The Heterogeneous Reaction of N_2O_5 with HBr on Ice Comparison with N_2O_5 +HCl

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Key Words: Chemical Kinetics / Heterogeneous Reactions / Interfaces

The heterogeneous reactions of N_2O_5 with HCl and HBr on ice have been studied in the temperature range 180 to 200 K using a Knudsen flow reactor.

The uptake of N_2O_5 on ice in the presence of HBr was found to be strongly dependent on the HBr concentration. For the highest HBr concentrations used a maximum uptake coefficient of N_2O_5 of $\gamma=0.11$ has been determined. We observed Br₂ and HONO in 80% yield as products with respect to N_2O_5 taken up. The uptake coefficient of N_2O_5 on ice in the presence of HCl was found to be $3.2 \cdot 10^{-2}$ and increased with increasing HCl concentration. ClNO₂ was detected as the sole reaction product with a maximum yield of 63% with respect to N_2O_5 consumed.

Hydrolysis of N_2O_5 resulting in HNO₃ was found to be competitive with the title reaction. For the case of the HBr reaction the branching ratio between Br₂ and HONO formation, on the one hand, and hydrolysis of N_2O_5 , on the other hand, has been determined. Mechanistic aspects of the heterogeneous reaction of N_2O_5 with HX have been discussed.

1. Introduction

It is now well recognized that the heterogeneous chemistry of HCl, ClONO₂ and N_2O_5 on frozen substrates such as polar stratospheric clouds is important with respect to the destruction of ozone in the winter stratosphere. Such processes are responsible for the formation of photoactive chlorine compounds [1–4] as well as for the denitrification of the lower stratosphere [5].

 N_2O_5 is a reservoir compound which converts NO_x (NO, NO₂) and NO₃ into the more stable reservoir species HNO₃ by undergoing heterogeneous hydrolysis on ice as well as on sulphate aerosols (reaction (1)) [6].

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{1}$$

The solubility of HX (X=Cl, Br) on or in ice is significant [7–9]. Therefore, heterogeneous reactions between HX and N_2O_5 on ice may take place which convert these halogen species into photochemically active forms according to reactions (2) and (3).

 $N_2O_5 + HCl \rightarrow HNO_3 + ClNO_2$ (2)

$$N_2O_5 + HBr \rightarrow HNO_3 + BrNO_2$$
 (3)

Previous studies of reactions (1) and (2) on ice at temperatures between 185 and 205 K resulted in an uptake coefficient of approximately 2 to $3 \cdot 10^{-2}$ for either reaction [4, 10, 11]. Only a slight increase in the uptake coefficient has been observed with increasing amount of HCl. ClNO₂, the product of reaction (2), has been qualitatively detected whereas the yields of ClNO₂ had not been measured in these studies. It remains unclear what the branching ratio between reaction (2) and hydrolysis of N₂O₅ (reaction (1)) is. The heterogeneous reaction of N₂O₅ with HBr has been studied only once where H_2O was adsorbed on cold glass and used as a substrate [8]. No product detection and identification had been attempted.

Heterogeneous activation of HBr is thought to play a minor role so far owing to its small concentration in the atmosphere [12]. Nevertheless, the general conclusion from previous studies involving HBr [8, 13–15] is that HBr reacts more efficiently on ice than the analogous HCl which may compensate somewhat for its low abundance.

An important aspect of a heterogeneous reaction involving HX is its mechanism. Previous studies [16–18] propose an ionic displacement mechanism at the solid-gas interface via a nucleophilic substitution. This implies that the pseudo first order rate constant for these reactions strongly depends on the amount of HX available at the interface.

In this study, experimental results on reactions (2) and (3) on ice at temperatures between 180 and 200 K are reported. Since not only the uptake of N_2O_5 but also the product yields of these reactions are quantified we are able to present branching ratios between the hydrolysis of N_2O_5 and the reaction of N_2O_5 with HX. Furthermore, some mechanistic aspects of the reactions are discussed.

2. Experimental Setup

The experiments were performed in a Teflon-coated Knudsen flow reactor operating in the molecular flow regime. This technique has been described in great detail in the literature [19]. Briefly, the gases under study were introduced into the Knudsen reactor from the gas handling system by using either a capillary for pressure reduction or a pulsed valve. The gases leave the Knudsen reactor through an escape orifice whose diameter (4, 8, 14 mm) determines the residence time and the densities of the molecules inside the Knudsen reactor. The rate constant

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Table 1

Characteristic parameters and relevant kinetic expressions

Definition	Value
Reactor volume V	$V = 2000 \text{ cm}^3$
Reactor surface area $A_{\rm R}$ (estimated)	$A_{\rm R} = 1300 \ {\rm cm}^2$
Sample surface area $A_{\rm S}$	$A_{\rm S} = 15.9 \ {\rm cm}^2$
Collision frequency for N_2O_5 with A_5 at room temperature	$\omega = 51 \text{ s}^{-1}$
Typical concentration range $N = F/V \cdot k_{esc}$, $F =$ flow into the reactor	$N = 1 - 1000 \cdot 10^{10} \text{ cm}^{-3}$
Orifice diameters	4, 8, 14 mm
Rate constant for effusive loss k_{esc} (theoretical value) (A_{H} = surface area of the orifice)	$k_{\rm esc} = (8RT/\pi M)^{1/2} \cdot A_{\rm H}/4 V$
k_{esc} for N ₂ O ₅ (experimental value)	0.39 s ⁻¹ (4 mm), 1.08 s ⁻¹ (8 mm), 3 s ⁻¹ (14 mm)
Rate constant for heterogeneous reaction from pulsed valve experiments (see text)	$k_{\rm uni} = k_{\rm dec} - k_{\rm esc}$
Rate constant for heterogeneous reaction from steady state experiments S_i (initial MS signal), S_f (final MS signal)	$k_{\rm uni} = (S_i / S_f - 1) \cdot k_{\rm esc}$
Uptake coefficient	$\gamma = k_{uni}/\omega$

for the effusive loss k_{esc} is given by the kinetic theory of gases and was routinely measured for each compound. The characteristic parameters and relevant kinetic expressions are given in Table 1.

The modulated effusive beam leaving the Knudsen cell is analysed by a quadrupole mass spectrometer (MS). The mass spectrometer settings were chosen to yield a sensi-tivity of approximately 10^{10} molecule/cm³ at a signal to noise ratio greater than 2. The mass spectra of all observed compounds are listed in Table 2. In addition, the apparatus was equipped with laser induced fluorescence detection. In the present work this technique was used to unambiguously detect NO2 after excitation at 403 nm and

Table	2	
Maga	amontanal I	de

Mass	spectral	data
	operate.	

broad band detection to the red of 500 nm with a detection limit of 10⁹ molecule/cm³. Details may be found in Ref. [19].

An isolation plunger allows the separation of the reactive surface from the reactor volume. Steady state experiments are performed by introducing into the reactor a constant flow of molecules across a capillary. By analysis of the change of the MS signal levels of the corresponding compounds upon opening and closing the sample chamber a value for the net uptake coefficient γ may be calculated. Real time experiments have been performed by introducing a pulse of N₂O₅ of 2 ms duration across a solenoid valve into the reactor and observing its decay. Comparison is made with a reference pulse while the reactive surface is isolated from the reactor volume. The rate constant for effusive loss k_{esc} is determined by fitting an exponential decay function to the experimental MS signal trace in the absence of reaction. Repeating the same procedure with the plunger lifted, thus with the sample exposed, a reactive pulse is obtained. The observed single exponential decay in the presence of a reactive surface is characterised by a new rate constant, k_{dec} , defined by $k_{dec} = k_{uni} + k_{esc}$ (Table 1).

We used a low temperature sample support in which the sample could be cooled down to 150 K. A programmable temperature controller maintained the final temperature to ± 0.5 K at an accuracy of ± 2 K. The absolute calibration of the low temperature support was performed using the literature values of the vapor pressure over ice in that temperature range. For preparing the ice samples approximately 5 ml of distilled water were poured into the sample support at ambient temperature and cooled down to the desired temperature in about 15 min and subsequently evacuated. Alternatively, the mounted sample support was cooled down to the desired temperature of typically 200 K followed by condensation of water from the gas phase $(F=10^{18} \text{ molecule/s})$. Recent studies showed that ice samples prepared by condensation have a higher porosity than bulk ice samples [20]. Nevertheless, uptake experiments of N₂O₅ in the presence or absence of HBr performed on these two different surfaces obtained identical results within experimental error. Also, no systematic difference in the uptake of HBr and HCl using

Species	Parent peak ^a)	Fragment ^a)	Fragment ^a)	Fragment ^a)	Fragment ^a)	
N ₂ O ₅		46 (100)	30 (55)			
HBr	80, 82 (100)	79, 81 (40)	()			
HCl	36 (100)	35 (14)				
BrNO ₂		93, 95 (1)	46 (100)	30 (80)	79 (10)	
CINO ₂		49 (1)	46 (100)	30 (50)	35 (10)	
Br ₂	160 (100)	79, 81 (17)	()		()	
HÕNO	47 (12)	30 (100)				
BrNO	109, 111 (12)	93, 95 (1.2)	79, 81 (10)	30 (100)		

^a) Ion mass with peak intensity in parentheses, given as percent of the most intense peak. The numbers in italics indicate the mass fragments which were used to monitor the species by MS.

the two different types of ice surfaces have been observed. The measured uptake coefficients agree well with previous studies [15, 21]. In some experiments we supplied an external flow of H_2O vapor to the Knudsen reactor in order to balance the water evaporating from the sample upon opening the sample volume. No differences, neither in the uptake coefficients nor in the rate of product formation, could be observed upon supplying an external flow of H_2O compared to no flow.

 N_2O_5 is prepared by oxidizing NO_2 with ozone as described by Fenter et al. [22]. After distillation of the raw product the impurities such as NO_2 and HNO_3 were measured to be less than 2%. The flow rate into the Knudsen reactor and thus the gas densities were determined by measuring the pressure change in a calibrated volume as a function of time.

3. Experimental Results

3.1 Heterogeneous Reaction of N_2O_5 in the Presence of HBr

The uptake kinetics of N_2O_5 in the presence of HBr on ice have been studied at temperatures of 180 to 200 K. Flow rates of N_2O_5 have been chosen to be between $3 \cdot 10^{14}$ and $3 \cdot 10^{15}$ molecule/s corresponding to densities of $5 \cdot 10^{10}$ to $2.5 \cdot 10^{12}$ molecule/cm³. Flow rates of HBr have been chosen to be between $1 \cdot 10^{14}$ and $4 \cdot 10^{15}$ molecule/s corresponding to densities of $2 \cdot 10^{10}$ to $2.5 \cdot 10^{12}$ molecule/ cm³. In a typical experiment, displayed in Fig. 1, the ice surface is doped with HBr prior to reaction. Upon exposing the ice surface to N_2O_5 the formation of Br₂ (*m/e* 160) and HONO (*m/e* 47) is observed. Due to the waning supply of HBr at the interface the rate of reaction (3) is decreasing. By adding a continuous flow of HBr at



Fig. 1

Steady state experiment at 200 K of the uptake of N_2O_5 on ice doped with HBr prior to reaction. At 50 s the ice surface is exposed to N_2O_5 resulting in an uptake of N_2O_5 (*m/e* 46, upper black trace). At the same time the products HONO (*m/e* 47, lower gray trace) and Br₂ (*m/e* 160, upper gray trace) appear. Due to the waning amount of HBr on the ice surface the rate of reaction decreases with time. At 270 s the HBr flow is turned on (*m/e* 80, lower black trace). The product signals increase whereas the N_2O_5 signal decreases indicating an increasing reaction rate

t=270 s the uptake rate of N₂O₅ is increasing again to a constant value. The expected primary product BrNO₂ (reaction (3)) or products of its decomposition such as NO_2 were not observed. The MS signal at m/e 95 (BrN⁺), when observed, was always accompanied by the MS signal at m/e 109 indicating that BrNO was formed. The MS signal at m/e 79 always equaled the sum of the contributions of HBr, Br2 and BrNO to the MS fragment intensity. Furthermore, NO₂, which is the expected decomposition product of BrNO₂, was not detected, a result which was verified by means of LIF detection of NO2. However, BrNO₂ is known to undergo rapid secondary reactions in the presence of Br⁻ [23, 24] which likely explains the fact that it was not observed. The reaction of BrNO₂ with HBr results in the observed products HONO and Br₂ (reaction (4)). Further reaction of HONO with excess HBr produces BrNO (reaction (5)) [15].

 $BrNO_2 + HBr \rightarrow Br_2 + HONO$ (4)

$$HONO + HBr \rightarrow BrNO + H_2O$$
(5)

The determination of the uptake coefficient of N₂O₅ was performed using the change in the MS signal at m/e 46 without further corrections. This method is applicable since N₂O₅ is the only compound contributing to this mass. Impurities of NO2 and HNO3 in the N2O5 sample were vanishingly small. Neither BrNO₂ nor NO₂ could be detected during the uptake of N₂O₅ and HONO has no detectable fragment at m/e 46. The rate of formation of HNO₃, product of reaction 3 and the hydrolysis of N_2O_5 (reaction (1)) was monitored at m/e 63. Under our experimental conditions no evaporation of HNO3 was detected during the uptake experiments. However, upon annealing the ice surface to 220 K after an uptake experiment desorption of HNO₃ from the surface was observed. The uptake of HNO₃ on ice at 200 K was studied in independent experiments. An uptake coefficient γ of 0.3 was measured in agreement with the literature [25-27].

The measured initial uptake coefficients of N₂O₅ on ice strongly depend on the HBr content of the surface. An example is presented in Fig. 2a and b. The left panel (Fig. 2a) shows an uptake experiment under concurrent flow conditions of HBr and N₂O₅ performed at a low flow rate of HBr ($F=1.5 \cdot 10^{14}$ molecule/s). Upon exposing a concurrent flow of HBr and N₂O₅ to the ice surface the formation of molecular bromine $(m/e \ 160)$ and HONO (m/e 47) is observed. By halting the HBr flow the products gradually disappear while the amount of N₂O₅ taken up decreases slightly. The measurement of the uptake coefficient of N₂O₅ yielded a value of $\gamma = 2.2 \cdot 10^{-2}$ which is close to the one obtained on a pure ice surface. The yields of Br₂ and HONO are 17 and 29%, respectively, in relation to the amount of N₂O₅ taken up and 25 and 45%, respectively, in relation to the amount of HBr taken up by the ice surface. Neither Br2 nor HONO [17] interact with the ice surface which was confirmed in additional experiments. A reference experiment of the uptake of Br₂ on a



Fig. 2

Steady state experiment of the uptake of N_2O_5 and HBr on an ice surface. The MS signals are converted in flow rates using the calibration factors determined in ancillary experiments. a) Left panel: ice surface exposed to a concurrent flow of HBr ($1.5 \cdot 10^{14}$ molec/s) and N_2O_5 ($F = 6.7 \cdot 10^{14}$ molec/s) at 200 K. At 30 s the plunger is lifted thus exposing the ice surface to the flow of reactants. At 170 s the HBr flow is halted resulting in a decrease of the MS signals of the products and of HBr. At 300 s the ice surface is isolated from the reactant flow. b) Right panel: same experiments as under a) but at higher HBr flow ($F = 9 \cdot 10^{14}$ molec/s). The plunger is lifted at 750 s and lowered at 920 s

HBr-doped ice surface resulted in an uptake coefficient of $5 \cdot 10^{-2}$ for Br₂ at 200 K which may explain the slightly lower yield of Br₂ compared to HONO. Although N₂O₅ is in excess with respect to HBr, not all HBr is consumed during the reaction. Furthermore, 71 to 83% of the N₂O₅ is lost by other processes, presumably hydrolysis reaction (1).

The right panel (Fig. 2b) displays an uptake experiment of N₂O₅ using a higher flow rate of HBr (F=9 $\cdot 10^{14}$ molecule/s) and the same flow rate of N₂O₅ as in the experiment presented in Fig. 2a (F=6.7 $\cdot 10^{14}$ molecule/s). The amount of N₂O₅ taken up is twice as large as for the experiment displayed in Fig. 2a and the yields of Br₂ and HONO are 59 and 87%, respectively, in relation to N₂O₅ taken up. Therefore, the reaction rate of reaction (3) has doubled when the HBr flow rate has been increased by a factor of 6.

Fig. 3 presents the uptake coefficient of N₂O₅ as a function of the reactive flow of HBr which is the flow of HBr retained by the surface, $F^{in}-F^{out}$. The experiments were performed at 180 and 200 K using two different flows of N₂O₅. At low HBr flow conditions the uptake coefficients are close to the ones determined on a pure ice surface. The uptake coefficient linearly increases with increasing HBr flow rate taken up by the substrate. At HBr flows taken up higher than 2.10¹⁵ molecule/s a limiting value for the uptake coefficient of N_2O_5 of $\gamma = 0.11$ and y=0.15 at 200 and 180 K, respectively, is obtained indicating pseudo first order conditions for reaction (3). It is remarkable that the limiting value is reached at more than 3-fold excess of HBr with respect to N₂O₅ although the stoichiometry of reactions (3) and (4) predicts a value of 2 for quantitative conversion of N₂O₅. Indeed, as is clearly shown below only 50% of the HBr taken up is available for reaction. This observation has already been made for other heterogeneous reactions involving HBr [15] and represents a distinct difference between the reac-





Uptake coefficient of N₂O₅ versus the reactive flow of HX (X=Br or Cl) defined as $F^{in}-F^{out}$. The experiments have been performed at a concurrent flow of HX and N₂O₅ at a residence time of N₂O₅ of 0.33 s (14 mm orifice). HBr/ice: \triangle : F (N₂O₅)=5.2·10¹⁴ molec/s, 180 K; \bigcirc : F (N₂O₅)=5.0·10¹⁴ molec/s, 200 K; \square : F (N₂O₅)=1.5·10¹⁵ molec/s, 200 K; \blacksquare : pure ice, 200 K; \blacksquare : ice doped with HNO₃, 200 K; \times : HCl/ice: the arrow indicates the uptake coefficient of N₂O₅ on a frozen 0.1 M HBr aqueous solution at 200 K

tivities of HBr and HCl. In the latter case all HCl taken up is available for heterogeneous reaction [17, 18].

An additional uptake experiment of N₂O₅ on 0.1 M aqueous HBr solution which should provide HBr in excess yielded an uptake coefficient of N_2O_5 of $\gamma = 0.10$ at 200 K close to the upper limit determined on an ice surface in the presence of an excess flow of HBr. The data displayed in Fig. 3 also point out the negative temperature dependence of the reaction. The uptake rate of HBr on ice is increasing with decreasing temperature. However, since the reactive flow of HBr, thus the flow of molecules to the surface is chosen as the independent variable the temperature dependence of the HBr uptake on ice is already taken into account. The uptake of N₂O₅ on ice is nearly temperature independent [28] and therefore the increasing uptake coefficient of N₂O₅ with decreasing temperature may reflect the temperature dependence of reaction (3).

No indications for surface saturation was found during the uptake of N_2O_5 on ice in the presence of HBr on the experimental timescale of several minutes. Repetitive exposure of the ice surface to N2O5 leads to identical results within experimental error. An uptake experiment of N₂O₅ (flow rate of 4.5.10¹⁴ molecule/s) on HNO₃-doped ice performed at 200 K in the presence of a reactive flow of HBr of 9.1.10¹⁴ molecule/s resulted in an uptake coefficient of $5.9 \cdot 10^{-2}$ for N₂O₅ (Fig. 3) indicating no inhibition of the reaction rate due to the presence of HNO₃. However, we observed a decrease of the uptake rate with increasing residence time thus increasing density of N₂O₅ inside the reactor which we attribute to saturation effects. Preliminary results on the interaction of N₂O₅ on pure ice show that the decrease of the rate of uptake with residence time is even stronger in the absence of HBr. These results point towards a complex uptake process of N₂O₅

Table 3				
Experimental results of steady	v state experiments	for the uptake of N ₂	O ₅ on ice in the	presence of HBr

T [K]	F ⁱ (HBr)	$F^{i}(N_{2}O_{5})$	F ^r (HBr)	$F^{r}(N_2O_5)$	$F(Br_2)$	F(HONO)	$\gamma(N_2O_5)$	Orifice
200	6.5·10 ¹⁴	9.0·10 ¹⁴		2.5·10 ¹⁴			4.4.10 ⁻²	14
200	6.5-10 ¹⁴	1.5·10 ¹⁵		$2.2 \cdot 10^{14}$			$5.5 \cdot 10^{-2}$	14
200	7.0·10 ¹⁴	$1.1 \cdot 10^{15}$	6.5·10 ¹⁴	3.8·10 ¹⁴	1.7·10 ¹⁴	$1.5 \cdot 10^{14}$	$3.4 \cdot 10^{-2}$	14
200	6.3·10 ¹⁴	$1.2 \cdot 10^{15}$	5.5·10 ¹⁴	4.2·10 ¹⁴	$1.5 \cdot 10^{14}$	$1.9 \cdot 10^{14}$	1.3·10 ⁻²	8
200	$4.7 \cdot 10^{14}$	$1.2 \cdot 10^{15}$	4.2·10 ¹⁴	4.4·10 ¹⁴	1.1·10 ¹⁴	1.2.1014	$5.5 \cdot 10^{-3}$	4
200	3.0-10 ¹⁴	7.9·10 ¹⁴	$2.7 \cdot 10^{14}$	$3.4 \cdot 10^{14}$	6.3·10 ¹³	7.9·10 ¹³	7.0·10 ⁻³	4
200	$4.4 \cdot 10^{14}$	1.5·10 ¹⁵	3.7·10 ¹⁴	5.1·10 ¹⁴	1.3.1014	1.0·10 ¹⁴	3.3·10 ⁻²	14
200	5.3·10 ¹⁴	$1.7 \cdot 10^{15}$	4.8·10 ¹⁴	8.2·10 ¹⁴	$1.5 \cdot 10^{14}$	$1.1 \cdot 10^{14}$	7.8·10 ⁻³	4
200	$2.4 \cdot 10^{14}$	2.9·10 ¹⁵	1.8·10 ¹⁴	6.9·10 ¹⁴	$1.1 \cdot 10^{14}$	1.4·10 ¹⁴	$2.5 \cdot 10^{-2}$	14
200	1.8·10 ¹⁴	2.3·10 ¹⁵	1.5·10 ¹⁴	$6.1 \cdot 10^{14}$	9.3·10 ¹³	$1.6 \cdot 10^{14}$	9.1·10 ⁻³	8
200	$1.3 \cdot 10^{14}$	1.9·10 ¹⁵	1.0.1014	$4.6 \cdot 10^{14}$	5.9·10 ¹³	1.0.1014	$2.0 \cdot 10^{-2}$	14
200	1.0.1014	1.9·10 ¹⁵	9.0·10 ¹³	5.3·10 ¹⁴	$6.2 \cdot 10^{13}$	7.9·10 ¹³	3.3·10 ⁻³	4
200	$1.5 \cdot 10^{14}$	$6.7 \cdot 10^{14}$	1.2·10 ¹⁴	$1.8 \cdot 10^{14}$	$3.0 \cdot 10^{13}$	5.3·10 ¹³	$2.2 \cdot 10^{-2}$	14
200	9.0·10 ¹⁴	6.9·10 ¹⁴	6.9·10 ¹⁴	$3.2 \cdot 10^{14}$	1.9·10 ¹⁴	$2.8 \cdot 10^{14}$	5.3·10 ⁻²	14
200	8.9·10 ¹⁴	7.5·10 ¹⁴	7.5·10 ¹⁴	4.7·10 ¹⁴	3.0·10 ¹⁴	3.8·10 ¹⁴	4.3·10 ⁻²	8
200	8.4·10 ¹⁴	4.3·10 ¹⁴	7.2·10 ¹⁴	$1.6 \cdot 10^{14}$	1.3.1014	$1.7 \cdot 10^{14}$	5.0·10 ⁻²	14
200	7.3·10 ¹⁴	$4.1 \cdot 10^{14}$	$6.4 \cdot 10^{14}$	$2.8 \cdot 10^{14}$	1.8·10 ¹⁴	$2.3 \cdot 10^{14}$	$4.7 \cdot 10^{-2}$	8
200	1.9·10 ¹⁵	5.3.1014	1.6·10 ¹⁵	3.3-10 ¹⁴	1.9·10 ¹⁴	$2.8 \cdot 10^{14}$	9.6·10 ⁻²	14
200	$2.3 \cdot 10^{14}$	5.8·10 ¹⁴	1.6·10 ¹⁴	3.3·10 ¹⁴			6.8·10 ⁻²	8
200	$2.2 \cdot 10^{15}$	6.4·10 ¹⁴	1.9·10 ¹⁵	$4.7 \cdot 10^{14}$	3.0·10 ¹⁴	3.3-10 ¹⁴	5.9·10 ⁻²	8
200	$2.3 \cdot 10^{15}$	5.8·10 ¹⁴	2.0·10 ¹⁵	4.9·10 ¹⁴	3.4·10 ¹⁴	4.1·10 ¹⁴	6.8·10 ⁻²	8
200	$1.1 \cdot 10^{15}$	1.6·10 ¹⁵	8.9·10 ¹⁴	$6.8 \cdot 10^{14}$	$2.2 \cdot 10^{14}$	2.3·10 ¹⁴	$4.8 \cdot 10^{-2}$	14
200	$2.8 \cdot 10^{15}$	5.7·10 ¹⁴	2.6·10 ¹⁵	4.6·10 ¹⁴	3.3·10 ¹⁴	1.9·10 ¹⁴	$3.1 \cdot 10^{-2}$	4
200	3.0·10 ¹⁵	5.6·10 ¹⁴	2.4·10 ¹⁵	3.5·10 ¹⁴	$1.8 \cdot 10^{14}$	$2.0 \cdot 10^{14}$	$1.0 \cdot 10^{-1}$	14
200	$1.1 \cdot 10^{15}$	4.5·10 ¹⁴	9.1·10 ¹⁴	$2.3 \cdot 10^{14}$	1.9·10 ¹⁴	2.0·10 ¹⁴	5.9·10 ⁻²	14 ^a)
180	$2.0 \cdot 10^{15}$	$3.7 \cdot 10^{14}$	1.9-1015	3.3·10 ¹⁴	$8.0 \cdot 10^{13}$	$1.6 \cdot 10^{14}$	$5.2 \cdot 10^{-2}$	4
180	$2.1 \cdot 10^{15}$	$3.2 \cdot 10^{14}$	$1.7 \cdot 10^{15}$	$2.3 \cdot 10^{14}$	$9.5 \cdot 10^{13}$	2.6·10 ¹⁴	1.5·10 ⁻¹	14
180	$1.0 \cdot 10^{15}$	$7.4 \cdot 10^{14}$	7.8·10 ¹⁴	3.8·10 ¹⁴	$2.6 \cdot 10^{14}$	3.3·10 ¹⁴	6.3·10 ⁻²	14
180	9.2·10 ¹⁴	5.4·10 ¹⁴	8.6·10 ¹⁴	3.9-10 ¹⁴	$1.2 \cdot 10^{14}$	1.8·10 ¹⁴	1.1·10 ⁻²	4
180	$2.6 \cdot 10^{15}$	5.6·10 ¹⁴	1.9·10 ¹⁵	3.9·10 ¹⁴	$3.8 \cdot 10^{14}$	4.9·10 ¹⁴	1.5·10 ⁻¹	14
180	$1.4 \cdot 10^{15}$	$5.1 \cdot 10^{14}$	1.0.10 ¹⁵	3.3·10 ¹⁴	2.8·10 ¹⁴	3.3·10 ¹⁴	1.1·10 ⁻¹	14
180	7.5.1014	5.1·10 ¹⁴	5.0·10 ¹⁴	$2.4 \cdot 10^{14}$	$1.4 \cdot 10^{14}$	8.6-10 ¹³	5.4·10 ⁻²	14
200	0.1 M HBr	4.4·10 ¹⁴		3.0·10 ¹⁴	$1.2 \cdot 10^{14}$	1.9·10 ¹⁴	1.0·10 ⁻¹	14 ^b)
200	0.1 M HBr	4.7·10 ¹⁴		4.1·10 ¹⁴	4.7·10 ¹³	3.1·10 ¹⁴	3.8·10 ⁻²	4 ^b)

 F^{i} : Continuous flow into the Knudsen cell [molecule/s], F^{r} : Flow to the surface defined by $F^{i}-F^{out}$ [molecule/s], orifice: diameter of escape orifice [mm]

^a) Ice surface previously exposed to HNO₃

^b) Frozen aqueous 0.1 M HBr solution

at higher densities and/or longer residence times which cannot simply be explained by saturation of the ice surface [28]. Experiments are underway to resolve this issue. In this work we focus on the results obtained at short residence times (0.3 s) resulting in a consistent picture. We will present the results for longer residence times only for the sake of completeness. All experiments are summarized in Table 3.

Pulsed valve experiments performed at 190 K resulted in an uptake coefficient of $\gamma = 0.15 \pm 0.04$ independent of the N₂O₅ density. The results are presented in Table 4 and typical experimental data are displayed in Fig. 4a. We again observed Br₂ (*m/e* 160) and HONO (*m/e* 47) as products. The decay of the product pulse of HONO agrees well with the calculated value of k_{esc} . Nitrous acid appeared without delay indicating a fast rate of reaction (4) (Fig. 4b). However, the decay of the product pulse of Br₂ expected to be the product of the same reaction is found not to be of single exponential type (Fig. 4b). The fact that Br₂ is taken up by the ice surface (see above) Table 4

Results of pulsed valve experiments for the uptake of N_2O_5 on ice in the presence of HBr at 190 K

F ⁱ	D	D ^r	D	D	γ	Orifice
(HBr)	(N ₂ O ₅)	(N ₂ O ₅)	(Br ₂)	(HONO)	(N ₂ O ₅)	
Doped Doped 1.4·10 ¹⁵ 2.3·10 ¹⁵ Doped Doped	$\begin{array}{r} 4.1\cdot10^{15}\\ 4.7\cdot10^{15}\\ 4.4\cdot10^{15}\\ 4.7\cdot10^{15}\\ 5.6\cdot10^{15}\\ 5.6\cdot10^{15}\\ 5.6\cdot10^{15}\end{array}$	$\begin{array}{r} 2.5 \cdot 10^{15} \\ 3.9 \cdot 10^{15} \\ 2.9 \cdot 10^{15} \\ 2.8 \cdot 10^{15} \\ 4.9 \cdot 10^{15} \\ 4.8 \cdot 10^{15} \end{array}$	1.4.10 ¹⁵ 9.6.10 ¹⁴	1.6·10 ¹⁵	$\begin{array}{c} 9.6 \cdot 10^{-2} \\ 1.1 \cdot 10^{-1} \\ 1.7 \cdot 10^{-1} \\ 9.6 \cdot 10^{-2} \\ 1.2 \cdot 10^{-1} \\ 1.0 \cdot 10^{-1} \end{array}$	14 4 14 14 14 14 4

 F^{i} : Continuous flow into the Knudsen cell [molecule/s], D: number of molecules (dose) obtained by integration of the corresponding pulse, D^{r} : number of molecules (dose) lost at the surface, orifice: diameter of escape orifice [mm]

may explain the non-exponential behaviour of the signal decay of Br_2 . The importance of this result will be discussed below.



Pulse of N₂O₅ exposed to an ice surface doped with HBr using the 4 mm orifice (residence time of N₂O₅ of 2.6 s) at 190 K. a) shows the reference and the reactive pulse of N₂O₅ indicating a rate constant for the loss at the surface of 5.9 s^{-1} resulting in an uptake coefficient of $\gamma = 0.12$. b) shows the product pulses of HONO (*m/e* 47) and Br₂ (*m/e* 160)

In order to obtain more mechanistic details on the reaction system HBr/N₂O₄/ice we have undertaken some additional experiments. By doping the ice surface with HBr previous to the uptake of N2O5 and subsequently exposing it to a flow of N₂O₅ a high initial uptake on the order of $\gamma = 0.1$ is observed. It decreased within a few minutes to the value of the uptake of N_2O_5 on a pure ice surface. The doping of the ice surface with HBr prior to reaction in a concurrent flow experiment only affects the initial uptake kinetics of N₂O₅. Whereas on an undoped ice surface it takes a few seconds until the new steady state signal of N₂O₅ is established at a simultaneous flow of HBr and N_2O_5 , the steady state value of γ is observed at once on an ice surface doped with HBr. This was already observed in previous studies of heterogeneous reactions involving HBr [15] and points towards a complex adsorption process for HBr.

On an ice surface doped with N_2O_5 and subsequently exposed to HBr no product formation is observed indicating that N_2O_5 is readily hydrolysed into products that are not reactive towards HBr. Whether the hydrolysis of N_2O_5 yielded HNO₃ or nitric acid hydrates under our experimental conditions cannot be answered in the present experiments. HNO₃, the product of reaction (1) and (3), is unreactive towards HBr. This was confirmed in an uptake experiment of HNO₃ onto a 0.1 M frozen HBr solution.

In Fig. 5 the yields of Br_2 and HONO with respect to HBr taken up on the ice substrate are displayed. For the



Fig. 5

Absolute yield of HONO and Br_2 vs reactive flow of HBr during the uptake experiments of N_2O_5 and HBr onto ice at 200 K and flow rates of N_2O_5 between $4 \cdot 10^{14}$ and $3 \cdot 10^{15}$ molec/s. For experimental details see Table 3. The solid line represents a yield of 25% of both HONO and Br_2 with respect to HBr consumed. By comparison, × represents the yield of ClNO₂ with respect to HCl consumed





Yield of HONO and Br₂ relative to N₂O₅ taken up onto the ice surface as a function of the ratio of the reactive flows of HBr and N₂O₅ at 200 K. For experimental details see Table 3. By comparison, \times represents the yields of ClNO₂ relative to N₂O₅ taken up as a function of the ratio of the reactive flows of HCl and N₂O₅

sake of simplicity the HONO yield always represents the sum of HONO and BrNO detected during the experiment. Both products, Br₂ and HONO, are formed at a 25% efficiency at low HBr flows indicating that even under excess N_2O_5 only 50% of the HBr is available for reaction following reactions (3) and (4) as already discussed above. At reactive HBr flows higher than $1\cdot 10^{15}$ molecule/s the yields of Br₂ and HONO become independent of HBr indicating conditions where HBr is in excess.

The fractional yields of Br_2 and HONO with respect to N_2O_5 reacted according to the reaction sequence (3) to (5) as a function of the ratio of HBr and N_2O_5 taken up on the ice surface are displayed in Fig. 6. At low ratios, thus for excess N_2O_5 in relation to HBr, the yields of HONO and Br_2 are on the order of 20% with respect to N_2O_5 consumed. Fig. 6 underlines the fact that under all accessible experimental conditions the relative yields of

both HONO and Br_2 are roughly equal with respect to N_2O_5 reacted. The relative yield of HONO and Br_2 increases linearly with increasing reactive HBr/N_2O_5 ratio which corresponds to increasing HBr concentrations at the surface. At HBr contents on the ice surface 2 to 3 times higher than N_2O_5 limiting yields of 75 and 80% of Br_2 and HONO, respectively, are obtained, which are however identical within experimental error. The average non unity yield of Br_2 and HONO even at excess HBr on the surface reflects the fact that hydrolysis of N_2O_5 on the ice is competitive with reaction of N_2O_5 with HBr.

3.2 Heterogeneouns Reaction of N₂O₅ in the Presence of HCl

The heterogeneous reaction of N_2O_5 in the presence of HCl has been studied before [4, 10, 11]. However, in order to directly compare the results for the heterogeneous reaction of N_2O_5 with HCl and HBr, we studied the system HCl/ N_2O_5 /ice, reaction (2), under the same experimental conditions as the reaction of N_2O_5 and HBr, reaction (3).

As recently shown by Flückiger et al. [21], a liquid layer is formed upon exposing HCl to an ice surface above a temperature-dependent threshold concentration. The experiments reported here have been performed at 200 K and HCl flows have been chosen to be either well below or above the threshold for the formation of a liquid layer. Table 5 summarizes the experimental data. Again, a dependence of the uptake coefficient of N2O5 on the N₂O₅ density is observed. At a HCl flow below threshold for the formation of a liquid layer the uptake coefficient of N₂O₅ is only slightly enhanced compared to the uptake on a pure ice surface (Fig. 3) in analogy to the results obtained at low flow rates of HBr. In the case where the interface consisted of a liquid layer of HCl/H2O both the yield of $CINO_2$ with respect to N_2O_5 and the uptake coefficient were enhanced. Due to the nature of our experiment the rate of evaporation of HCl from the ice surface is larger at short residence times (14 mm orifice) compared to long residence times (4 mm orifice). Therefore less HCl is available on the ice surface for shorter residence times compared to longer ones. This fact is reflected in the lower reactive flows of HCl for short residence times (Table 5) leading to a lower enhancement of the uptake coefficient of N₂O₅.

No abrupt change in reactivity has been observed in going from a quasi liquid layer (low HCl flow, first two entries in Table 5) to a liquid layer (high HCl flow, last two entries in Table 5). The uptake kinetics follow the same trend as the heterogeneous reactions of $ClONO_2$ +HCl [18] or N₂O₅+HBr on ice, as presented above. These results indicate that the actual state of the surface (liquid or quasi-liquid state of HCl) is less important of a parameter for the rate of a bimolecular heterogeneous reaction involving HCl, compared to the actual concentration of HCl at the interface. Were the reactive uptake Table 5

Experimental results for the uptake of N_2O_5 on ice in the presence of HCl at T=200 K

F^{i}	F^{i}	F^{r}	F^{r}	F	γ γ	Orifice	-
	(N_2O_5)	(HCI)	(N_2O_5)	$(CINO_2)$	$(1_{2}U_{5})$		
$7.6 \cdot 10^{14}$	1.1.1015	1.6·10 ¹⁴	$4.1 \cdot 10^{14}$	$2.4 \cdot 10^{13}$	3.5.10-2	14	
$6.9 \cdot 10^{14}$	$1.0 \cdot 10^{15}$	$4.0 \cdot 10^{14}$	4.2·10 ¹⁴	$2.0 \cdot 10^{14}$	4.8·10 ⁻³	4	
$2.1 \cdot 10^{15}$	6.6·10 ¹⁴	$2.4 \cdot 10^{14}$	2.3·10 ¹⁴	$7.8 \cdot 10^{13}$	$3.2 \cdot 10^{-2}$	14	
2.0·10 ¹⁵	6.6·10 ¹⁴	1.5·10 ¹⁵	4.6-10 ¹⁴	$2.9 \cdot 10^{14}$	$1.7 \cdot 10^{-2}$	4	
						-	

 F^i : Continuous flow into the Knudsen cell [molecule/s], F^r : flow to the surface defined by $F^i - F^{out}$ [molecule/s], orifice: diameter of escape orifice [mm]

rates sensitive to a phase change an abrupt change of γ with HCl density would have been expected.

4. Discussion

The experimental results presented here deal with the heterogeneous reaction of N2O5 with HBr and HCl on ice. We have clearly shown that the rate constant for both reactions depended on the HX concentration present on the ice surface and that hydrolysis of N2O5 is a competitive process. The reaction of N2O5 with HCl has been studied before and our results on the uptake coefficient of N₂O₅ agree well with literature data [4, 10, 11]. The reaction of N2O5 with HBr has been studied by Hanson and Ravishankara [8] using water adsorbed on cold walls as a substrate. Using a fast-flow reactor they found an uptake coefficient of $5 \cdot 10^{-3}$ which is 5 times lower than the lowest value we have found. However, their experimental conditions are completely different from ours so that a comparison may not be appropriate. Since we measured the heterogeneous reaction of N2O5 with HBr over a wide range of concentrations and experimental procedures we are able to draw some conclusions concerning the mechanism and the nature of the heterogeneous interaction which we will discuss below.

As already mentioned in the previous section the primary product of reaction (3), $BrNO_2$ has not been observed. We only detected secondary reaction products, namely HONO and Br_2 which have been produced by the reaction of $BrNO_2$ with excess HBr according to reaction (4). The stoichiometry of the suggested mechanism, reaction (3) and (4), is supported by the mass balance shown in Fig. 5. On an ice surface hydrolysis may also be an efficient loss process for $BrNO_2$, reaction (6) [24]. However, HOBr was not detected because it undergoes a rapid reaction with HBr forming Br_2 , reaction (7) [29].

$$BrNO_2 + H_2O \rightarrow HOBr + HONO$$
 (6)

$$HOBr + HBr \rightarrow Br_2 + H_2O \tag{7}$$

The sum of reactions (6) and (7) is the same as reaction (4) and from the present experiments we can not determine whether Br_2 is formed in reaction (4) directly or

stepwise via reaction (6) and (7). The slow formation of Br₂ in the steady state experiments (Fig. 2) and its nonexponential decay in the pulsed valve experiment compared to that of HONO (Fig. 4) may be an argument in favor of reactions (6) and (7). On the other hand, during the pulsed valve experiments Br₂ is produced without significant delay (Fig. 4) compared to HONO which may indicate simultaneous formation of the two products. Furthermore, we observed a non-negligible rate of uptake of Br₂ on ice in the presence of HBr which may also explain its complex behaviour. This result is surprising because Br₂ does not interact at all with a pure ice surface. One possible explanation may be that in the presence of bromide Br3 is formed on the ice surface. The observed interaction of Br₂ with ice/HBr may perhaps explain the slightly lower average yield of Br₂ (75%) compared to HONO (80%) according to Fig. 6. The interaction of HONO with a HBr-doped ice surface resulted in the formation of BrNO (reaction (5)) which does not interact with the ice surface [15]. This reaction, however, only occurs at excess HBr as it is a secondary reaction involving HONO. By taking the sum of the yields of HONO and BrNO we make sure that we detect the total amount of HONO generated. Based on the yields of HONO and Br₂ with respect to N₂O₅ taken up we are able to obtain a branching ratio for reaction (1) and (3).

For a steady state experiment the flow of N_2O_5 to the surface (reactive flow, $F^r = F^{in} - F^{out}$) may be expressed as

$$\frac{F^{r}(N_{2}O_{5})}{V} = (k_{3}^{*}[HBr] + k_{1}') \cdot [N_{2}O_{5}]$$
(I)

and the product flows as:

$$\frac{F(\mathrm{Br}_2)}{V} = \frac{F(\mathrm{HONO})}{V} = k_3^*[\mathrm{HBr}] \cdot [\mathrm{N}_2\mathrm{O}_5] \tag{II}$$

V represents the volume of the Knudsen reactor (Table 1), k_3^* the rate constant for reaction (3) and k_1' the pseudo first order rate constant for hydrolysis (reaction (1); $k_1'=k_1\cdot[H_2O]$. The term (k_3^* [HBr]+ k_1') corresponds to the measured loss rate constant k_{uni} (Table 1) of N₂O₅ in the presence of HBr within our simple reaction scheme stating the competition between reaction (1) and (3). Combining equation I and II yields expression III:

$$\frac{F(\text{HONO})}{F^{r}(N_{2}O_{5})} \cdot k_{\text{uni}} = k_{3}^{*}[\text{HBr}]$$
(III)

The calculated values for the pseudo first order rate constants k'_1 and k'_3 [HBr] are displayed in Fig. 7. The rate constant for hydrolysis of N₂O₅ (reaction (1)) can be calculated using the simple algebraic expression $k_{uni}-k'_3$ [HBr]. A mean value of $k'_1=1\pm0.5$ s⁻¹ which corresponds to a reaction probability of $\gamma=(2\pm1)\cdot10^{-1}$ for the hydrolysis of N₂O₅ on ice at 200 K is obtained in excellent agreement with literature data [4, 10, 11]. The fact



Fig. 7

Rate constant for the reaction of N_2O_5 with HBr on an ice surface and the rate constant for the hydrolysis of N_2O_5 vs the reactive flow of HBr at 200 K. The rate constante k_3^* [HBr] has been determined by applying Eq. (III) to the experimentally obtained overall rate constant k_{uni} . The term $k_{uni} - k_3^*$ [HBr] corresponds to the rate constant for hydrolysis of N_2O_5 on ice, k_1^* [H₂O]

that the rate constant for hydrolysis stays constant regardless of the HBr concentration on the ice surface leads us to conclude that hydrolysis and reaction with HBr are completely independent of each other and thus competitive. The pseudo first order rate constant for reaction (3), k_3^* [HBr], is linearly increasing with the HBr reactive flow and reaches a limiting value of 5.6 s⁻¹ which corresponds to a reaction probability of $\gamma = 0.11$ at 200 K. This upper limit of k_{uni} correspond to the point where the HBr concentration on the ice surface is high enough to ensure pseudo first order conditions.

The uptake of HBr on ice leads to ionic dissociation [30]. Therefore we propose a nucleophilic substitution mechanism for the reaction of HBr with N₂O₅, reaction (3), with Br⁻ reacting as the nucleophile (reaction (8)). It seems unlikely that N₂O₅ dissociates prior to reaction with Br⁻ into NO₃⁻ and NO₂⁺ as suggested in the literature [31]. On ice N₂O₅ is readily hydrolyzed at temperatures above 170 K and no evidence for the formation of crystalline ionic N₂O₅ was found [32]. Therefore we propose a concerted S_N2-type nucleophilic attack of Br⁻ on covalent N₂O₅.

$$Br- + N2O5 → [Br ··· NO2 ··· NO3]- → BrNO2 + NO3- (8)$$

BrNO₂ undergoes a fast subsequent reaction with HBr adsorbed at the surface according to reaction (4) or (6) followed by reaction (7). The nitrate ion NO₃ is hydrated perhaps forming nitric acid hydrates. This substitution mechanism has already been discussed for other reactions involving HX [16–18]. The fact that we have to apply a concurrent flow of HBr and N₂O₅ in order to obtain the highest uptake rates for N₂O₅ points towards an efficient interfacial reaction at the solid-gas interface.

The heterogeneous reaction of N_2O_5 with HCl is very similar to the one involving HBr. As shown in the previous chapter, both uptake rates are enhanced relative to

the uptake on pure ice by a factor of 5 at long residence times (see Tables 3 and 5, 4 mm orifice) at flows (F^{i}) of HCl and HBr increasing from $7 \cdot 10^{14}$ to $2 \cdot 10^{15}$ molecule/s. However, at short residence times, that same increase of the flow rate of HCl and HBr does not have the same effect on the uptake rate of N_2O_5 . In the case of the HCl reaction no significant increase in the uptake rate of N₂O₅ is observed upon increasing F^{i} (HCl), whereas y increases by a factor of 2 to 3 for the HBr system. This observation represents a significant difference between the systems involving HCl and the ones involving HBr. The adsorbed HCl taken up on the ice gives rise to a vapor pressure which is supported by a desorption rate of HCl from the ice surface thus reducing the net uptake of HCl in contrast to HBr where no desorption rate from the surface has been observed [21]. Therefore, a critical parameter of the rate of reaction (2) and (3) is the net uptake of HX on the ice surface supporting the assumption of true interfacial reaction.

Another difference between reactions involving chlorine compared to those involving bromine is the reactivity of the products. The only reaction product we observed in the reaction between HCl and N_2O_5 was the primary product ClNO₂ which is stable under our experimental conditions. In the analogous reaction with HBr the primary product, BrNO₂, was not observed at all as we only detected the secondary products HONO, Br₂ and BrNO. The difference in the behaviour of the two molecules BrNO₂ and ClNO₂ can be rationalized by considering the different oxidation state of the halogen atom: Br being in the oxidation state +I whereas Cl is formally in the –I state. This causes a higher reactivity of BrNO₂ towards negatively charged species like Br⁻ leading to the observed product Br₂.

5. Conclusion

We have shown in this work that the rate constant for the reaction of N_2O_5 strongly depends on the HX content on the ice surface. The kinetics (Fig. 3) as well as the mass balance (Figs. 5 and 6) of both systems, namely HBr/ice and HCl/ice, are identical within experimental error.

At the highest HBr concentrations used in this study we observed a fast rate of uptake of N_2O_5 corresponding to $\gamma=0.1$, that is 5 times higher than the uptake of N_2O_5 on pure ice. Hydrolysis of N_2O_5 is competitive with reaction with HX. Therefore one potentially important result for atmospheric modeling is the measured branching ratio for reaction (1) vs reaction (2) or (3). At the lowest HBr concentration reaction (3) resulting in HONO and Br₂ occurs to the extent of 20%, whereas the hydrolysis of N_2O_5 is favored to the extent of 80%. At high HBr concentrations 80% of the N_2O_5 reacts with HBr whereas only 20% is hydrolyzed. The reaction of N_2O_5 with HCl behaves similarly.

The products Br_2 and HONO may play a role in the partitioning of bromine species as well as nitrogen species. Moreover, the formation of the easily photolyzed

HONO may affect atmospheric OH concentration [33]. N_2O_5 nighttime concentrations in the lower stratosphere are of the same order as the N_2O_5 concentrations used in this study [34]. To our knowledge, no measurements of atmospheric HBr concentrations are available between the altitude of 8 and 15 km. Model studies estimate concentrations between 10^7 and 10^8 molecule/s cm³ [35, 36] which are two orders of magnitude lower than the one used in this study which makes it difficult to assess the atmospheric implication of reaction (3). However, under certain atmospheric conditions, HBr may accumulate on ice particles and efficiently convert N_2O_5 into HONO and Br₂ thus effectively contributing to an additional source of OH free radicals as well as bromine atoms.

Funding for this work was generously provided by the Office Fédéral de l'Education et de la Science (OFES), supporting the "Environment and Climate" program of the European Community within the framework of the projects HALOTROP and COBRA. We thank professor H. van den Berg for his lively interest and input.

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(Received: January 30, 1998 final version: March 23, 1998) E 9808