Article:

Antonsen, Simen, Bunkan, Arne J.C., D'Anna, Barbara et al. (12 more authors) (2017) Atmospheric Chemistry of tert-butylamine and AMP. Energy Procedia. pp. 1026-1032. ISSN 1876-6102

https://doi.org/10.1016/j.egypro.2017.03.1248

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 114 (2017) 1026 – 1032

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Atmospheric chemistry of *tert*-butylamine and AMP

Simen Antonsen[a], Arne J. C. Bunkan[b], Barbara D´Anna[c], Philipp Eichler[d],Naomi Farren[e], Mattias Hallquist[f], Jacquiline F. Hamilton[e],Hampus Kvarnliden[f], Tomáš Mikoviny[b], Markus Müller[c],Claus J. Nielsen[b]*, Yngve Stenstrøm[a], Wen Tan[b], Armin Wisthaler[b], Liang Zhu[b]

[a]*Norwegian University of Life Science, Department of Chemical Biotechnology and Food Science, NO-1432 Aas, Norway*
[b]*Department of Chemistry, University of Oslo, P.O.Box. 1033 Blindern, NO-0315 Oslo, Norway*
Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69629 Villeurbanne, France

[d]*Institute of Ion Physics and Applied Physics, University of Innsbruck, Austria*
[e]*Wolfson Atmospheric Chemistry Laboratory, University of York, York YO10 5DD, N Yorkshire, England*
[f]*University of Gothenburg, Department of Chemistry and Molecular Biology, Atmospheric Science, SE-41296 Gothenburg, Sweden*

Abstract

The atmospheric chemistry of $(CH_3)_3CNH_2$ (*tert*-butylamine, *t*BA) and $(CH_3)_2(CH_2OH)CNH_2$ (2-amino-2-methyl-1-propanol, AMP) has been studied by quantum chemistry methods and in photo-oxidation experiments in the EUPHORE chamber in Valencia (Spain). Aerosol formation and composition has been quantified. Yields of nitramines and other products in the photo-oxidations have been determined and complete photo-oxidation schemes including branching between the major reaction routes have been obtained.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: Amines; nitramines; atmospheric chemistry; photo-oxidation;

---

* Corresponding author. Tel.: +47-22855680.
E-mail address: claus.nielsen@mail.uio.no

Peer-review under responsibility of the organizing committee of GHGT-13.
doi:10.1016/j.egypro.2017.03.1248

1. Introduction

Implementation of amine-based Carbon Capture technology results in small, but yet significant emission of amines to the environment. The concern is that the amines emitted subsequently will undergo photo-oxidation resulting in formation of potentially carcinogenic nitrosamines and nitramines. The Norwegian Institute for Public Health (NIPH) has recommend upper limits ensuring minimal or negligible risk of cancer for the public from exposure to these substances. NIPH concludes that the total amount of nitrosamines and nitramines should not exceed 0.3 ng/m^3 in air and 4 ng/L in drinking water.[1] To realize such low ambient concentrations requires intimate knowledge of the atmospheric chemistry and strict limits on the allowed amine emissions.

AMP (2-Amino-2-methyl-1-propanol) and *tert*-butylamine, *t*BA, differ from other amines studied in the ADA projects[2-4] in lacking hydrogen atoms attached to the carbon atom in alpha-position – the primary amino group is attached to a tertiary carbon atom. There is no reliable quantitative information in the open literature on products formed in the photo-oxidation of AMP and similar amines. Carter reported results from photo-oxidation studies of AMP and reported ~80% H-abstraction from the amino group;[5] a "lumped photo-oxidation mechanism" was also presented. This model was later used by CSIRO in their atmospheric dispersion calculations.[6] Azzi *et al.*[6] also reported results from mixed AMP + NO_x + VOC photo-oxidation experiments from which no information concerning the branching ratio N-H : C-H in the initial abstraction step can be extracted. There is no mechanistic information on *t*BA photo-oxidation available in the literature.

2. Experimental

The photo-oxidation experiments were part of a campaign carried out in the period June 1 – June 26, 2015, in chamber B at the European Photoreactor Facility (EUPHORE) in Valencia, Spain (longitude -0.5, latitude 39.5). The EUPHORE facility includes two ~200 m^3 hemispherical outdoor chambers constructed from Teflon film for photochemical studies, offering a range of analytical instrumentation for *in situ* and on-line detection of chemical components and particles in the chamber, and monitors for actinic flux.[7]

A commercial PTR-TOF 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) was used for on-line organic trace gas measurements.[8] The instrument was operated at 100 Td (1 Td = 10^{-17} V cm^{-2} molecule^{-1}) in a 10 s integration mode; the drift tube was kept at a temperature of 100 °C and a pressure of 2.4 mbar. The analyzer was interfaced to the EUPHORE chamber via a 200 cm long Siltek®/Sulfinert®-treated stainless steel (inner diameter 2.16 mm) sampling tube kept at 80 °C. The inlet flow was set to 50 sccm. The PTR-TOF 8000 instrument was calibrated for toluene using a dynamically diluted VOC standard (Apel-Riemer Environmental Inc., Boulder, CO, USA) containing approximately 1 ppmV of toluene with an accuracy of ± 5%. The instrument was also calibrated for amines using a commercial liquid calibration unit (LCU, Ionicon Analytik GmbH, Innsbruck, Austria) for evaporation of a gravimetrically prepared aqueous standard in nitrogen. Instrumental response factors for potential photo-oxidation products of *t*BA and AMP were theoretically derived using ion-molecule collision rates of H_3O^+ ions with the respective analyte molecules.[9] An empirical instrumental correction factor was applied to account for mass discrimination effects in the ion detection and kinetic energy effects in the collision rate calculations.

Chemical analysis of semi-volatile submicron particles was obtained with a PTR-TOF 8000 instrument interfaced to a CHARON inlet.[10] The CHARON inlet strips off gas-phase analytes, enriches the particle concentration in the PTR-ToF-MS subsampling flow and vaporizes the particles prior to analysis by PTR-ToF-MS. The vaporization temperature used in this study was 140 °C. The CHARON inlet was interfaced to the EUPHORE chamber using Siltek®/Sulfinert®-treated stainless steel tubing (total length: 415 cm, 40 cm extending into the chamber, ID: 4.57 mm). The inlet included a thermodenuder section immediately upstream of the gas-phase denuder of the CHARON set-up. The PTR-ToF-MS drift tube was kept at a temperature of 130 °C and a pressure of 2.40 mbar (100 Td). The entire set-up was calibrated using size-selected ammonium nitrate particles. Reference spectra were obtained for the *t*BA and AMP nitrate salts.

The time-of-flight Aerodyne Aerosol Mass Spectrometer (AMS) allows real-time and *in situ* analysis of fine and ultrafine particles. The instrument investigates size distribution and chemical composition of particles between 0.03 to 1.0 μm on a 1 min basis. The methodology used within c-TOF AMS is fully described in Drewnick *et al.*[11] The particles are sampled through a critical orifice (diameter 100μm) at 80 cm^3 min^{-1} and focused by an aerodynamic lens which blocks all particles larger than 1 μm in diameter. Then they enter a vacuum chamber where a mechanical chopper allows a packet of particles (beam chopped) to be accelerated according to their vacuum aerodynamic diameter (D_{va}) and thereby giving size distribution data. The particles are then sent to the vaporization-ionization chamber where the non-refractory (NR) components of the particles are flash-vaporized on a hot surface (~600 °C) and ionized by electron impact (35 eV). Resultant positively charged ions are guided into the time-of-flight mass spectrometer. The collected mass spectra (m/z from 4 to > 300 in a minute scale) give information on the chemical composition (nitrate, sulphate, chloride, potassium, ammonium, aliphatic organic, PAHs) using a "fragmentation table".

Thermosorb/N air sampling cartridges (Ellutia, Cambridge) were used for the quantitative analysis of nitramines. The cartridge contains a solid adsorbent to collect the nitrosamines and nitramines, and an amine trap and nitrosation inhibitor to prevent artificial analyte formation. The Thermosorb/N cartridges were connected to the chamber using a 50 cm length of ¼" Sulfinert coated tubing, with an in-line particulate filter (2 μm) installed before the cartridge. Sampling was performed at 1 L min^{-1} for 60 minutes at various time intervals throughout each experiment. The cartridges were eluted using 3 mL of DCM/methanol (3:1, *v/v*) for the analysis of nitramines. The elution efficiency was estimated by vapor spiking the cartridges with the target compound; recovery of the *t*BA-nitramine was 54% whereas only 5% of the AMP-nitramine was recovered. The solvent extracts were evaporated under a gentle stream of nitrogen, redissolved in 1 mL ethyl acetate, and analysed by two-dimensional gas chromatography nitrogen chemiluminescence detection (GCxGC-NCD). A series of blank Thermosorb/N cartridges were analysed and the target compound was not found in any of these samples.

At the end of each experiment the chamber was closed and the aerosol formed was collected onto 47 mm diameter quartz microfiber filters at a flow rate of 48 L min^{-1} for 60 min. The filters were stored at -18 °C until further analysis. Three quarters of each filter was analyzed using two-dimensional gas chromatography nitrogen chemiluminescence detection (GCxGC-NCD). The filters were extracted into ethyl acetate using pressurized liquid extraction, and concentrated to a final volume of 1 mL prior to injection into the GC. The remaining quarter of the filter was analyzed for nitrate salts of tBA and AMP using ion chromatography. The filter was dissolved in deionized water (2 mL) and sonicated at RT for 30 min. The liquid extract was filtered (0.22 μm) prior to analysis.

Chemical synthesis procedures for the nitramines and other reference compounds will be reported elsewhere.

3. Theoretical methods

3.1. Quantum calculations

Stationary points on the potential energy surface for the reactions of OH with *t*BA and AMP were characterized in M06-2X[12] calculations employing the aug-cc-pVTZ[13-14] basis set. Pre and post reaction complexes were located by following the reaction path (IRC) from the saddle points. The energies of the stationary points were then improved with explicitly correlated coupled cluster singles and doubles calculations with perturbative triples scaled as recommended in the Molpro manual, denoted CCSD(T*)-F12a.[15-16] Reaction enthalpies were calculated using the G4 model chemistry.[17] Additional dipole moments and isotropic polarizabilities serving as input to prediction of ion-molecule reaction rate coefficients[18] were obtained in B3LYP calculations. The coupled cluster calculations were performed in Molpro 2012.1[19-20] whereas the DFT and G4 calculations were performed in Gaussian 09.[21]

3.2. Kinetics calculations

Master equation calculations were carried out using the program MESMER 3.0[22] (Master Equation Solver for Multi-Energy-well Reactions) to simulate the kinetics of the OH radical reactions with *t*BA and AMP as well as to estimate the branching´s in the subsequent degradation steps. The required input parameters for the stationary points were obtained from the electronic structure calculations, whereas the energy transfer in collisions with N_2, $\langle \Delta E_{down} \rangle$, was set to 250 cm^{-1}.

4. Results

Six *t*BA and six AMP photo-oxidation experiments were carried out in the EUPHORE reactor in Valencia in June 2015. Full reports of the results obtained are in progress and will be offered elsewhere. In the present communication we only give selected examples from our studies.

4.1. Tert-Butylamine

The atmospheric photo-oxidation of *t*BA is dominated by reaction with the OH radical that abstracts a hydrogen atom from either one of the $–CH_3$ groups or from the $–NH_2$ group. The reaction is characterized by pre- and post-reaction Van der Waals adducts and submerged barriers. Fig. 1 illustrates the stationary points on the potential energy surface of the initial steps in the OH radical reaction with *t*BA and the atmospheric photo-oxidation mechanism following H-abstraction from one of the $–CH_3$ groups. The theoretical study shows that the nitrosamine and nitramine of tBA will be formed in the atmospheric photo-oxidation of tBA, but that the nitrosamine spontaneously re-arranges and $(CH_3)_3CNHNO \rightarrow (CH_3)_3CN{=}NOH \rightarrow (CH_3)_2C{=}CH_2 + N_2 + H_2O$.

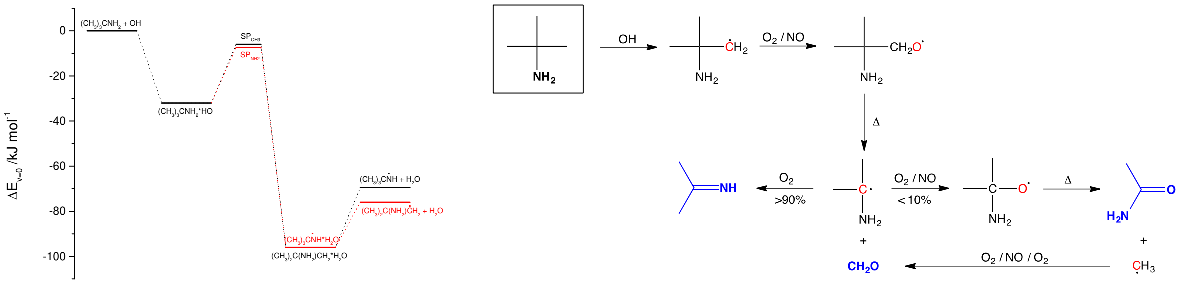

Fig. 1. (Left) Potential energy surface of the initial steps in the OH radical reaction with tBA. Results from CCSD(T*)-F12a/aug-cc-pVTZ// M06-2X/aug-cc-pVTZ. (Right) Mechanism the atmospheric photo-oxidation following H-abstraction from one of the CH_3-groups. The chemical compounds in boldface typeset have been detected in the experiments.

The air was sampled on Thermosorb/N cartridges at regular intervals during the photo-oxidation experiments. Fig. 2 illustrates the pleasing agreement between the off-line results and the on-line PTR-ToF-MS results.

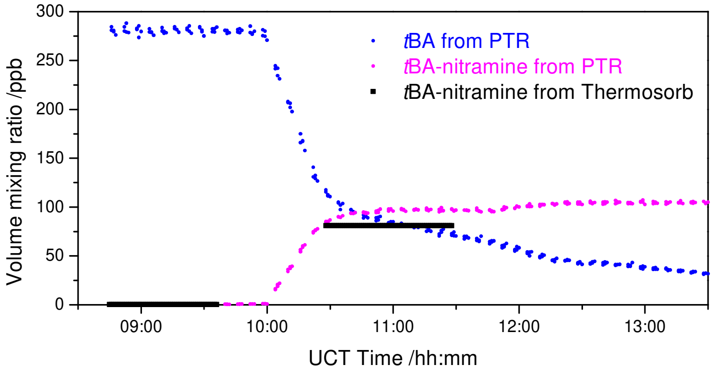

Fig. 2. Comparison of off-line and on-line results during a *t*BA photo-oxidation experiment (on June 2, 2015). Chamber opened at 09:42 and closed at 11:48.

Aerosol formation was observed in all photo-oxidation experiments. A major part of the particles is found to be the amine-nitric acid salt, but other organic components were unambiguously identified by the CHARON system. Fig.

3 shows an example of the aerosol growth and the chemical constituents found in the particles by evaporation at 140 °C.

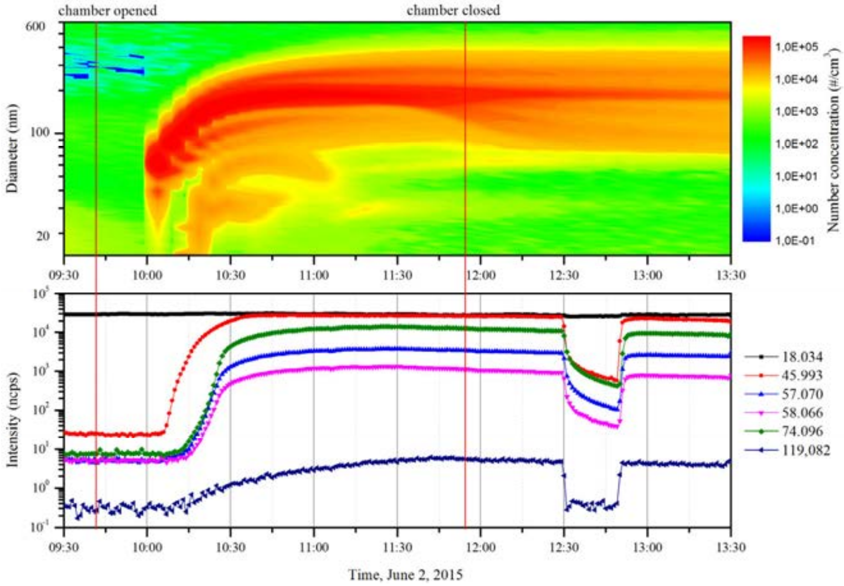

Fig. 3. *t*BA photo-oxidation experiment (on June 2, 2015). Chamber opened at 09:42 and closed at 11:48. (Top) Particle number and size distribution during the experiment. (Bottom) CHARON primary ion signals from the aerosol. Ion signals m/z 18.034 (NH_4^+), m/z 45.993 ($H_2NO_3^+$), m/z 57.084 ($C_4H_9^+$ fragment from protonated *t*BA) , m/z 58.066 ($C_3H_8N^+$, protonated $(CH_3)_2C{=}NH$), m/z 74.096 ($C_4H_{12}N^+$, protonated *t*BA) and m/z 119.082 ($C_4H_{11}N_2O_2^+$, protonated *t*BA-nitramine).

4.2. AMP

The atmospheric photo-oxidation of AMP is dominated by reaction with the OH radical that abstracts a hydrogen atom from either one of the $-CH_3$ groups, from the $-CH_2OH$ group or from the $-NH_2$ group. The reaction is characterized by pre- and post-reaction Van der Waals adducts and submerged barriers for the H-abstraction reactions involving $-NH_2$ and CH_2 in $-CH_2OH$; there is a small barrier to abstraction from the CH_3-groups and a medium high barrier to abstraction from OH in $-CH_2OH$. H-abstraction from the CH_3-groups and the OH-group will therefore only be of minor importance at atmospheric conditions.

AMP will also form both the corresponding nitrosamine and the nitramine during atmospheric photo-oxidation; but, again, the nitrosamine spontaneously re-arranges: $(CH_3)_2(CH_2OH)CNHNO \rightarrow (CH_3)_2(CH_2OH)CN{=}NOH \rightarrow CH_2{=}C(CH_3)CH_2OH + N_2 + H_2O$. Focusing on the nitramine formation, an average number for the nitramine yield was found to be (0.4 ± 0.2) % of reacted AMP per ppbV NO_2 present in the air. Fig. 4 illustrates the AMP loss and the AMP-nitramine formation during a photo-oxidation experiment (the NO_2 mixing ratio increased from around 10 to 30 ppbV during the experiment due to the addition of the OH pre-cursor isopropylnitrite).

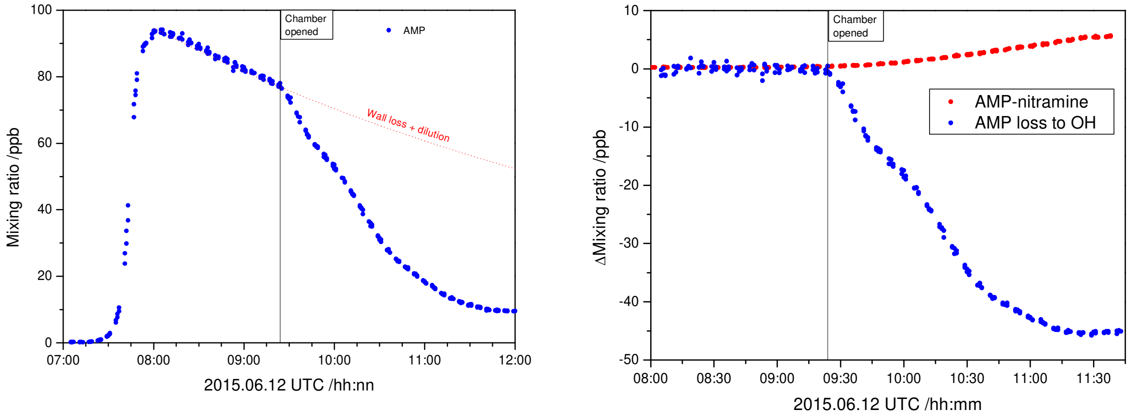

Fig. 4. Time profile of AMP during the AMP photo-oxidation experiment on 2015.06.12 from which a nitramine yield of (0.4 ± 0.2) % of reacted AMP per ppbV NO_2 present was extracted. Results from PTR-ToF-MS.

The composition of the aerosol formed during the experiments was not only analysed by AMS and CHARON, but also by GCxGC-NCD and ion chromatography. The ion chromatography results for the AMP aerosol show that the major constituent is the AMP nitrate; the GCxGC-NCD chromatogram, Fig. 5, shows the presence of the AMP nitramine as well as other nitrogen containing compounds in the aerosol.

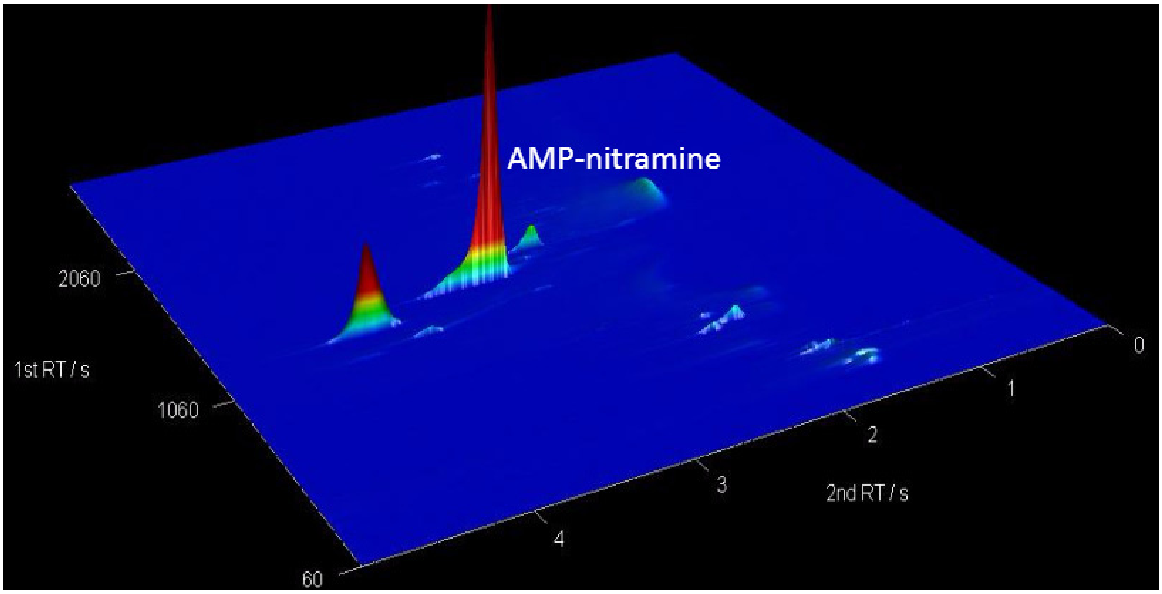

Fig. 5. GCxGC-NCD chromatogram to show AMP-NO_2 and other organic nitrogen compounds in the collected aerosol

Acknowledgements

This work is part of the Atmospheric Chemistry of Amines project (ACA) supported by CLIMIT program under contract 244055, and has received additional support from the Research Council of Norway through a Centre of Excellence Grant (Grant No. 179568/V30).

References

[1] Låg M, Lindeman B, Instanes C, Brunborg GPS. Health effects of amines and derivatives associated with CO_2 capture. The Norwegian Institute of Public Health 2011.

[2] Nielsen CJ, D'Anna B, Dye C, George C, Graus M, Hansel A, Karl M, King S, Musabila M, Müller M, Schmiedbauer N, Stenstrøm Y, Wisthaler, A. Atmospheric Degradation of Amines (ADA). Summary Report: Gas phase photo-oxidation of 2-aminoethanol (MEA) NILU OR 8/2010, ISBN 978-82-425-2172-9; NILU: 2010.

[3] Nielsen CJ, D'Anna B, Karl M, Aursnes M, Boreave A, Bossi R, Bunkan AJC, Glasius M, Hansen AMK, Hallquist M, Kristensen K, Mikoviny T, Maguta MM, Müller M, Nguyen Q, Westerlund J, Salo K, Skov H, Stenstrøm Y, Wisthaler A, Summary Report: Photo-oxidation of Methylamine, Dimethylamine and Trimetahylamine. Climit project no. 201604; NILU OR 2/2011, ISBN 978-82-425-2357-0; NILU: 2011.

[4] Nielsen CJ, D´Anna B, Bossi R, Bunkan AJC, Dithmer L, Glasius M, Hallquist M, Hansen AMK, Lutz A, Salo K, Maguta MM, Nguyen Q, Mikoviny T, Müller M, Skov H, Sarrasin E, Stenstrøm Y, Tang Y, Westerlund J, Wisthaler A. Atmospheric Degradation of Amines (ADA); ISBN 978-82-992954-7-5, http://urn.nb.no/URN:NBN:no-30510; University of Oslo: Oslo, 2012.

[5] Carter WPL. Reactivity estimates for selected consumer product compounds; Center for Environmental Research and Technology, College of Engineering, University of California, Riverside, California 92521: February 19, 2008.

[6] Azzi M, Angove D, Campbell I, Cope M, Emmerson K, Feron P, Patterson M, Tibbett ASW. Assessing Atmospheric Emissions from Amine based CO2 PCC Process and their Impacts on the Environment – A Case Study. Volume 2: Atmospheric chemistry of MEA and 3D air quality modelling of emissions from the Loy Yang PCC plant.; CSIRO Australia: 2014.

[7] Becker KH. The European Photoreactor EUPHORE, Design and Technical Development of the European Photoreactor and First Experimental Results, Final Report of the EC-Project Contract EV5V-CT92-0059; 1996.

[8] Jordan A, Haidacher S, Hanel G, Hartungen E, Mark L, Seehauser H, Schottkowsky R, Sulzer P, Mark TD. A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS). Int J Mass spectrom 2009; 286:122-128.

[9] Su T, Chesnavich WJ. Parametrization of the ion-polar molecule collision rate constant by trajectory calculations. J Chem Phys 1982; 76:5183-5.

[10] Eichler P, Müller M, D'Anna B, Wisthaler A. A novel inlet system for online chemical analysis of semi-volatile submicron particulate matter. Atmos Meas Tech 2015; 8:1353-1360.

[11] Drewnick F, Hings S, DeCarlo P, Jayne J, Gonin M, Fuhrer K, Weimer S, Jimenez J, Demerjian K, Borrmann S, Worsnop D. A New Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS) - Instrument Description and First Field Deployment. Aerosol Sci Technol 2005; 39:637-658.

[12] Zhao Y, Truhlar DG. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. Theor Chem Acc 2008; 120:215-241.

[13] Dunning TH Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. J Chem Phys 1989; 90:1007-23.

[14] Kendall RA, Dunning TH, Harrison RJ. Electron-Affinities of the 1st-Row Atoms Revisited - Systematic Basis-Sets and Wave-Functions. J Chem Phys 1992; 96:6796-6806.

[15] Adler TB, Knizia G, Werner HJ. A simple and efficient CCSD(T)-F12 approximation. J Chem Phys 2007; 127:221106.

[16] Knizia G, Adler TB, Werner H-J. Simplified CCSD(T)-F12 methods: Theory and benchmarks. J Chem Phys 2009; 130:054104.

[17] Curtiss LA, Redfern PC, Raghavachari K. Gaussian-4 theory. J Chem Phys 2007; 126:084108.

[18] Su T. Parametrization of kinetic energy dependences of ion–polar molecule collision rate constants by trajectory calculations. J Chem Phys 1994; 100:4703.

[19] Werner HJ, Knowles PJ, Knizia G, Manby FR, Schütz M, Celani P, Korona T, Lindh R, Mitrushenkov A, Rauhut G, Shamasundar KR, Adler TB, Amos RD, Bernhardsson A, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Goll E, Hampel C, Hesselmann A, Hetzer G, Hrenar T, Jansen G, Köppl C, Liu Y, Lloyd AW, Mata RA, May AJ, McNicholas SJ, Meyer W, Mura ME, Nicklass A, O'Neill DP, Palmieri P, Peng D, Pflüger K, Pitzer R, Reiher M, Shiozaki T, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T, Wang, M. MOLPRO, version 2012.1, a package of ab initio programs, 2012.

[20] Werner HJ, Knowles PJ, Knizia G, Manby FR, Schtz M. Molpro: a general purpose quantum chemistry program package. WIREs Comput Mol Sci 2012; 2:242-253.

[21] Frisch MJT, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr. JA, Peralta JE, Ogliaro, F, Bearpark , Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ö, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, Revision C.01, Gaussian, Inc.: Wallingford CT, 2009.

[22] Glowacki DR, Liang CH, Morley C, Pilling MJ, Robertson SH. MESMER: An Open-Source Master Equation Solver for Multi-Energy Well Reactions. J Phys Chem A 2012; 116:9545-9560.