamines on air quality with the help of atmospheric chemistry multiphase box models and dispersion models. Such models should simulate the key steps of possible chemical conversions in the atmospheric multiphase system but they rely heavily on accurate measurements or predictions of phase transfer parameters, kinetic constants and product distributions. Substantial information can be found on gas phase processes and aqueous phase processes involving the OH radical as one of the main atmospheric oxidants. But kinetic data on other important aqueous oxidants such as NO_3 radical or O_3 is scarce (Nielsen et al., 2012). Both NO_3 and O_3 can

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represent potentially important nighttime sinks for organic compounds. Only few measurements exist for aqueous ozone reactions with amines or nitrosamines. Depending on their pK_a and pH value, amines will be protonated or neutral in the aqueous phase, but most amines will be protonated in the atmospheric aqueous phase having pK_a values between 8 and 10 (Nielsen et al., 2012) and because of common pH-values of cloud and particles in the range of 1 to 7 (Herrmann, 2003). Small rate coefficients have been determined for neutral amines and protonated amines were unreactive towards O_3 (Hoigné and Bader, 1983b). For nitrosamine reactions with O_3, kinetic studies are limited to only nitrosodimethylamine (NDMA) where reported rate coefficients range from 0.052 to ~10 $M^{-1}\ s^{-1}$ (Hoigné and Bader, 1983b; Lee et al., 2007). To close the aforementioned knowledge gaps for O_3 and NO_3 reactivity, kinetic experiments have been undertaken with a series of amines and their corresponding nitrosamines, namely dimethylamine (DMA), diethanolamine (DEA), pyrrolidine (PYL) and nitrosodimethylamine (NDMA), nitrosodiethanolamine (NDEA) and nitrosopyrrolidine (NPYL). The obtained kinetic data are aimed for implementation into existing tropospheric cloud and particle chemistry models. Warning: precautionary measures should be implemented when working with the highly toxic nitrosamines!

2. Material and methods

2.1. No$_3$ radical reactions

The NO_3 reactivity with amines and nitrosamines was measured with a laser flash photolysis long path absorption setup (Fig. 1). The chosen method of NO_3 radical generation was $S_2O_8^{2-}$ photolysis at 351 nm due to the large UV-absorption of the nitrosamine reactants at shorter wavelengths. $S_2O_8^{2-}$ was added as $K_2S_2O_8$ in a concentration of 0.03 M NO_3^- in the form of $NaNO_3$ in a concentration of 0.1 M. The pH of the solutions was kept at pH = 4 for nitrosamines and amines. $S_2O_8^{2-}$ photolysis produces sulfate radicals:

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^- \qquad (R-1)$$

which then react with excess nitrate to form NO_3 radical:

$$SO_4^- + NO_3^- \rightarrow NO_3 + SO_4^{2-} \qquad (R-2)$$

followed by the reaction of NO_3 radical with the added reactant, amine or nitrosamine.

$$NO_3 + R \rightarrow \text{products} \qquad (R-3)$$

The decay of the NO_3 radical was followed by cw-laser spectroscopy at 632 nm. The 632 nm analytical HeNe-laser light was passed 3 times through the cell (d = 6 cm) to increase the absorption path to 18 cm. The measured intensity values from decay trace were plotted as $\ln(\ln(I_0/I_t))$ vs. time and the k_{1st} was obtained by linear regression. Pseudo first order rate coefficients (k_{1st}) have been measured at a series of different reactant concentrations in excess over NO_3 radical to obtain the second order rate coefficients (k_{2nd}) from a plot of k_{1st} vs. reactant concentration. Temperatures were varied to determine effects of T on the rate coefficient. The obtained results are given with an experimental error calculated with the student-t factor for the 95% confidence level. The experimental set-up was equipped with ventilations at three different positions as safety precaution (see Fig. 1). Experimental solutions with nitrosamines and radical precursors were prepared under a fumehood in sealable plastic volumetric flasks. All exhaust air was collected, separately removed from the laboratory and actively after-treated.

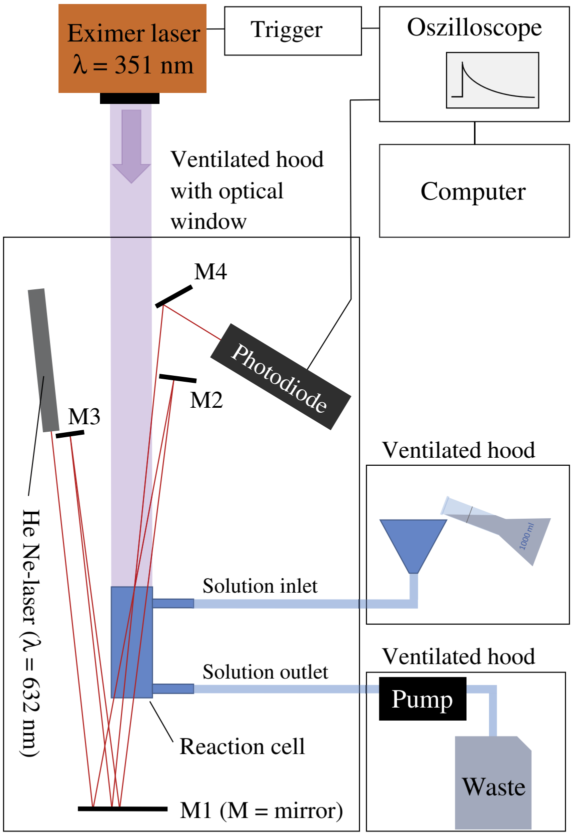

Fig. 1. Simplified scheme of experimental set-up to investigate NO_3 radical reactivity with $S_2O_8^{2-}$ photolysis at 351 nm as NO_3 generation method, ventilation system to work with hazardous volatile substances.

2.2. Ozone reactions

In aqueous solution, ozone undergoes a series of decomposition reactions initiated by hydroxide ion, OH^- (Kilpatrick et al., 1956; Sehested et al., 1991; Staehelin et al., 1984; Tomiyasu et al., 1985). The initial OH^- reaction can be suppressed by applying a low pH in the experiments, but the decomposition reactions are not completely blocked. Therefore, phosphate buffer has been used to adjust pH = 2 in the experimental solutions for both amine and nitrosamine reactions. The remaining experimental problem is to measure a very slow reaction with amines or nitrosamines on top of non-avoidable slow side reactions. Therefore, O_3 kinetic experiments always involved measurements of a blank solution with ozone besides the actual measurement of O_3 + reactant. All experiments were performed under a fumehood