

Atmospheric Chemistry – Dark Chemistry Final report

Tel-Tek report no. 2211030-DC06 v2

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Abstract	<i></i>	

The present report summarises the findings and conclusions from the *Atmospheric Chemistry* – *Dark Chemistry* project. The project has provided sound scientific data that fill the knowledge gaps relating to amine dark chemistry. The recommendation is that there is no need for further amine dark chemistry studies.

The project has achieved its targets.

We have reviewed this report and find it in accordance w	vith Tel-Tek's quality system
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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
2	HSE
3	Activities
	3.1 Activity 1: Evaluation of the overall status and approach taken to atmospheric chemistry
	3.2 Activity 2: Specification of the dark atmospheric conditions at Mongstad7
	3.3 Activity 4: Kinetic studies of NO ₃ radical reactions with selected amines, nitrosamines and nitramines
	3.4 Activity 5: Box modelling - Comparison of amine+OH and amine+NO ₃ chemistry 8
	3.5 Activity 6: Formation rate data
4	Conclusions and recommendations
5	Literature 11
An	nex 1. Experimental results
An	nex 2. Updated NO ₃ structure activity relationship15

1 SCOPE OF SERVICES

The overall objective of the study is to improve the understanding of the dark chemistry of amines in the gas phase and provide data for air quality model implementation. 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. To specify the dark atmospheric conditions at Mongstad including
 - a. The atmospheric processes at night time that can affect the fate of amines
 - b. The concentrations of reactive species, including, but not limited to NO_3 , NO, NO_2 , H_2O

Typical concentrations of NO_3 and other important species during summer and winter time shall be specified.

- 4. To propose a plan for experimental investigation of the most significant topics within dark chemistry
- 5. To assess dark kinetics and yields for nitrosamine and nitramine formation for selected amines
- 6. To compare the kinetics of daytime and night time conditions
- 7. To recommend conservative and generic figures for dark chemistry representing upper bound nitrosamine and nitramine formation kinetics in the dark

2 HSE

The project involved handling of hazardous chemicals and was carried out as required by statutes and regulations.

The University of Castilla-la Mancha is a Governmental institution that follows HSE rules and regulations according to Spanish Law. All compounds under study, including possible degradation products, are treated as toxic compounds. All of them have been handled on vacuum lines. A Safe Job Analysis has also been carried out. The compounds have been studied in a closed reactor where they were completely oxidized through reaction with NO_3 radicals. No accidents have occurred during the project lifetime.

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 – Dark Chemistry* project comprised 6 activities of which activity 3 was setting up an experiment plan. This activity will not be commented further. The results from the other 5 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 have special relevance to the *Atmospheric Chemistry – Dark Chemistry* project:

1. Amine + NO_3 kinetics: There are no experimental data available. Kinetic data and information from estimates of the gas phase NO_3 radical concentration in the Mongstad area are needed to quantify the importance of NO_3 radical chemistry. It is emphasized that the amine + NO_3 reactions may be very important.

There is sparse data concerning the amount of nitrosamines/nitramines that can be formed in the gas phase photo-oxidation of secondary amines. The branching in the initial H-abstraction reaction will differ for OH, Cl and NO₃, but the subsequent reactions of the formed amino radical and the amount of nitramine formed will be the same independent of the initial oxidant. There is no simple and sound way to predict the CH:NH branching ratio in the initial hydrogen abstraction reaction in secondary amines.

- 2. *Amine* + *HONO kinetics*: *More data is clearly needed to elucidate the general nitrosamine homogeneous and surface assisted formation kinetics.*
- 3. Nitrosamine + NO_3 kinetics: The nitrosamine reaction with NO_3 radicals essentially takes place at night when there is no photolysis. The additional loss process may or may not be important, but experimental data are needed to establish this.
- 4. Nitramine + NO_3 kinetics: Any additional nitramine loss process may be important to the overall budget. Experimental kinetic data for nitramine + NO_3 reactions are clearly needed to establish the validity of the OH-NO₃ reactivity correlation for nitramines.

All of the abovementioned knowledge gaps have been effectively and successfully addressed in the "Atmospheric Chemistry – Dark Chemistry"-project.

3.2 Activity 2: Specification of the dark atmospheric conditions at Mongstad

A comprehensive study to characterize the dark atmospheric conditions at Mongstad is presented in the Tel-Tek report no. 2211030-DC01, Atmospheric Chemistry – Dark Chemistry. Nighttime Chemistry in the Mongstad Area: Literature Study and Model Simulations.²

The work includes a literature study on coastal NO₃ radical measurements. Model calculations on the European scale were carried out employing the chemistry transport model COSMO-MUSCAT,³ which previously have been validated by simulations on the European and regional scales. The gas phase chemistry is described by the RACM-MIM2 mechanism,^{4,5} which contains relatively detailed NO₃ and organic chemistry. COSMO-MUSCAT has produced hourly time-series for the whole year 2006 for j_{NO2} , NO, NO₂, OH, NO₃ and other relevant species. The simulation results cannot reproduce the Mongstad measurements exactly due to the coarse horizontal grid resolution of $28 \times 28 \text{ km}^{2.6}$ However, the data sets are ideal for process evaluation and assessing the importance of photolysis, and of OH and NO₃ reactions in the Mongstad area. The time series are available in various formats.

3.3 Activity 4: Kinetic studies of NO₃ radical reactions with selected amines, nitrosamines and nitramines

The "Atmospheric Chemistry – Dark Chemistry"-project involved 4 experimental activities:

- Kinetic studies of NO_3 radical reactions with methylamine, dimethylamine and trimethylamine.
- Kinetic studies of the NO₃ radical reactions with 2 simple nitrosamines ((CH₃)₂NNO and (CH₃CH₂)₂NNO).
- Kinetic studies of the NO₃ radical reactions with 4 simple nitramines (CH₃NHNO₂, CH₃CH₂NHNO₂, (CH₃)₂NNO₂ and (CH₃CH₂)₂NNO₂).
- "Dark experiments" employing the EUPHORE reactor, in which the time-evolution of dimethylamine-NO-NO₂-HONO mixtures were studied.

The results from these experiments are documented in the Tel-Tek report no. 2211030-DC03, *Atmospheric Chemistry – Dark Chemistry. EUPHORE, UCLM and UiO experiments.*⁷

The obtained rate coefficients for NO_3 reactions with amines, nitrosamines and nitramines are included in Annex 1 (page 13), and only a short presentation of the main results will be given here. For more detailed information on the experiments the reader should consult Tel-Tek report no. 2211030-DC03.⁷

The NO₃ radical reactions with amines are fast (see Table A1 in Annex 1, page 13). However, in a clean coastal/rural environment like the Mongstad area, the concentration of NO₃ is relatively low and on an annual basis, the NO₃ radical will only account for around 5 % of the total amine gas phase photo-oxidation. During the dark winter months, the relative importance of NO₃ radical reactions increase, but in the winter period the atmospheric oxidative capacity is generally low.

In summary, the NO₃ radical reaction with amines will not be very important to the fate of amines emitted from a CCS plant in the Mongstad area. Consequently, the open issue of C-H / N-H branching in the initial hydrogen abstraction reaction is of no real importance.

The NO_3 radical reactions with nitrosamines and nitramines are slow (see Tables A2 and A3 in Annex 1, page 13). In short, the reactions are so slow that they can be ignored.

The "dark experiments" at EUPHORE were designed to elucidate the postulated homogeneous and heterogeneous reactions between amines and $NO/NO_2/HONO$. The experiments showed, unambiguously, that amines do not react with $NO/NO_2/HONO$ in the gas phase forming nitrosamines, but that heterogeneous (or surface assisted) reactions do take place, and that these reactions lead to formation of nitrosamines. The rate with which these surface reactions take place is so low that they can be neglected under any relevant atmospheric condition.

3.4 Activity 5: Box modelling - Comparison of amine+OH and amine+NO $_3$ chemistry

The activity is described in the Tel-Tek Report no. 2211030-DC05, *Atmospheric Chemistry – Dark Chemistry. Comparison of amine+OH and amine+NO₃ chemistry.*⁸

Box-model simulations were used to evaluate the atmospheric removal of amines by reaction with NO_3 radicals *vs*. OH radicals. Amine reaction with OH radicals is clearly the major atmospheric gas phase loss process. In absolute numbers only around 5 % of the total amine emitted is removed by reaction with NO_3 radicals in the Mongstad area. However, the NO_3 radicals are responsible for a large fraction of amine removal during the winter season at Mongstad.

Box-model simulations confirm that the dominant gas phase loss process for nitrosamines is direct photolysis, and that only a few per cent of nitrosamines will be removed by reaction with OH radicals. On a yearly basis, the amount nitrosamine removed by reaction with OH radicals is around 3 %.

Reaction with OH radicals is the dominant atmospheric gas phase loss process for nitramines. The lifetime of dimethylnitramine with respect to reaction with OH will be around 3 days in the Mongstad area; larger aliphatic nitramines will typically have lifetimes of around 1 day.

3.5 Activity 6: Formation rate data

The obtained experimental data were evaluated and analysed in relation to extending a recently developed structure activity relationship (SAR) for NO₃ radical reaction with organics.⁹ This is described in the Tel-Tek Report no. 2211030-DC04, *Atmospheric Chemistry – Dark Chemistry. Nitroso- and nitramine formation data.*¹⁰

SAR parameters were derived for NO_3 reactions with nitrosamines and nitramines, and it is now possible to estimate the reactivity of these compound classes towards NO_3 . The relevant part of the updated NO_3 -SAR⁹ is included in Annex 2, page 15.

Amines are not included in the NO_3 -SAR. An alternative method is proposed for estimating the rate coefficient for NO_3 reaction with amines in general. The method is based on an established correlation between the rate coefficients of OH and NO_3 reactions with the same substrates:

- 1. Calculate the rate coefficient for OH reaction with the amine using the Kwok-Atkinson SAR^{11}
- 2. Use the NO₃-OH correlation of Wayne *et al.*: $\log k_{\text{NO3}} = 21.6 + 3.32 \cdot \log k_{\text{OH}}$.¹²

4 CONCLUSIONS AND RECOMMENDATIONS

The *Atmospheric Chemistry – Dark Chemistry* project has supplied scientifically sound data as the basis for addressing severe knowledge gaps relating to dark chemistry in the Mongstad region.

1. Amine + NO₃ kinetics:

There are now experimental kinetic data available for the NO₃ reaction with amines. There is also simulation data for the NO₃ radical concentration in the Mongstad area. Although the amine+NO₃ reactions are fast, the NO₃ radical concentration is too low in the Mongstad area for NO₃-chemistry to be very important, it is estimated that around 5 % of the total amine emitted will be removed by reaction with NO₃ radicals in the Mongstad area. Consequently, there is no urgent need to determine the branching ratio in the initial H-abstraction reaction will by NO₃. Such a study will be both lengthy and costly. It is suggested to use a worst-case scenario branching, such that all amine+NO₃ reactions will lead to formation of the amino radical. The subsequent reactions are well known from previous studies, see *e.g.* ADA.^{13,14}

Recommendation: No need for further studies. Simplified NO_3 chemistry should be included in dispersion modelling.

2. Amine + HONO kinetics:

There is now irrevocable data showing that the rate coefficient for homogeneous gas phase reaction between amines and HONO, proposed by Rolle and Gnauk,¹⁵ is orders of magnitude too high; the reaction has no relevance for atmospheric conditions. Also the proposed heterogeneous or surface assisted reactions between amines and NO/NO₂/HONO have been demonstrated to be of no importance under atmospheric conditions.

Recommendation:	No	need	for	further	studies.	No	need	to	include	amine	+
	NO/	NO_2/H	ONO	reaction	s in dispe	rsion	model	ling			

3. Nitrosamine + NO₃ kinetics:

There are now experimental kinetic data available for the NO₃ reaction with nitrosamines. The reactions are very slow and of no importance to the situation in the Mongstad region.

Recommendation:	No need for further studies. No need to include nitrosamine $+ NO_3$
	reactions in dispersion modelling.

4. Nitramine + NO₃ kinetics:

There are now experimental kinetic data available for the NO_3 reaction with nitramines. The reactions are slow and of no importance to the situation in the Mongstad region.

Recommendation: No need for further studies. No need to include nitramine $+ NO_3$ reactions in dispersion modelling.

5. Nitrosamine + OH kinetics:

Box-model simulations show that the reaction is of minor importance.

Recommendation: No need for further studies. No need to include nitrosamine + OH reactions in dispersion modelling.

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ANNEX 1. EXPERIMENTAL RESULTS

The Atmospheric chemistry – dark chemistry project has generated kinetic data for NO₃ radical reaction with 3 amines. The experimental rate constants are compared to the corresponding amine + OH data in Table A1. The experimental results are documented in the Tel-Tek report no. 2211030-DC03, Atmospheric Chemistry – Dark Chemistry. EUPHORE, UCLM and UiO experiments.⁷ There are no other kinetic data for amine + NO₃ reactions in the literature.

Table A1. Co	mparison of experimental 1	rate constants a	at 295-300 K	K for the reaction	s of OH
and NO ₃ radic	als with amines.				
Compound	$k_{\rm OH}$ /cm ³ molecule ⁻¹ s ⁻¹	Ref.	$k_{\rm NO3}$ /cm ³	³ molecule ⁻¹ s ⁻¹	Ref.

Compound	$k_{\rm OH}$ /cm ³ molecule ¹ s ⁻¹	Ref.	$k_{\rm NO3}$ /cm ³ molecule ¹ s ¹	Ref.
CU.NU.	$(2.20 \pm 0.22) imes 10^{-11}$	16	$(0.7\pm0.5) imes10^{-13}$	7
	$(1.73 \pm 0.11) imes 10^{-11}$	17		
$(CH_3)_2NH$	$(6.54 \pm 0.66) imes 10^{-11}$	18	$(2.0 \pm 1.0) imes 10^{-13}$	7
	$(6.49 \pm 0.64) imes 10^{-11}$	17		
$(CH_3)_3N$	$(6.09 \pm 0.61) imes 10^{-11}$	18	$(5.0 \pm 1.0) imes 10^{-13}$	7
	$(3.58 \pm 0.22) imes 10^{-11}$	17		

The Atmospheric Chemistry – Dark Chemistry project has generated kinetic data for NO_3 radical reaction with 2 nitrosamines. Table A2 compares the new data with existing data for the OH radical reaction with nitrosamines. The experimental results are documented in the Tel-Tek report no. 2211030-DC03, Atmospheric Chemistry – Dark Chemistry. EUPHORE, UCLM and UiO experiments.⁷ There are no other data on nitrosamine + NO_3 kinetics in the literature.

Table A2. Comparison of experimental rate coefficients at 296-300 K for the reactions of nitrosamines with OH and NO₃ radicals.

	5			
Compound	k _{OH}	Ref.	$k_{\rm NO3}$	Ref.
	$/cm^3$ molecule ⁻¹ s ⁻¹		$/cm^3$ molecule ⁻¹ s ⁻¹	
(CH ₃) ₂ NNO (NDMA)	$(2.4 \pm 0.4) \times 10^{-12}$	19	$(1.4 \pm 0.6) \times 10^{-16}$	7
	$(3.6 \pm 0.1) \times 10^{-12}$	20		
(CH ₃ CH ₂) ₂ NNO (NDEA)	1.77×10^{-11} a		$(5.1 \pm 2.1) \times 10^{-16}$	7
^a Estimated using the OH-SA	R of Kwok and Atkinso	n ¹¹		

Estimated using the OH-SAR of Kwok and Atkinson.

The Atmospheric chemistry – Dark Chemistry project has generated kinetic data for NO_3 radical reaction with 4 nitramines. Table A3 compares the new data with existing data for the OH radical reaction with nitramines. The experimental results are documented in the Tel-Tek report no. 2211030-DC03, Atmospheric Chemistry – Dark Chemistry. EUPHORE, UCLM and UiO experiments.⁷ There are no other data on nitramine + NO_3 kinetics in the literature.

Table A3. Comparison of experimental rate coefficients at 296-300 K for the reactions of nitrosamines with NO_3 radicals.

Compound	k _{OH}	Ref.	$k_{ m NO3}$	Ref.
	/cm ³ molecule ⁻¹ s ⁻¹		$/cm^3$ molecule ⁻¹ s ⁻¹	
CH ₃ NHNO ₂ (MNA)	$(7.7 \pm 0.7) \times 10^{-13}$	14	$(1.5\pm0.5) imes10^{-15}$	7
$(CH_3)_2NNO_2(DMNA)$	$(3.6 \pm 0.5) \times 10^{-12}$ $(3.5 \pm 0.5) \times 10^{-12}$	19 14	$(2.3 \pm 1.5) \times 10^{-15}$	7
	$(3.3 \pm 0.3) \times 10$	11	15	
CH ₃ CH ₂ NHNO ₂ (ENA)	1.0×10^{-11} a		$(2.5 \pm 1.1) \times 10^{-15}$	7
(CH ₃ CH ₂) ₂ NNO ₂ (DENA)	$1.9 imes 10^{-11}$ a		$(4.0 \pm 1.8 \) imes 10^{-15}$	7

^aEstimated using the OH-SAR of Kwok and Atkinson, Ref. 11.

ANNEX 2. UPDATED NO₃ STRUCTURE ACTIVITY RELATIONSHIP

The initial step in NO₃ radical reaction mechanisms generally parallel the corresponding OH radical reaction mechanisms, suggesting a possible correlation between NO₃ and OH radical reaction rates. Sabljic and Güsten²¹ examined the correlation of NO₃ and OH radical rate coefficients for reaction with 57 various aliphatic compounds and derived the following equation: log $k_{NO3} = 18.86 + 3.05 \cdot \log k_{OH}$, where the rate constants are in units of cm³ molecule⁻¹ s⁻¹. This equation is appropriate only for aliphatic compounds.

Atkinson established a general Structure-Activity Relationship (SAR) for OH radical reaction with organics²² that later was extended to nitrosamines and nitramines.²³ In this SAR the total OH radical reaction rate constant is given by:

 $k_{total} = k$ (H-atom abstraction from C-H and O-H bonds)

- + k(OH radical addition to >C=C< and -C=C- bonds)
- + k(OH radical addition to aromatic rings)
- + k(OH radical interaction with -NH₂, >NH, >N-, >NNO, -SH and -S- groups)

The calculation of overall H-atom abstraction rate constants is based upon the estimation of $-CH_3$, $-CH_2$ -, >CH-, and -OH group rate constants. The $-CH_3$, $-CH_2$ -, and >CH- group rate constants depend on the identity of the substituents around those groups, with

$$k(CH_3-X) = k_{prim} \cdot F(X)$$

$$k(X-CH_2-Y) = k_{sec} \cdot F(X) \cdot F(Y)$$

$$k(X-CH(Y)-Z) = k_{tert} \cdot F(X) \cdot F(Y) \cdot F(Z)$$

where k_{prim} , k_{sec} , and k_{tert} are the rate constants per –CH₃, -CH₂-, and >CH- group for a "standard" substituent, *X*, *Y*, *Z* are the substituent groups; and *F*(*X*), *F*(*Y*), and F(*Z*) are the corresponding substituent factors. The standard substituent group is chosen to be X = Y = Z = -CH₃, *F*(-CH₃) = 1.00 by definition.²² It was assumed that the majority of the initial OH radical reaction proceeds via OH radical addition to the N-atom, followed by a number of decomposition reactions of the adduct leading to products. In the latest update of the SAR¹¹ the following parameters relevant to the present work are presented in Table 3.1.

Group	$k_{298}/10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Substituent Group X	F(X)
-CH ₃ (k_{prim})	0.136	-NH ₂ , >NH, >N-, >NNO, >NNO ₂ ^a	9.3
$>$ CH ₂ (k_{sec})	0.934	-CH ₃	1.0
$>$ CH- (k_{tert})	1.94	-CH ₂ -, >CH-, >C<	1.23
-OH	0.14	-OH	3.5
RNH_2	21		
R_2NH	63		
R ₃ N	66		
R ₂ NNO	0		
R_2NNO_2	1.3		

Table 3.1. SAR-parameters for OH radical reaction with organics.

^a It should be noted that the OH-SAR for nitrosamines and nitramines is based on kinetic data for only one nitrosamine, $(CH_3)_2NNO$, and one nitramine, $(CH_3)_2NNO_2$, and that it therefore should be used with caution for these compound classes.

In connection with a review of NO₃ radical reactions with organics Atkinson reported a correlation of the H-atom abstraction rate coefficients per equivalent C-H bond for the room temperature reactions of NO₃ and OH radicals with a series of alkanes and aldehydes; a least-squares analysis lead to (in cm³ molecule⁻¹ s⁻¹ units): ln $k_{NO3} = 6.498 + 1.611 \cdot \ln k_{OH}$. This

equation was then used to extrapolate a Structure-Activity Relationship (SAR) for NO₃ radical reactions from the existing general SAR for OH radical reaction with organics,^{22,23} to give the group rate constants $k_{NO3}^{prim} = 7.0 \times 10^{-19}$, $k_{NO3}^{sec} = 1.5 \times 10^{-17}$ and $k_{NO3}^{tert} = 8.2 \times 10^{-17}$ cm³ molecule⁻¹ s⁻¹, and substituent factors $F_{NO3}(X) = [F_{OH}(X)]^{1.611}$.

Grosjean and Williams²⁴ derived a correlation for NO₃ and OH radical reactions with unsaturated aliphatics (in cm³ molecule⁻¹ s⁻¹ units): $\log k_{OH} = 0.204 - 7.69 \cdot \log k_{NO3}$. Atkinson later implemented the same methodology for estimating NO₃ radical rate constants for olefins as for estimating OH radical addition to olefins.²⁵

Very recently, Kerdouci *et al.*⁹ published a structure-activity relationship, based on paramerization of the molecular structure according to the group-additivity method of Atkinson.^{22,23} The proposed SAR includes alkanes, alkenes, dienes, terpenes and saturated and unsaturated oxygenated compounds including alcohols, ketones, ethers and esters. The following parameters relevant to the present work are presented in Table 3.2.

Tuble 3.2. Shire parameters for off fudical federion with organics.						
Group	k_{298} /cm ³ molecule ⁻¹ s ⁻¹	Substituent Group X	F(X)			
-CH ₃ (k_{prim})	$1.00 imes 10^{-18}$	-CH ₃	1			
$>CH_2(k_{sec})$	$2.56 imes 10^{-17}$	-CH ₂ -	1.02			
>CH- (k_{tert})	$1.94 imes 10^{-16}$	>CH-	1.61			
OH	$2.00 imes 10^{-17}$	>C<	2.03			
RNH_2	?	-OH	18			
R_2NH	?	-NH ₂ , >NH, >N-, >NNO, >NNO ₂ ^{a,b}	36			
R ₃ N	?					
R ₂ NNO	0 ^b					
RNHNO ₂	$1.5 imes 10^{-15}$ b					
R_2NNO_2	$2.2 imes 10^{-15}$ b					

Table 3.2. SAR-parameters for OH radical reaction with organics.

^a Assuming $F_{NO3}(X) = [F_{OH}(X)]^{1.611}$ (Atkinson, Ref. ²⁶). ^b This work.

Wayne *et al.*¹² carried out a systematic analysis of NO₃ radical reactivity and reported correlations between NO₃ and OH radical reactivity for both abstraction and addition reactions and reported a correlation of log $k_{\text{NO3}} = -5.13 + 0.947 \cdot \log k_{\text{OH}}$ for H-abstraction reactions and log $k_{\text{NO3}} = 21.6 + 3.32 \cdot \log k_{\text{OH}}$ for addition reactions.