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# Photo-oxidation of two Amines for Use in CO<sub>2</sub> Capture:

Experimental Studies  
in the  
European Photo Reactor EUPHORE

Matthias Karl<sup>1</sup>, Christian Dye<sup>1</sup>, Armin Wisthaler<sup>1,2</sup>, Norbert  
Schmidbauer<sup>1</sup>,  
Tomas Mikoviny<sup>2</sup>, Matteo Lanza<sup>2</sup>,  
Barbara D'Anna<sup>3</sup>, Aurelie Meme<sup>3</sup>,  
Monica Vázquez-Moreno<sup>4</sup>, Amalia Muñoz<sup>4</sup>,  
Mila Ródenas Garcíá<sup>4</sup>, and Esther Bórras<sup>4</sup>

<sup>1</sup> NILU – Norsk institutt for luftforskning

<sup>2</sup> Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck

<sup>3</sup> IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de LYON, Villeurbanne, France.

<sup>4</sup> Instituto Universitario CEAM-UMH - EUPHORE, Valencia, Spain



**Scientific report**

# **Summary report**

# Photo-oxidation of two Amines for Use in CO<sub>2</sub> Capture: Experimental Studies in the European Photo Reactor EUPHORE

Matthias Karl<sup>1</sup>, Christian Dye<sup>1</sup>, Armin Wisthaler<sup>1,2</sup>, Norbert Schmidbauer<sup>1</sup>, Tomas Mikoviny<sup>2</sup>, Matteo Lanza<sup>2</sup>, Barbara D'Anna<sup>3</sup>, Aurelie Meme<sup>3</sup>, Monica Vázquez-Moreno<sup>4</sup>, Amalia Muñoz<sup>4</sup>, Mila Ródenas García<sup>4</sup>, and Esther Bórras<sup>4</sup>

<sup>1</sup> NILU – Norsk institutt for luftforskning, Kjeller, Norway

<sup>2</sup> Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Austria

<sup>3</sup> IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de LYON, Villeurbanne, France.

<sup>4</sup> Instituto Universitario CEAM-UMH - EUPHORE, Valencia, Spain

## Abstract

The present study aimed at the identification and quantification of toxic compounds (nitrosamines and nitramines) resulting from the photochemical oxidation of the two amines for use in CO<sub>2</sub> capture and the determination of their chemical production yields under various NO<sub>x</sub> mixing ratios in sunlit chamber experiments. Kinetic and product studies on the reaction of two alkanol amines for use in CO<sub>2</sub> Capture, in the following referred to as Amine-1 and Amine-2, with hydroxyl (OH) radicals have been carried out in chamber B of the photo reactor facility EUPHORE in Valencia, Spain, in the time of 02-19 April 2013. The rate constant determined for reaction OH + Amine-1 was determined in the study to be  $(2.6 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , at  $296 \pm 1 \text{ K}$ . The rate constant for reaction OH + Amine-2 was determined to be  $(10.3 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $295 \pm 1 \text{ K}$ . The systematic uncertainty of the determined rate constant values is estimated to be 25% due to the uncertainties of the wall loss determination. The obtained results of the product studies suggest that about 30 % of the reaction between Amine-1 and OH radicals takes place at the amino group ( $-\text{NH}_2$ ). In all experiments the concentrations of nitramines and nitrosamines were determined by an off-line method (collection on Thermosorb cartridges and subsequent analysis by UHPLC-MS) and an on-line method (PTR-ToF-MS). Considering the uncertainties of the two measurement methods, the conversion yield of Amine-1-nitramine for low NO<sub>x</sub> conditions typical for Mongstad is estimated to range from 1.4% to 4.1%. The candidate for the first generation nitrosamine forming the photo-oxidation of Amine-1 (Amine-1-nitrosamine candidate) was identified by analysis of Thermosorb/N samples in the Amine-1 product yield experiments. The photo-oxidation experiments with Amine-2 gave no indication that a nitrosamine is formed in the OH-reaction of this amine.

## 1. Introduction

Photochemical experiments at European Photochemical Reactor (EUPHORE) in Valencia, Spain were used in the “Atmospheric Degradation of Amines” (ADA) projects to revise and update theoretical reaction mechanisms describing the OH-initiated oxidation of certain amines (Nielsen et al., 2010; 2011a; 2011b; 2012). In comparison to ADA projects, the present study has a very limited scientific scope: The identification and quantification of toxic compounds (nitrosamines and nitramines) resulting from the photochemical oxidation of the two amines and the determination of their production yields under various NO<sub>x</sub> mixing ratios in sunlit chamber experiments in the photo reactor EUPHORE.

The use of amines as reagents in chamber photo-oxidation studies presents a series of experimental challenges including wall losses, wall reactions and sample carry-over between different experiments. The chamber wall surfaces represent a sink for gas-phase alkanolamines; they are in a thermodynamic adsorption/desorption equilibrium with the adsorbed amines. The chamber wall surface can also act as a catalyst for heterogeneous reactions, for examples between amines and nitrous acid, known to form nitrosamines. The low surface-to-volume ratio, close to  $1 \text{ m}^{-1}$ , of the chamber and the good infrastructure at EUPHORE facilitated the study of the photo-oxidation of amines. Heterogeneous reactions on the chamber wall surfaces as well as the sample carry over between experiments were of minor importance in the EUPHORE experiments.

We report rate constants of the two amines in the reaction with OH radicals and product yields of nitrosamines and nitramines that form in the OH-initiated oxidation of the two amines. Provided errors of concentrations and yields refer to *systematic error*, and provided errors of derived rate constants refer to *random error* of the data analysis. The *systematic error* of rate constants is also provided.

## 2. Experimental

Kinetic and product studies on the reaction of two alkanol amines for use in CO<sub>2</sub> Capture - in the following referred to as Amine-1 and Amine-2 - with hydroxyl (OH) radicals have been carried out in chamber B of the photo reactor facility EUPHORE in Valencia, Spain, in the time of 02-19 April 2013. In total 14 experiments with the two amines were carried out in the EUPHORE facility. Experiments with Amine-1 were performed at high NO<sub>x</sub> and low NO<sub>x</sub> conditions to evaluate the relevance of reaction pathways that may compete with the formation of nitrosamines and nitramines. Experiments with Amine-2 were performed under high NO<sub>x</sub> conditions, with varying aerosol loads present at the beginning of the experiments. The NO<sub>x</sub> dependence of the nitrosamine and nitramine yields of Amine-2 was not further investigated because it was expected that the photo-oxidation of Amine-2 follows the reaction pathways in the N-abstraction channel based on the current understanding. Due to the cloudy conditions in springtime, the chemical isopropyl nitrite (CAS no. 541-42-4) was used to accelerate photochemistry in the experiments.

Typically, only one experiment for product yield determination was done on one day. Experiments typically started with 0.5 hour to 1 hour stand-time after injection of the amine was completed to observe losses of the amine to the chamber wall surfaces in the dark. The flushing/cleaning of the chamber was done overnight to reduce the concentrations of all gas phase compounds and particle concentrations to values close or below the instrument detection limits is done overnight with a high air flow of 3.0-3.5 m<sup>3</sup>/min. The total flushed air volume corresponds to several times the chamber volume (204 m<sup>3</sup>). Typical concentrations that could be achieved after e.g. 4 hours (corresponding to 720-840 m<sup>3</sup> air) of flushing are ca. 1 ppbv NO<sub>x</sub>, 1 ppbv O<sub>3</sub>, 1 µg/m<sup>3</sup> aerosol mass, < 1 ppbv amine, <0.1 pptv nitrosamines and nitramines; which were acceptable for the start of a new amine photo-oxidation experiment.

The deployed analytical methods to determine gas-phase concentrations of amines and their oxidation products were on-line high mass resolution Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS), High Temperature Proton-Transfer-Reaction Mass Spectrometry (HT-PTR-MS), Fourier Transformation Infrared Spectrometry (FT-IR), and in addition off-line ultra-high performance liquid chromatography mass spectrometry (UHPLC-MS) analysis of Thermosorb/N cartridges. Air samples were drawn from the chamber onto commercial Thermosorb/N cartridges at a flow rate of 3 liters per minute. Sampling was usually conducted for 30 minutes in the dark chamber before opening of the chamber canopy, during the sunlit experiment, and after the closing of the chamber canopy.

Measurement of total aerosol concentration and aerosol size distribution is done with a scanning mobility particle sizer (SMPS) composed of a differential mobility analyzer (DMA) with a condensation particle counter (CPC). In addition, a time-of-flight Aerodyne aerosol mass spectrometer (AMS) was used to measure time series of concentration of total aerosol, nitrate aerosol and organic aerosol (only in the experiments with Amine-2).

For the injection of amines into the dark chamber a new injection device developed and constructed by NILU was deployed. The new amine injection system has been successfully used to inject 2-aminoethanol (MEA) into the EUPHORE chamber during the NILU "MEATEST" campaign (24-31 July 2010) and allows injection of a predefined exact amount of amine with high precision (Karl et al., 2012). The injections system is build with a Harvard 22 syringe pump system with air stream heating which allows for transfer of a known amount of the alkanolamines into the chamber. The quantification of amine mixing ratios in the chamber air relied on measurements with the HT-PTR-MS and FT-IR instruments.

For the seeded experiments to study the impact of background aerosol on nitramine production yields, a defined initial seed aerosol was generated at experiment start by atomizing an aqueous ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) solution. Condensable products that form in the photo-oxidation of amines will condense on the seed particles. This method also allows for a better quantification of the yield of secondary organic aerosol than it would be possible in experiments without seed aerosol, because the presence of seed aerosol generally suppresses nucleation of new particles. Nucleation generally complicates the determination of aerosol yields. The introduction of aerosol seed (ammonium sulfate) with concentration of  $\sim 70 \mu\text{g}/\text{m}^3$  using an aerosol spray generator took only a few minutes.

Previous CCM (Carbon Capture Mongstad) projects on the analysis of nitramines have been focused on the chemical analysis of emission related matrices, such as the water-wash from CO<sub>2</sub> capture. CCM has not established a reference method for the quantification of nitramines in mixtures of amines and NO<sub>x</sub> in air. US EPA has evaluated Thermosorb/N (US EPA method 521; [http://www.epa.gov/microbes/documents/m\\_521.pdf](http://www.epa.gov/microbes/documents/m_521.pdf)) as being a suitable adsorbent for nitrosamines. US EPA has recommended HPLC for analysis of

nitramines in the trace analysis of explosive residues in water, soil and sediment (US EPA method 8330A;

<http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8330a.pdf>). No method from US EPA is available regarding analysis of nitrosamines and nitramines in air at humidity levels relevant for photo-oxidation chamber experiments.

Identification and quantification of nitrosamines and nitramines in this study has been done by on-line and off-line methods. Off-line ultra-high performance liquid chromatography mass spectrometry (UHPLC-MS) was used for the analysis of Thermosorb/N cartridges. Mass spectral interpretation included a targeted analysis for the first-generation nitrosamines and nitramines forming in the oxidation of Amine-1 and Amine-2. A commercial PTR-TOF 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was used for on-line measurements of nitrosamines and nitramines. The PTR-ToF-MS instrument has been described in detail by Jordan et al. (2009). The instrument was operated at a pulsing frequency of 33 kHz. The spectral integration time was 10 s. The electric field applied to the drift tube was periodically switched in 80 s intervals, i.e. measurements were performed at two alternating E/N-values of 50 and 90 Td ( $1 \text{ Td} = 10^{-17} \text{ Vcm}^{-2} \text{ molecule}^{-1}$ ), respectively. Here, E is the electric field strength across the drift tube (V/cm), and N is the gas number density ( $\text{molecules/cm}^3$ ). The double-mode operation was used to detect possible fragmentation of the product ions.

Table 1 provides a summary of the detection limits of the on-line method (PTR-ToF-MS) and the off-line method (Thermosorb/N + HPLC-MS) for the four nitrosamines / nitramines of interest. For the compounds where no reference standard was available, the term “candidate” was used to emphasize that the identification is not 100% certain. The evaluation of uncertainty in this study follows the definitions given in the EURACHEM/CITAC Guide CG 4 (Ellison et al., 2000). For the off-line method (Thermosorb/N collection and analysis by UHPLC/MS) the measurement uncertainty of Amine-1-nitramine is strictly following the EURACHEM definition, and the *expanded uncertainty* with coverage factor of two is provided.

*Table 1: Method Limit of Detection (LoD) for nitramines and nitrosamines in this study.*

Compound	PTR-ToF-MS (online method)	Thermosorb/N + HPLC-MS analysis (offline method) *
<b>Amine-1-nitramine</b>	~ 10 pptV	0.6 pptV
<b>Amine-1-nitrosamine candidate</b>	~ 10 pptV	2 pptV
<b>Amine-2-nitramine candidate</b>	~ 10 pptV	10 pptV
<b>Amine-2-nitrosamine candidate</b>	~ 10 pptV	10 pptV

\* LoD refer to 100 l sample.

The theoretical calibration error of the measurement of Amine-1-nitramine by the online method (PTR-ToF-MS) was  $\pm 25\%$ . The calibration factor of the PTR-ToF-MS for Amine-1-nitramine was derived theoretically from ion-molecule collision theory. The collision rate of  $\text{H}_3\text{O}^+$  and Amine-1-nitramine was calculated using the quantum-chemically calculated dipole moment and isotropic molecular polarizability of Amine-1-nitramine. The nominal calibration error of the collision rate calculation is  $\pm 25\%$  which is the main uncertainty contribution in the Amine-1-nitramine calibration. The *expanded uncertainty* of the PTR-ToF-MS measurement, as defined by EURACHEM/CITAC has not been evaluated to a full extent in the frame of this study, main point being that the uncertainty contribution from the heated inlet line and real calibration has not been investigated.

The chemical analysis of the Thermosorb/N samples were performed with a Agilent UHPLC/MS q-TOF (model 1290 Infinity/6550). The compound separation was accomplished by reversed phase chromatography. The instrument was calibrated with authentic Amine-1-nitramine reference standard (purity  $>99\%$ ). The *expanded uncertainty with a coverage factor of 2* is estimated to be  $\pm 28\%$  and the linearity is 4 orders of magnitude. The mass accuracy is better than 1 ppm and mass resolution is higher than 20 000 for the Amine-1-nitramine. Positive or negative artefact formation from particle deposition and/or from evaporation of particles from the Thermosorb/N cartridge was not investigated.

A control experiment with the reference standard of Amine-1-nitramine was performed. The intention of the experiment was to determine the fragmentation ratio of Amine-1-nitramine in the PTR-ToF-MS instrument in the absence of other gaseous compounds and particle phase. The injected amount of the Amine-1-nitramine reference standard was taken from a stock solution which had a concentration of 219 g/l in water. The stock solution has been diluted by 1500 (to give 146 mg/l) and 1 ml from the diluted solution was injected. The injection of 146  $\mu\text{g}$  of the reference standard of Amine-1-nitramine (in 1 ml aqueous solution) into the EUPHORE chamber was done using the amine injection system.

### 3. Results

#### *Control Experiment*

For the first time during an amine photo-oxidation campaign in EUPHORE, a comparison of the online instruments with the reference standard of a nitramine compound was carried out in a control experiment. The control experiment with the first generation nitramine that forms in the photo-oxidation of Amine-1 (in the following referred to as Amine-1-nitramine) allowed to evaluate the fragmentation of this compound in the PTR-ToF-MS. In all experiments the concentrations of nitramines and nitrosamines of the two amines were determined in parallel by the offline method (collection on Thermosorb cartridges and subsequent analysis by UHPLC-MS) and the online method (PTR-ToF-MS). It was possible to determine the mass spectral information for both the low-E/N and high-E/N mode of the PTR-ToF-MS operation. Protonated Amine-1-nitramine strongly fragments at the C-N bond upon protonation. The main finding of the control experiment is that

protonated Amine-1-nitramine does fragment under typical PTR-MS operating conditions.

### *Kinetic Studies*

Kinetic studies to determine the rate constant of the OH-reaction between Amine-1 and Amine-2. Kinetic experiments were performed as a relative rate experiment, using 1,3,5-Trimethylbenzene (1,3,5-TMB) as reference compound with known OH-rate constant. This method has been successfully applied by Karl et al. (2012) to determine the rate constant of the MEA + OH reaction.

The rate constant determined for reaction OH + Amine-1 was determined in the study to be  $(2.6 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , at  $296 \pm 1 \text{ K}$ . The rate constant for reaction OH + Amine-2 was determined to be  $(10.3 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at  $295 \pm 1 \text{ K}$ . The systematic uncertainty of the determined rate constant values is estimated to be 25% due to the uncertainties of the wall loss determination.

### *Product Studies*

Amine-1-nitramine was unambiguously identified and quantified by UHPLC/MS and PTR-ToF-MS in all analyzed photo-oxidation experiments with Amine-1. The discrepancy between the measured Amine-1-nitramine mixing ratios obtained from the offline and the online determination was relatively large, but still within the overall uncertainties of both methods. The evaluation of the missing uncertainty contributions of the respective method was beyond the scope of this study. It is therefore recommended to carry out future research on the comparison of the off-line and the on-line method quantification of nitramines derived from the oxidation of alkanolamines.

Production yields of Amine-1-nitramine in the OH-initiated oxidation of Amine-1 were determined based on the offline and the online measurement of Amine-1-nitramine and on FT-IR data of Amine-1 (accuracy  $\pm 22\%$ ). Amine-1-nitramine yields based on the FT-IR data and the UHPLC-MS data the production yield of Amine-1-nitramine in the photo-oxidation of Amine-1 was estimated to be 14 ( $\pm 5.2$ ) % for high  $\text{NO}_x$  conditions, 2.3 ( $\pm 0.9$ ) % for low  $\text{NO}_x$  conditions, and 1.6 ( $\pm 0.6$ ) % in the mixture experiment with Amine-1 and Amine-3 (Amine-3 has been studied in previous photo-oxidation experiments at EUPHORE). Amine-1-nitramine yields based on the FT-IR data and the PTR-ToF-MS data the production yield of Amine-1-nitramine in the photo-oxidation of Amine-1 was estimated to be 21 ( $\pm 7$ ) % for high  $\text{NO}_x$  conditions, 3.0 ( $\pm 1.1$ ) % for low  $\text{NO}_x$  conditions, and 4.1 ( $\pm 1.4$ ) % in the Amine-1 / Amine-3 mixture experiment.

The candidate for the first generation nitrosamine forming the photo-oxidation of Amine-1 (Amine-1-nitrosamine candidate) was identified by UHPLC-MS in the Amine-1 product yield experiments. The estimated mass-based yield for Amine-1-nitrosamine candidate for high  $\text{NO}_x$  was  $0.85 \text{ }^{+1.7}_{-0.6} \%$  and for low  $\text{NO}_x$  was  $0.01 \text{ }^{+0.02}_{-0.01} \%$ . Based on the available information obtained from PTR-ToF-MS it is concluded that no unequivocally evidence was found for the formation of Amine-1-nitrosamine from the reaction of Amine-1 with OH radicals.

The candidate for the first generation nitramine forming the photo-oxidation of Amine-2 (Amine-2-nitramine candidate) was identified by UHPLC-MS and PTR-ToF-MS in the Amine-2 product yield experiments. Based on the FT-IR data and the UHPLC-MS data the production yield of Amine-2-nitramine candidate in the photo-oxidation of Amine-2 was estimated to be 6.7 ( $+13.4$ )<sub>-4.4</sub> % without seed aerosol and 1.0 ( $+2.0$ )<sub>-0.7</sub> % with seed aerosol (ammonium sulphate). The yield from PTR-ToF-MS data for the seeded experiment was in agreement with the offline yield determination, with 0.7 ( $+1.3$ )<sub>-0.4</sub> %.

The candidate for the first generation nitrosamine forming the photo-oxidation of Amine-2 (Amine-2-nitrosamine candidate) was not identified by UHPLC-MS above detection limit in the Amine-2 product yield experiments. No signal corresponding to the exact m/z of protonated Amine-2-nitrosamine was detected by PTR-ToF-MS in any of the experiments. Amine-2-nitrosamine is unlikely to be observed because the primary nitrosamine group is anticipated to rapidly undergo isomerization to a hydroxy diazo group which reacts with O<sub>2</sub>.

#### *Product yield summary*

In Table 2 an overview of the product yields of Amine-1-nitramine, Amine-1-nitrosamine candidate, and Amine-2-nitramine candidate determined in experiments of this study using either measurement data from the Thermosorb/N analysis by UHPLC/MS (off-line method) or from PTR-ToF-MS (on-line method). The respective systematic uncertainty of the determined yields due to the uncertainties of the analytical method and the uncertainties of the model calculation are provided for each yield estimate, as absolute error. For low NO<sub>x</sub> and high NO<sub>x</sub> experiments, respectively, the obtained yield of the Amine-1-nitramine according to the off-line method and the on-line method quantification were rather similar. However the Amine-2-nitramine candidate could only be quantified with a large uncertainty since the reference standard of this nitramine was not available. Therefore no reliable conclusion can be drawn based on comparing the yields.

*Table 2: Percentage production yields of Amine-1-nitramine, Amine-1-nitrosamine candidate, and Amine-2-nitramine candidate. Amine-1-nitrosamine candidate and Amine-2-nitramine candidate were only tentatively identified. Provided uncertainty in brackets reflects overall accuracy of the yield determination. Long dash indicates that no unambiguous signal at the compound m/z could be identified. Blackened boxes indicate that no experiments for the corresponding combination have been performed during the campaign in EUPHORE.*

Conditions	UHPLC-MS			PTR-ToF-MS		
	Amine-1-Nitramine	Amine-1-Nitrosamine candidate	Amine-2-Nitramine candidate	Amine-1-Nitramine	Amine-2-Nitrosamine candidate	Amine-2-Nitramine candidate
Low NO <sub>x</sub>	2.3 (±0.9)	0.01 ( <sup>+0.02</sup> <sub>-0.02</sub> )		3.0 (±1.1)	—	
High NO <sub>x</sub>	14.0(±5.2)	0.85 ( <sup>+1.7</sup> <sub>-0.6</sub> )	6.7 ( <sup>+13.4</sup> <sub>-4.4</sub> )	21.0 (±7.4)	—	—
High NO <sub>x</sub> , seed aerosol			1.0 ( <sup>+2.0</sup> <sub>-0.7</sub> )			0.7 ( <sup>+1.3</sup> <sub>-0.4</sub> )
High NO <sub>x</sub> , amine mixture	1.6 (±0.6)	~0.002 (±0.002)		4.1 (±1.4)	—	

#### 4. Discussion

There is contradicting evidence for Amine-1-nitramine being a sticky compound that undergoes adsorption to and desorption from the chamber walls and partitioning to particles. It could not be clarified whether non-zero concentrations of Amine-1-nitramine in the background chamber air before experiment start stem from carry-over of the Amine-1-nitramine itself or from carry-over of Amine-1 which subsequently was oxidized to Amine-1-nitramine. A conclusive answer can only be obtained in further studies. Until then, all statements and conclusions related to the stickiness of Amine-1-nitramine should be regarded as preliminary, since it has only been confirmed for the conditions of a laboratory experiment. In this laboratory experiment (recovery experiment), the sampling collection efficiency and the recovery of Amine-1-nitramine on Thermosorb/N cartridges was evaluated. The recovery experiment demonstrated that Amine-1-nitramine is lost to Silcosteel at room temperature, in a relatively low zero air flow of 1.8 lpm and with significant amount of methanol and no other species being present in the matrix. For the data analysis of the campaign only experiments were selected that did not suffer from carry-over of the amines of previous experiments or from the potential desorption of Amine-1-nitramine from the chamber walls.

High load of particles (200-1200 µg m<sup>-3</sup>) formed in all experiments, with the aerosol mass increasing steadily throughout experiment time. The loss of amines to the particles can therefore not be neglected and has to be investigated further.

The loss of the amine to particles will increase the potential error of the yield quantification.

## 5. Conclusions

Based on model simulations of photo-oxidation experiments using Amine-1 data by FT-IR and Amine-1-nitramine data by PTR-ToF-MS it is concluded that about 30% of the reaction with OH radicals takes place at the amino group ( $-\text{NH}_2$ ), to form the first-generation nitramine and nitrosamine, about 65% take place at the  $-\text{CH}_2\text{OH}$  group, to form an amino aldehyde, and about 5% lead to the formation of ammonia ( $\text{NH}_3$ ) following a mechanism that has still to be clarified. The H-abstraction at one of the  $\text{CH}_3$  groups appears to be negligible (less than 1%). An alternative explanation for the formation of  $\text{NH}_3$  in the experiments could be surface reactions on particles or displacement of ammonium from particles. It is emphasized that the branching ratio at the amino group determined using concentrations of Amine-1-nitramine measured by PTR-ToF-MS is in the same order of magnitude as in the previously postulated mechanisms for the OH-reaction of Amine-1. The recommendation to use the highest obtained yield for Amine-1-nitramine (corresponding to 30% H-abstraction at  $-\text{NH}_2$ ) for atmospheric dispersion simulations is driven by the intention to provide a “worst case” estimate for the environmental impact assessment of amines emitted from  $\text{CO}_2$  capture.

Results obtained in the photo-oxidation experiments on the gas-phase reaction of the two amines with the OH radical, i.e. rate constants and branching ratio provide information for use in dispersion modelling of the atmosphere at Mongstad. For a full evaluation of the environmental impact of the two selected amines for use in  $\text{CO}_2$  capture, other atmospheric processes such as uptake of amines by aerosol, partitioning of amines to the aqueous phase of clouds, dry deposition, and wet deposition have to be taken into consideration. The ambient formation yields of nitrosamines and nitramines from the oxidation of gaseous amines in the boundary layer at Mongstad will therefore depend on the level of  $\text{NO}_x$ , the actinic flux, relative humidity and background aerosol level and composition. It is noted that the actual nitramine production yield in the Mongstad region will more correspond to the yield determined for low  $\text{NO}_x$  conditions. Considering the uncertainties of the two measurement methods, the conversion yield of Amine-1-nitramine for low  $\text{NO}_x$  conditions is estimated to range from 1.4% to 4.1%.

## Acknowledgement

This project has received financial support from Gassnova through CLIMIT project no. 225764 and from Aker Engineering & Technology AS, Department of Clean Carbon.

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*Associated with CIENS and the Fram Centre*  
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REPORT SERIES SCIENTIFIC REPORT	REPORT NO. OR 44/2013	ISBN: 978-82-425-2615-1 (print) 978-82-425-2616-8 (electronic) ISSN: 0807-7207	
DATE 2.12.2013	SIGN. 	NO. OF PAGES 10	PRICE NOK 150.-
TITLE Photo-oxidation of two Amines for Use in CO <sub>2</sub> Capture:  Experimental Studies in the European Photo Reactor EUPHORE		PROJECT LEADER Matthias Karl  NILU PROJECT NO. O-112126	
AUTHOR(S) Matthias Karl, Christian Dye, Armin Wisthaler, Norbert Schmidbauer, Tomas Mikoviny, Matteo Lanza, Barbara D'Anna, Aurelie Meme, Monica Vázquez-Moreno, Amalia Muñoz, Mila Ródenas García, and Esther Bórras		CLASSIFICATION * A  CONTRACT REF. Aker Engineering & Technology AS Purchase Agreement no. PO-343	
QUALITY CONTROLLER: Leonor Tarrasón, Aasmund Fahre Vik			
REPORT PREPARED FOR Aker Engineering & Technology AS 160326-FE&T Clean Carbon Snarøyveien 20, PO Box 222 NO-1326 Lysaker, Norway			
ABSTRACT The present study aimed at the identification and quantification of toxic compounds (nitrosamines and nitramines) resulting from the photochemical oxidation of the two amines (Amine-1 and Amine-2) for use in CO <sub>2</sub> capture and the determination of their chemical production yields under various NO <sub>x</sub> mixing ratios in sunlit chamber experiments at the photo reactor facility EUPHORE in Valencia, Spain. Considering the uncertainties of the two applied nitramine measurement methods, the conversion yield of Amine-1-nitramine for low NO <sub>x</sub> conditions typical for Mongstad is estimated to range from 1.4% to 4.1%. The candidate for the first generation nitrosamine forming the photo-oxidation of Amine-1 (Amine-1-nitrosamine candidate) was identified by analysis of Thermosorb/N samples in the Amine-1 product yield experiments.			
NORWEGIAN TITLE Foto-oksidasjon av to aminer for bruk ved CO <sub>2</sub> -fangst. Eksperimentelle studier i den europeiske foto-reaktoren "EUPHORE".			
KEYWORDS			
Air Quality	Carbon Capture and Storage		Health Effects
ABSTRACT (in Norwegian) Denne artikkelen presenter identifisering og kvantifisering av giftige forbindelser (nitrosaminer og nitraminer) som dannes som følge av den luftkjemiske degradering av to aminer (Amin-1 og Amin-2). Disse aminer blir brukt for karbonfangst. Eksperimenter ble gjennomført under forskjellige NO <sub>x</sub> blandingsforhold i det solbelyste kammer ved "European Photochemical Reactor" EUPHORE i Valencia (Spania). Når man tar i betraktning usikkerheten i de to anvendte nitramine målemetoder, er produktutbytte av Amin-1-nitramine for lav-NO <sub>x</sub> forhold typiske for Mongstad anslått å variere fra 1.4% til 4.1%. Kandidaten for den første generasjonen nitrosamine dannet i foto-oksidasjon av Amin-1 (Amin-1-nitrosamine kandidat) ble identifisert ved analyse av Thermosorb/N prøvene i Amin-1 produktutbytte eksperimenter.			

\* Classification  
A Unclassified (can be ordered from NILU)  
B Restricted distribution  
C Classified (not to be distributed)

REFERENCE: O-112126  
DATE: NOVEMBER 2013  
ISBN: 978-82-425-2615-1 (print)  
978-82-425-2616-8 (electronic)

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