Atmospheric Chemistry – Nitrosamine Photolysis

Final report

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Abstract

The present report summarises the findings and conclusions from the *Atmospheric Chemistry – Nitrosamine Photolysis* project. The project has provided sound scientific data that fill the knowledge gaps relating to nitrosamine gas phase photolysis. The recommendation is that there is no need for further nitrosamine gas phase photolysis studies.

The project has achieved its targets.

We have reviewed this report and find it in accordance with Tel-Tek's quality system

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Keywords

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Open – report can be cited, given proper citation, **Internal** – report is internal, **Confidential**

About the Atmospheric Chemistry project

Gassnova has awarded Tel-Tek a contract (no. 257430177) for the project "Atmospheric chemistry". The project has four sub-projects:

- Aqueous phase chemistry
- Nitrosamine photolysis
- Dark chemistry
- Chlorine chemistry

Tel-Tek has entered a consortium agreement with universities and research institutions to carry out the project:

- University of Oslo. Norway
- Leibniz-Institut für Troposphärenforschung. Germany
- Universität Innsbruck. Austria
- IRCELYON. France
- Universidad de Castilla-La Mancha. Spain
- Georgia Tech. USA
- Norwegian University of Life Sciences. Norway

Quality Assurance

The data and results in this report has been quality controlled and verified according to generally accepted principles for publication in internationally recognised scientific journals. This statement also includes the reports within the project that is used as a basis for the conclusions and recommendations in this report.

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CONTENTS

1 Scope of services 5

2 HSE 5

3 Activities 6

3.1 Activity 1: Evaluation of the overall status and approach taken to atmospheric chemistry 6

3.2 Activity 2: Sensitivity of NO_2-photolysis rates at Mongstad, Norway due to surface albedo and cloud optical thickness 6

3.3 Activity 4: Photolysis experiments at EUPHORE 6

3.4 Activity 5: Importance of nitrosamine photolysis 7

3.5 Activity 6: Gas phase photolysis rate expression 7

3.6 Activity 7: Relative rate studies of amine+OH reactions 7

4 Conclusions and recommendations 8

5 Literature 9

Annex 1: Experimental results from the project 10

1 SCOPE OF SERVICES

The overall objective of the study is to enable implementation of a lower bound nitrosamine gas phase rate expression in a reactive dispersion model. The sub goals are stated as:

1. To evaluate the overall status and approach taken to atmospheric chemistry as described in “Basis for the TQP4 call-off 2 Studies on Atmospheric Chemistry, CO2 Capture Mongstad memo, 2010”.
2. To identify any significant topics that are either erroneous or missing.
3. The gas phase nitrosamine natural photolysis rates shall be investigated for a set of nitrosamines.
4. The importance of photolysis for the nitrosamine concentration in air as a function of time shall be analysed.
5. A gas phase photolysis rate expression for nitrosamines shall be recommended for implementation in a reactive dispersion model.

2 HSE

The project involved handling of hazardous chemicals and was carried out as required by statutes and regulations. The Standard Operational Procedure (SOP) in the CEAM (EUPHORE) laboratories is that all compounds studied, including possible degradation products, are treated as toxic/potentially carcinogenic. The SOP also includes that all toxic/carcinogenic and/or suspected explosive compounds are handled in well-ventilated fume hoods using gloves, laboratory coats and safety goggles. A Safe Job Analysis has been conducted, and a participant meeting arranged and documented.

The Standard Operational Procedure (SOP) in the UiO laboratory is that all compounds under study, including possible degradation products, are treated as potentially carcinogenic unless other information is available. The SOP also includes that all toxic/carcinogenic compounds are handled on vacuum lines. A Safe Job Analysis has been conducted and documented.

The University of Oslo is a Governmental institution that follows HSE rules and regulations according to Norwegian Law. UiO is not required to produce HSE data sheets for compounds synthesized for research purpose. The HSE-manual can be found here:

http://www.kjemi.uio.no/intern/organisasjonsutvikling/hms/hse-manual/

No accidents or near accidents have occurred during the project lifetime.

3 ACTIVITIES

The *Atmospheric Chemistry – Nitrosamine Photolysis* project comprised 6 activities of which activity 3 was setting up an experiment plan. This activity will not be commented further. An additional activity was added during the project lifetime. The results from these 6 activities are summarized in the following sections.

3.1 Activity 1: Evaluation of the overall status and approach taken to atmospheric chemistry

The overall status and approach taken to atmospheric chemistry as described in "Basis for the TQP4 call-off 2 Studies on Atmospheric Chemistry, CO2 Capture Mongstad memo, 2010" has been evaluated (Scope of services, items 1 and 2). The evaluation is presented in the Tel-Tek report no. 2211030-NP01, *Atmospheric Chemistry - Review of atmospheric amine chemistry relevant to Mongstad*.[1]

The report pointed out a number of important topics for which data were missing. The following has special relevance to the *Atmospheric Chemistry – Nitrosamine Photolysis* project:

1. ***Nitrosamine photolysis**: More data is clearly needed to establish general nitrosamine gas phase photolysis kinetics.*

The abovementioned knowledge gap has effectively and successfully been addressed in the *Atmospheric Chemistry – Nitrosamine Photolysis* project.

3.2 Activity 2: Sensitivity of NO_2-photolysis rates at Mongstad, Norway due to surface albedo and cloud optical thickness

A thorough study to evaluate NO_2-photolysis rates at Mongstad is presented in the Tel-Tek report no. 2211030-NP02, *Sensitivity of NO_2-photolysis rates at Mongstad, Norway due to surface albedo and cloud optical thickness for summer, winter and equinox conditions*.[2]

NO_2-photolysis rates were calculated for the area around Mongstad, and the influence of ground albedo and cloud optical thickness investigated. The photolysis rates are increased by up to a factor of 3 when the ground is fully covered with fresh snow. Cloud cover affects the photolysis NO_2-rate in a non-linear fashion. The relative change of the photolysis rate between clear sky and cloud scenarios is larger for good UV-absorbers (water, forest) compared to good UV-reflectors (snow). The effect of shading by clouds and ground albedo can be as large as the annual summer-winter variation in the photolysis rate. In short, it is very challenging to model NO_2-photolysis rates on short timescales and small grid sizes.

3.3 Activity 4: Photolysis experiments at EUPHORE

The Tel-Tek technical report no. 2211030-NP03, *Atmospheric Chemistry – Nitrosamine Photolysis. Report from experiments at EUPHORE,*[3] is a voluminous report documenting the photolysis experiments with 3 nitrosamines at EUPHORE and the primary data obtained. The report also includes documentation of UiO experiments to obtain absolute infrared absorption cross sections for the 3 nitrosamines. All experiments were completed successfully.

3.4 Activity 5: Importance of nitrosamine photolysis

Nitrosamine formation and removal by photolysis in the Mongstad region has been simulated in box model calculations. This is documented in the Tel-Tek Report no. 2211030-NP05, *Atmospheric Chemistry – Nitrosamine Photolysis. Importance of nitrosamine photolysis*.[4]

The box model simulations were based on data from from activity 2 (see above), and from the *Atmospheric Chemistry – Dark Chemistry* project.[5] The simulations show significant annual variations and suggest that the annual average volume mixing ratio of nitrosamine from amine emitted directly from plant is less 0.3‰ of the amine emitted. The previous result from the ADA-2010 project was around 20 times higher, ca. 0.6%.[6] The difference in results is linked to the new, improved information on j_{NO2} in the Mongstad area, and to the fact that the ADA-2010 estimates were based on higher NOx-levels and on a lower NO_2:NO ratio of 2:1. The simulations further suggest that amount of nitrosamine emitted directly from plant on the average will be reduced by 50% during 30 minutes.

3.5 Activity 6: Gas phase photolysis rate expression

The analyses of the EUPHORE nitrosamine photolysis experiments are documented in the Tel-Tek Report no. 2211030-NP04, *Atmospheric Chemistry – Nitrosamine Photolysis. Gas phase photolysis expression*.[7]

The three series of nitrosamine photolysis experiments were analysed to derive the photolysis rate relative to that of NO_2, and the branching ratios of the corresponding amino radical reactions with NO, NO_2 and O_2. Within the experimental error the relative photolysis rates of $CH_3CH_2N(NO)CH_3$, $CH_3CH_2CH_2N(NO)CH_3$ and $CH_3CH_2CH_2CH_2N(NO)CH_3$ are the same. The study suggests to use $j_{Nitrosamine}/j_{NO2}$ = 0.32±0.03 as a general gas phase photolysis rate expression for nitrosamines (there are no data available to the Tel-Tek *Atmospheric Chemistry – Nitrosamine Photolysis* project challenging this). The complete set of parameters describing the formation and photolysis of the three nitrosamines, and the subsequent reactions of the amino radicals are listen in Annex 1, page 10.

3.6 Activity 7: Relative rate studies of amine+OH reactions

The analyses of the EUPHORE experiments are documented in the Tel-Tek Report no. 2211030-NP06, *Atmospheric Chemistry – Nitrosamine Photolysis. Relative Rate studies of Amine+OH reactions.*[8]

The rate coefficients for OH reaction with CH_3NHCH_3, $CH_3CH_2NHCH_3$ and $CH_3CH_2CH_2NHCH_3$ at 298 K were determined and compared with predictions of the Atkinson structure activity relastionship for OH radical reactions with organics.[9,10] The experimental results and SAR predictions are in agreement, taking the experimental uncertainties into consideration, and the new experimental results confirm that the OH rate coefficient for reaction with amines increase with increasing length of the alkyl chain. The experimental results are included in Annex 1, page 10.

4 CONCLUSIONS AND RECOMMENDATIONS

The *Atmospheric Chemistry – Nitrosamine Photolysis* project has supplied scientifically sound data as the basis for addressing severe knowledge gaps relating to the fate and impact of nitrosamines in the Mongstad region.

Nitrosamine photolysis:
There is now an extensive, high-quality experimental data set available for gas phase nitrosamine photolysis under very different conditions (actinic flux and NOx). All results point to a relative photolysis rate coefficient of $j_{\mathrm{Nitrosamine}} = (0.32 \pm 0.03) \times j_{\mathrm{NO2}}$. There are no data available to the project that challenge using $j_{\mathrm{Nitrosamine}} = 0.32 \times j_{\mathrm{NO2}}$ for all nitrosamines in dispersion modelling.

Recommendation:	*No need for further studies. Use $j_{Nitrosamine} = 0.32 \times j_{NO2}$ in dispersion modelling.*

5 LITERATURE

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ANNEX 1: EXPERIMENTAL RESULTS FROM THE PROJECT

The processes occurring during nitrosamine photolysis is summarized by the following scheme:

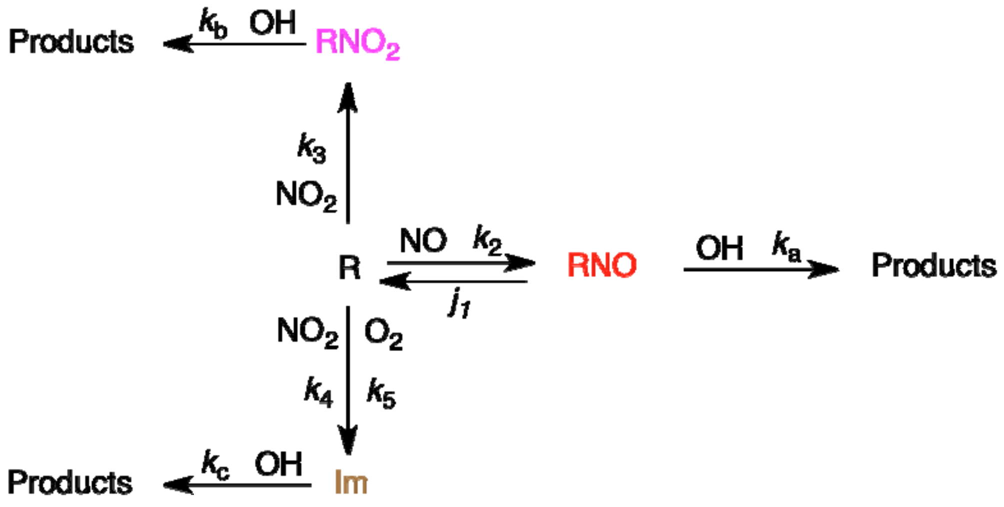

Table A1. Parameters describing nitrosamine photolysis.

	MeEtNNO	MePrNNO	MeBuNNO	NDMA [a]
j_{rel}	0.322 ± 0.005	0.3155 ± 0.0029	0.339 ± 0.005	0.53,[11] 0.25 [12]
k_2/k_3	0.95 ± 0.10	0.608 ± 0.032	0.94 ± 0.06	0.26,[13] 0.75 [12]
k_4/k_3	0.055 ± 0.009	0.004 ± 0.012	0.0	0.22 ± 0.06,[13] 0.10 [12]
$k_5/k_3\,/10^{-7}$	5.26 ± 0.06	6.46 ± 0.11	8.11 ± 0.09	3.90 ± 0.28,[13] 3.0 [12]
$k_a\,/10^{-11}$	1.01	1.33	1.47	
$k_b\,/10^{-11}$	1.14	1.46	1.60	
$k_c\,/10^{-11}$	15.9 ± 1.3	8.3 ± 0.5	17.0 ± 1.5	
$k_d\,/10^{-7}$	6.5 ± 1.5	2.2 ± 0.5	6.0 ± 1.8	
$N_{exp}\,/\,N_{Obs}$	7 / 4485	7 / 5909	6 / 5280	
rms /ppbV	11.4	3.8	3.1	

[a] NDMA, nitroso dimethylamine.

Table A2. Experimental relative rate coefficients and absolute rate coefficients (/cm^3 $molecule^{-1}$ s^{-1}) for the reactions of MeMeNH, MeEtNH, MePrNH with OH radicals.

Compound	Exp.no.	Reference compound	k_{rel}	k_{ref}	$k_{Amine+OH}$ /10^{-11}
MeMeNH	1	1,3,5-TMB [a]	1.391 ± 0.010	5.24×10^{-11}	7.2_9
	2	1,3,5-TMB	1.455 ± 0.025	5.24×10^{-11}	7.6_2
	1	THF [b]	4.17 ± 0.10	1.5×10^{-11}	6.2_6
	2	THF	5.03 ± 0.19	1.5×10^{-11}	7.5_5
					(7.2 ± 1.4)
					(6.54 ± 0.66) [14]
					(6.49 ± 0.64) [15]
MeEtNH	1	1,3,5-TMB	1.588 ± 0.012	5.24×10^{-11}	8.3_2
	2	1,3,5-TMB	1.432 ± 0.019	5.24×10^{-11}	7.5_0
	1	THF	4.68 ± 0.12	1.5×10^{-11}	7.0_2
	2	THF	4.98 ± 0.19	1.5×10^{-11}	7.4_7
					(7.6 ± 1.5)
MePrNH	1	1,3,5-TMB	1.841 ± 0.012	5.24×10^{-11}	9.6_5
	2	1,3,5-TMB	1.436 ± 0.021	5.24×10^{-11}	7.5_2
	1	THF	5.51 ± 0.14	1.5×10^{-11}	8.2_7
	2	THF	5.01 ± 0.20	1.5×10^{-11}	7.5_2
					(8.2 ± 1.6)

[a] Rate coefficient for OH reaction with 1,3,5-trimethylbenzene (1,3,5-TMB) from Ref. [16].
[b] Rate coefficient for OH reaction with tetrahydrofurane (THF) from Ref. [9].