A MECHANISM FOR PHOTOCHEMICAL REACTIONS IN THE QUASI-LIQUID LAYER OF SNOW CRYSTALS IN POLAR REGIONS

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1 INTRODUCTION

Photochemical processes in snow have recently attracted considerable scientific interest.[1] Field and laboratory experiments have been reported regarding the influence of photochemical processes in the snow on concentrations of species like nitrogen oxides (NO_x), hydrogen peroxide (H_2O_2), and formaldehyde (HCHO). Field measurements have studied the following processes in the surface snow: 1. the production of NO_x in the snow and the release to the atmosphere, 2. the bi-directional exchange of H_2O_2 and HCHO between the atmosphere and the snow, and 3. the impact of the emission on the composition of the atmospheric boundary layer in snow-covered regions.[1-15]

Among the manifold reactions in snow the photolysis of nitrate (NO_3^-) is now the best characterized reaction due to a range of laboratory experiments. These studies have been used to extract information about the absorption coefficients and quantum yields of NO_3^- in ice as a function of wavelength,[16] the formation of products like the hydroxyl radical (OH)[16, 17] and nitrite (NO_2^-),[17-19] and the release of NO_x to the gas phase.[18, 20-23] Limited information regarding the absorption coefficients and the formation of OH radicals can also be found for the photolysis of H_2O_2.[24] Investigations regarding the photolytic decomposition of further compounds with a potential relevance for photochemical processes in surface snow are limited to studies, in which reactions of HCHO and NO_2^- have been examined.[19, 25, 26]

These results have demonstrated that snow photochemistry involves several complex chemical processes. Such a system can only be accounted for with a comprehensive reaction mechanism. Therefore, we used available experimental and field data to assemble a comprehensive reaction mechanism for surface snow. In addition, rate constants for the reactions involved for typical polar conditions in summer at snow temperatures of −20 °C are presented together with typical initial concentrations of the stable compounds involved in the mechanism. First simulations are performed for typical summer conditions in Greenland and results of these calculations are presented.

2 LABORATORY STUDIES OF PHOTOCHEMICAL REACTIONS IN ARTIFICIAL SNOW

We developed an experimental set-up to investigate single photochemical reactions in artificial snow samples. Details of the experiments and the preparation of the snow samples have previously been described.[19, 25] Snow samples were prepared by spraying solutions of purified water containing single impurities into liquid nitrogen. Photolytic reactions of H_2O_2, HCHO, NO_3^- and NO_2^- have been investigated under comparable experimental conditions.[19, 25] The results demonstrated that under the applied conditions NO_2^- was produced during the NO_3^- photolysis. However, the photolysis of NO_2^- also led to the formation of significant amounts of NO_3^-. The photolysis of H_2O_2 in the snow was observed for a wide range of initial H_2O_2 concentrations in the snow. In contrast, a first-order decrease of HCHO was only observed with high initial concentrations well beyond the range of HCHO concentrations observed in natural snow samples. The obtained experimental photolysis rates are summarized in Table 1.

3 PHOTOCHEMICAL MECHANISM FOR SNOW

Jacobi et al.[26] presented a reaction mechanism for the transformation of NO_3^- and NO_2^- in snow using several series of laboratory experiments investigating the photolysis of NO_3^- and NO_2^- in artificial snow samples. Using the experimental results, rate constants were determined for the involved photolysis reactions of NO_3^- and NO_2^- and the transfer of both compounds from the snow to the gas phase for the applied experimental conditions. The calculations were performed with the assumptions that all of the impurities were located in the so-called quasi-liquid layer (QLL)[27] at the surface of the snow crystals and that the reactions occur in this liquid-like medium. Although it is known that the formation of QLL appears close to the melting point,[27] impurities can enhance the disorder in the surface layer leading to a thicker QLL also at much lower temperatures. For example, the results of Cho et al.[28] indicate that the presence of sodium chloride in the snow with typical concentrations found in coastal polar snow samples leads to the formation of a significant QLL even at temperatures as low as -20 °C.[26] Since further ions are omnipresent in snow even in polar regions, the presence of a QLL on the snow crystals at these low snow temperatures is likely.

Subsequently, the obtained photolysis rate constants were adjusted for Arctic summer conditions as observed on the Greenland ice sheet. Further calculations with the adjusted rate constants demonstrated that under natural conditions the formation of nitrogen oxides

Table 1 *Experimental photolysis rates in artificial snow for several investigated compounds. Rates were obtained for –20 °C.*

Compound	Photolysis rate h^{-1}	Reference
NO_3^-	1.2	26
NO_2^-	30	26
H_2O_2	0.48	19
HCHO	0.1	19

in the snow is dominated by NO_2, which is either generated directly by the photolysis of NO_3^- or by the reaction of NO_2^- with the hydroxyl radical (OH). Due to the quick transformation of NO_2^- to NO_2 the NO_2^- concentrations remain low. Consequently, even if the pH of the QLL would be low enough to favor the formation of nitrous acid (HONO), the HONO generation in the QLL remains probably negligible.

The full and simplified mechanisms for the transformation of NO_3^- and NO_2^- and the production of NO_x in snow presented by Jacobi et al.[26] take only into account reactions of N-containing compounds. However, the importance of the role of the OH radical for the reactions in the QLL is well known. Further laboratory studies indicated that the photolysis of H_2O_2 is probably the most important OH source in the QLL.[24] Thus, a comprehensive reaction mechanism needs to consider a complete set of OH sources and sinks.

The importance of the OH radical for the chemical reactions in the QLL becomes obvious if the calculated QLL concentrations are compared to levels calculated for tropospheric cloud droplets. For example, Herrmann et al.[29] demonstrated that OH levels in the tropospheric aqueous phase reach maximum values between 1 and $2 \cdot 10^{-12}$ M (= mol dm^{-3}) depending mainly on the concentrations of organic compounds. In contrast, the OH levels in the calculations presented by Jacobi et al.[26] increase to levels on the order of $1 \cdot 10^{-9}$ M in the QLL for conditions in surface snow in Greenland. This number represents an upper limit for the OH concentrations since a rage of reactions, which are significant OH sinks in the tropospheric aqueous phase, are not included in the previously presented mechanism. Among these reactions are mainly the reactions with organic compounds. However, knowledge about concentrations of single organic compounds in the snow is still very limited.[e.g. 7] Currently, only formaldehyde concentrations in snow have been investigated in detail at several polar locations.[5, 10, 11, 30-32] The reported concentrations range from 0.05 to $1.2 \cdot 10^{-6}$ M. A more comprehensive characterization of the organic content is available also for Summit station. Measurements of total organic carbon and

Table 2 *Reported concentrations of organic components in snow samples from Summit station collected in June 2000.*[7]

Compound or class of compounds	Concentration	
	µg L^{-1}	µM
Total organic carbon (TOC)	1850	3.7[a]
Inorganic Carbon	1080	17.7[b]
Formaldehyde	35.7	1.19
Acetate	21.8	0.369
Propionate	5.9	0.080
Formate	3.9	0.087
Methanesulfonate	0.6	0.006
Lactate	0.4	0.004

[a] Since Grannas et al.[33] reported that the molecular mass of the organic carbon in snow can reach values of higher than 1 kDa, we used an estimated average molecular mass of 500 Da to translate the measured TOC concentration into µM.

[b] Assuming that the inorganic carbon is dominated by carbonate.

several individual components were performed using surface snow samples collected in June 2000.[7] The reported concentrations are summarized in Table 2.

An updated reaction mechanism with additional reactions and estimated rate coefficient adjusted to conditions encountered at Summit station in Greenland in June 2000 is presented in Table 3. In addition to the chemistry of N-containing compounds, we included further sources and sinks of the OH radical.

The reaction rate for the photolysis rate of H_2O_2 (R8) was calculated using data from previously published laboratory experiments of photolysis reactions of NO_3^- and H_2O_2 in artificial snow for comparable experimental conditions (Table 1). Therefore, the obtained experimental rate constant of 0.48 h^{-1} for the H_2O_2 photolysis was divided by a factor of 400 similar to the procedure for the photolysis rate of NO_3^- as described in Jacobi et al.[19, 26] The HCHO photolysis reaction in snow is probably negligible under natural conditions and is not included in the reaction mechanism.

According to modeling studies regarding the tropospheric aqueous phase the reaction of hydrated formaldehyde ($CH_2(OH)_2$) with OH represents an important OH sink.[e.g. 29] Using temperature dependent kinetic data for this reaction,[29] a rate constant of $5.4 \cdot 10^8$ M^{-1} s^{-1} is calculated for –20 °C. Since the used kinetic data was obtained in bulk aqueous solutions, the reaction (R9) involves the attack of the OH radical on the hydrated formaldehyde $CH_2(OH)_2$. It was suggested that formaldehyde in snow is mainly present in the non-hydrated form HCHO.[14] Nevertheless, we include the aqueous phase rate constant since it seems likely that the hydration of the HCHO molecules can occur in the QLL of the snow crystals. Due to the presence of the high concentration of organic compounds in the snow[7] the reaction of these compounds with OH are also included (Table 3). Since most of the individual organic compounds are not identified, reactions with single organic reactants cannot be included. We rather use a general reaction (R10) with an estimated rate constant on the order of $1 \cdot 10^8$ M^{-1} s^{-1}. This rate constant represents in average for the reaction of the OH radical with several organic compounds in the aqueous phase.[28]

Table 3 *Recommended reactions with rates estimated for -20 °C for a comprehensive mechanism for reactions occurring in natural surface snow.*

	Reaction	Rate constants	Reference
(R1)	$NO_3^- (+ H^+) \xrightarrow{h\nu} NO_2 + OH$	$8.3 \cdot 10^{-7}$ s^{-1}	26
(R2)	$NO_3^- \xrightarrow{h\nu} NO_2^- + O$	$1.7 \cdot 10^{-7}$ s^{-1}	26
(R3)	$NO_3^- + O \rightarrow NO_2^- + O_2$	$2 \cdot 10^8$ M^{-1} s^{-1}	26
(R4)	$O (+ O_2) \rightarrow O_3$	$1.2 \cdot 10^6$ s^{-1}	26
(R5)	$NO_2^- + OH \rightarrow NO_2 + OH^-$	$1 \cdot 10^{10}$ M^{-1} s^{-1}	26
(R6)	$NO_2 + OH \rightarrow H^+ + NO_3^-$	$5 \cdot 10^9$ M^{-1} s^{-1}	26
(R7)	$NO_2 \rightarrow NO_2$ gas	9.7 s^{-1}	26
(R8)	$H_2O_2 \xrightarrow{h\nu} 2$ OH	$3.3 \cdot 10^{-7}$ $s^{-1 a}$	See text
(R9)	$CH_2(OH)_2 + OH \rightarrow$ prod.	$5.4 \cdot 10^8$ M^{-1} s^{-1}	29
(R10)	ORG + OH $\rightarrow$ prod.	$1 \cdot 10^8$ M^{-1} s^{-1}	See text

[a] The photolysis rate is extrapolated relative to the total NO_3^- photolysis rate using the ratio of the experimental photolysis rates reported by Jacobi et al.[19, 26]

To start simulations of reactions in surface snow initial concentrations of the involved stable species are needed. Table 4 gives a summary of concentrations of NO_3^-, H_2O_2, HCHO, and organic compounds (ORG) observed in surface snow samples collected at Summit station in the summer of the year 2000. Assuming that all photochemical reactions take place in the QLL these concentrations need to be translated into QLL concentrations. As described by Jacobi et al.[26] the impurities are confined to the very small volume of the QLL leading to significantly higher concentrations. Such an enrichment factor representing the summer conditions at Summit was used to obtain the initial NO_3^- concentration in the QLL for the simulation of processes in natural snow.[26] Applying the same factor of $1.94 \cdot 10^{-5}$ representing the ratio of the QLL to the total volume of the snow, the QLL concentrations for the further compounds can be calculated (Table 4). In the case of H_2O_2 this value possibly represents only an upper limit. Previous studies have shown that larger fractions of the H_2O_2 incorporated in snow can also be located within the snow crystal.[5]
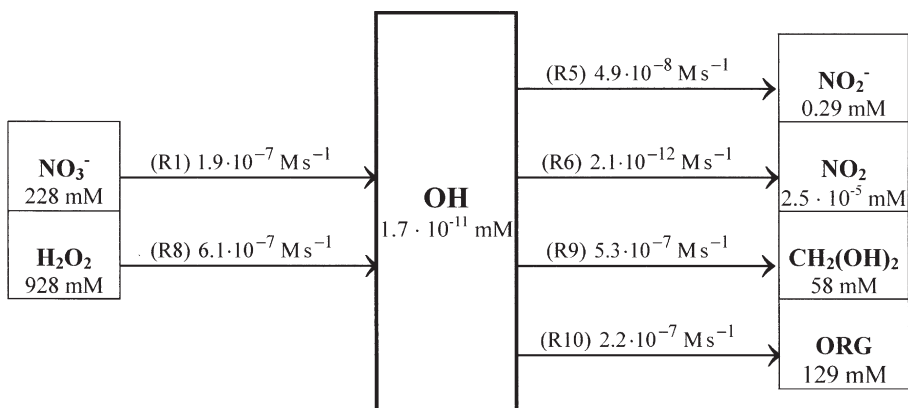
4 MODEL CALCULATIONS

We performed simulations for the QLL with the photochemical mechanism summarized in Table 3 using the commercial software FACSIMILE,[34] which uses an implicit integration scheme for stiff differential equations[35] with a self-adjusting time step. This software is able to translate a reaction mechanism into a set of dependent differential equations for the concentrations of all involved species. Further input parameters include reaction rate constants and initial concentrations if necessary. Additional details about the software can be found on the AEA Technology website (www.aeat.co.uk/mcpa/areas/software/facsimil.htm).

Calculations were started with initial concentrations as shown in Table 4. Initial concentrations of all further compounds were set to zero. Results of the calculations are shown in Figure 1. We present numbers obtained after a simulation period of 100 min with constant reaction rates. Although concentrations of the stable compounds H_2O_2, NO_3^-, HCHO, and ORG steadily decrease due to the photolysis reactions or the reactions with OH, calculated concentrations remain relatively constant over longer periods. For example, concentrations of the stable compounds changed less than 1% after the simulation of 100 min (Figure 1) compared to the initial concentrations (Table 4).

Table 4 *Concentrations of stable compounds included in the reaction mechanism as observed in the snow at Summit station in the summer of the year 2000.*

Compound	Observed Concentration µM	QLL concentration mM	Reference
NO_3^-	4.4	230	26
NO_2^-	0	0	26
H_2O_2	18	930	9
HCHO	1.19	61	7
ORG	2.5 [a]	130	7

[a] The concentration for the sum of organic compounds was calculated as the difference of the total organic content and the formaldehyde measurements shown in Table 1.

Figure 1   *Sources and sinks of OH calculated for the QLL of surface snow. Numbers are*
calculated after a simulation period of 100 minutes. Numbers in brackets refer
to reactions as shown in Table 2.

The calculations clearly demonstrate the strong impact of the organic compounds on the OH levels in the QLL. The reactions of OH with HCHO and ORG clearly dominate the OH sinks. The additional OH production due to the photolysis of H_2O_2 cannot outweigh this OH sink. As a result the OH concentrations are significantly lower as compared to the calculations with the N-containing compounds alone.[26]

Nevertheless, the production of OH in the QLL is dominated by the photolysis of H_2O_2. The OH source strength is more than a factor of three higher than the OH production due to the NO_3^- photolysis. This is in agreement with the results presented by Chu and Anastasio.[24]

5 CONCLUSIONS

The experiments and model calculations regarding photochemical processes in surface snow clearly demonstrate that photochemical transformations in the snow are very diverse. As in the atmospheric gas and liquid phase, the OH radical plays a critical role in these transformations. However, the sinks of this radical are not well defined. The reactions with organic compounds are probably the most important OH destruction reactions. However, due to the limited information of the concentrations of single organic compounds in snow it is currently impossible to assemble a detailed mechanism for snow chemistry. Therefore, we decided to introduce a class of compounds, which represents organic material. Additional investigations of organic components in snow can be used to further refine the mechanism.

The comprehensive reaction mechanism presented here includes only ten reactions. Assuming that the conditions at Summit are typical summer conditions for both polar regions we suggest using these reactions together with the recommended rates as a basic set of reactions for further modeling studies of photochemical processes in surface snow. Stable compounds include NO_3^-, H_2O_2, HCHO, and organics in snow. For the first three compounds snow concentration measurements for several polar locations are available in the literature. Therefore, this mechanism can be introduced into one-dimensional models to investigate the impact of photochemical reactions in the snow for a given location in detail.

A further introduction into regional or global models will be helpful for the evaluation of the impact of the surface snow reactions on a larger spatial scale.

The applicability of the recommended mechanism is possibly limited by different snow properties. For example, since the reactions occur in the QLL of the snow crystals, changes in the specific surface area (SSA) during the metamorphosis of the snow can also alter concentrations of the impurities. A strong interaction between chemical and physical properties of the snow can be expected. Therefore, further studies taking also into account physical snow properties like density and SSA are needed to verify the proposed transformations by photochemical reactions in the snow.

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