

Gas phase atmospheric bromine photochemistry

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Abstract. This paper reviews the current knowledge of gas phase bromine photochemistry and presents a budget study of atmospheric bromine species. The effectiveness of the ozone catalytic loss cycles involving bromine is quantified by considering their chain length and effectiveness. The chain effectiveness is a new variable defined as the chain length multiplied by the rate of the cycle's rate-limiting step. The chain effectiveness enables a fair comparison of different catalytic cycles involving species which have very different concentrations. This analysis clearly shows that below 25 km the BrO/ClO and BrO/HO₂ cycles are among the most important ozone destruction cycles.

Introduction

This paper is a review of gas phase bromine photochemistry and is intended to complement the companion paper [Lary *et al.* this issue] which considers heterogeneous bromine photochemistry. Bromine enters the atmosphere by a variety of natural and anthropogenic processes. The three main bromine source gases that can reach the stratosphere (i.e. are not removed from the troposphere by rainout, reaction with OH or photolysis) are CH₃Br, CBrClF₂ and CBrF₃. The most abundant of these source gases is methyl bromide (CH₃Br) whose natural source is mainly due to oceanic biological processes. In these, mainly algal, processes CH₃Br is formed together with other species such as CH₂Br₂, CHBr₃, CH₂BrCl and CHBrCl₂. The oceans are a significant natural source of CH₃Br [Singh *et al.*, 1983]. Measurements of larger tropospheric northern hemisphere mixing ratios suggest a large land based northern hemisphere source of CH₃Br which could well be anthropogenic [Penkett *et al.*, 1985; Reeves and Penkett, 1993]. The main industrial use of CH₃Br is as a fumigant, particularly for the treatment of soils. CH₃Br is also used in quarantine treatments and in insect and rodent control.

The wide variety of CH₃Br measurements made over the last decade in different parts of the world [Berg *et al.*, 1984; Rasmussen and Khalil, 1984; Penkett *et al.*, 1985; Cicerone *et al.*, 1988; Fabian *et al.*, 1994; Kaye *et al.*, 1994] suggest that the natural background concentration of CH₃Br in the troposphere is approximately 10 pptv. CH₃Br concentrations of up to 15 pptv have also been observed; these are likely to reflect the effect of anthropogenic sources.

The first study of atmospheric bromine chemistry was by Yung *et al.* [1980], who pointed to the general importance of atmospheric bromine chemistry and to the catalytic destruction of ozone by the ClO/BrO cycle. Bromine has been shown to play a significant role ($\approx 20\%$) in the formation of the ozone hole in polar stratospheric regions [McElroy *et al.*, 1986]. The contributions to ozone loss from bromine reactions are largest below about 20 km [e.g., Poulet *et al.*, 1992; Garcia and Solomon, 1994]. Bromine plays an important role in stratospheric ozone depletion despite being much less abundant than chlorine [World Meteorological Organization (WMO), 1992].

When atmospheric bromine chemistry is compared to chlorine chemistry, it can be seen that much more bromine is present in the active forms Br and BrO than chlorine is present in their counterparts Cl and ClO. Consequently, bromine has a greater potential to destroy stratospheric ozone than does chlorine [e.g. WMO, 1990,1992].

Section 2 describes the photochemical model used in this study, which contains a detailed photochemistry scheme. Section 3 gives a budget study of atmospheric bromine species based on the current knowledge of gas phase bromine chemistry. Section 4 considers the effectiveness of the various ozone-destroying catalytic bromine cycles. Section 5 summarizes the main conclusions.

Model Description

The column model used in this study is a version of a new suite of models called AUTO-CHEM. The model included a total of 53 species. No family or photochemical equilibrium assumptions are made. Of the 53 species, 51 species are integrated separately with a 15 minute time step, namely: O(¹D), O(³P), O₃, N, NO, NO₂, NO₃, N₂O₅, HONO, HNO₃, HNO₃(s), HO₂NO₂, Cl, Cl₂, ClO, ClOO, OClO, Cl₂O₂, ClNO₂,

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ClONO_2 , HCl , $\text{HCl}_{(s)}$, HOCl , H , OH , HO_2 , H_2O_2 , CH_3 , CH_3O_2 , $\text{CH}_3\text{O}_2\text{NO}_2$, CH_3OOH , CH_3O , HCHO , HCO , Br , Br_2 , BrO , BrONO_2 , BrONO , HBr , HOBr , BrCl , H_2 , H_2O , $\text{H}_2\text{O}_{(s)}$, CO , CO_2 , CH_4 , N_2O , CH_3Br and CF_2Cl_2 . O_2 and N_2 are included but not time integrated. The version of AUTO-CHEM used in this study contains a total of 236 reactions, 129 bimolecular reactions, 27 trimolecular reactions, 42 photochemical reactions and 38 heterogeneous reactions. The rate constants for the reactions were taken from *Atkinson et al.* [1992] and *DeMore et al.* [1994].

The time integration scheme used is an adaptive timestep *Burlisch-Stoer* scheme [*Stoer and Burlisch*, 1980] specifically designed for integration of stiff systems after *Press et al.* [1992]. The time integration package is as accurate as the often used *Gear* [1971] package but faster. Photolysis rates are calculated by using full spherical geometry and multiple scattering as described by *Lary and Pyle* [1992a,b] after *Meier et al.* [1982], *Nicolet et al.* [1982] and *Anderson* [1983]. The average photolysis rate over a model time step is calculated using 10 point gaussian quadrature as described by *Press et al.* [1992].

AUTO-CHEM has also been used to perform for the first time four-dimensional variational analysis of chemical species [*Fisher and Lary*, 1995] and to examine the effect of the reaction $\text{OH} + \text{ClO} \rightarrow \text{HCl} + \text{O}_2$ on polar ozone photochemistry [*Lary et al.*, 1995].

Gas Phase Bromine Chemistry

This section examines the budgets of reactive bromine species as predicted by our current understanding of the gas phase kinetics of bromine. Figure 1 is a reaction scheme of atmospheric bromine photochemistry. Het-

erogeneous nitrogen and chlorine reactions are considered in these calculations but not heterogeneous bromine reactions. Heterogeneous bromine reactions are the subject of the companion paper *Lary et al.* [this issue]. The reactive bromine species included in AUTO-CHEM are Br , Br_2 , BrO , BrONO , BrONO_2 , HBr , HOBr and BrCl .

Figure 2 shows the calculated midlatitude photochemical lifetimes of these species for local noon at equinox, and Figure 3 shows the calculated midlatitude partitioning of reactive bromine species for local noon at equinox.

It can be seen from Figure 2 that in marked contrast to their chlorine counterparts all of the bromine species are short-lived. Figure 3 shows that typically the most abundant inorganic bromine species in the lower stratosphere are BrO , BrONO_2 and HOBr . Each of the reactive bromine species will now be considered in turn.

BrONO_2

BrONO_2 has a photochemical lifetime of a few minutes throughout the sunlit middle atmosphere (the solid squares in the right-hand panel of Figure 2). The relatively short lifetime of BrONO_2 is due to the photolysis of BrONO_2 , which occurs in the visible region of the spectrum. Consequently, BrONO_2 is very close to photochemical steady state in the sunlit atmosphere. The recent study of *Burkholder et al.* [1995] measured the absorption cross section of BrONO_2 in the important tail region between about 390 nm and 500 nm extending the previous measurements of *Spencer and Rowland* [1978]. As pointed out by *Burkholder et al.* [1995], if the products are BrO and NO_2 then BrONO_2 will not be involved in catalytic ozone destruction. Photolysis would merely reverse the formation of BrONO_2 . How-

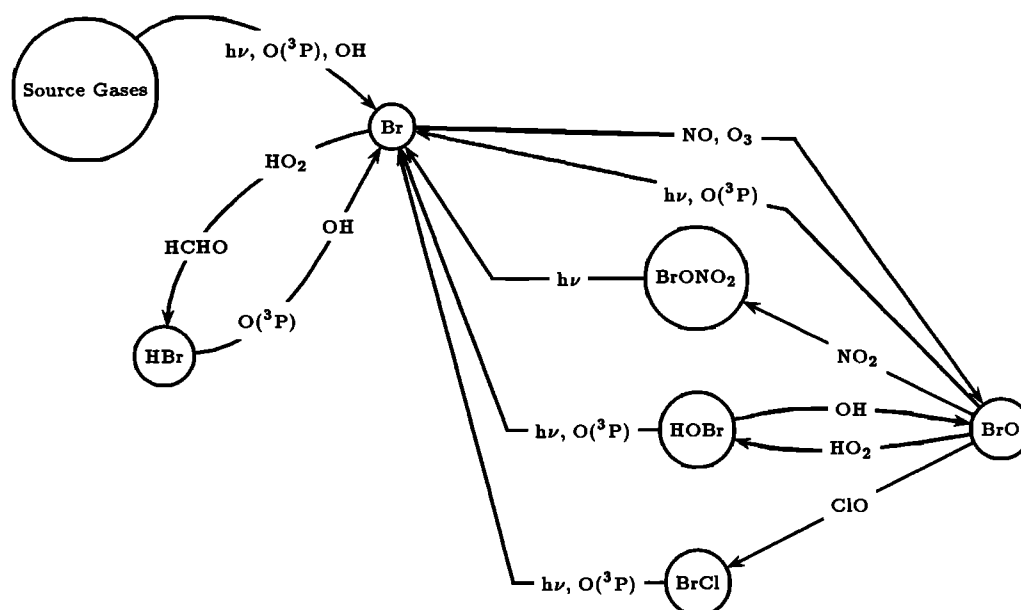


Figure 1. Schematic of atmospheric bromine photochemistry.

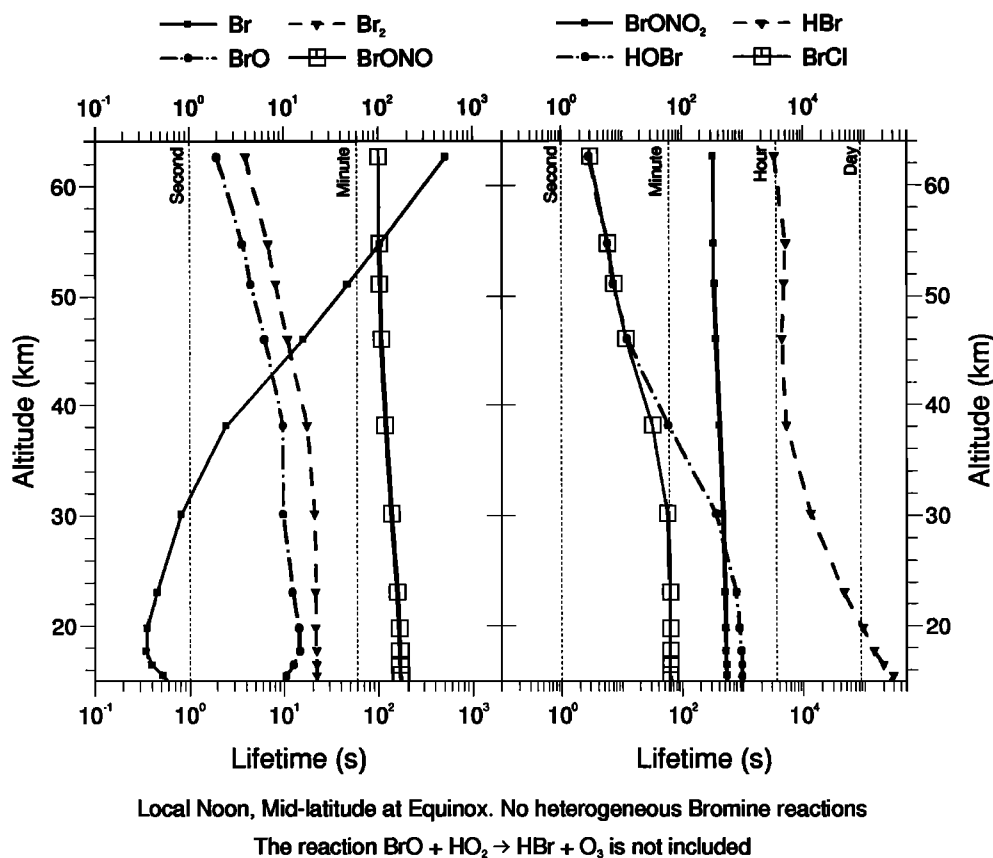


Figure 2. The calculated midlatitude photochemical lifetimes of reactive bromine species for local noon at equinox. Heterogeneous bromine reactions were not included in these calculations. These simulations do not include the reaction $\text{HO}_2 + \text{BrO} \rightarrow \text{HBr} + \text{O}_3$.

ever, if the products are Br and NO_3 , then an important catalytic destruction of ozone can occur. This catalytic destruction of ozone will be considered in the next section.

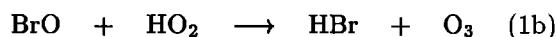
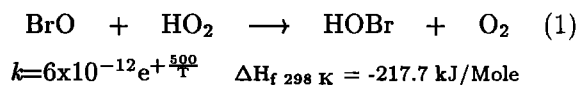
BrONO_2 is produced by the three-body reaction of BrO with NO_2 . Because BrONO_2 has a relatively short lifetime, the BrONO_2 concentration responds very rapidly to any change in NO_2 , as occurs, for example, due to denoxification on surfaces. The rate recommended for the formation of BrONO_2 by *DeMore et al.* [1992] is based on kinetic measurements made by *Thorn et al.* [1993] and *Danis et al.* [1990]. These measurements were made at over 260 K and so quite large temperature extrapolations are involved when considering lower stratospheric temperatures. It would therefore be valuable to have further measurement studies of this reaction at the colder temperatures experienced in the lower stratosphere.

The companion paper *Lary et al.* [this issue] shows that the catalytic hydrolysis of BrONO_2 on sulfate aerosols is an important sink of BrONO_2 in the lower stratosphere.

HOBr

In the sunlit atmosphere, HOBr is almost in immediate photochemical steady state with a lifetime of sev-

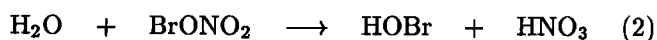
eral minutes in the lower stratosphere decreasing to a few seconds in the upper stratosphere (the solid circles in the right-hand panel of Figure 2). In the sunlit lower stratosphere HOBr represents between approximately 20% and 30% of the total BrO_y =total inorganic bromine (the solid circles in the right-hand panel of Figure 3). The main source of HOBr is the reaction



Possible minor channel $\Delta H_f \text{ }_{298 \text{ K}} = -31.8 \text{ kJ/Mole}$

The units of this, and all subsequent rate constants, are molecules $\text{cm}^{-3} \text{ s}^{-1}$. Recent laboratory measurements of reaction (1) were made by *Poulet et al.* [1992] and of reaction (1b) by *Mellouki et al.* [1994]. The effect of HBr production by reaction (1b) is considered below in the subsection on HBr.

As can be seen in the companion paper *Lary et al.* [this issue], in the troposphere and lower stratosphere, the heterogeneous production of HOBr on sulfate aerosols can play an important role:



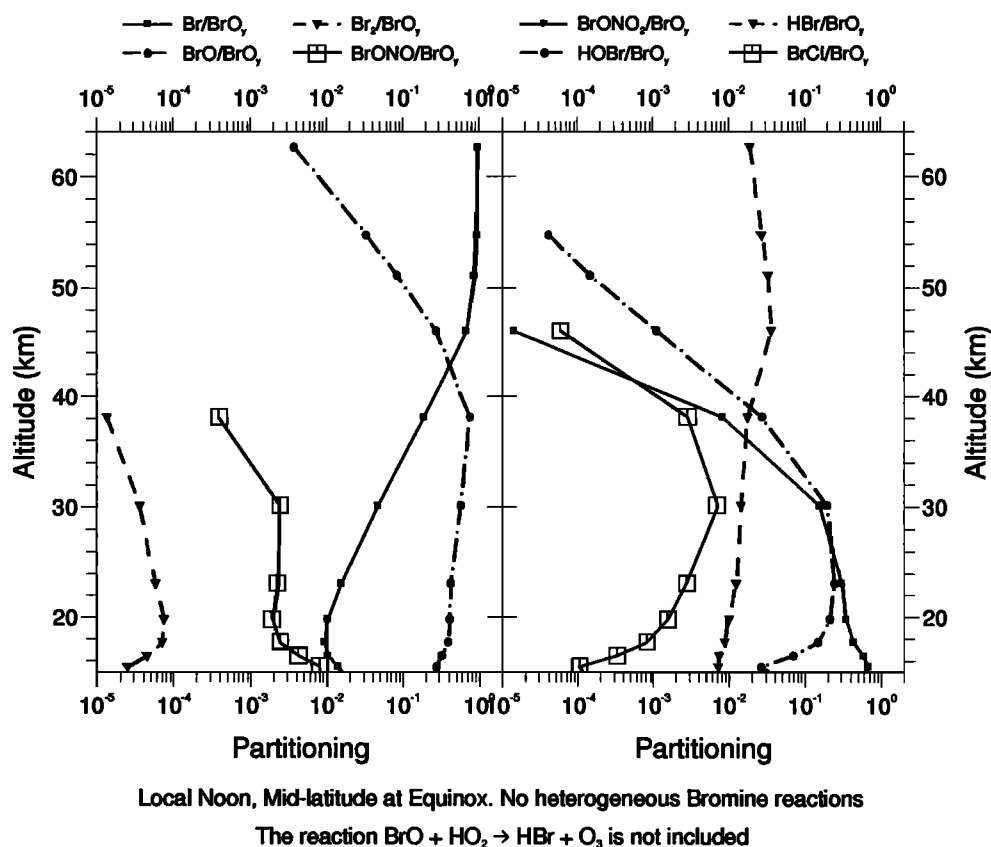
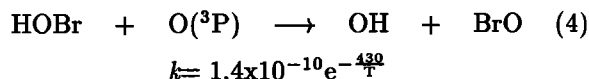
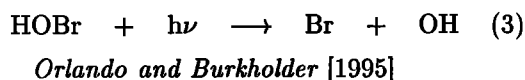


Figure 3. The calculated midlatitude partitioning of reactive bromine species for local noon at equinox.

(see also *Fan and Jacob* [1992] and *Hanson and Ravishankara* [1995]). HOBr destruction is due to photolysis and the reaction with $\text{O}(^3\text{P})$. The rate constant for the reaction of HOBr with $\text{O}(^3\text{P})$ has recently been determined by *Nesbitt et al.* [1995].

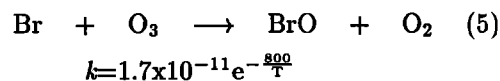


Below approximately 25 km photolysis is the most important loss of HOBr, whereas above this altitude the reaction with $\text{O}(^3\text{P})$ is the main loss of HOBr [*Nesbitt et al.*, 1995]. This confirms the findings of *Nesbitt et al.* [1995]. The lifetime of HOBr varies from about 15 minutes in the sunlit lower stratosphere to a few seconds in the upper stratosphere. This is based on calculations using the HOBr absorption cross section which have recently been measured for the first time by *Orlando and Burkholder* [1995].

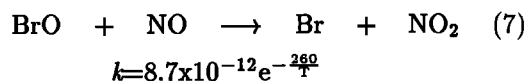
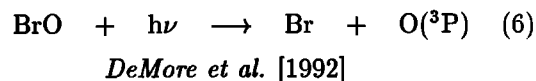
BrO

The most abundant bromine species in the sunlit lower stratosphere is normally BrO, which has a lifetime of a few seconds (the solid circles in the left hand

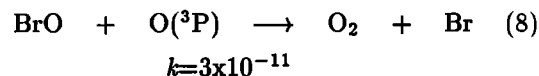
panel of Figure 2). Typically, at 20 km, approximately 40% of BrO_y is in the form of BrO rising to a peak of about 75% at around 40 km (the solid circles in the left-hand panel of Figure 3). The main source of BrO is the reaction



In the sunlit lower stratosphere the main destruction of BrO is by photolysis (the peak BrO absorption is at around 325 nm) and reaction with NO



In the upper stratosphere the main loss of BrO is due to the reaction



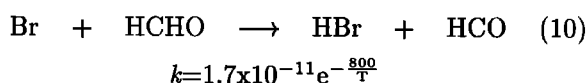
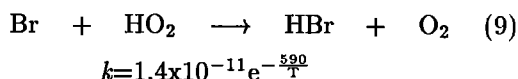
In the lower stratosphere the reaction of BrO with ClO contributes a few percent to the loss rate of BrO. Close to the ground the reaction of BrO with HO_2 , men-

tioned above, contributes about 10% to the total loss of BrO, as does the formation of BrONO₂. As will be discussed later, the reaction of BrO with ClO is also important for catalytic ozone destruction.

HBr

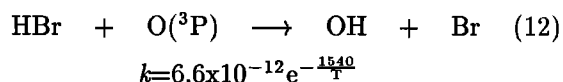
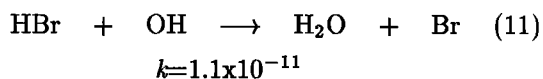
Although HBr is the longest lived BrO_y reservoir, it still has a lifetime of only about a day in the sunlit midlatitude lower stratosphere, decreasing to an hour in the upper stratosphere (the triangles in the right-hand panel of Figure 2). The lifetime does increase at high latitudes during winter where there is less sunlight. According to our current understanding, generally only a small percent of BrO_y in the lower stratosphere is in the form of HBr (the triangles in the right-hand panel of Figure 3). However, in the troposphere, HBr is generally a larger fraction of the total BrO_y. Typically between about 10% and 40% of tropospheric BrO_y can be in the form of HBr if heterogeneous bromine reactions are not considered and if it is assumed that there is negligible production of HBr by reaction (1B) above. However, as will be seen in the companion paper *Lary et al.* [this issue], if heterogeneous bromine reactions do occur HBr may be only a very small fraction of the total BrO_y present both in the troposphere and lower stratosphere.

HBr is produced mainly by the reactions



At around 20 km at equinox in the sunlit lower stratosphere reactions (9) and (10) make a significant contribution to HBr production. However, as shall be seen later, the reaction of Br with HCHO can sometimes become the most important source of HBr in the lower stratosphere. In the upper stratosphere the importance of reaction (10) decreases and reaction (9) is the main source of HBr, whereas the main source of HBr in the model troposphere is reaction (10). In the very low stratosphere and troposphere the higher aldehydes probably also play a role in producing HBr.

Below about 50 km, HBr is destroyed mainly by reaction with OH. Above 50 km the reaction of HBr with O(³P) also becomes an important loss of HBr.



The partitioning of reactive bromine is very sensitive to the branching ratio of reaction (1) in the lower stratosphere. Even a very small yield of HBr will in-

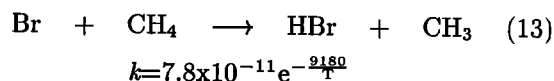
crease the HBr concentration at the expense of HOBr. To illustrate this, Figure 4 shows that an HBr yield of only 0.1% would double the HBr concentration at 20 km and a yield of 1% would give a tenfold increase in HBr at 20 km. If it were assumed that reaction (1b) had a yield of 0.1%, then between 60% and 70% of the HBr produced at around 20 km would be due to reaction (1b); if the yield is 1% then between 80% and 90% of the HBr produced at around 20 km is due to reaction (1b). The partitioning of reactive bromine is affected by the assumed yield of HBr from reaction (1) up to about 50 km, above this altitude the effect on the HBr concentration is relatively small.

Garcia and Solomon [1994] have recently examined the effect of assuming different branching ratios for reaction (1). They found that the BrO abundance was critically dependent on the yield of HBr. Their comparison between model calculations and observations suggests that the yield must be substantially less than 5%.

Laboratory measurements of reaction (1) were made by *Poulet et al.* [1992]. They pointed out that HBr is a possible product of this reaction but stated that the only product they observed at 298 K was HOBr suggesting a negligible yield for HBr. They did not preclude the formation of HOBr at the lower temperatures of the stratosphere. Reaction (1b) is a four-centered reaction and because of the required reaction geometry these reactions are generally very slow. An upper limit on the yield of HBr from reaction (1b) has recently been determined by *Mellouki et al.* [1994] by measuring an upper limit for the reverse reaction. The limits were measured at 301 K and 441 K and were extrapolated to low temperatures. They found that the yield of HBr from reaction (1b) is negligible throughout the stratosphere. It is likely that less than 0.01% of reaction (1) yields HBr as a product.

Since the yield of HBr from reaction (1) would affect the fraction of BrO_y in the form of BrO it would also affect the OCIO concentration, since OCIO is produced mainly by reaction (15). Increasing the yield of HBr from reaction (1) from 0% to 1% would reduce the large nighttime OCIO column by just over 16% at midlatitudes.

Our current understanding of bromine photochemistry suggests that the main sources of HBr are reactions (9) and (10). For all of these reactions both the reactants are present in the atmosphere in relatively small concentrations. This is in contrast to HCl, which is formed mainly by the reaction of Cl with the relatively abundant CH₄. The extensive literature review of *Baulch et al.* [1981] quotes a rate constant for the analogous bromine reaction which is very slow at stratospheric temperatures



A reaction which may play a role in the troposphere

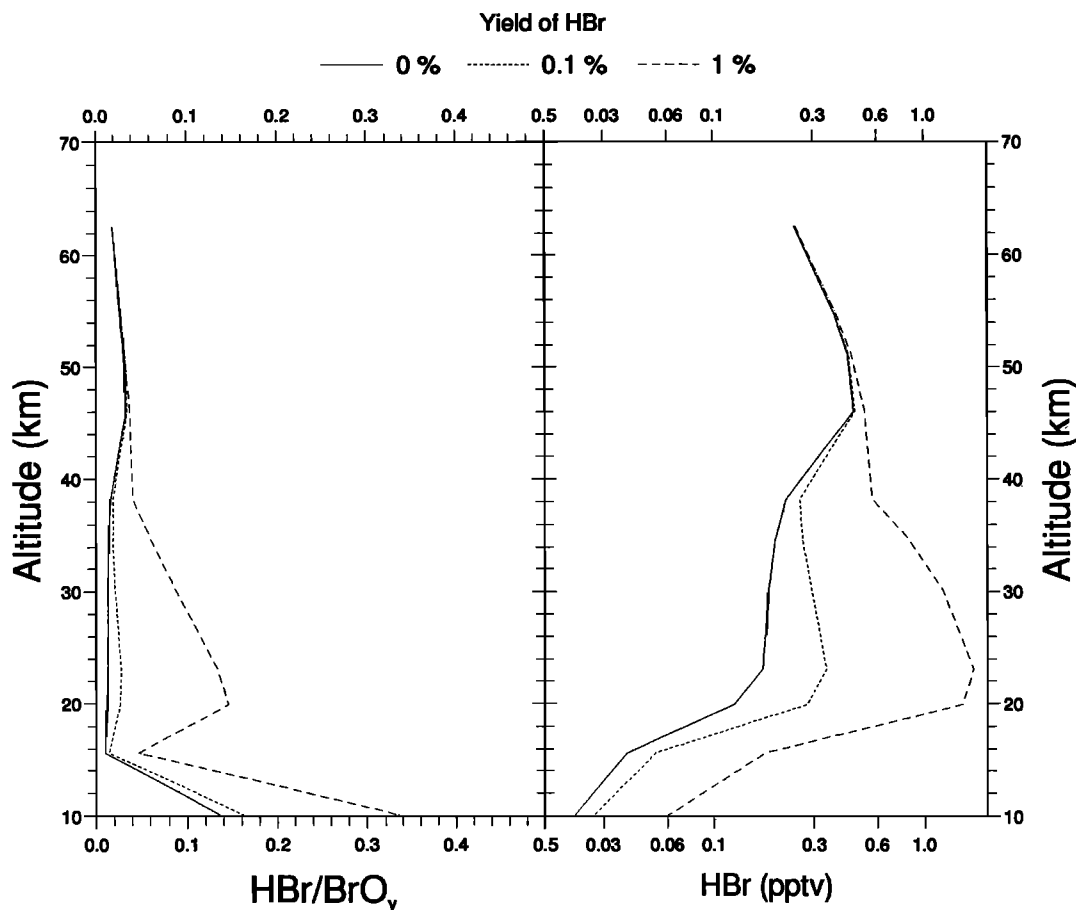
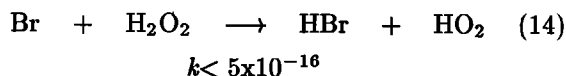


Figure 4. The calculated midlatitude concentration and fraction of BrO_y present as HBr for local noon at equinox if 0%, 0.1% and 1% of the reaction of HO_2 with BrO yields HBr. Heterogeneous bromine reactions were not included in these calculations.

and lower stratosphere is



There have been five different studies of reaction (14) by *Leu* [1980], *Posey et al.* [1981], *Heneghan and Benson* [1983], *Toohey et al.* [1987] and *Mellouki et al.* [1994]. Apart from *Heneghan and Benson* [1983] all show that Br has a very low reactivity towards H_2O_2 . *Mellouki et al.* [1994] suggest that this discrepancy may have been due to some reactive impurity from the microwave discharge source used by *Heneghan and Benson* [1983].

Mellouki et al. [1994] also considered the loss of HBr due to its reaction with HO_2 . They concluded that there was no measurable evidence for this reaction. If there is an additional source of HBr which could proceed at a rate comparable to reaction (1), it would considerably affect our understanding of the partitioning of reactive bromine.

Br

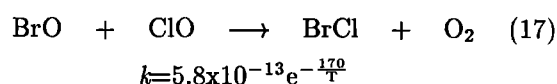
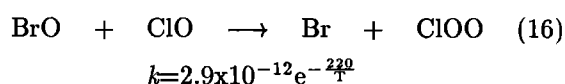
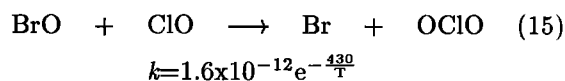
Br constitutes about 1% of BrO_y in the sunlit lower stratosphere, where it is in photochemical steady state with a lifetime of about half a second (the solid squares

in the left-hand panel of Figure 2). At 30 km approximately 10% of BrO_y is in the form of Br rising to over 90% above 50 km (the solid squares in the left-hand panel of Figure 3). This is in contrast to Cl, which in the lower stratosphere typically constitutes only around 0.001% of the total ClO_y (=Total inorganic chlorine), increasing to about 4% in the upper stratosphere. As one descends through the group of halogens from fluorine through to iodine, the partitioning shifts towards the more reactive species. Throughout most of the middle atmosphere the most important loss of Br is reaction with O_3 and the two most important sources of Br are the photolysis of BrO (reaction (6)) and the reaction of BrO with NO (reaction (7)). In the upper stratosphere the reaction of BrO with $\text{O}(^3\text{P})$ is the most important source of Br (reaction (8)). Two channels of the reaction of BrO with ClO contribute a few percent to the production of Br in the sunlit lower stratosphere (reactions (15) and (15) below), as does the photolysis of HOBr and BrONO_2 .

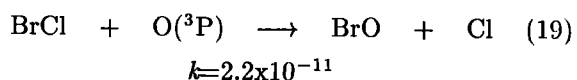
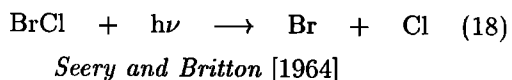
BrCl

The lifetime of BrCl in the sunlit lower stratosphere is approximately a minute (the open squares in the right-hand panel of Figure 2). During the day BrCl

generally constitutes much less than 1% of BrO_y in the lower stratosphere (Figure 3) when no heterogeneous reactions have occurred on polar stratospheric clouds (PSCs) for a long time. When PSCs, or cold sulfate aerosols, are encountered, the BrCl concentration rapidly increases and BrCl can become a sizable fraction of the total BrO_y . BrCl is typically the major nighttime reservoir of BrO_y when PSCs are present. The gas phase production of BrCl is almost entirely due to reaction (17):



The reaction of BrO with ClO is an important reaction as it is the first step in the catalytic loss of ozone due to the cycle described in the next section. The loss of BrCl below about 30 km is almost entirely due to photolysis, the peak BrCl absorption is at around 375 nm (*Seery and Britton* [1964], *R. A. Cox*, private communication [1993]). Above about 30 km the main loss of BrCl is due to the reaction with $\text{O}(^3\text{P})$. This reaction is not normally included in numerical models but its rate was determined by *Clyne et al.* [1976].



Catalytic Cycles

There are several important chain reactions involving atmospheric bromine species. These chains can propagate after an initiation step transforming reactants into products by repeated cycles of the chain. The length of these cycles is limited by termination steps which destroy the chain centre, or radical, involved in the cycle. The chain length is a measure of how many times the cycle is executed before the chain centre is removed. The chain length, \mathcal{N} , is usually 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 chain center, k_{dest} .

$$\text{chain length, } \mathcal{N} = k_{\text{rls}}/k_{\text{dest}} \quad (20)$$

In the atmosphere there are a very large number of interacting and competing cycles occurring. Therefore, a more useful definition has been used which defines the chain length in terms of the destruction of the long-

lived source gases, such as CH_3Br , instead of in terms of the production or destruction of a specific chain centre, such as Br or BrO . Because the chain length is a ratio of two rates it is dimensionless.

If a particular radical is involved in a catalytic cycle which has a very long chain length, but it is only present in small concentrations, the effectiveness of the cycle will be limited. It is therefore useful to define a new variable, which shall be called the chain effectiveness, as the chain length multiplied by the rate of the cycle's rate-limiting step. The chain effectiveness enables a fair comparison to be made of different catalytic cycles involving species which have very different concentrations.

$$\text{chain effectiveness, } \mathcal{E} = k_{\text{rls}} \mathcal{N} \quad (21)$$

This section considers the chain length and chain effectiveness of the various atmospheric bromine catalytic cycles as a function of altitude compared with other catalytic cycles which are of importance in the atmosphere. Because this paper focuses on the gas phase chemistry of atmospheric bromine, the situation chosen was noon for midlatitudes at the equinox.

As was seen earlier, all of the atmospheric bromine species are relatively short lived. Therefore, the termination steps of the gas phase bromine cycles which involve the formation of HBr or BrONO_2 are not very effective since the Br or BrO can easily be liberated from these species. In fact, BrONO_2 is itself involved in the catalytic heterogeneous destruction of ozone [*Lary et al.*, this issue], so formation of BrONO_2 is not even the termination of a chain. This is in marked contrast to the Cl/ClO and NO/NO_2 catalytic cycles, where the formation of the reservoirs HCl and HNO_3 is an effective termination of the chain reactions. Consequently, the bromine chain reactions tend to have longer chain lengths than their chlorine counterparts. Catalytic ozone loss can be due to several cycles involving bromine (Figure 5), which will now be considered in turn.

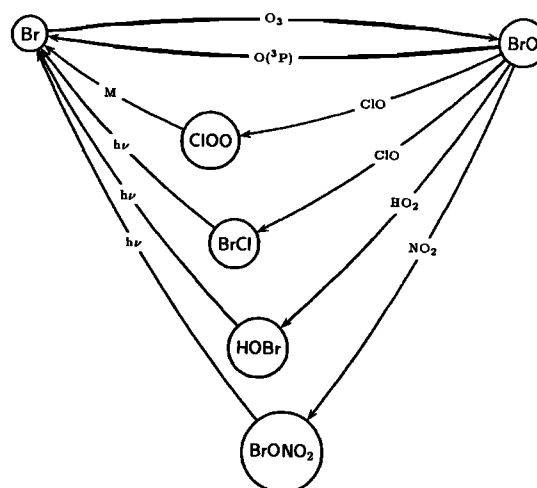


Figure 5. The bromine gas phase catalytic ozone destruction cycles.

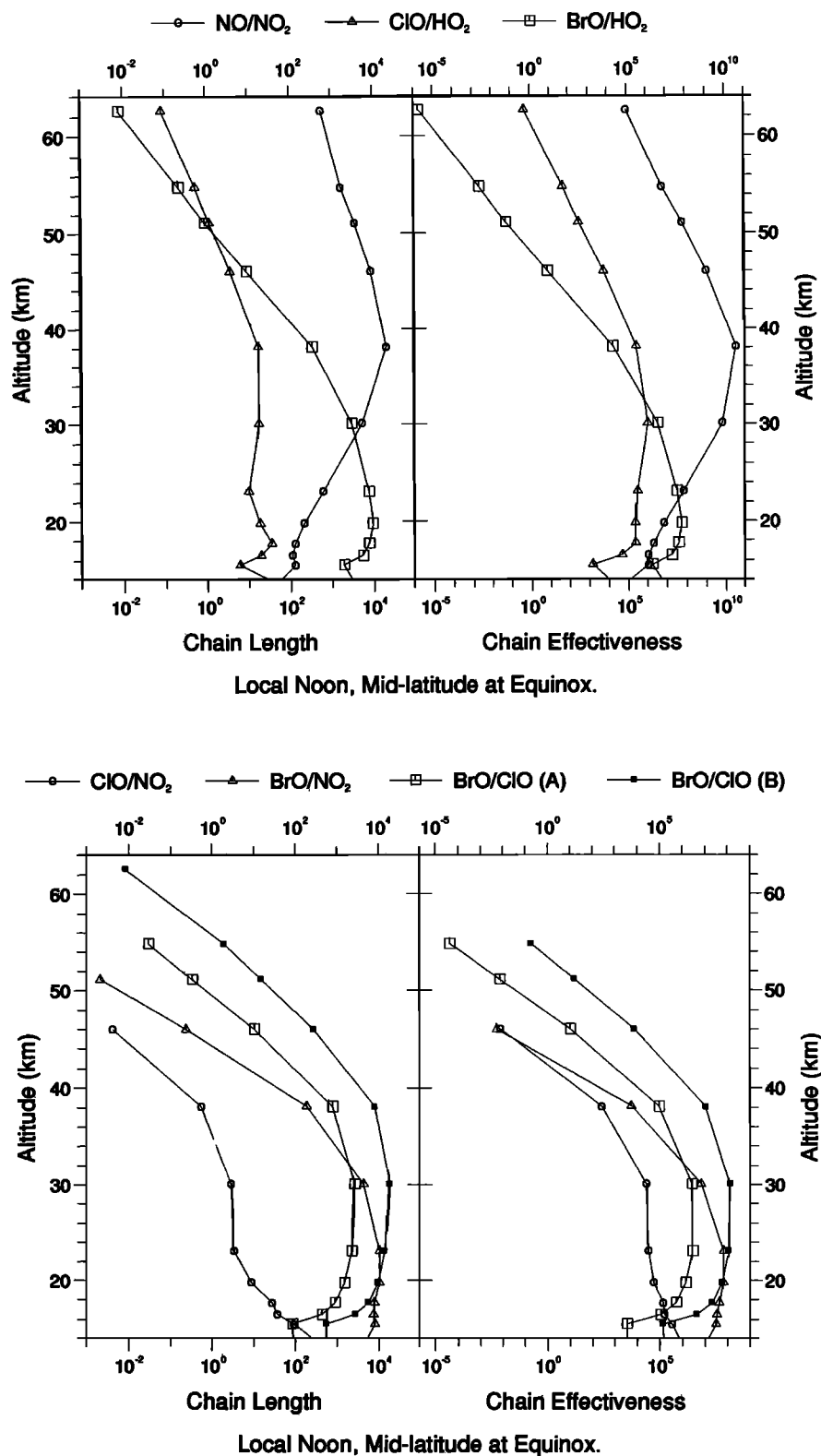
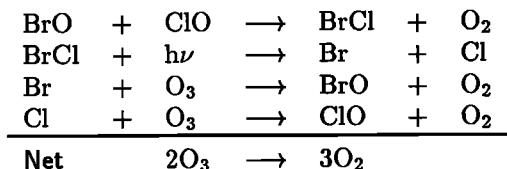


Figure 6. The calculated midlatitude chain length and chain effectiveness of various catalytic cycles for local noon at equinox. The chain effectiveness is the chain length multiplied by the rate of the cycle's rate-limiting step and has units of molecules cm⁻³ s⁻¹.

BrO/ClO

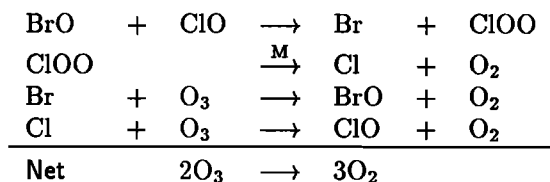
In polar regions the coupling of BrO and ClO chemistry via the BrO/ClO catalytic cycle is particularly important. The coupling is also important at midlatitudes. The BrO/ClO cycle can operate via two routes. One route, here referred to as route A, results in the formation of BrCl:



Depending on the physical conditions, in the low stratosphere below about 15 km the rate-limiting step is the formation of BrCl. However, higher up in the stratosphere it is the photolysis of BrCl.

In the sunlit stratosphere between 15 and 35 km this cycle has a chain length of approximately 10^3 with the chain length decreasing above 35 km (Figure 6). The chain effectiveness of this cycle is approximately 10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ between about 17 and 30 km (Figure 6). This can be compared to the NO/NO₂ catalytic cycle [Crutzen, 1970; Johnston, 1971], which is the most important ozone loss cycle at 38 km where it has a chain length of 10^4 and a chain effectiveness of approximately 10^{10} molecules $\text{cm}^{-3} \text{s}^{-1}$, decreasing to 10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ at 17 km and 10^2 molecules $\text{cm}^{-3} \text{s}^{-1}$ at 10 km (Figure 6).

The alternative cycle, here referred to as route B, is much more effective than route A and involves the formation of ClOO:

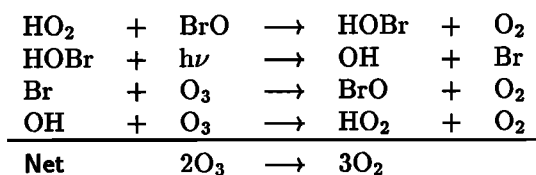


The rate-limiting step is the formation of ClOO. Throughout the sunlit lower stratosphere this cycle has a chain length of approximately 10^4 (Figure 6). The chain effectiveness of this cycle is approximately 10^8 molecules $\text{cm}^{-3} \text{s}^{-1}$ between about 20 and 30 km (Figure 6). Route B of the ClO/BrO catalytic cycle is approximately an order of magnitude more effective at destroying ozone between 16 and 20 km than the NO/NO₂ catalytic cycle.

The efficiency of the BrO/ClO cycle is reduced by the alternate channel of the BrO + ClO reaction which yields OClO (reaction (15)). OClO is photolyzed to give an oxygen atom, this channel constitutes a null cycle.

BrO/HO₂

The BrO/HO₂ catalytic cycle involves the formation of HOBr.

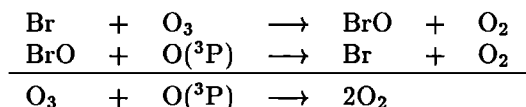


Below about 15 km the rate-limiting step is the photolysis of HOBr; above this the formation of HOBr is the rate limiting step. In the sunlit lower stratosphere this cycle has a long chain length of approximately 10^3 (Figure 6). The chain effectiveness of the BrO/HO₂ catalytic cycle is greater than 10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ between 13 and 30 km. The chain length and effectiveness decrease above 35 km. The BrO/HO₂ catalytic cycle is approximately 2 orders of magnitude more effective at destroying ozone at 12 km than the NO/NO₂ catalytic cycle, and twice as effective at 20 km.

The analogous ClO/HO₂ catalytic cycle has a much shorter chain length of less than 50 above 15 km, where the rate-limiting step is the photolysis of HOCl (Figure 6). The ClO/HO₂ chain length is approximately 10^2 close to the tropopause and in the troposphere, where the rate-limiting step is the reaction of OH with O₃. Between 15 and 20 km the BrO/HO₂ cycle is between 1 and 2 orders of magnitude more effective than the ClO/HO₂ cycle at destroying ozone, even though BrO is much less abundant than ClO. This finding emphasizes the importance of atmospheric bromine for catalytic ozone destruction.

Br/BrO

The Br/BrO catalytic cycle increases in length from 10^2 in the lower stratosphere to 10^4 in the upper stratosphere (Figure 6).



At all sunlit altitudes the reaction of BrO with O(³P) is the rate limiting step. The chain effectiveness increases from 10^3 molecules $\text{cm}^{-3} \text{s}^{-1}$ at 12 km to 10^9 molecules $\text{cm}^{-3} \text{s}^{-1}$ at 38 km (Figure 7). The analogous Cl/ClO has a shorter chain length, which increases from 10 in the lower stratosphere to 10^3 in the upper stratosphere and has a chain effectiveness which increases from 10^2 molecules $\text{cm}^{-3} \text{s}^{-1}$ at 12 km to 10^{10} molecules $\text{cm}^{-3} \text{s}^{-1}$ at 38 km. Consequently at 38 km the NO/NO₂ cycle is the main ozone loss cycle but above this the Cl/ClO cycle is the main ozone loss cycle [Stolarski and Cicerone, 1974; Molina and Rowland, 1974].

BrO/NO₂

As was recently pointed out by Burkholder *et al.* [1995], if the products of BrONO₂ photolysis are Br and NO₃, then a very effective BrONO₂ catalytic cycle can exist, namely

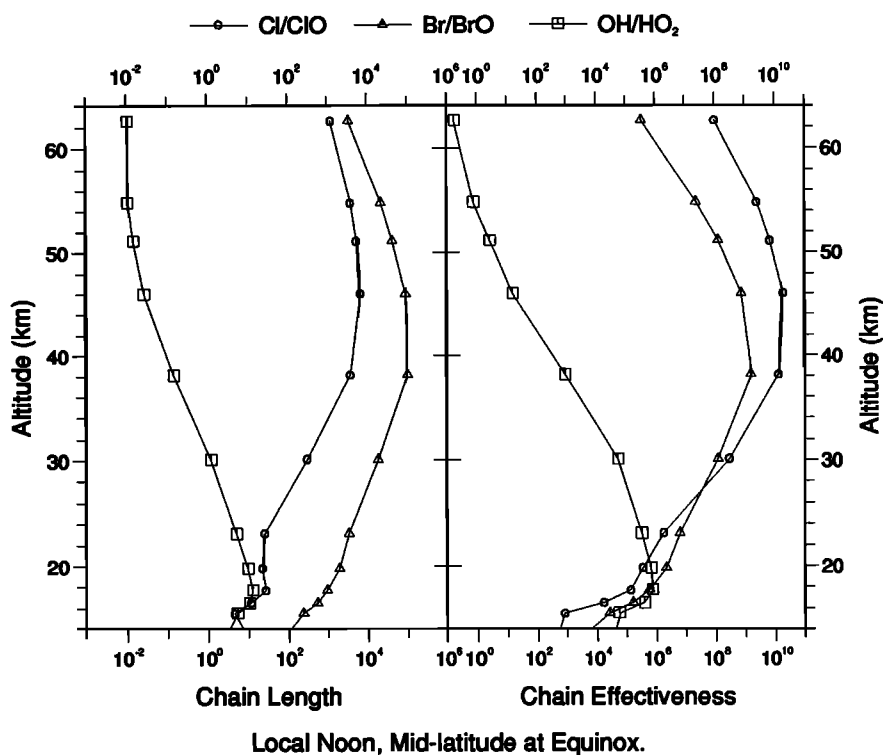
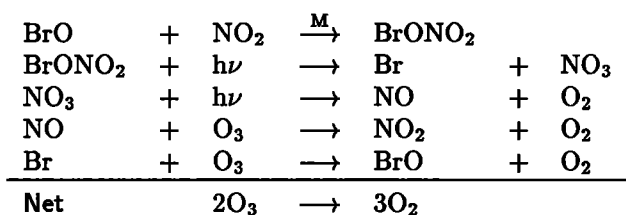


Figure 7. The calculated midlatitude chain length and chain effectiveness of various catalytic cycles for local noon at equinox.



Depending on the conditions, the rate-limiting step of the cycle is the photolysis of BrONO₂ or of NO₃ to NO. If it is assumed that the main BrONO₂ photolysis products are Br and NO₃ then the BrO/NO₂ cycle between about 15 km and 30 km has a chain length of more than 10³. The chain length decreases above 30 km. The chain effectiveness is approximately 10⁷ molecules cm⁻³ s⁻¹ between about 15 and 30 km (Figure 6). This result can be compared to the analogous ClO/NO₂ cycle [Toumi *et al.*, 1993] which has a chain length of about 10² at the tropopause decreasing to only 3 at 40 km, and a chain effectiveness of 10⁵ molecules cm⁻³ s⁻¹ close to the tropopause decreasing to 10² molecules cm⁻³ s⁻¹ at 38 km. This finding emphasizes the point made by Toumi *et al.* [1993] that the ClO/NO₂ cycle is only important for high levels of ClONO₂. For typical levels of BrONO₂ and ClONO₂ the BrO/NO₂ cycle is more effective at removing ozone than the analogous ClO/NO₂ cycle.

Summary

The current knowledge of gas phase bromine chemistry has been reviewed and two gas phase reactions

not normally considered have been found to be important in the upper stratosphere. They are the reactions of O(³P) with BrCl and HOBr whose rates were measured by Clyne *et al.* [1976] and Nesbitt *et al.* [1995], respectively.

The effectiveness of the ozone catalytic loss cycles involving bromine has been quantified by considering their chain length and effectiveness. The chain effectiveness is a new variable defined as the chain length multiplied by the rate of the cycle's rate-limiting step. The chain effectiveness enables a fair comparison of different catalytic cycles involving species which have very different concentrations.

It is shown that in the low stratosphere the most effective ozone loss cycles are the BrO/HO₂ and BrO/ClO cycles. Both catalytic cycles have long chain lengths of greater than 10³ and a chain effectiveness of between 10⁶ and 10⁸ molecules cm⁻³ s⁻¹ in the lower stratosphere. The cycles are therefore effective ozone destruction cycles even when no PSCs are present.

If it is assumed that the main photolysis products of BrONO₂ are Br and NO₃, then the BrO/NO₂ cycle between about 15 km and 30 km has a chain length of at least 10³. The chain length decreases above 30 km. This cycle will only be effective for ozone loss if BrONO₂ photolysis leads to the production of Br and NO₃. This conclusion agrees with the recent findings of Burkholder *et al.* [1995] and can be compared to the analogous ClO/NO₂ cycle [Toumi *et al.*, 1993], which has a chain length of about 10² at the tropopause decreasing to only 3 at 40 km.

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