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Report

257430179 Atmospheric Chemistry - Chlorine Chemistry

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ABSTRACT

Executive summary

The goal of this study is to investigate the significance of the reactions of chlorine radicals with three classes of generic amines, primary, secondary and tertiary. The overall aim is to include the data in larger dispersion models for investigation of the importance of chlorine reactions relative to other removal processes for amines in the atmosphere. The rates of reaction of representative amines with Cl have been be investigated in the laboratory using the relative rate method using two different photoreactor chambers using FT-IR and GC-MS as detection methods. The experiments proved challenging but upper limit rate constants were determined and the conclusion is that amine reactions with chlorine are very fast (of the order of ~10-11 molecules cm-3 s-1).

Product studies of the reactions of the generic amines with Cl have been carried out using a GC-MS experimental setup with a chemical desorption system. There were no observations of unexpected products of the reaction. Nitrosamines were not seen as a product of amine + Cl reactions, even with NOx present. Branching ratios for the reactions of chlorine with the C-H and N-H groups of the amines were determined by quantum chemistry and found to be around 50/50 indicating that chlorine reactions have the potential to form nitrosamines by reaction at the N-H site. The chemical reactions and the obtained rate information are implemented in a box model which shows that the chlorine degradation is negligible overall but might still be significant locally by the coast. A model with sufficient spatial detail might capture the localized contribution from chlorine chemistry.

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Table of contents

1 Executive summary

The goal of this study is to investigate the significance of the reactions of chlorine radicals with three classes of generic amines, primary, secondary and tertiary. The overall aim is to include the data in larger dispersion models for investigation of the importance of chlorine reactions relative to other removal processes for amines in the atmosphere. The rates of reaction of representative amines with Cl have been be investigated in the laboratory using the relative rate method using two different photoreactor chambers using FT-IR and GC-MS as detection methods. The experiments proved challenging but upper limit rate constants were determined and he conclusion is that amine reactions with chlorine are very fast (of the order of ~10^{-11} molecules cm^{-3} s^{-1}).

Product studies of the reactions of the generic amines with Cl have been carried out using a GC-MS experimental setup with a chemical desorption system. There were no observations of unexpected products of the reaction. Nitrosamines were not seen as a product of amine + Cl reactions, even with NO_x present. Branching ratios for the reactions of chlorine with the C-H and N-H groups of the amines were determined by quantum chemistry and found to be around 50/50 indicating that chlorine reactions have the potential to form nitrosamines by reaction at the n-H site. The chemical reactions and the obtained rate information are implemented in a box model which shows that the chlorine degradation is negligible overall but might still be significant locally by the coast. A model with sufficient spatial detail might capture the localized contribution from chlorine chemistry.

2 Atmospheric chemistry of chlorine species

There is very little available data for the gas-phase reactions of the nitrosamines and nitramines that are potential amine degradation products. A single study of the OH reactions of N-nitrosodimethyl amine and dimethylnitramine has been carried out with the reaction rates found to be 3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 4.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Thus, the reactions are a factor of 10 slower than for the amines but still considered fast overall. There is no data for either Cl or NO_3 reactions for these compounds. Nitrosamines are known to photolyze rapidly even at ground level and the atmospheric lifetime of these compounds are expected to be determined by photolysis and on the order of a few hours when there is sunlight available. Nitramines do not have absorption features in the spectral region relevant for the troposphere and do not photolyze. The lifetime of nitramines is likely determined by OH reactions and uptake into the aqueous phase.

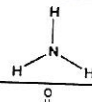
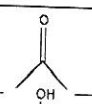
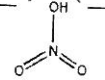
Reactive halogen species, including chlorine radicals are formed photochemically from sea salt during daylight hours in coastal areas. Under certain conditions, the concentrations of reactive chlorine can reach levels where they might be a contributing removal process for amines and amine degradation products at the Mongstad location. Chlorine radicals is the most important halogen species reacting with hydrocarbons and other trace gases in the atmosphere, but concentrations of chlorine vary significantly on a daily and yearly basis.

The process degradation products identified for the four parent amines (MEA, Piperazine, AMP and MDEA) include aldehydes, organic acids, amides, nitrosamines, nitramines, alcohols and other aliphatic amines. Of particular

concern for human health effects and the environment are nitrosamines and nitramines and well as certain amides and aldehydes. These compounds are known to be carcinogenic, and their emission levels and atmospheric residence times need to be determined for risk assessment. In the following we consider only gas phase photochemical processes that remove these compounds, and for many compounds, the primary atmospheric gas phase removal process is reaction with the hydroxyl radical (OH). OH radicals are formed photochemically during the daylight hours, and the average concentration in the Mongstad region is ~5×10^5 molecules cm^{-3}. In addition, the chlorine radical (Cl) can be a significant removal process in coastal areas as it is produced photochemically from sea salt aerosol (SSA) and reacts very rapidly with most organic compounds. In many cases the Cl reaction rate is one or two orders of magnitude faster than the OH reaction rate, which is balanced by the much higher average OH concentrations in the atmosphere. Cl is only present in significant amounts in coastal areas.

Chlorine radicals react with organic species by hydrogen abstraction in an analogous way to OH, and in most cases the reaction pathways can be expected to be similar. However, the branching ratios might be very different. Chlorine is a large radical and is more subject to molecular steric hindrance than is OH. Known data for OH reaction rates with amines indicate that OH reacts fast with amines, of the order of 10^{-11} cm3 molecule s-1.[1] There is currently no available rate data in the literature for the reactions of amines with Cl radicals or indeed other reactive halogen species. Cl rate data is available for some of the identified degradation products including ammonia, formaldehyde, acetaldehyde and formic and acetic acid.[2] For all other process degradation products including the nitrosamines and nitramines there's no available data.

Table 1. Identified amine process degradation products and the reaction rates with OH and Cl.

Name	CAS	Structure	Formula	OH reaction rate (cm^3 $molec.^{-1}$ s^{-1})	Cl reaction rate (cm^3 $molec.^{-1}$ s^{-1})
NH3	7664-41-7		NH_3	1.60×10^{-13} [2]	1.08×10^{-11} [3]
Formaldehyde	50-00-0		HCHO	8.20×10^{-12} [2]	8.2×10^{-11} [2]
Acetaldehyde	75-07-0		CH_3CHO	1.52×10^{-11} [4]	7.2×10^{-11} [2]
Formic acid/formate	64-18-6		HCOOH	4.50×10^{-13} [2]	2.0×10^{-13} [2]
Acetic acid/acetate	64-19-7		CH_3COOH	4.00×10^{-13} [2]	2.81×10^{-14} [2]
Acetone	67-64-1		CH_3COCH_3	2.80×10^{-12} [2]	2.30×10^{-12} [5]
Nitric acid/Nitrate	7697-37-2		HNO_3	1.50×10^{-13} [2]	2.00×10^{-16} [2]

The observed process degradation products of the parent amines can degrade in the gas phase after emission and form further secondary degradation products. The main concern for health and safety are nitramines and nitrosamines. These are formed in the photochemical degradation of an amine by H-abstraction from the amine group by a radical followed by reaction with NO and NO_2. The simplest reaction scheme for a primary or secondary amine is as follows:

$$R_2NH + X \longrightarrow R_2N\cdot + HX \quad (R3)$$
$$R_2N\cdot + NO \longrightarrow R_2NNO \quad (R4)$$
$$R_2N\cdot + NO_2 \longrightarrow R_2NNO_2 \quad (R5)$$

In this case the H-abstraction occurs from the amine nitrogen, but it can also occur from the alkyl groups which leads to complex degradation schemes, but no important pathways to form nitrosamines and nitramines. Formation of these compounds can only happen via hydrogen-shift reactions in some degradation products that aren't energetically feasible under atmospheric conditions. The branching ratio between H-abstraction from the nitrogen and the alkyl groups is needed to assess the potential to form nitramines and nitrosamines. For alcohols, abstraction from the OH-group is a very minor pathway, but there are very few reliable studies of the extent of H-abstraction from the amine hydrogen. A single available study of the dynamics of the branching ratio for Cl with methylamine, has indicated that the branching ration between hydrogen abstraction from the NH_2 group and abstraction from the CH_3 group was about 48 to 52%respectively.[6] This is sharp contrast to the branching ration for the OH-reaction which shows that hydrogen abstraction from the amine group is a minor pathway. It is therefore important to explore the branching ratios of the chlorine reactions in order to investigate the possible products formed. Some secondary degradation products, including amides, have the mechanistic potential to form nitramines. The product yield and lifetimes of these compounds should ideally be considered. This can be studied by quantum chemical mechanistic studies and experimental product studies.

The atmospheric lifetime of a molecule is the measure for how long an emitted or produced compound remains in the atmosphere until it is destroyed or removed. In terms of human exposure to harmful compounds the atmospheric lifetime is a determining factor for the risk assessment of a species. How long a molecule resides in the atmosphere is governed by many different complex processes such as transport, gas phase chemistry, aerosol and cloud chemistry, photolysis, emission and deposition. In order to better understand these processes one can use models to solve mathematical equations that represent these processes. In this way, many scenarios can be explored without performing costly laboratory experiments or field measurements. Results from the models can be used to identify the processes most important to validate. Atmospheric models range in scale from global models to small box models and cover times scales ranging from fractions of seconds to several years. Larger models include atmospheric physics and transport, whereas smaller models are useful for studying individual processes in more detail. A box model can be useful for modelling the chemistry specifically in the marine boundary layer with reactions that are known to be important in that environment, without taking transport into account.

The atmospheric lifetime of a molecule with respect to OH degradation is usually expressed as $\tau_{OH}=1/(k(OH)*[OH])$, where $k(OH)$ is the rate of reaction with OH and [OH] is the average tropospheric OH concentration. The lifetime with respect to Cl degradation can be expressed In a similar way, although this number will be less meaningful since high Cl concentration are very localized.

3 Specification of atmospheric concentrations of chlorine

Whether it is necessary to consider active chlorine as a removal process for amines and degradation products depends on the rates of reaction and concentrations of chlorine species in the environment. In general the average concentration of Cl radicals in the troposphere is much lower than that of OH radicals, so it follows that the OH radical reactions are generally a much more important removal process. However, locally in coastal areas peak Cl concentrations can approach levels comparable to OH concentrations (table 2) and because most hydrocarbons react an order of magnitude faster with Cl than OH, it can be a significant removal process. The specific location of the Mongstad plant is in a coastal area (within 5-10 km of the seashore) which means that it is necessary to take Cl removal into account when estimating the overall lifetime of the amines and amine derivatives. In the case of amines, the reactions with HCl is also likely to contribute given that they are strong bases and can form imminium salts upon reaction with HCl. HCl is an important halogen species in the marine troposphere and it is produced from sea spray. It is the main source of Cl radicals by reaction with OH radicals (see below).

In the marine boundary layer, wave movement in the sea generates airborne droplets of seawater from which the water can evaporate leaving the dissolved solid material behind in the form of aerosol. Most of this solid material is NaCl and gas phase photochemical reactions with molecules such as H_2SO_4, HNO_3, N_2O_5 and $ClONO_2$ lead to the formation of Cl_2 and $ClNO_2$ both of which produce Cl radicals when photolyzed.

Active chlorine is produced by the following reactions:

$$N_2O_5 + NaCl_{(s)} \rightarrow ClNO_2 + NaNO_{3(s)}$$
$$2NO_2 + NaCl_{(s)} \rightarrow NOCl + NaNO_{3(s)}$$
$$ClONO_2 + NaCl_{(s)} \rightarrow Cl_2 + NaNO_{3(s)}$$

With $ClNO_2$, NOCl and Cl_2 being precursors of Cl by photolysis.

HCl is formed via:

$$2NaCl + H_2SO_4 \leftrightarrow Na_2SO_4 + 2HCl$$
$$NaCl + H_2SO_4 \leftrightarrow NaHSO_4 + HCl$$
$$NaCl + HNO_3 \leftrightarrow NaNO_3 + HCl$$

HCl itself is the main source of Cl radicals by reaction with OH:

$$HCl + OH \rightarrow Cl + H_2O$$

The exact mechanisms of these reactions and their relative importance are poorly defined at present. It is also very likely that aqueous phase chemistry can produce reactive chlorine species from NaCl and some evidence of these processes has been published. In addition, Cl can be produced from photochemical degradation of organic halogen compounds such as CH_3Cl and $CHCl_3$ but this is considered a minor contribution compared to sea salt aerosol (SSA).[7]

The direct measurement of Chlorine radicals in the atmosphere is very difficult. Estimates of chlorine concentrations are generally made by varying methods. One is measuring the reactive decay of well-known organic compounds and deducing the Cl concentration from the known concentration of OH radicals.[8] Another method is measuring Cl_2 and ClO and other chlorine species concentrations by mass spectrometry techniques and laser spectroscopy and estimating the Cl concentration from the photolysis of these species. These techniques are not easy to employ in the field however, and that's is why there are relatively very few measurements of Chlorine concentrations. Available measurements are summarized in table 2.

Table 2. Available data for the concentration of chlorine radicals. Cl* denotes the sum of chlorine species (Cl_2, Cl, ClO, $ClONO_2$, HOCl, $ClNO_2$) which is reported by some studies. The global average OH concentration is ~$1x10^6$ molecules/cm^3. HCl concentrations are generally 5-10 times higher than Cl concentrations.

Species	Conditions	Concentration molecules/cm^3	Location
Cl	Coastal Peak	$1x10^5$	Miami, Florida[9]
Cl*	Peak	$2.5x10^{10}$	Cape Verde[10]
Cl*	Coastal Peak	$1x10^{10}$	Maine, USA[11]
Cl	Coastal Peak	$4x10^4$	Maine, USA[12]
Cl	Southern Hemisphere Peak	<1000	Southern Hemisphere[8]
Cl	Average marine BL	$1.8x10^3$	Global[13]
Cl	Peak	$3x10^3$	Taiwan[14]

Cl	Hemispheric daily average	$2.6x10^3$	Southern Hemisphere[7]
Cl	Peak	$3.9x10^5$	Long Island, New York[15]

It can be seen that global average values of Cl radicals are of the order of 10^3 molecules/cm^3, which is a factor 10^3 lower than for OH indicating that overall OH is a much more important reactant.

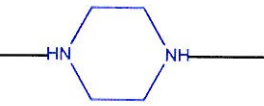
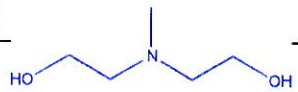
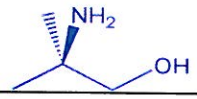
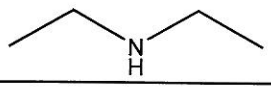
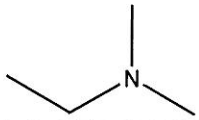
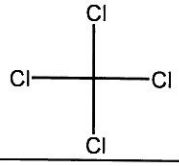
However, local daytime peak values reach 10^5 molecules/cm^3 which means that in a coastal environment at daytime when photolysis is high, Cl reactions compete with OH reactions. For the purpose of modelling the lifetimes of amines in the atmosphere, it would be most useful to use average coastal Cl concentrations of 5-$10x10^3$ molecules/cm^3. This should provide a reasonable average contribution from Cl reactions. However, it should be kept in mind that in summer at midday, the Cl induced removal is likely to be much higher. In the winter, when Cl radical production is at a minimum, the contribution is likely to be insignificant. At all times of year, reactions of amines with HCl can be expected to take pace and it is important to consider this process as well.

4 Experimental studies

The amines selected for study are the generic amines identified during Amine 4: 2-ethanolamine, piperazine and N-methyldiethanol amine. These represent the three generic classes of amines, primary, secondary and tertiary. The aim is that the rate data obtained for these compounds will form the basis for recommendations for other compounds within the same class. These compounds have relatively low volatilities which is an advantage when using the chemicals on an industrial scale. The vapour pressures of 2-ethanol amine (MEA) and piperazine might be expected to be high enough to achieve a sufficient concentration of reactants in the photoreactor chamber. In the case of N-methyldiethanol amine, it may prove necessary to heat the cell by 15-30 °C above room temperature in order to have a sufficiently high concentration of the compound. As an alternative to the three generic amines, amines with higher vapour pressures can be studied. Propylamine, diethylamine and N,N-dimethylamine are proposed as alternatives for primary, secondary and tertiary amines.

The amines selected for study in this project are classified as corrosive and some of their degradation products are possible/query mutagens. A leakage tested vacuum line situated in an efficient fume hood was employed for all the gas handling procedures. Carbon tetrachloride, which is used for Cl radical generation is a mutagen and is handled in a closed system. The amounts of compound used for spectroscopic analysis are however, very small. Standard issue laboratory gloves and coats were worn for protection and disposable pipettes used during the handling. The waste gases from the reaction chamber were pumped out through a liquid nitrogen cooled cold trap which traps the remaining amines and reaction products after the experiment has been completed. The cold trap is removed from the gas line and left to thaw in the fume hood overnight.

Table 3: The chemical structures and vapour pressures of the selected generic amines and other reactants used in this study.

Name	CAS	Structure	P(20 °C) Torr	BP (K)	Safety
2-ethanolamine (MEA), primary	141-43-5		0.2	443	Harmful/corrosive
Piperazine, secondary	110-85-0		0.8	418	Risk of impaired fertility/harm to the unborn child
N-methyl diethanolamine (MDEA), tertiary	105-59-9		0.01	520	Harmful/corrosive
2-amino-2-methylpropanol (AMP)	124-68-5		<1	165	Harmful/corrosive
Diethylamine	109-89-7		182	328	Harmful/corrosive
N,N-dimethylethylamine	598-56-1		418	310	Harmful/corrosive
Carbon tetrachloride	56-23-5		89.6	350	Toxic/ mutagen

4.1 Experimental equipment

A photochemical reactor for studies of atmospheric kinetics and spectroscopy has been built at the Copenhagen Centre for Atmospheric Research. This reactor was used for reaction rate measurements. The reactor consists of a vacuum FTIR spectrometer coupled to a 100 L quartz cylinder by multipass optics mounted on electropolished stainless steel end flanges, surrounded by UV-A, UV-C and broadband sun lamps in a temperature-controlled housing. A vacuum FTIR interferometer (Bruker IFS 66v/s) with a maximum resolution of 0.125 cm^{-1}, and equipped

with liquid nitrogen cooled InSb and MCT detectors, is connected to reaction chamber via a system of optics under vacuum.

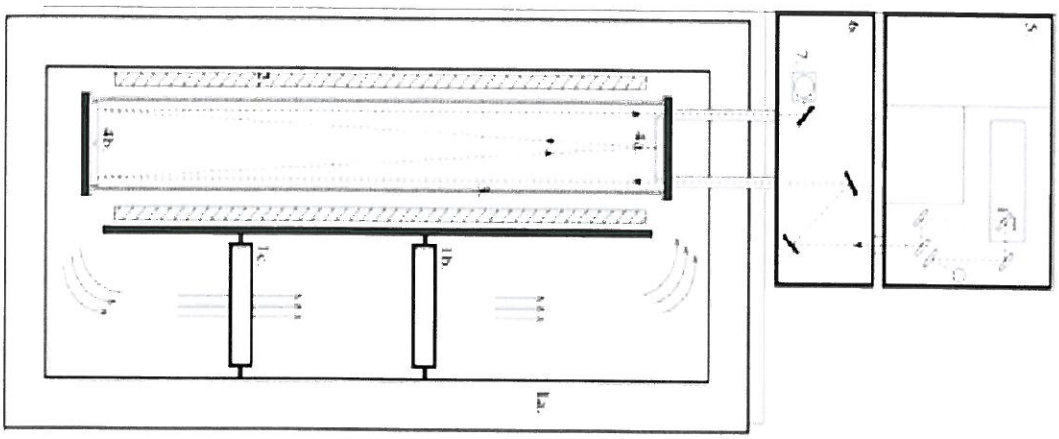


Figure 1: Schematic of the photochemical reactor at the University of Copenhagen. The reactor consists of multi-pass optics reaction cell and a spectrometer for detecting the chemicals. The cell is equipped with different lamps for a large range of wavelengths and the absorption path length is 80 m.

The selected amines were introduced into the cell via a gas handling system along with the reference compound, carbon tetrachloride and bath gas. The experiments were carried out at atmospheric pressure, 1013 mbar, using dry technical air as the bath gas (80%N_2, 20%O_2). The chlorine radicals are produced by irradiation of carbon tetrachloride by UVC light[1]:

$$CCl_4 + h\nu \longrightarrow CCl_3 + Cl \quad (200\,nm \leq \lambda \leq 280\,nm)$$

The accuracy of the experiment is essentially determined by the quality of the IR spectra. Sensitivity is increased by using multi-pass White-type optics which allow path lengths of 8-90 m to be achieved in the cell. This makes it possible to work with concentrations at the ppb level which is desirable when dealing with harmful chemicals and has the advantage of resembling atmospheric conditions. The signal to noise ratio is improved by the addition of 64 scans for each recorded spectrum.

Relative rate experiments were also carried out in a coolable photoreactor equipped with online and off-line GC-MS detection. The systems used an Agilent Technologies 6850 network GC system. The photoreactor consists of a standard commercial box freezer equipped with UVA and UVC lamps and reflective coating (Figure 2a). The reacting gases are introduced into a UV transparent Teflon vessel and irradiated. The products are monitored on

[1] CCl_4 is chosen as a source of Cl radicals instead of Cl_2, because it is very stable until photolyzed. Cl_2 decomposes to some extent in tubing and on the rector walls in the presence of trace amounts of water to form HCl which reacts with the amines.

the GC-MS either by sampling directly from the Teflon reaction vessel. The amines selected for study were introduced into the Teflon vessel along with molecular chlorine and the reference compound cyclohexane.

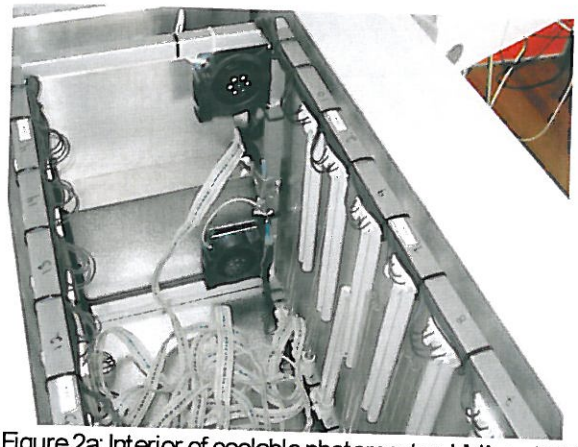


Figure 2a: Interior of coolable photoreactor. UVA and UVC lamps are mounted on the sides.

Figure 2b: Agilent Technologies 6850 GC-MS. A direct sampling module is connected in the middle.

4.2 Data analysis

The relative rate method is used to measure the reaction rate of the amine relative to reference compounds with well-known reaction rates with chlorine radicals. The decays of the concentrations of the reacting species are measured simultaneously as a function of reaction time and rate is k_A and k_B:

$$A + Cl \xrightarrow{k_A} products$$
$$B + Cl \xrightarrow{k_B} products$$

Assuming that there are no loss processes other than these reactions and that there are no other processes producing the reactants, the following relation is valid:

$$\ln\left\{\frac{[A]_0}{[A]_t}\right\} = \frac{k_A}{k_B}\ln\left\{\frac{[B]_0}{[B]_t}\right\}$$

where $[A]_0$, $[A]_t$, $[B]_0$ and $[B]_t$ denote the concentrations of the compounds A and B at times zero and t, respectively. A plot of $\ln([A]_0/[A]_t)$ vs. $\ln([B]_0/[B]_t)$ will thus give the relative photolysis rate coefficient $k_{rel} = k_A/k_B$ as the slope. The reaction mixture is irradiated in steps to provide typically 7-10 points on the plots. After each irradiation period an infrared spectrum is recorded and the change in concentrations of the amine and reference compound determined.

The reference compound is chosen to have a rate similar to or at least with the same order of magnitude as the amine being studied. As these are unknown, as a first guess reference compounds with reaction rates similar to the OH reaction rates determined for these generic amines will be used. For these amine studies, ethylene and cyclohexane were appropriate reference. The method and instrumentation is described in detail in [16].

Table 4. Experiments performed in the Teflon photochemical reactor. The amines studied were the compounds that were amenable to handling in this reaction chamber.

Reaction	OH Reaction rate (EPI Suite)	Reference compounds	Reference rate (NIST) molec. cm^{-3} s^{-1}
MEA + Cl	3.55E-11	C2H4 High + Low NO_x	9.30E-11
Piperazine + Cl	1.69E-10	C6H12	2.4e-10
MDEA + Cl	9.70E-11	C6H12 C2H4	2.4e-10 9.30E-11
DEA + Cl	6.45E-11	C6H12	2.4e-10
N-Ethyldimethylamine + Cl	7.7e-11	C6H12	2.4e-10
AMP + Cl	2.5e-11	C6H12	2.4e-10

4.3 Experimental errors

The major experimental error sources are the monitored sample pressures (ca. 0.5%), the optical path length of the absorption cell (ca. 1.0%), the sample temperature (ca. 1.0%) and the baseline drift in the single beam spectra (ca. 1.0%). The error propagation thus indicates overall expected standard deviations in the order of ca. 3% for the

evaluated relative concentrations in the infrared spectra. Each individual experiment will be carried out at least 3 times to reduce the error on the final reaction rate.

4.4 Experimental results

The initial experiments in the FT-IR based photoreactor were carried out with MEA, DEA and MDEA. The data indicated a very fast reaction of the amines with chlorine with the compound completely gone after a few minutes of reaction time. However the reaction product, most likely imminium salts were rapidly deposited on the multipass mirrors of the cell making it necessary to clean the cell after each experiment. It was decided that the Teflon reaction vessel with GC-MS detection would be more suitable as the Teflon bags can be more easily flushed and are disposable. The GC-MS analysis turned out to be problematic for some of these very polar compounds, particularly for PIPA and AMP. However by manual fitting of the relative rate data it was possible to obtain usable data for the smaller amines, albeit with somewhat higher errors bars than we would have liked. Every time the amine reacts with Cl an HCl molecule is formed which reacts very rapidly with amines. It was therefore necessary to correct the data for HCl reaction by assuming a 1:1 reaction ratio for Cl and HCl. The data is summarized in table 5.

Table 5. The experimentally determined upper limit rate constants for amine reaction with Cl radicals. The data have been corrected for reaction with HCl in the chamber.

Name	CAS	Reaction rate (Cl)
DEA	109-89-7	4.7e-11 (3.2)
N-Ethyldimethylamine	598-56-1	8.4e-11 (4.5)
MEA	141-43-5	3.6e-11 (4.1)
MDEA	105-59-9	9.7e-11 (3.8)
PIPA	110-85-9	- >5e-11
AMP	124-68-5	- >5e-11

PIPA and AMP were not possible to study in the Teflon reaction vessel. Upper limit for rate constants come from photoreactor experiments alone. This included HCl, so it denotes degradation by $Cl^{\bullet}$.

4.5 Product studies

The reaction products of the Teflon reaction chamber experiments were studied by GC-MS with chemical desorption following sampling on Thermosorb/N air sampling cartridges. The products are listed in table 6 for MEA and in table 7 for DEA. These amines were chosen because they were the compounds most suited for GC-MS analysis and with the simplest expected product range. The products of the reaction also include the imminium salts which were deposited in the Teflon bag/reaction chamber and not collected on the sampling cartridges. It cannot be ruled out that the salts react with other compounds in the vessel including Cl radicals to form products of their own.

For both MEA and DEA it should be noted that no nitrosamines or nitramines were observed amongst the products. For each cartridge 5-7 litres of air from the reaction vessel were collected in order to collect even the smallest amounts of compound. The sensitivity of the method should be sufficient to observe a 1-2%conversion to nitrosamines butthey were not observed. It's possible that any nitrosamines formed were destroyed too rapidly to be collected..

Table 6. Product studies, MEA Teflon reaction vessel experiments. Observed degradation products.

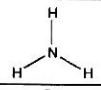
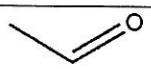
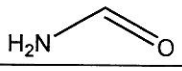
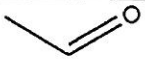
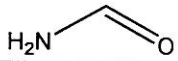
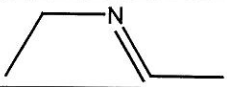
Name	CAS	Structure
NH3	7664-41-7	
Formaldehyde	50-00-0	
Acetaldehyde	75-07-0	
Formic acid/formate	64-18-6	
Acetic acid/acetate	64-19-7	
Formamide	75-12-7	

Table 7. Observed degradation products, DEA experiments by Teflon reaction vessel experiments.

Name	CAS	Structure
Formaldehyde	50-00-0	
Acetaldehyde	75-07-0	
Formic acid/formate	64-18-6	
Formamide	75-12-7	
NH3	7664-41-7	
N-ethyl ethylimine ? (uncertain)		

5 Branching ratios

The chlorine reactivity of the nitrogen bound hydrogen relative to the carbon bound hydrogens is very important because hydrogen abstraction from the N-H group can lead to nitrosamine formation via a very direct pathway whereas as C-H abstraction requires several reaction steps to form nitrosamines. Quantum chemistry methods can be used to estimate the relative energies of the reactant and transition states for the two different reaction sites. The geometries of the stationary points along the reaction path have been calculated at the University of Copenhagen for a primary and secondary amine using the Gaussian 09 suite of programs available at the STENO cluster at DCSC (Danish Centre for Scientific Computing at Copenhagen University).

The vibrational frequencies are calculated by these methods and used to characterize the stationary points (a minimum or a saddle point) and to estimate the zero point vibrational energy (ZPE). The reactant and transition state energies were calculated at the CCSD level using several basis sets. The coupled cluster method is computationally heavy with calculations taking 1-2 weeks for piperazine, however previous studies have shown that this level is the most accurate for this kind of study. The results from CCSD/aug-cc-pVTZ calculations yields negative reaction barriers of the order of -15 kJ/mol for PIPA (secondary) and CH_3NH_2 (primary) for both the N-H and C-H reaction sites. The C-H/N-H branching ratios are 46/54 and 51/49 for PIPA and CH_3NH_2 respectively.

This agrees well with published experimental data that show a C-H to N-H branching ratio of 48/52 for CH_3NH_2[6] OH and Cl reactivities can in general be expected to be similar, however the OH C-H to N-H branching ratio has been determined to be around 75/25 for some amine compounds. The higher reactivity towards C-H is caused by an interaction between the OH radical hydrogen and the lone pair in the R2-N-H group which activates the C-H towards reaction. In conclusion, it might be expected that chlorine radicals will tend to react more at the N-H bond than OH and therefore have a higher potential to form nitrosamines. The importance of this effect depends on the overall contribution of Cl reaction.

6 Box Modelling

6.1 The Box Model

The determined upper limit rate constants for the reaction of chlorine radicals with amines have been implemented in a tropospheric box model using the **Kintecus chemical kinetics simulation program**[17]. The Kintecus simulation software includes a compiler to model the reactions of atmospheric chemical kinetic and equilibrium processes.[18] For the present purposes, the box model has been constructed to evaluate the removal of the studied amines by chlorine radicals and by reaction with hydroxyl radicals. Elements of this model can be incorporated in a larger scale meteorological model.

The model includes 169 chemical reactions, including the Ox, HOx, NOx and hydrocarbon chemistry that drives the concentration of reactive species in the atmosphere. The model includes methane, ethane, propane and isoprene as hydrocarbon species. All of these compounds react with the OH radical and the reactions with NO_3 and Cl radicals have also been incorporated. The reaction rate constants have been taken from the established kinetics databases (JPL Photochemical Database, IUPAC Gas Kinetic Data Evaluation)[2, 19]. The core chemistry of the model is given in appendix A.

For the amines, the OH reaction rates have been determined experimentally for some of the compounds, namely AMP, and DMA. For the rest, an alternative is to use OH reaction rate constants predicted by quantitative structure-activity relationship (QSAR) calculations employed by the EPI Suite™ [2, 19]. However, since this QSAR approach is known to be inaccurate and likely overestimates the rate constants for amines and nitrosamines, we have chosen instead to use the experimental value for the amines for which they are available. The model scenarios have been carried out with a starting concentration of 1 ppm for each of the amines. Initial concentrations of other atmospheric species (hydrocarbons, H_2O, NO_x, etc.) have been taken from the literature[20].

6.2 Seasonal scenarios for chlorine chemistry

The chlorine reactions of amines depends on the availability of sunlight as the OH reaction does. It is therefore expected that the contribution of chlorine radical removal of amines is largest in the spring summer when there is

plenty of light. The production of other active chlorine species is less well understood, but is also likely to be photolysis dependent. The exception might be HCl which efficiently removes amines. The model scenarios shown the seasonal variation based on the variation in the photolysis rate of Cl_2. The scenarios assume that the production of Cl_2 remains constant which is a conservative estimate since the release of Cl_2 from SSA is a photochemical process.

Since this is a zero-dimensional box-model the spatial distribution of reactive species is not taken into account. The model employs an averaged chlorine concentration, however, locally the concentration might be significantly higher. The scenarios in figures 3a-3d show the chlorine contribution compared to OH for the degradation of amines for June, September, December and March. These scenarios have been run with the Cl_2 concentration set so that the Cl concentrations match observations of $1.8x10^3$ molecules/cm^3 in the marine boundary layer. Figure 4 shows the removal of MEA by OH and Cl exclusively showing that OH is a much more important removal process overall.

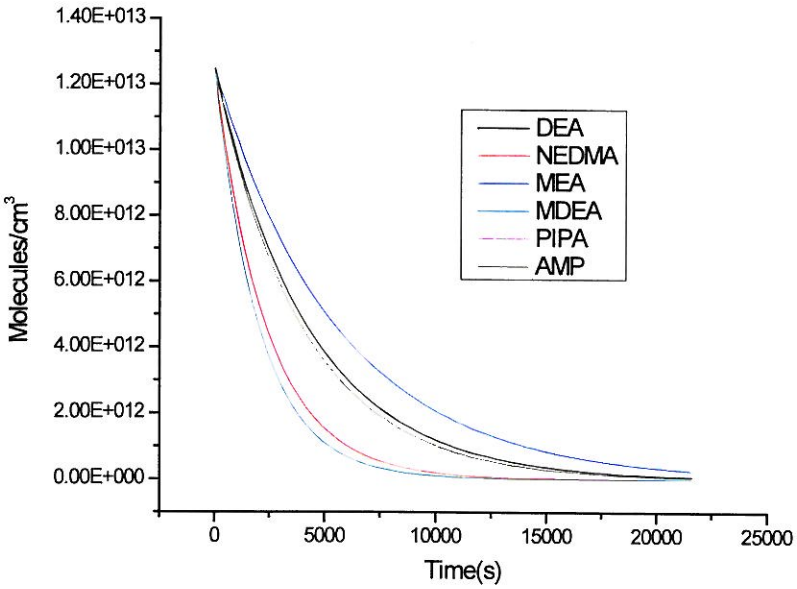


Figure 3a. Model scenario for amine oxidation by OH and Cl in June.

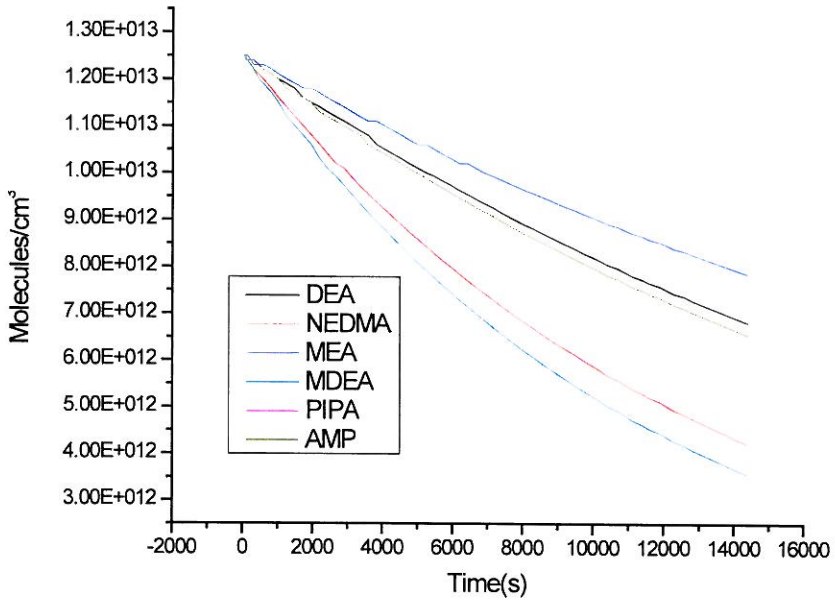


Figure 3b. Model scenario for amine oxidation by OH and Cl in March.

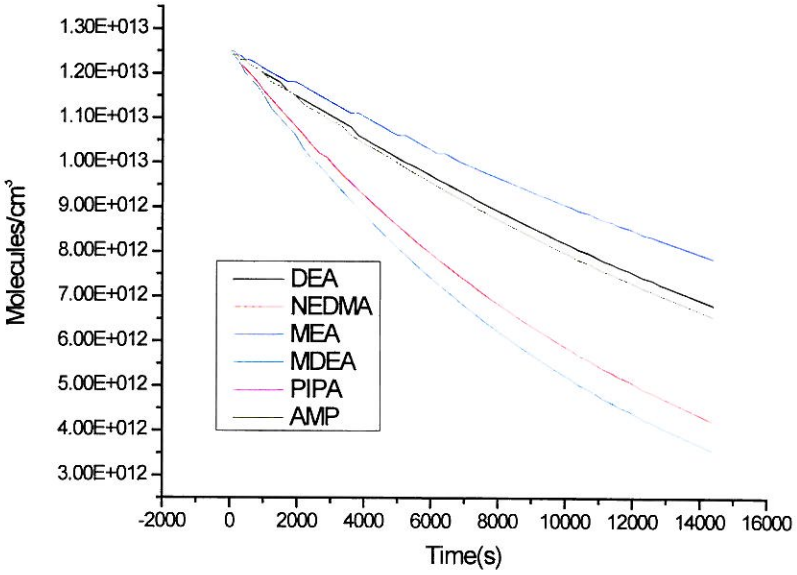


Figure 3c. Model scenario for amine oxidation by OH and Cl in September.

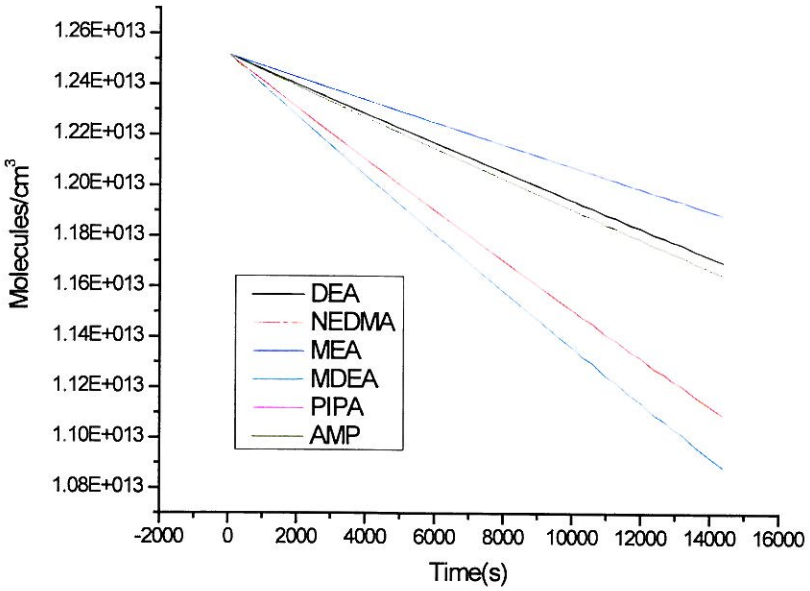


Figure 3d. Model scenario for amine oxidation by OH and Cl in December.

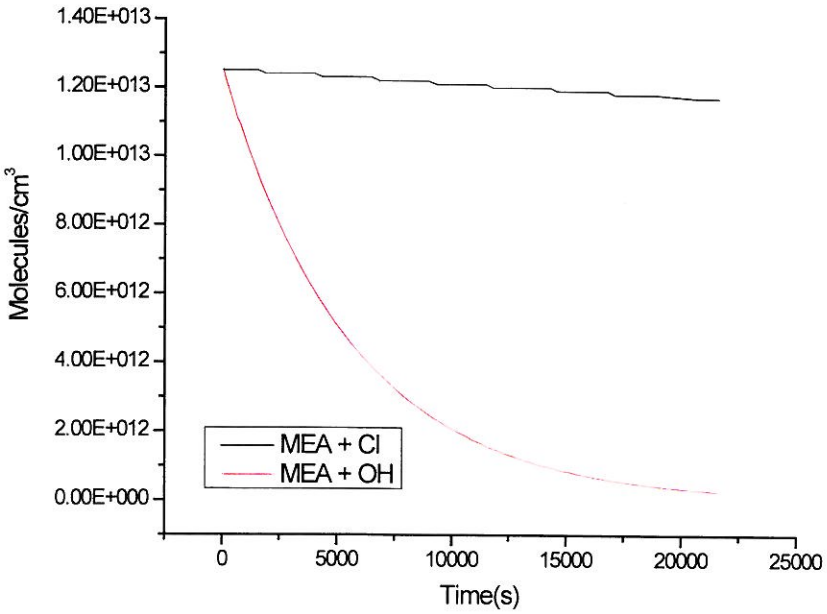


Figure 4. Model scenario for amine oxidation by OH and Cl respectively in June. The OH removal is more important in this and other scenarios studied.

7 Conclusion

The reactions of chlorine radicals with several amines including primary, secondary and tertiary species were studied experimentally and theoretically. The rates of reaction of representative amines with Cl have been be investigated in the laboratory using the relative rate method using two different photoreactor chambers using FT-IR and GC-MS as detection methods. The experiments proved challenging but upper limit rate constants were determined and he overall conclusion is that amine reactions with chlorine are very fast (of the order of ~10^{-11} molecules cm^{-3} s^{-1}).

Product studies of the reactions of the generic amines with Cl have been carried out using a GC-MS experimental setup with a chemical desorption system. There were no observations of unexpected products of the reaction. Nitrosamines were not seen as a product of amine + Cl reactions, even with NO_x present. Branching ratios for the reactions of chlorine with the C-H and N-H groups of the amines were determined by quantum chemistry and found to be around 50/50 indicating that chlorine reactions have the potential to form nitrosamines by reaction at the H-H site. The chemical reactions and the obtained rate information are implemented in a box model which shows that the chlorine degradation contributes about 5%to the overall amine loss but might still be significant locally by the coast. A model with sufficient spatial detail might capture the localized contribution from chlorine chemistry.

For the purpose of modelling chlorine chemistry in a larger dispersion model, two approaches may be taken. One is to include chlorine specific chemistry as shown in the box model used in the present study. This is more detailed and accurate, but likely computationally demanding. A detailed model should ideally include the HCl reaction and subsequent removal of the salt formed.

The contribution from chlorine radical removal as shown by the box model is not very large when using average chlorine concentrations. The reaction of amines with HCl is likely to be at least as important as Cl in the marine boundary layer as field measurements have shown that there is a factor 10-1000 more HCl. Another approach might be to augment the OH concentration in the model to account for an addition sink by Cl reaction. The model could include an additional OH source in coastal areas (e.g. within 5 km of the coast) corresponding to the average coastal Cl concentration. This would provide the effect of an additional removal process for amines, but it would not include any chlorine specific details such as the difference in branching ratio and reaction rate between the OH and Cl reactions. Based on a 5%contribution to the overall amine removal, this approach should be sufficient at least for initial evaluations.

8 Abbreviaitons

MEA	2-ethanolamine
DEA	Diethylamine
MDEA	N-methyl diethanolamine
DMA	Dimethylamine
PIPA	Piperazine
AMP	2-amino-2-methylpropanol
ZPE	Zero point energy
GC-MS	Gas chromatogrpahy mass spectrometry
FT-IR	Fourier transform infrared (spectroscopy)
SSA	Sea salt aerosol
UV-A, UV-C	Ultraviolet, A-region and C-region
CCSD	Coupled cluster singles and doubles

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10 Appendix

Appendix A is provided as a separate spreadsheet.

APPENDIX A

2,71E-05	0	0 O3 ==> O2 + O1D	Photo
9,27E-03	0	0 NO2 ==> NO + O	Photo
2,97E-05	0	0 HCHO ==> H + HCO	Photo
4,60E-05	0	0 HCHO ==> H2 + CO	Photo
2,31E-02	0	0 NO3 ==> NO + O2	Photo
1,82E-01	0	0 NO3 ==> NO2 + O	Photo
4,22E-05	0	0 N2O5 ==> NO3 + NO2	Photo
7,10E-10	0	0 N2O5 ==> NO3 + NO + O	Photo
6,91E-06	0	0 H2O2 ==> OH + OH	Photo
2,04E-03	0	0 HNO2 ==> NO + OH	Photo
5,89E-07	0	0 HNO3 ==> NO2 + OH	Photo
3,75E-06	0	0 HNO4 ==> NO2 + HO2	Photo
1,40E-03	0	0 HONO ==> OH + NO	Photo
4,93E-06	0	0 CH3CHO ==> CH3 + HCO	Photo
4,00E-12	0	0 CH3CHO ==> CH4 + CO	Photo
1,00E-24	0	0 CH3CHO ==> CH3CO + H	Photo
1,48E-05	0	0 C2H5CHO ==> C2H5 + HCO	Photo
7,15E-05	0	0 CHOCHO ==> products	Photo
1,00E-04	0	0 CH3COCHO ==> products	Photo
4,86E-07	0	0 CH3COCH3 ==> products	Photo
5,34E-06	0	0 CH3OOH ==> CH3O + OH	Photo
8,33E-07	0	0 CH3ONO2 ==> CH3O+NO2	Photo
6,13E-07	0	0 PAN ==> products	Photo
2,46E-03	0	0 Cl2 ==> Cl + Cl	Photo
1,00E-24	0	0 ClOO ==> products	Photo
4,16E-05	0	0 ClONO2 ==> Cl + NO3	Photo
7,90E-06	0	0 ClONO2 ==> ClO + NO2	Photo
#			
1,50E-04	0	0 NitrosoDMA ==> (CH3)2N + NO	Nitrosamine photolysis
1,40E-04	0	0 NitrosoPIPA ==> C5H10N + NO	Nitrosamine photolysis
2,70E-04	0	0 DinitrosoPIPA ==> C4H8N2NO + NO	Nitrosamine photolysis
1,40E-04	0	0 Nitrosomorpholine ==> C4H8NO + NO	Nitrosamine photolysis
1,70E-04	0	0 NitrosoDEA ==> products + NO	Nitrosamine photolysis
1,80E-04	0	0 NitrosoMAE ==> products + NO	Nitrosamine photolysis
#			
3,00E-12	0	0 NitrosoDMA + OH ==> products	Nitrosamine oxidation
2,00E-12	0	0 NitrosoPIPA + OH ==> products	Nitrosamine oxidation
2,00E-12	0	0 DinitrosoPIPA +OH ==> products	Nitrosamine oxidation
2,00E-12	0	0 Nitrosomorpholine +OH ==> products	Nitrosamine oxidation
2,00E-12	0	0 NitrosoDEA + OH ==> products	Nitrosamine oxidation
2,00E-12	0	0 NitrosoMAE + OH ==> products	Nitrosamine oxidation
#			
1,00E-11	0	0 HOC2H4NH2 + OH ==> HOC2H4NH + H2O	Amine
1,00E-11	0	0 HOC2H4NH2 + OH ==> HOC2H3NH2 + H2O	Amine
6,56E-11	0	0 (CH3)2NH + OH ==> NitrosoDMA	Amine
#			
1,00E-11	0	0 (CH3)2NH + Cl ==> NitrosoDMA	Amine
4,70E-11	0	0 DEA + Cl ==> products	Amine

8,40E-11	0	0	NEDMA + Cl ==> products	Amine
3,60E-11	0	0	MEA + Cl ==> products	Amine
9,70E-11	0	0	MDEA + Cl ==> products	Amine
5,00E-11	0	0	PIPA + Cl ==> products	Amine
5,00E-11	0	0	AMP + Cl ==> products	Amine
#				
1,00E-11	0	0	(CH3)2NH + OH ==> NitrosoDMA	Amine
4,70E-11	0	0	DEA + OH ==> products	Amine
8,40E-11	0	0	NEDMA + OH ==> products	Amine
3,60E-11	0	0	MEA + OH ==> products	Amine
9,70E-11	0	0	MDEA + OH ==> products	Amine
5,00E-11	0	0	PIPA + OH ==> products	Amine
5,00E-11	0	0	AMP + OH ==> products	Amine
#				
1,10E-10	0	0	O1D + H2 ==> OH + H	HOx
2,20E-11	0	-1,2	O + OH ==> O2 + H	HOx
3,00E-11	0	-2	O + HO2 ==> OH + O2	HOx
1,40E-12	0	20	O + H2O2 ==> OH + HO2	HOx
1,40E-10	0	4,7	H + O3 ==> OH + O2	HOx
8,10E-11	0	0	H + HO2 ==> OH + OH	HOx
1,60E-12	0	9,4	OH + O3 ==> HO2 + O2	HOx
5,50E-12	0	20	OH + H2 ==> H2O + H	HOx
1,68E-11	0	2,4	OH + OH ==> H2O2	HOx
4,80E-11	0	-2,5	OH + HO2 ==> H2O + O2	HOx
1,10E-14	0	5	HO2 + O3 ==> OH + O2 + O2	HOx
#				
3,60E-12	0	-2,24	HO2 + NO ==> NO2 + OH	NOx
4,37E-12	-3,2	0	HO2 + NO2 ==> HO2NO2	NOx
1,30E-12	0	-3,8	OH + HO2NO2 ==> H2O + NO2 + O2	NOx
1,40E-12	0	0	O3 + NO ==> NO2 + O2	NOx
1,40E-13	0	20,54	O3 + NO2 ==> NO3 + O2	NOx
5,35E-11	-3,9	0	NO2 + NO3 ==> N2O5	NOx
1,50E-11	0	-1,7	NO + NO3 ==> NO2 + NO2	NOx
8,50E-13	0	24,5	NO3 + NO3 ==> NO2 + NO2 + O2	NOx
6,70E-11	0	0	O1D + N2O ==> NO + NO	NOx
4,90E-11	0	0	O1D + N2O ==> N2 + O2	NOx
6,70E-11	0	0	O1D + N2O ==> NO + NO	NOx
4,90E-11	0	0	O1D + N2O ==> N2 + O2	NOx
8,51E-18	-0,6	0	O1D + N2 ==> N2O	NOx
3,00E-17	0	0	O + HNO3 ==> OH + NO3	NOx
3,00E-16	0	0	O + N2O5 ==> NO2 + NO2 + O2	NOx
4,37E-12	-3,2	0	HO2 + NO2 ==> HO2NO2	NOx
1,30E-12	0	-3,8	OH + HO2NO2 ==> products	NOx
1,40E-12	0	0	O3 + NO ==> NO2 + O2	NOx
1,40E-13	0	20,54	O3 + NO2 ==> NO3 + O2	NOx
5,35E-11	-3,9	0	NO2 + NO3 ==> N2O5	NOx

1,50E-11	0	-1,7	NO + NO3 ==> NO2 + NO2	NOx
8,50E-13	0	24,5	NO3 + NO3 ==> NO2 + NO2 + O2	NOx
3,00E-16	0	0	O + N2O5 ==> NO2 + NO2 + O2	NOx
1,70E-11	-2	0	OH + NO ==> HONO	NOx
6,00E-12	0	0	OH + HONO ==> H2O + NO2	NOx
3,00E-11	0	0	O + NO ==> NO2	NOx
6,50E-12	0	-1,2	O + NO2 ==> NO + O2	NOx
2,19E-12	-2	0	O + NO2 ==> NO3	NOx
1,00E-11	0	0	O + NO3 ==> NO2 + O2	NOx
3,00E-17	0	0	O + HNO3 ==> OH + NO3	NOx
3,00E-16	0	0	O + N2O5 ==> NO2 + NO2 + O2	NOx
1,70E-11	-2	0	OH + NO ==> HONO	NOx
6,08E-11	-4,4	0	OH + NO2 ==> HNO3	NOx
2,20E-11	0	0	OH + NO3 ==> HO2 + NO2	NOx
1,80E-11	0	3,9	OH + HONO ==> H2O + NO2	NOx
1,40E-13	0	0	OH + HNO3 ==> NO3 + H2O	NOx
#				
1,50E-13	0	0	CO + OH ==> CO2 + H	C Chemistry
2,45E-12	0	14,8	CH4 + OH ==> CH3 + H2O	C Chemistry
1,09E-11	0	0	CH3 + O2 ==> CH3O2	C Chemistry
3,80E-13	0	-6,49	CH3O2 + HO2 ==> CH3OOH + O2	C Chemistry
2,80E-12	0	-2,37	CH3O2 + NO ==> CH3O + NO2	C Chemistry
9,60E-12	0	0	CH3O + O2 ==> HCHO + HO2	C Chemistry
8,20E-12	0	-0,33	HCHO + OH ==> HCO + H2O	C Chemistry
5,20E-12	0	0	HCO + O2 ==> CO + HO2	C Chemistry
1,00E-12	0	-1,58	CH3OOH + OH ==> HCHO + OH + H2O	C Chemistry
4,40E-12	0	-3,03	CH3CHO + OH ==> CH3CO + H2O	C Chemistry
5,00E-12	0	0	CH3CO + O2 ==> CH3COO2	C Chemistry
2,36E-09	0	0	CH3COO2 + NO2 ==> PAN	C Chemistry
5,36E-12	0	6	CH3OH + OH ==> CH2OH + H2O	C Chemistry
1,34E-12	0	6	CH3OH + OH ==> CH3O + H2O	C Chemistry
2,66E-12	0	-2	CH3OOH + OH ==> CH3O2 + H2O	C Chemistry
1,14E-12	0	-2	CH3OOH + OH ==> CH2OOH + H2O	C Chemistry
4,00E-14	0	0	OH + PAN ==> products	C Chemistry
9,10E-12	0	0	CH2OH + O2 ==> HCHO + HO2	C Chemistry
3,90E-14	0	9	CH3O + O2 ==> HCHO + HO2	C Chemistry
4,00E-12	0	-0,7	CH3O + NO ==> HCHO + HNO	C Chemistry
7,40E-11	0	-1,2	O1D + CO2 ==> O + CO2	C Chemistry
1,50E-10	0	0	O1D + CH4 ==> CH3 + OH	C Chemistry
1,00E-10	0	0	O + CH3 ==> CH3O	C Chemistry
3,40E-11	0	16	O + HCHO ==> OH + HCO	C Chemistry
1,80E-11	0	11	O + CH3CHO ==> CH3CO + OH	C Chemistry
1,10E-11	0	14	CH4 + Cl ==> CH3 + HCl	C Chemistry
8,20E-11	0	0,28	HCHO + Cl ==> HCO + HCl	C Chemistry
#				
2,80E-11	0	0	O1D + Cl2 ==> ClO + Cl	ClOx
1,50E-10	0	0	O1D + HCl ==> OH + Cl	ClOx

1,00E-11	0	33	O + HCl ==> OH + Cl	ClOx
3,00E-11	0	-0,7	O + ClO ==> Cl + O2	ClOx
2,40E-12	0	9,6	O + OClO ==> ClO + O2	ClOx
4,62E-12	-1,1	0	O + OClO ==> ClO3	ClOx
2,70E-11	0	5,3	O + Cl2O ==> ClO + ClO	ClOx
1,70E-13	0	0	O + HOCl ==> OH + ClO	ClOx
2,90E-12	0	8	O + ClONO2 ==> products	ClOx
1,40E-12	0	9	OH + Cl2 ==> HOCl + Cl	ClOx
1,10E-11	0	-1,2	OH + ClO ==> HO2 + Cl	ClOx
4,50E-13	0	-8	OH + OClO ==> HOCl + O2	ClOx
2,60E-12	0	3,5	OH + HCl ==> H2O + Cl	ClOx
3,00E-12	0	5	OH + HOCl ==> H2O + ClO	ClOx
2,40E-12	0	12,5	OH + ClNO2 ==> HOCl + NO2	ClOx
1,20E-12	0	3,3	OH + ClONO2 ==> products	ClOx
1,80E-11	0	-1,7	HO2 + Cl ==> HCl + O2	ClOx
4,80E-13	0	-7	HO2 + ClO ==> HOCl + O2	ClOx
2,50E-12	0	6	NO + OClO ==> NO2 + ClO	ClOx
6,56E-14	-1,5	0	Cl + O2 ==> ClOO	ClOx
2,90E-11	0	2,6	Cl + O3 ==> ClO + O2	ClOx
3,70E-11	0	23	Cl + H2 ==> HCl + H	ClOx
1,10E-11	0	9,8	Cl + H2O2 ==> HCl + HO2	ClOx
2,40E-11	0	0	Cl + NO3 ==> ClO + NO2	ClOx
6,40E-12	0	-2,9	ClO + NO ==> NO2 + Cl	ClOx
5,00E-17	0	0	NO3 + HCl ==> HNO3 + Cl	ClOx
1,40E-17	0	0	ClO + O3 ==> ClOO + O2	ClOx
1,00E-18	0	0	ClO + O3 ==> NO2 + Cl	ClOx
1,00E-12	0	15,9	ClO + ClO ==> Cl2 + O2	ClOx
3,00E-11	0	24,5	ClO + ClO ==> ClOO + Cl	ClOx
3,50E-13	0	13,7	ClO + ClO ==> OClO + Cl	ClOx
2,19E-12	-1,6	0	Cl + NO ==> ClNO	ClOx
3,16E-11	-2	0	Cl + NO2 ==> ClONO	ClOx
4,37E-12	-2	0	Cl + NO2 ==> ClNO2	ClOx
4,37E-12	-3,4	0	ClO + NO2 ==> ClONO2	ClOx
5,35E-13	-3,1	0	ClO + ClO ==> Cl2O2	ClOx
4,62E-12	-4,7	0	OClO + O ==> ClO3	ClOx
1,51E-12	-3,1	0	ClO + OClO ==> Cl2O3	ClOx
3,16E-14	-3,8	0	CO + Cl ==> ClCO	ClOx

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