Heterogeneous atmospheric bromine chemistry

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Abstract. This paper considers the effect of heterogeneous bromine reactions on stratospheric photochemistry. We have considered reactions on both sulfate aerosols and on polar stratospheric clouds (PSCs). It is shown that the hydrolysis of $BrONO_2$ on sulfate aerosols enhances the HOBr concentration, which in turn enhances the OH and HO_2 concentrations, thereby reducing the HCl lifetime and concentration. The hydrolysis of $BrONO_2$ leads to a nighttime production of HOBr, making HOBr a major nighttime bromine reservoir. The photolysis of HOBr gives a rapid increase in the OH and HO_2 concentration at dawn, as was recently observed by *Salawitch et al.* [1994]. The increase in the OH and HO_2 concentration, and the decrease in the HCl concentration, leads to additional ozone depletion at all latitudes and for all season. At temperatures below 210 K the bulk phase reaction of HOBr with HCl in sulfate aerosols becomes important. The most important heterogeneous bromine reactions on polar stratospheric clouds are the mixed halogen reactions of HCl with HOBr and $BrONO_2$ and of HBr with HOCl and $ClONO_2$.

Introduction

The recent World Meteorological Organization (WMO) assessment [1992] reported that for the first time there are statistically significant decreases in ozone in all seasons in both the northern and southern hemispheres at middle and high latitudes during the 1980s and that most of this decrease is occurring in the lower stratosphere. This finding has also been supported by trends derived from ozonesondes [*Logan*, 1994]. This paper shows that at least part of this ozone loss is likely to be due to in situ heterogeneous bromine reactions.

The atmospheric chemistry of reactive bromine species is characterized by their short lifetimes. The longest-lived reactive bromine species is HBr, which has a lifetime of up to a day but constitutes only a small fraction of the total reactive bromine (BrO_y) present in the atmosphere [*Lary*, 1995]. In contrast, the longest-lived reactive chlorine species is HCl which typically has a lifetime of over a week in the lower stratosphere and often constitutes the largest fraction of the total reactive chlorine (ClO_y) present in the atmosphere.

Heterogeneous chlorine reactions are important because they provide a mechanism, not provided by gas

phase chemistry, for the rapid conversion of HCl into $ClO_x (=Cl+ClO+2Cl_2O_2)$. Since the timescale for HCl production is several days it is only recycled slowly. Therefore, the heterogeneous reactions considerably perturb the chlorine partitioning. In contrast, because bromine species are short-lived heterogeneous bromine reactions are important as they allow the formation of catalytic cycles for the conversion of H_2O into HO_x $(=OH+HO_2)$, HCl into ClO and NO_x $(=NO+NO_2)$ into HNO_3, as well as for the rapid recycling of the bromine reservoir species $BrONO_2$ and HBr. This leads to ozone loss at all latitudes and for all seasons, particularly when high loadings of sulfate aerosol are present in the atmosphere.

Calculation of Heterogeneous Reaction Rates

Table 1 shows the heterogeneous bromine reactions used in this study. This set of reactions was constructed by analogy with the known heterogeneous chlorine reactions. Recently, reactions (1) and (2) in Table 1 have been studied by *Abbatt* [1994] on ice. The measured γ values are very similar to the value of 0.3 for the reaction HOCl with HCl on water ice [*Hanson and Ravishankara*, 1991; *Abbatt and Molina*, 1992].

Reactions (1) to (3) in Table 1 have been treated as bulk phase reactions on sulfate aerosols because of

Table 1. Heterogeneous Bromine Reactions Used in This Study

Reaction								$\Delta H_{298\,K}$ kJ/Mole	Surface Type	γ A	γ I	γ II
(R1)		HBr	+	HOBr	$\longrightarrow$	Br_2	+ H_2O	-95.3	A,I,II	B	0.1	$0.12^\dagger$
(R2)	*	HCl	+	HOBr	$\longrightarrow$	BrCl	+ H_2O	-55.6	A,I,II	B	0.1	$0.25^\dagger$
(R3)	*	HBr	+	HOCl	$\longrightarrow$	BrCl	+ H_2O	-115.8	A,I,II	B	0.1	0.3
(R4)		HBr	+	$BrONO_2$	$\longrightarrow$	Br_2	+ HNO_3	-118.2	I,II		0.3	0.3
(R5)	*	HCl	+	$BrONO_2$	$\longrightarrow$	BrCl	+ HNO_3	-78.5	I,II		0.3	0.3
(R6)	*	HBr	+	$ClONO_2$	$\longrightarrow$	BrCl	+ HNO_3	-107.3	I,II		0.3	0.3
(R7)	*	H_2O	+	$BrONO_2$	$\longrightarrow$	HOBr	+ HNO_3	-22.9	A,I,II	$0.4^\ddagger$	0.006	0.3
(R8)		HBr	+	N_2O_5	$\longrightarrow$	BrONO	+ HNO_3	-5.6	I,II		$0.005^\S$	$0.005^\S$

The assumed radii used in this study for sulfate aerosol (A), PSC I (I) and PSC II (II) are 0.1 μm, 0.1 μm, 10 μm respectively. B, a bulk phase reaction. $\star$, a key reaction.

§From *Hanson and Ravishankara* [1992].

†From *Abbatt* [1994].

‡From *Hanson and Ravishankara* [1995].

their diffusoreactive length. For example, as mentioned by *Danilin and McConnell* [1995], the diffusoreactive length of reaction (2) exceeds 1 μm for 60 wt % H_2SO_4 solution. The rates of the bulk phase reactions are calculated as a function of temperature by using a Henry's law coefficient and an aqueous phase bimolecular rate coefficient as described by *Cox et al.* [1994]. The bulk phase reactions are fastest at cold temperatures and for high water concentrations and are therefore most important in the region close to the tropopause or wherever the temperature falls below 210 K.
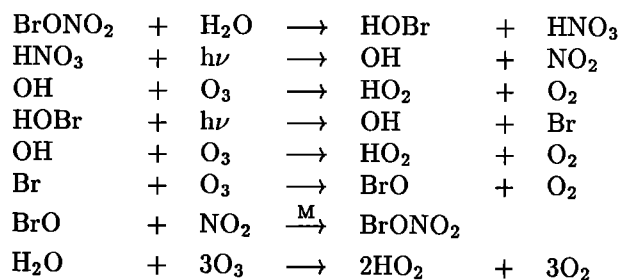
In each case the bimolecular rate coefficient for the liquid phase reaction is taken to be 10^5 M^{-1} s^{-1}. The effective Henry's law coefficient for HCl is calculated as a function of temperature and effective hydrogen concentration in the manner described by *Cox et al.* [1994]. The effective Henry's law coefficient for HBr is calculated after *DeMore et al.* [1994] (see also *Brimblecombe and Clegg* [1988]). The effective Henry's law coefficient for HOBr is taken to be 10^6 M/atm in accordance with the results of *Hanson and Ravishankara* [1995] at 210 K. In marked contrast to the hydrolysis of $ClONO_2$ on sulfate aerosols, the hydrolysis of $BrONO_2$ on sulfate aerosols (reaction (7) in Table 1) is not a strong function of temperature [*Hanson and Ravishankara*, 1995] (see Figure 3 later). *Hanson and Ravishankara* [1992] studied the heterogeneous reaction of HBr with N_2O_5 (reaction (8) in Table 1). Where γ values were unavailable, the γ values used for the bromine reactions were taken to be the same as those of their chlorine analogues.

The key heterogeneous bromine reactions are marked with a large star in Table 1. They involve the relatively abundant bromine species HOBr and $BrONO_2$. The net effect of these reactions is to convert BrO_y from $BrONO_2$ and HBr into HOBr and BrCl. The HOBr can subsequently be photolyzed or heterogeneously converted into BrCl.

Heterogeneous Bromine Catalytic Cycles

The hydrolysis of $BrONO_2$ is the rate-limiting step of a catalytic cycle in which H_2O is split and converted into HO_2. Three ozone molecules are destroyed for each molecule of $BrONO_2$ hydrolyzed.

Cycle A

$BrONO_2$	+	H_2O	$\longrightarrow$	HOBr	+	HNO_3
HNO_3	+	$h\nu$	$\longrightarrow$	OH	+	NO_2
OH	+	O_3	$\longrightarrow$	HO_2	+	O_2
HOBr	+	$h\nu$	$\longrightarrow$	OH	+	Br
OH	+	O_3	$\longrightarrow$	HO_2	+	O_2
Br	+	O_3	$\longrightarrow$	BrO	+	O_2
BrO	+	NO_2	$\xrightarrow{M}$	$BrONO_2$		
H_2O	+	$3O_3$	$\longrightarrow$	$2HO_2$	+	$3O_2$

Cycle A is represented schematically in Figure 1. Cycle A has a long chain length for enhanced levels of sulfate aerosol reaching a peak of over 10^3 between
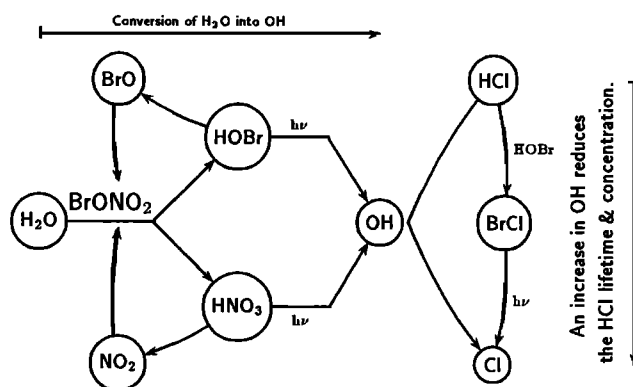

Figure 1. Reaction scheme showing the effects of $BrONO_2$ hydrolysis on sulphate aerosols.

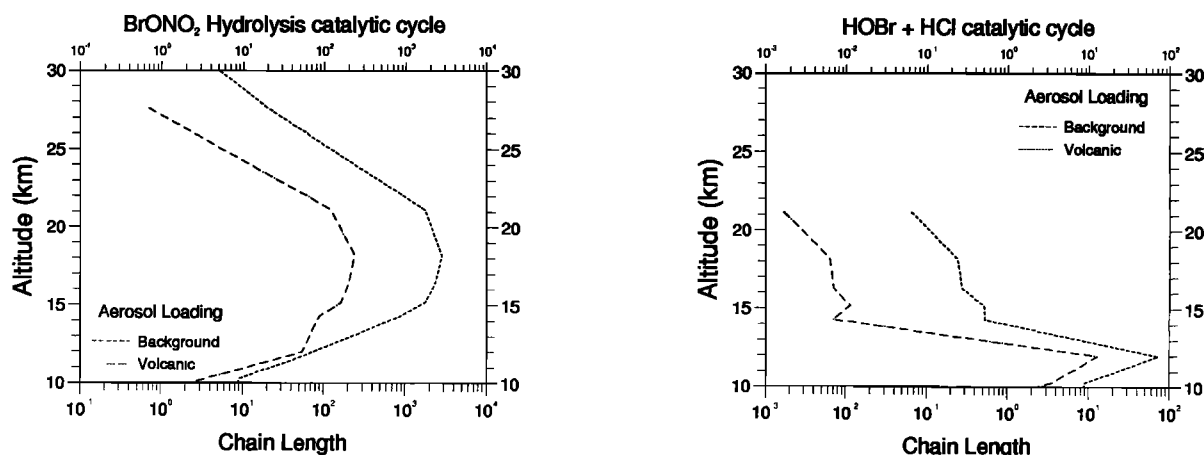**Figure 2.** The chain lengths of the ozone destroying $BrONO_2$ hydrolysis and the $HOBr+HCl$ catalytic cycles for background and volcanic loadings of sulphate aerosol.

about 15 km and 20 km (Figure 2). The chain length is a measure of how many times the cycle is completed before the chain center is removed. Because the chain length is a ratio of two rates, it is dimensionless. It is discussed in more detail in the companion paper [Lary, this issue] where it is defined as the rate of propagation (the rate of the rate-limiting step), k_{rls} divided by the rate of production or destruction of the source gases, k_{dest}.

$$\text{chain length, } \mathcal{N} = \frac{k_{rls}}{k_{dest}} \qquad (1)$$

The rate of the rate-limiting step reaches a peak of approximately 1600 molecules cm^{-3} s^{-1} close to 18 km for enhanced levels of sulfate aerosol, and approximately 150 molecules cm^{-3} s^{-1} for background levels of sulfate aerosol.

The sticking coefficient for hydrolysis of $BrONO_2$ on sulfate aerosols is not temperature dependent. Cycle A can proceed whenever sunlight is present. It is therefore important for ozone loss at all latitudes and for all seasons in the lower stratosphere. For example, over a 40-day mid-latitude simulation of a vertical profile in a one-dimensional model at the equinox, including heterogeneous bromine reactions reduced the ozone column by 11.2% for volcanic aerosol loadings and by 5.4% for background aerosol loadings. The ozone loss due to heterogeneous bromine reactions took place in the troposphere and the lower stratosphere. Although this study did not include the effects of rain out in the troposphere, it is clear that heterogeneous bromine reactions are also important in the troposphere [Fan and Jacob, 1992; Finlayson-Pitts et al., 1990; McConnell et al., 1992; Toumi, 1994].
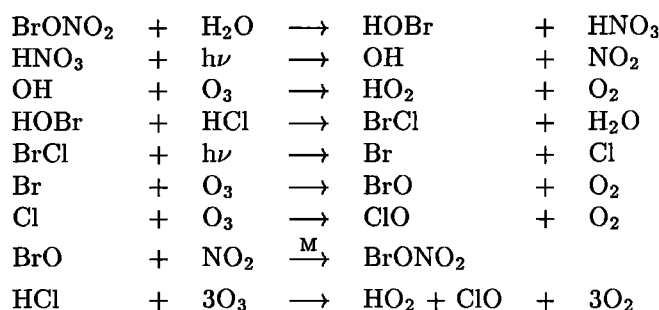
Cycle A enhances the OH concentration and thereby indirectly couples the atmospheric chemistry of chlorine and bromine, because the increase in the OH con-

centration can reduce the HCl lifetime by up to a factor of 3. The reduced HCl lifetime, and the accompanying increase in the ClO_x concentration, alters the $ClONO_2/HCl$ ratio, enhancing the effectiveness of the two gas phase ClO/BrO catalytic cycles.

Both the production and destruction of HNO_3 involve OH. However, owing to the relative rates of these two reactions, the increase in the OH concentration increases the production of HNO_3 more than it enhances the HNO_3 destruction. As a result the ratio of the HNO_3 production timescale to the HNO_3 loss timescale increases from between 1.5 and 2 in the lower stratosphere to approximately 3 when heterogeneous bromine reactions on enhanced loadings of sulfate aerosols are included for noon at mid-latitudes at equinox. This increase in OH leads to an increase in the HNO_3 concentration at the expense of the NO_2 concentration.

At cold temperatures the HOBr formed by $BrONO_2$ hydrolysis can react with HCl within sulfate aerosols to produce BrCl instead of being photolyzed. This cycle couples the atmospheric chemistry of chlorine and bromine, releasing active chlorine from HCl. Each time the cycle is executed, HCl is converted into ClO and three ozone molecules are destroyed.

Cycle B

$BrONO_2$	+	H_2O	$\longrightarrow$	HOBr	+ HNO_3
HNO_3	+	$h\nu$	$\longrightarrow$	OH	+ NO_2
OH	+	O_3	$\longrightarrow$	HO_2	+ O_2
HOBr	+	HCl	$\longrightarrow$	BrCl	+ H_2O
BrCl	+	$h\nu$	$\longrightarrow$	Br	+ Cl
Br	+	O_3	$\longrightarrow$	BrO	+ O_2
Cl	+	O_3	$\longrightarrow$	ClO	+ O_2
BrO	+	NO_2	$\xrightarrow{M}$	$BrONO_2$	
HCl	+	$3O_3$	$\longrightarrow$	$HO_2 + ClO$	+ $3O_2$

The rate of the bulk phase reactions (1) to (3) in Table 1 are a strong function of both the temperature

and the water vapor concentration. Therefore cycle B is only effective in the cold temperatures found in the very low stratosphere. For enhanced aerosol loadings it has a chain length approaching 100 (Figure 2).

Figure 3 shows that the hydrolysis of $BrONO_2$ on sulfate aerosols is effective over a wide range of temperatures. It can be seen that in absolute terms it has a relatively low rate, underlining the fact that its importance is due to its being part of a catalytic cycle. It is interesting that even though the sticking coefficient is not a function of temperature, the absolute rate of $BrONO_2$ hydrolysis in units of molecules cm^{-3} s^{-1} is temperature dependent (Figure 3). This is because the $BrONO_2$ concentration is very sensitive to the amount of NO_2 present, which is in turn a function of the temperature and ozone concentration [Lary, 1991; Lary et al., 1994]. A similar effect is observed in the rate of N_2O_5 hydrolysis (Figure 3). By comparing the rates of $BrONO_2$, N_2O_5 and $ClONO_2$ hydrolysis shown in Figure 3 it illustrates that the reduction in NO_x and enhancement in HNO_3 that occurs when $BrONO_2$ hydrolysis is included is not due to the hydrolysis of $BrONO_2$ alone, a relatively slow process, but is also due to the increase in OH released by the photolysis of the HOBr that is formed.

In agreement with the findings of Hanson and Ravishankara [1995] it was found that at temperatures below approximately 210 K the fastest stratospheric heterogeneous bromine reaction is the bulk phase reaction of HOBr with HCl. At the tropopause and below, the high water concentrations enable the bulk phase reaction of HOBr with HCl to proceed very rapidly.

Diurnal Cycles

The hydrolysis of $BrONO_2$ has a marked effect on the shape of the $BrONO_2$ and HOBr diurnal cycles (Figure 4). During the day $BrONO_2$ is rapidly produced by the three-body reaction of BrO with NO_2, and the hydrolysis of $BrONO_2$ is not fast enough to compete with the photolysis of $BrONO_2$. Therefore at mid-latitudes $BrONO_2$ hydrolysis has a relatively small effect on the daytime $BrONO_2$ concentration. However, after sunset, $BrONO_2$ production ceases and any $BrONO_2$ present is converted into HOBr on the timescale of a few hours, so that at the end of the night little $BrONO_2$ remains if enhanced aerosol loadings are present (Figure 4). $BrONO_2$ would otherwise be a major BrO_y reservoir as the reaction of BrO with NO_2 goes to completion. Consequently, the largest difference in the calculated $BrONO_2$ concentration due to heterogeneous bromine reactions occurs just before dawn (Figure 4).

The increase in HOBr is due to the hydrolysis of $BrONO_2$ during the night causes a sudden increase in the OH and HO_2 concentrations at dawn as HOBr is rapidly photolyzed (Figure 4). This sudden dawn in-

crease in OH and HO_2 is in agreement with the recent SPADE observations of OH and HO_2 reported by Salawitch et al. [1994]. The simulations shown in Figure 4 used the initial conditions given in table 1 of Salawitch et al. [1994] and assumed 14 pptv of BrO_y. Salawitch et al. [1994] explained the sudden increase in OH and HO_2 at sunrise by the heterogeneous conversion of HO_2NO_2 into HONO. However, Figure 4 shows that at least part of the sudden sunrise increase in OH and HO_2 is due to $BrONO_2$ hydrolysis enhancing the HOBr concentration. Hanson and Ravishankara [1995] mentioned that $BrONO_2$ hydrolysis produces enough HOBr during the night to give a release of OH at dawn.

When using the HOBr cross sections of Orlando and Burkholder [1995] the inclusion of heterogeneous bromine reactions leads to a slightly lower BrO concentration for a short period immediately after dawn as HOBr is photolyzed slightly more slowly than $BrONO_2$. The decrease in BrO in the short period just after dawn would not occur if HOBr photolysis was faster than $BrONO_2$ photolysis. The bulk phase reaction of HOBr with HCl proceeds at night causing a slow, but steady, increase of BrCl during the night (Figure 4). At high latitudes in the cold stratosphere under volcanic conditions the reaction of HOBr with HCl proceeds at a much higher rate, leading to a coupling of bromine and chlorine chemistry (see also Danilin and McConnell [1995]).

Partitioning of Reactive Species

The inclusion of heterogeneous bromine reactions alters the Br/BrO, Cl/ClO, NO/NO_2 and OH/HO_2 ratios as well as altering the absolute concentrations of these species. There is an increase in the BrO_x, ClO_x and HO_x concentrations and a decrease in the NO_x concentration. The Br/BrO ratio is reduced when heterogeneous bromine reactions are included due to the decrease in the NO concentration, and hence the rate of the reaction of BrO with NO. The Cl/ClO ratio is reduced when heterogeneous bromine reactions are included due to the decrease in the NO concentration, and hence the rate of the reaction of ClO with NO. The NO/NO_2 ratio is reduced when heterogeneous bromine reactions are included due to the increase in the ClO, BrO, HO_2 and CH_3O_2 concentrations, and hence, the rate of their reactions with NO. The OH/HO_2 ratio is reduced when heterogeneous bromine reactions are included due to the decrease in the NO concentration and the increase in the ClO concentration. This decreases the rate of the reaction of HO_2 with NO and increases the rate of the reaction of ClO with OH.

During periods of enhanced aerosol loading the HCl/ClO_y ratio is reduced owing to the increase in OH by the catalytic hydrolysis of $BrONO_2$ and a corresponding decrease in the HCl lifetime and concentration (Figure 5). The effect is most pronounced in the lower stratosphere. The decrease in the HCl/ClO_y ratio is accompanied
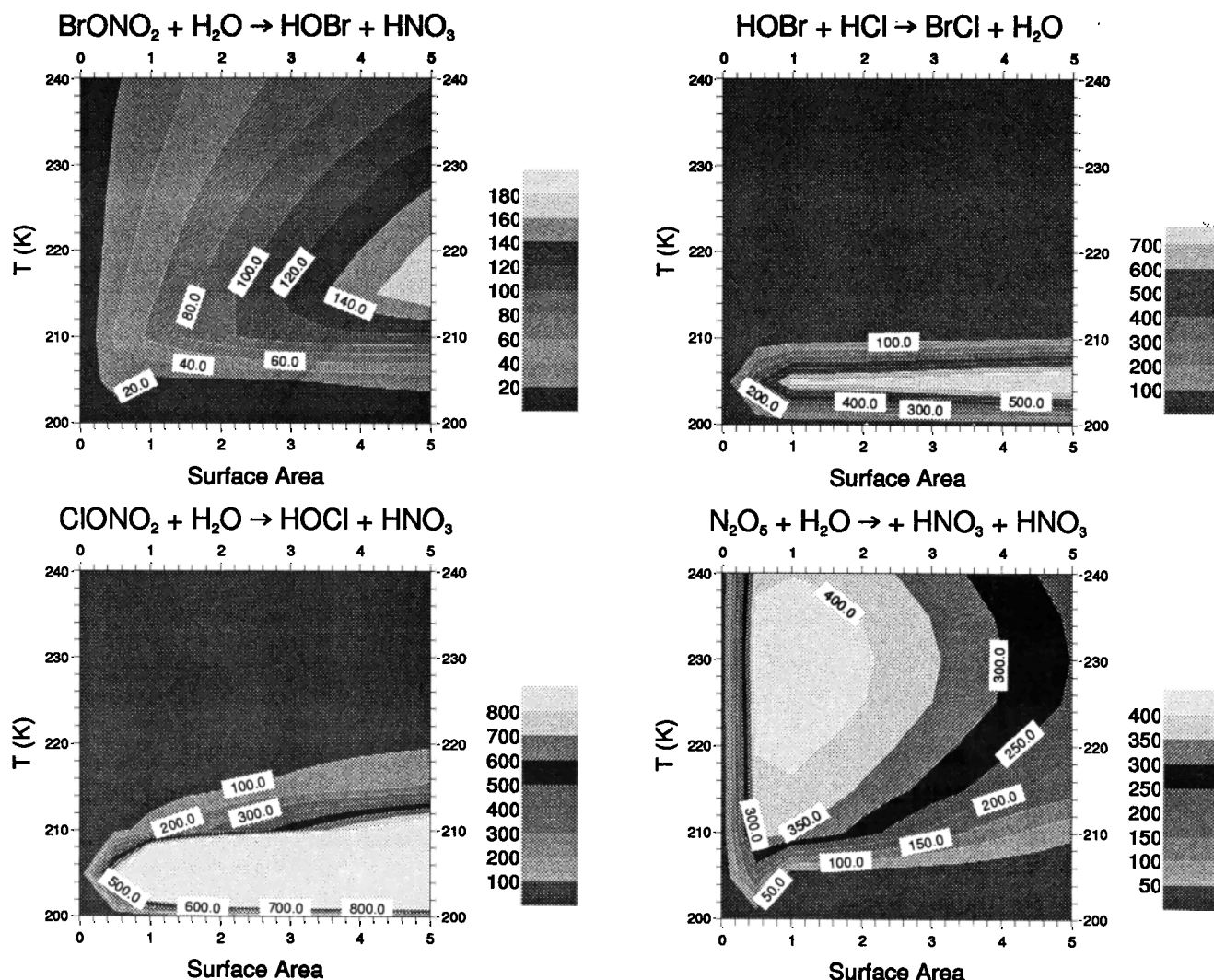
Figure 3. The absolute rate of heterogeneous reaction on sulphate aerosols at noon in units of molecules cm^{-3} s^{-1} as a function of temperature in K and aerosol surface area in units of $\mu m^2/cm^3$. The results shown are for the end of a 2-week simulation where an air parcel at 150 mb, 45°N at equinox was kept at a given temperature with a given aerosol surface area present throughout the simulation. Please note that each plot has a different contour interval.

by an increase in the ClO/ClO_y and $HOCl/ClO_y$ ratios (Figure 5). It would be useful to have simultaneous measurements of HCl, $ClONO_2$ and HOCl against which to critically test the photochemistry. Because the γ value for the hydrolysis of $BrONO_2$ is not temperature dependent, the reduction in the HCl/ClO_y ratio by this mechanism is primarily dependent on the aerosol loading and is not critically dependent on temperature, latitude or solar zenith angle.

Since including heterogeneous bromine reactions affects the fraction of BrO_y in the form of BrO it also affects the OClO concentration. The increase in the OClO column at warmer mid-latitudes due to the inclusion of heterogeneous bromine reactions is much greater than the increase at colder high latitudes. As will be seen later, this is because the inclusion of heterogeneous bromine reactions has a smaller effect on the partition-

ing of reactive bromine species at cold temperatures. For a 2-week simulation, at the equinox at 45°N, including heterogeneous bromine reactions increased the midnight OClO column by a factor of just over 2 for background levels of sulfate aerosol and by a factor of almost 3 for enhanced levels of sulfate aerosol. In contrast, at high latitudes the increase in the OClO column is of the order of 10%. This reinforces the finding of Sessler et al. [1995] that the OClO concentration is not a simple function of both ClO and BrO.

Gas Phase Catalytic Ozone Loss

In addition to forming the catalytic cycles A and B already described, heterogeneous bromine reactions enhance the coupling between chlorine and bromine chemistry which occurs due to the two gas phase ClO/BrO
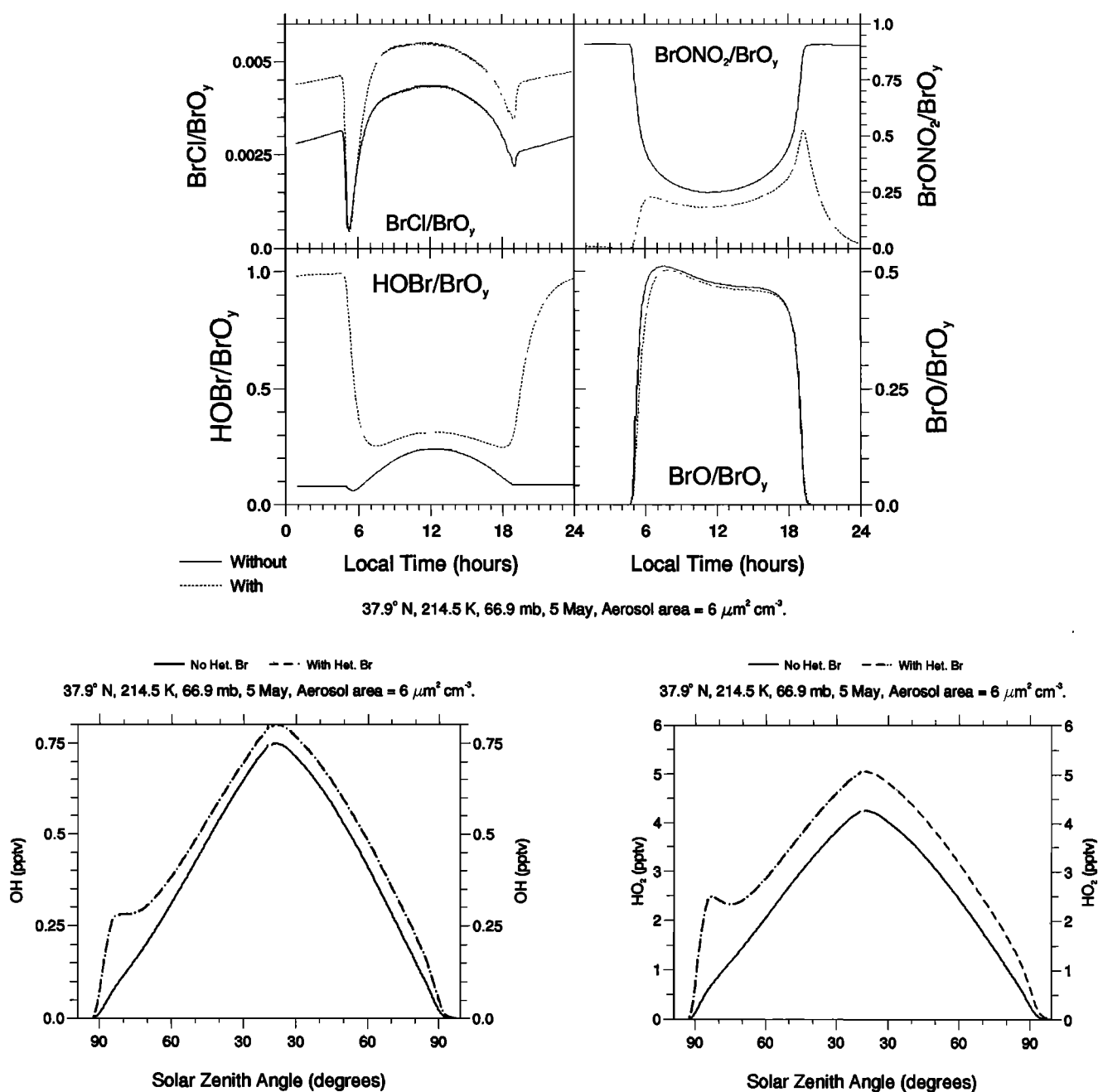
Figure 4. The effect of heterogeneous bromine reactions on sulfate aerosols on the shapes of diurnal cycles. The solid line is for a simulation which includes no heterogeneous bromine reactions, and the dashed line is for a simulation which does include heterogeneous bromine reactions. The initial conditions were taken from Table 1 of *Salawitch et al.* [1994].

catalytic ozone destruction cycles. The chain length of these two gas phase ClO/BrO cycles is increased by nearly an order of magnitude from 10^5 to 10^6 when heterogeneous bromine reactions are included.

The chain length of the BrO/HO$_2$ catalytic cycle is approximately 10^4 and is not significantly affected by heterogeneous bromine reactions. However, there is a decrease in the importance of the BrO/NO$_2$ ozone destruction catalytic cycle due to the hydrolysis of BrONO$_2$ on sulfate aerosols. The BrO/NO$_2$ cycle was high-

lighted by *Burkholder et al.* [1995] and is also examined by *Lary* [1995] together with a description of the gas phase catalytic bromine cycles. The BrO/NO$_2$ cycle only leads to ozone loss if the products of BrONO$_2$ photolysis are Br and NO$_3$.

To examine the effect of heterogeneous bromine reactions on lower stratosphere, mid-latitude, ozone loss, a set of idealized model simulations were performed. The numerical model is called AUTOCHEM and is described in *Lary et al.* [1995] and *Lary* [this issue]. In
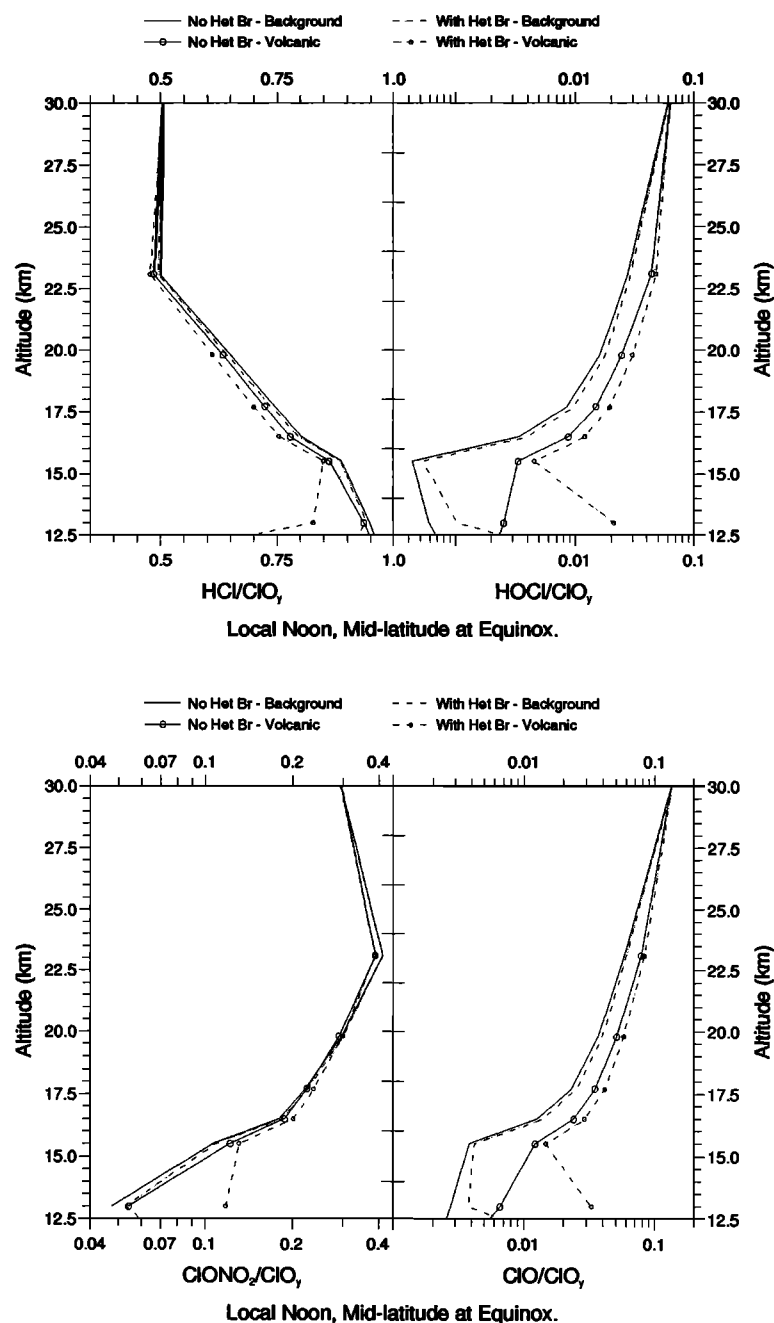
Figure 5. The effect of heterogeneous bromine reactions on sulfate aerosols on the calculated chlorine partitioning. The solid line is for no heterogeneous bromine reactions, and the dashed line is for with heterogeneous bromine reactions. The circles are for a volcanic aerosol loading.

these simulations the temperature of a stationary box was varied between 210 K and 198 K (Figure 6). This range of temperatures was chosen so that chlorine and bromine activation might occur on cold stratospheric aerosols *without* PSCs forming. For the first 10 days of the simulation the temperature was kept at 205 K. For the next ten days of the simulation the temperature was kept at 200 K. Then for 60 days the temperature was kept at 198 K. The partitioning of bromine species during these simulations are shown in Figure 6.

When heterogeneous bromine reactions are not considered, the ozone concentration has decreased by 283 ppbv for background levels of aerosol and by 1430 ppbv for volcanic levels of aerosol by the end of this idealized 100-day simulation (Figure 6). When heterogeneous bromine reactions are considered, the extra chlorine and bromine activation which occurs leads to an additional ozone depletion of approximately 60 ppbv for background levels of aerosol (an increase of 21%) and an additional 62 ppbv for volcanic levels of aerosol
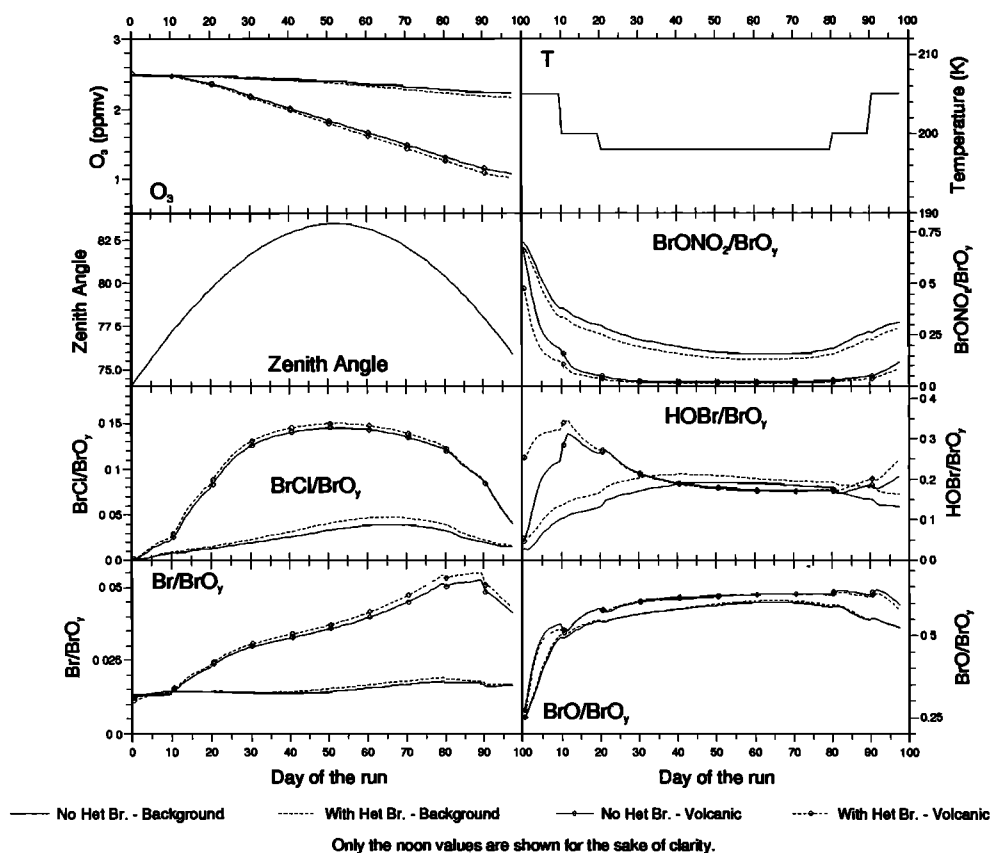
Figure 6. The effect of heterogeneous bromine reactions on the calculated noon partitioning of BrO_y for idealized box model simulations for an air parcel at 60°N at 55 mb with background and volcanic aerosol loadings. The simulations start in autumn and go through to spring. The solid line in each case is for no heterogeneous bromine reactions, and the dashed line is for with heterogeneous bromine reactions. The circles are for a volcanic aerosol loading. Note, that only the noon partitioning is shown because the amplitude of the diurnal cycles is so large that it hampers a comparison of the two simulations over such a long (100 days) period.

(an increase of 4.3%). Heterogeneous bromine reactions therefore contribute to mid-latitude, indeed all latitude, ozone loss in the lower stratosphere. Because the hydrolysis of $BrONO_2$ is not temperature dependent, it enhances ozone loss throughout the year and at all latitudes.

Figure 7 shows that when heterogeneous bromine reactions are included there is an increase in ClO_x by day 20, as well as an increase in the HO_x and BrO_x concentrations. There is a coupling between chlorine and bromine chemistry which leads to chlorine as well as bromine activation. There has also been a drop in the NO_x and HCl concentrations. This is in agreement with the findings of *Danilin and McConnell* [1995].

The additional chlorine and bromine activation which occurs is due to heterogeneous bromine reactions on PSCs is not as significant as that due to heterogeneous bromine reactions on sulfate aerosols. This is not a reflection of the sticking coefficients but underlines the fact that the bromine species are much shorter-lived than their chlorine counterparts. Since $BrONO_2$ and HOBr have such short lifetimes, the drop in the NO_2 and HO_2 concentrations which occurs immediately a

PSC is encountered also leads to a corresponding drop in the $BrONO_2$ and HOBr concentrations. When a model simulation is performed with an air parcel in a PSC for extended periods of time, the calculated HBr and $BrONO_2$ concentrations are virtually zero, and the HOBr concentration is very small. As a result, after an extended period in PSCs, the fastest PSC reaction is that of HCl with HOBr. However, this has a rate which is between 1 and 2 orders of magnitude less than the analogous bulk phase reaction in cold sulfate aerosols shown in Figure 3.

Consequently, whether or not heterogeneous bromine reactions are included, when PSCs are present there is relatively little bromine present as $BrONO_2$ and HOBr to react heterogeneously, and so a large fraction of the reactive bromine present is converted into BrCl. However, a heterogeneous reaction involving BrCl on PSCs could be significant. At present the authors know of no heterogeneous BrCl reactions. In the presence of sunlight BrCl is of course rapidly photolyzed to release Br and Cl, so any heterogeneous BrCl reaction would be most important at night.
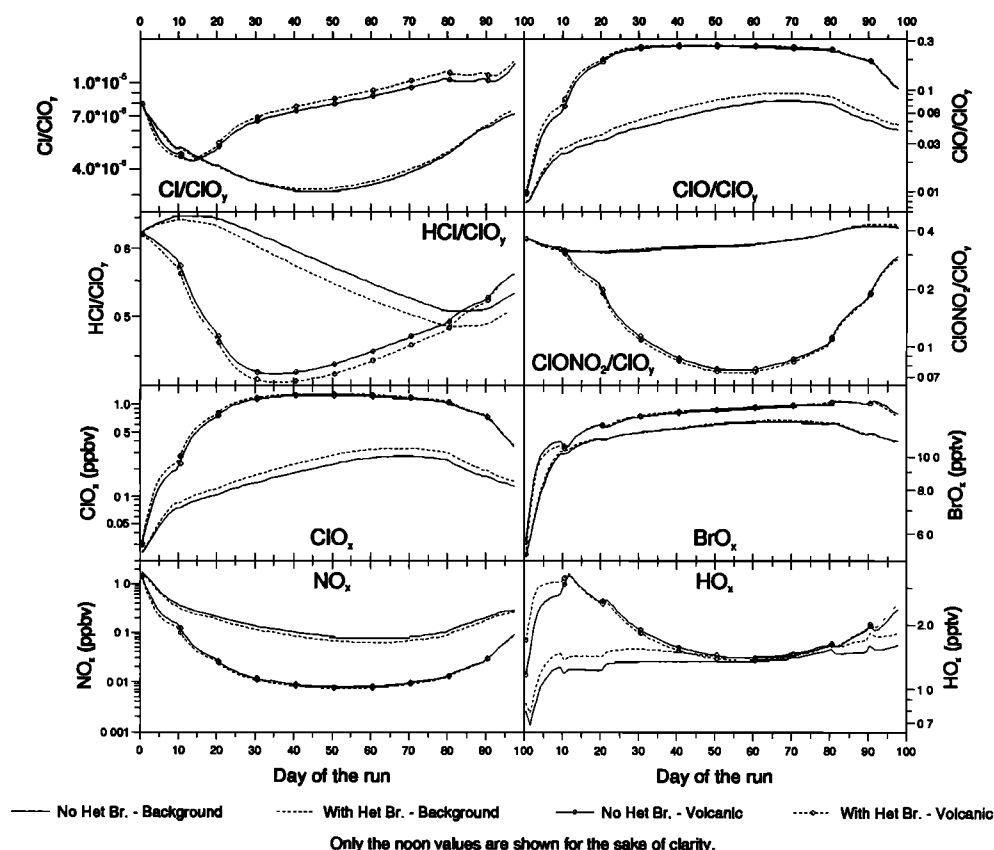
The most noticeable effect of including heterogeneous

Figure 7. The effect of heterogeneous bromine reactions on the calculated noon partitioning of ClO_y and the NO_x, HO_x, ClO_x and BrO_x volume mixing ratios for idealized box model simulations for an air parcel at 60°N at 55 mb with background and volcanic aerosol loadings. The simulations start in autumn and go through to spring. The solid line in each case is for no heterogeneous bromine reactions, and the dashed line is for with heterogeneous bromine reactions. The circles are for a volcanic aerosol loading. Note, that only the noon partitioning is shown because the amplitude of the diurnal cycles is so large that it hampers a comparison of the two simulations over such a long (100 day) period.

bromine reactions in the model is the dramatic drop in the HBr concentration. Although HBr usually only represents a small fraction of BrO_y, after prolonged PSC processing the enhanced levels of Cl lead to an enhancement in methane oxidation and consequently the concentration of HO_2. The enhanced HO_2 concentration can lead to an enhanced production of HBr, such that if heterogeneous bromine reactions are not included, more than 20% of BrO_y can be in the form of HBr. When there is rapid removal of HBr by heterogeneous bromine reactions, HBr does not represent a significant fraction of BrO_y.

The relative importance of the various heterogeneous bromine reactions on PSCs varies with the conditions, but the most important heterogeneous reactions tend to be the mixed halogen reactions, particularly reactions (2), (3) and (5) in Table 1, namely, the heterogeneous reactions of of HCl with HOBr and $BrONO_2$ and HBr with HOCl. This is just a reflection of the fact that the most abundant bromine species which undergo heterogeneous reactions are generally $BrONO_2$ and HOBr, and that HCl is an important chlorine reser-

voir. Consequently, simply from concentration considerations, the heterogeneous reactions of $BrONO_2$ and HOBr with HCl are important. In contrast, the reactions of HBr with HOCl and $ClONO_2$ are key reactions in the model because they keep the HBr concentration small. It would be valuable to have more laboratory studies of these reactions. It is important to note that the model description of bromine partitioning would change dramatically if there is a significant source of HBr which exists in reality which has not been included in the model. The model currently predicts that where aerosols are present the HBr concentration should be small. It would therefore be valuable to have observations of HBr with which the model could be compared. If these observations show that HBr is in fact present in appreciable quantities in regions where sulfate aerosols are present, it means that there is an important additional source of HBr.

In the next section the wide range of situations encountered on the 475 K isentropic surface during early 1993 are considered. Associated with the wide range of temperatures present on the 475 K isentropic surface

T on the 475.0 K isentrope
ECMWF analysis – 22 February 1993 – Time:12 00 GMT

PV on the 475.0 K isentrope.
ECMWF analysis – 22 February 1993 – Time:12 00 GMT
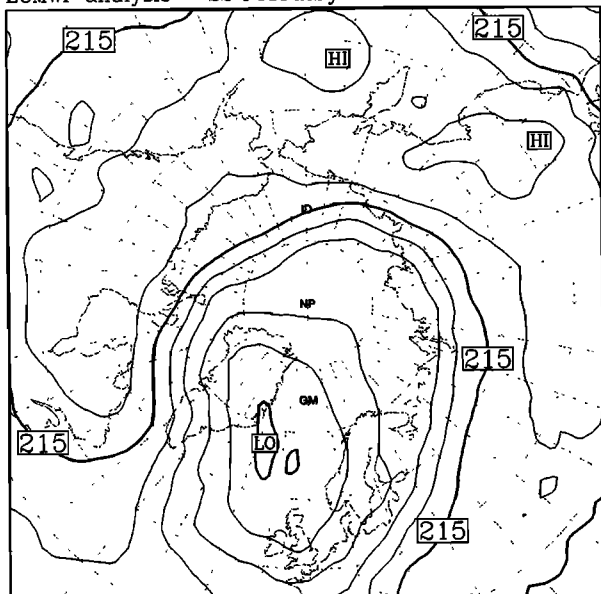
Contour from 190 to 225 by 5
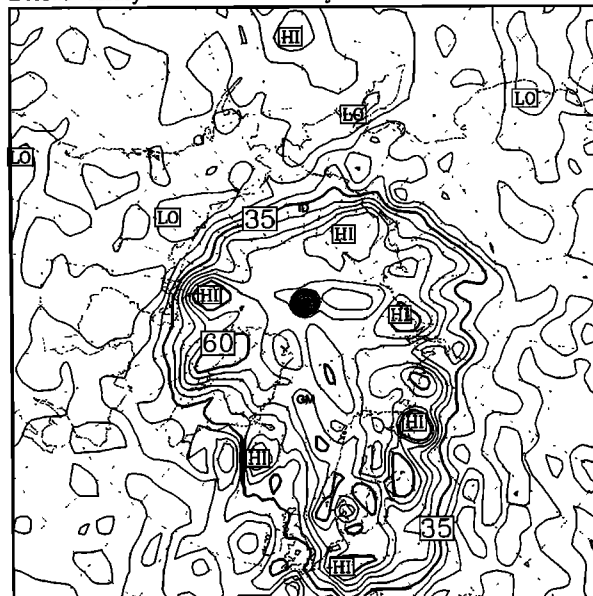
Contour from 10 to 60 by 5

Figure 8. The ECMWF temperature and PV analysis for the 475 K isentropic surface at 12 GMT for the February 22, 1992.

there are quite large variations in pressure, with much lower pressures in the cold regions.

Isentropic Model Simulations of the Winter of 1993

Relative to the interannual variability observed in the northern hemisphere lower stratospheric temperatures, the winter of 1992-1993 can be classed as long and cold. PSCs were present in the lower stratosphere from early December 1992 until late February 1993 [Chipperfield, 1994]. During January the vortex was centered on the pole, but during February, distortions to the vortex ensured that air parcels traveling around its edge made excursions to sunlit latitudes. For example, Figure 8 shows the potential vorticity (PV) and temperature fields at 475 K on February 22, 1993. On this day the polar vortex is distorted and descends over Europe. The lowest temperatures of 190 K occur to the east of Greenland, permitting PSCs to form in this region.

This section considers the effect of heterogeneous bromine reactions by including them in a two-dimensional single level isentropic model, SLIMCAT, described by Chipperfield et al. [1993, 1994, 1995], Chipperfield [1994] and Lary et al. [1995]. This model was run at an altitude of 475 K using winds analysed by the European Centre for Medium-Range Weather Forecasts (ECMWF) from 1 January, 1993, until 1 March, 1993. The two-dimensional model also has a detailed chemical scheme with the heterogeneous bromine reactions included as described above. Six model simulations

were performed (Table 2). Simulations SC1 (without heterogeneous bromine reactions) and SC2 (with heterogeneous bromine reactions) assumed a 0% yield for HBr from the reaction of HO_2 with BrO (reaction (1b) discussed by Lary [this issue] and referred to as reaction (1b) hereafter). Simulations SC3 and SC4 were similar to experiments SC1 and SC2 respectively, but reaction (1b) was assumed to have a 1% channel. Finally, experiments SC5 and SC6 were similar to SC1 and SC2, respectively, but with an enhanced aerosol loading of 15 $\mu m^2/cm^3$.

By comparing experiments SC1 and SC2 it was seen that inclusion of the heterogeneous bromine reactions significantly modified the partitioning of BrO_y species (not shown). As already observed, including heterogeneous bromine reactions gives additional ozone loss at all latitudes. The peak additional accumulated ozone loss predicted over the 2-month integrations was approximately 21 ppbv at northern midlatitudes (1.0%, Figure 9(a)). The additional loss decreased at northern high latitudes and was a minimum at the center of the north polar vortex. Therefore the most important effect of including heterogeneous bromine reactions in experiment SC2 is due to the reactions on sulfate aerosols with a minor effect due to reactions on PSCs.

Experiments SC5 and SC6 were initialized with an aerosol loading of 15 $\mu m^2/cm^3$, corresponding to conditions after a moderate volcanic eruption. Figure 10 shows the distribution of bromine species from the two-diemsional model on February 22, 1993, from run SC6 (with heterogeneous bromine reactions). The total

Table 2. Summary of SLIMCAT Model Experiments

Run	Heterogeneous Bromine Reactions	Aerosol Area $\mu m^2/cm^3$	Quantum Yield of reaction (1B)
SC1	no	1	0
SC2	yes	1	0
SC3	no	1	0.01
SC4	yes	1	0.01
SC5	no	15	0
SC6	yes	15	0

abundance of BrO_y at the center of the vortex is around 20 pptv. In the sunlit vortex the main bromine species is BrO with a peak mixing ratio of 9 pptv. Figure 10(b) shows that the main nighttime reservoir of BrO_y in the PSC-processed vortex is BrCl with peak mixing ratio of around 15 pptv. Owing to the rapid hydrolysis of $BrONO_2$ on sulfate aerosols, HOBr is the main nighttime reservoir outside the PSC-processed region, but the mixing ratio inside the vortex is lower. The maximum mixing ratio of HOBr in the sunlit polar vortex is around 6 pptv. Figure 10(d) shows the distribution of HBr from run SC6 with heterogeneous bromine reactions included. The highest values of only 0.006 pptv occur within the PSC region. Without heterogeneous bromine reactions (run SC5, not shown) the HBr mixing ratio is much higher but still only 0.3-0.5 pptv at mid-latitudes, decreasing inside the polar vortex to around 0.2 pptv (not shown). However, these mixing ratios are still low, and HBr is only a minor component of the total inorganic bromine at this altitude. The two-dimensional model has a simpler CH_4 oxidation scheme than the box model and so does not produce as much HBr as the box model in PSC regions (see above). The low abundance of HBr and $BrONO_2$ predicted in run SC5 (and also run SC1) in the Arctic polar vortex limits the effect of the heterogeneous bromine reactions which occur on PSCs.

Comparison of run SC5 and run SC6 shows the effect of including heterogeneous bromine reactions under volcanic aerosol loading. In early March the difference in ozone between run SC6 and SC5 is around 25 ppbv in the northern polar vortex, around 40 ppbv at northern mid-latitudes, and interestingly, a maximum of 150 ppbv during summer at the high southern latitudes (Figure 9(b)). This is due to the enhanced HO_x concentration (Figure 11(e)) which has been produced by the catalytic hydrolysis of $BrONO_2$ (cycle A). This finding emphasizes that heterogeneous bromine reactions can catalytically enhance ozone loss at all latitudes in all seasons.

Figure 11 shows the difference in some bromine species, ClO_x and HO_2 between SC5 and SC6. As was found in the earlier idealized simulations, in regions of PSC processing there is an almost complete removal of HBr (not shown). HBr has also been completely removed at mid-latitudes. The only region where HBr remains is coincident with the PSC region between Iceland and Scandinavia (Figure 10). The HBr has been reduced by up to 0.5 pptv. The bromine released from the HBr has been photochemically repartitioned among the major bromine species, as would be expected from their short lifetimes. On February 22 the largest increase in BrO between runs SC6 and SC5 of 2.5 pptv also occurs at high southern latitudes, while in the northern hemisphere the increase is similar to that seen between the background aerosol runs SC2 and SC1 (not shown). The heterogeneous removal of HBr has led to a small increase in BrO of around 0.1 pptv inside
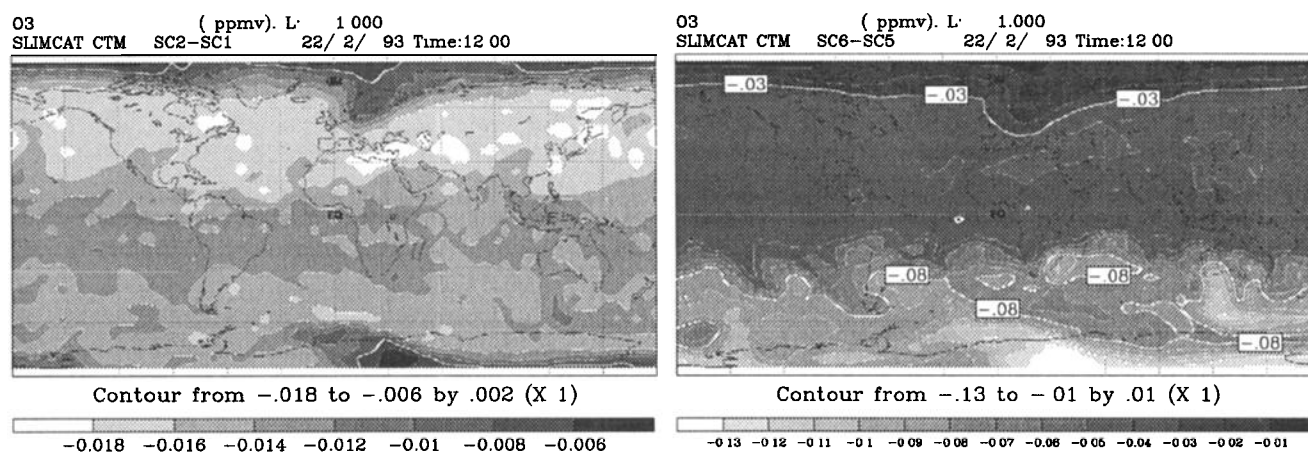
O3   (ppmv). L·   1 000
SLIMCAT CTM   SC2-SC1   22/ 2/ 93 Time:12 00

Contour from −.018 to −.006 by .002 (X 1)

−0.018   −0.016   −0.014   −0.012   −0.01   −0.008   −0.006

O3   (ppmv). L·   1.000
SLIMCAT CTM   SC6-SC5   22/ 2/ 93 Time:12 00

Contour from −.13 to − 01 by .01 (X 1)

−0 13 −0 12 −0 11 −0 1 −0 09 −0 08 −0 07 −0.06 −0 05 −0.04 −0 03 −0 02 −0 01

Figure 9. Difference in the ozone mixing ratio (ppmv) near the end of the 2-month simulations between (a) SC2 and SC1 and (b) SC6 and SC5. Different contour intervals are used in Figures 9(a) and 9(b).
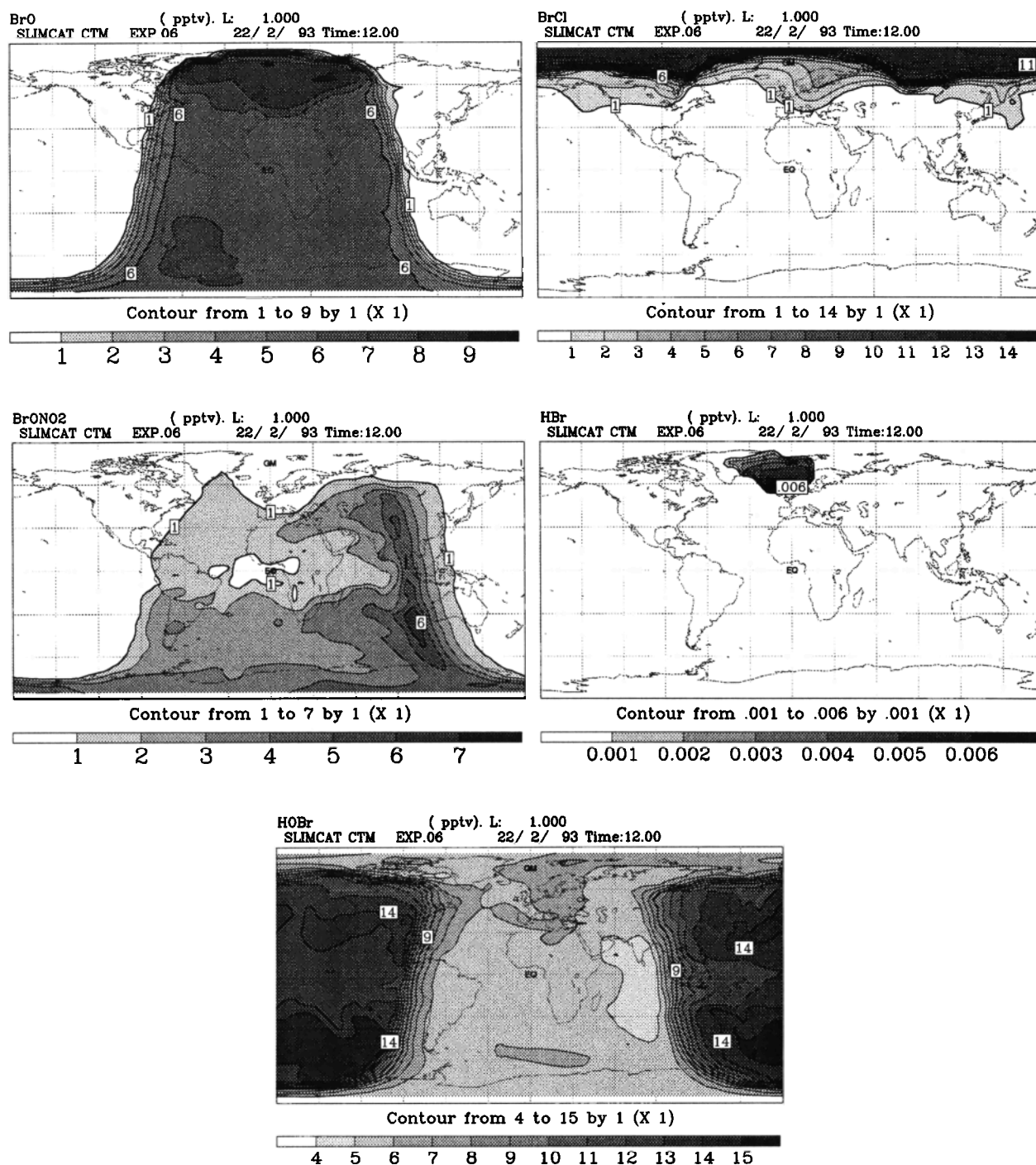
Figure 10. Mixing ratio (pptv) of (a) BrO, (b) BrCl, (c) BrONO$_2$, (d) HBr and (e) HOBr at 475 K on February 22, 1993, from the two-dimensional model run with heterogeneous bromine reactions and volcanic aerosol loading (SC6).

the polar vortex. As was observed in the earlier idealized experiments, including heterogeneous bromine reactions slightly reduces the BrO concentration immediately after dawn (Figure 11(a)) as HOBr is photolyzed at a slightly slower rate than BrONO$_2$. The heterogeneous hydrolysis of BrONO$_2$ on sulfate aerosols efficiently converts BrONO$_2$ to HOBr. With the higher aerosol loading the nighttime conversion of BrONO$_2$ to HOBr is more rapid and effectively complete at an

early stage of the night. The conversion of BrONO$_2$ is also rapid during the day and accounts for the reduction of 7 pptv of BrONO$_2$ at high southern latitudes. As well as the increase in BrO there is an increase of 4 pptv in HOBr. Under high aerosol loading the rates of the heterogeneous bromine reactions compete with the rapid daytime gas phase reactions which normally control the BrO$_y$ partitioning. Figure 11 shows that this conversion is most effective at night. Just before sunrise
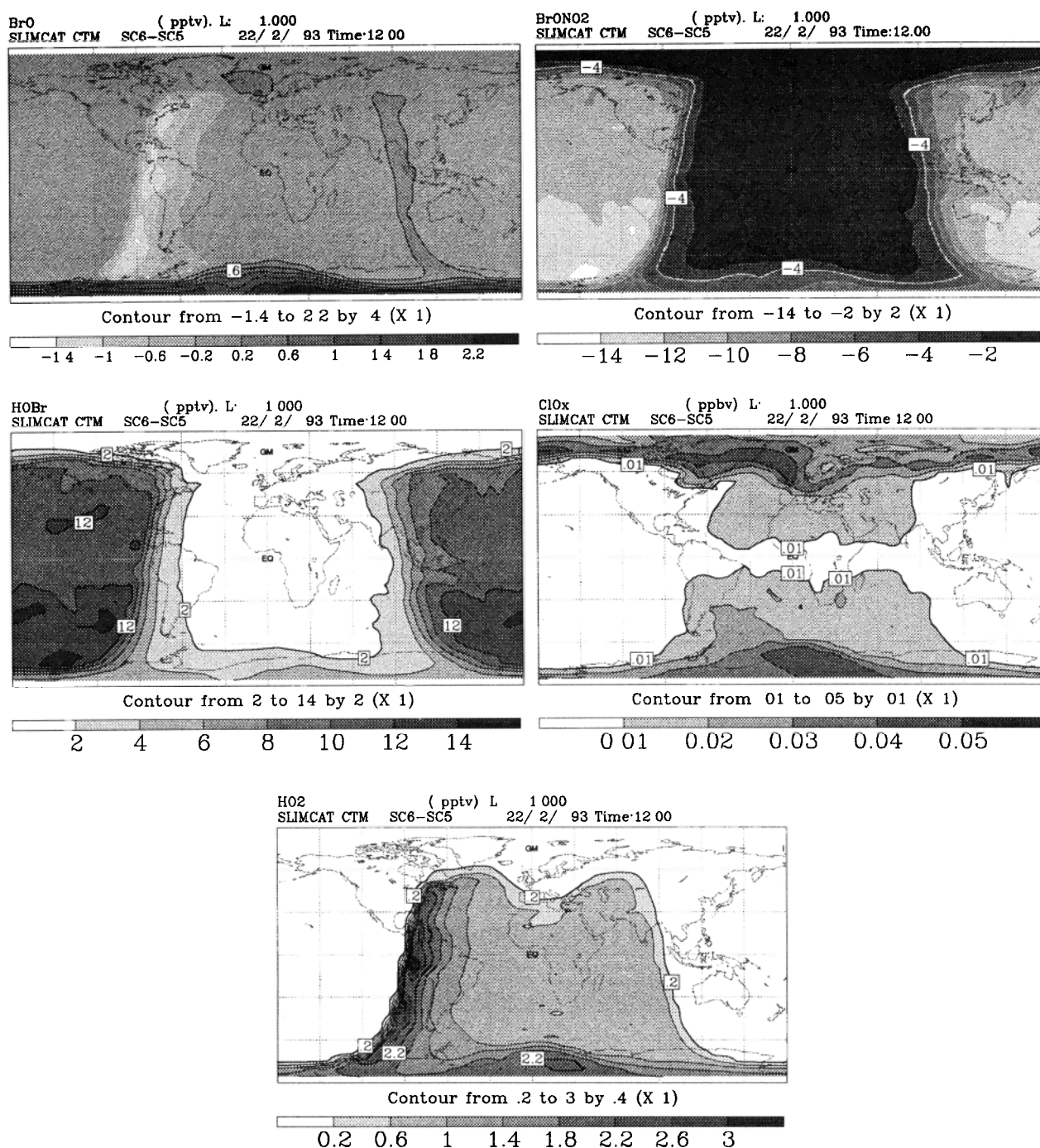
Figure 11. Difference in mixing ratio (pptv) between the two-dimensional model run with heterogeneous bromine reactions minus run without (SC6-SC5) for (a) BrO, (b) $BrONO_2$, (c) HOBr (d) ClO_x and (e) HO_2 at 475 K on 22 February 1993. The simulations used a volcanic aerosol loading.

there is 12 pptv more of HOBr in run SC6. During the daytime, photochemical reactions rapidly partition the BrO_y species and produce $BrONO_2$, and so the heterogeneous reactions have a much smaller effect than the gas phase reactions which normally control the BrO_y partitioning. There is up to 50 pptv more ClO_x in run SC6 at high southern latitudes and in PSC regions in the north polar vortex. Finally, HO_2 has increased by up to 2.2 pptv just after sunrise and during polar day in the southern hemisphere.

The catalytic increase in OH due to the hydrolysis of $BrONO_2$ leads to a reduction in the HCl lifetime and the HCl/ClO_y ratio. This can be seen in Figure 12 which shows the HCl/ClO_y ratio for simulations SC2 and SC6. The substantial reduction in the mid-latitude HCl/ClO_y ratio is particularly noticeable in the simu-
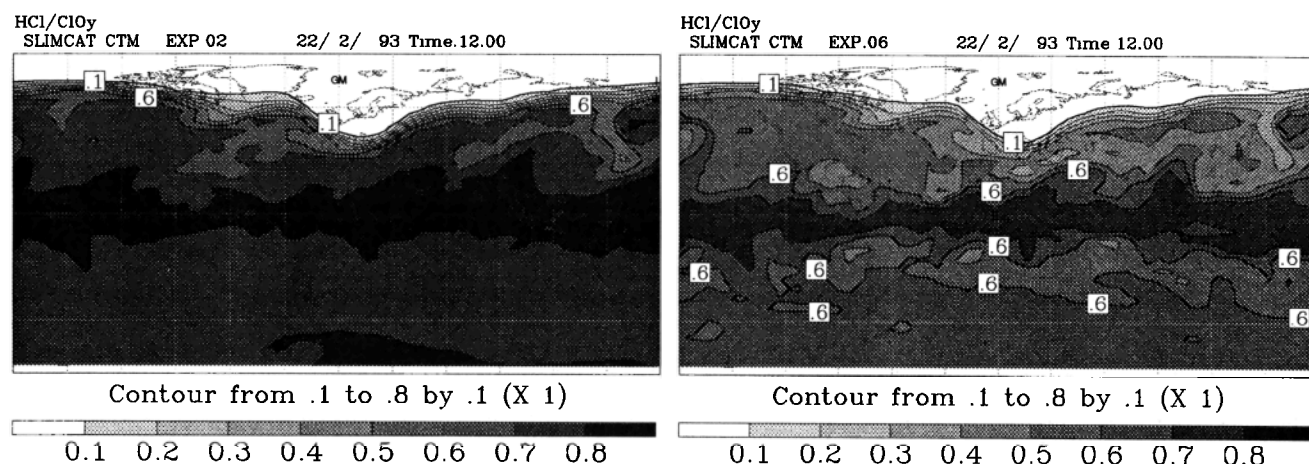
Figure 12. The HCl/ClO_y ratio for simulations SC2 (background aerosol loading) and SC6 (enhanced aerosol loading) at 475 K on February 22, 1993.

lation with a volcanic aerosol loading (SC6). In agreement with the results presented earlier, the HCl/ClO_y ratio is approximately between 0.4 and 0.6 throughout much of the mid-latitudes, as opposed to a value of between approximately 0.7 and 0.8 in simulations SC1 and SC2. For simulation SC6 the HCl/ClO_y ratio is also low in the summer hemisphere, with values typically between 0.5 and 0.6.

As discussed by Lary [this issue], it is unlikely that reaction (1b) proceeds. However, to investigate the possible importance of such a source of HBr simulations SC3 and SC4 were performed. A Comparison of experiments SC1 and SC3 showed the effect of including reaction (1b) with a 1% channel. Run SC3 has less polar ozone destruction than run SC1, the largest difference at the end of the run being 23 ppbv (around 1%, not shown) at the edge of the polar vortex. This is a larger effect on polar O_3 than that from including the heterogeneous bromine reactions alone. The inclusion of reaction (1b) increased HBr in the polar vortex by around 2 pptv (and by up to 4 pptv at mid-latitudes) at the expense of BrO_x (BrO + BrCl). This decrease in BrO reduces the ozone depletion.

When reaction (1b) is included in the model, the additional inclusion of the heterogeneous bromine reactions had a larger effect in the polar region. The increase in HBr due to reaction (1b) enables the heterogeneous reactions to recycle the additional HBr into BrO_x. The largest difference in accumulated O_3 loss between runs SC4 and SC3 is 45 ppbv (around 2%) at the edge of the polar vortex in early March. The additional loss at mid-latitudes is around 20 ppbv, similar to but slightly less than the difference between runs SC2 and SC1 above. However, the additional depletion inside the polar vortex is now greater than that at mid-latitudes. This increase offsets the reduced ozone depletion due to the inclusion of reaction (1b) as the levels of BrO were similar between runs SC2 and SC4. Therefore, with only a 1% channel, reaction (1b) would have a

significant effect, although there is no evidence for this channel from laboratory studies. A review of the kinetic measurements of (1b) is given by Lary [this issue]. Although the work of Mellouki et al. [1994] shows that reaction (1b) is in fact very slow, a comparison of SC1 and SC2 with SC3 and SC4 (not shown) illustrated that an additional source of HBr would substantially affect our view of the partitioning of bromine species.

These simulations with the two-dimensional isentropic model for early 1993 have confirmed the results from the idealized box model runs above. The effect of the heterogeneous bromine reactions on PSCs is small. The most important heterogeneous bromine reaction is the hydrolysis of $BrONO_2$. Under nonvolcanic conditions the reaction led to an additional O_3 depletion at northern mid-latitudes of up to 18 ppbv during the 2-month model run. With a volcanic aerosol loading the northern mid-latitude ozone depletion increased to 40 ppbv, while in the southern hemisphere, significant additional ozone depletion of over 130 ppbv was produced along with changes to ClO and HO_2.

Summary

Figure 13 summarizes the main gas phase and heterogeneous atmospheric photochemistry of bromine described in this paper and the companion paper Lary [this issue].

The effects of heterogeneous bromine reactions on sulfate aerosols and polar stratospheric clouds (PSCs) have been examined by using a range of photochemical models under a wide variety of conditions. The most important aerosol reactions were found to be the hydrolysis of $BrONO_2$, and, for temperatures below 210 K and/or high water concentrations, the bulk phase reaction of HOBr with HCl. These reactions take part in two catalytic ozone destruction cycles. Each cycle destroys three ozone molecules per cycle and enhance the HO_x, BrO_x, ClO_x and HNO_3 concentrations while
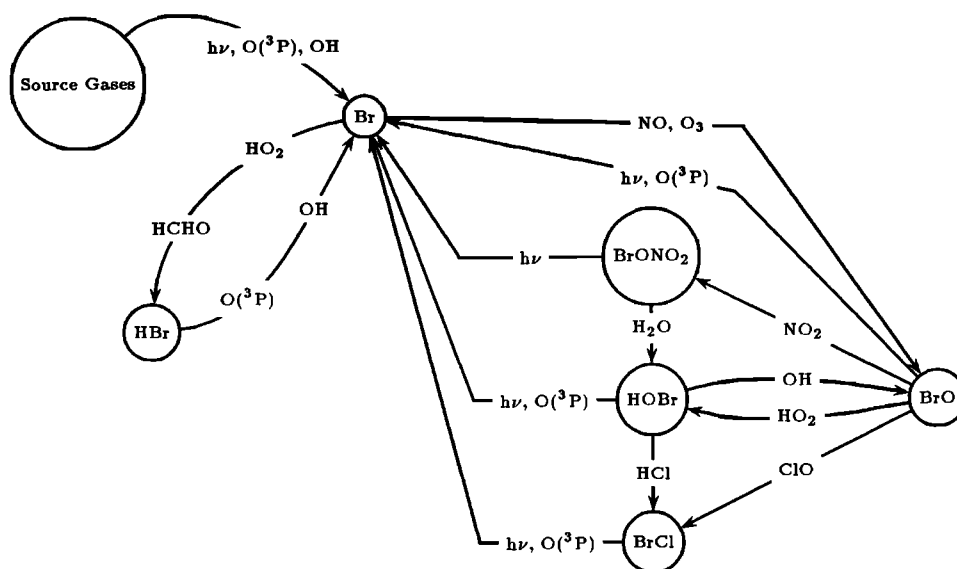
Figure 13. A schematic of atmospheric bromine photochemistry.

reducing the HCl and NO_x concentrations. The additional ClO_x and BrO_x activation that results enhances the effectiveness of the two gas phase ClO/BrO cycles whose chain lengths can increase by an order of magnitude for enhanced aerosol loadings due to the hydrolysis of $BrONO_2$. The catalytic $BrONO_2$ hydrolysis cycle is shown to be important for lower stratosphere ozone loss at all latitudes, with a chain length of greater than 10^3 for enhanced aerosol loadings. The enhancement in the OH concentration can substantially reduce the HCl lifetime and HCl/ClO_y ratio in the lower stratosphere. The nighttime hydrolysis of $BrONO_2$ leads to a nighttime enhancement of HOBr, so that at dawn HOBr photolysis leads to a rapid rise in OH and HO_2 as has recently been observed by *Salawitch et al.* [1994].

For a simulation of the winter of 1992-1993 on the 475 K isentropic surface constrained by ECMWF analyses, under nonvolcanic conditions the hydrolysis of $BrONO_2$ led to an additional O_3 depletion at northern mid-latitudes of up to 18 ppbv during the 2-month model run. With a volcanic aerosol loading the northern mid-latitude ozone depletion increased to 40 ppbv, while in the summer of the southern hemisphere significant additional ozone depletion of over 130 ppbv was produced along with changes to ClO and HO_2.

On PSCs the most important heterogeneous bromine reactions are the mixed halogen reactions of HCl with HOBr and $BrONO_2$ and HBr with HOCl and $ClONO_2$.

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