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Catalytic destruction of stratospheric ozone

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Abstract. This paper presents a review of the main ozone destroying catalytic cycles operating in the stratosphere. Particular attention is paid to the kinetic aspects of these cycles such as the rate limiting step and chain length. Although it is an important kinetic parameter, the chain length of the various cycles is seldom considered when the various catalytic cycles are discussed. This survey highlights that in the low stratosphere the cycles involving HO_2 and halogens (notably bromine) are particularly important. In approximate order of effectiveness the most important ozone loss cycles in the polar lower stratosphere are the BrO/ClO, HO_2/BrO, and OH/HO_2 cycles.

Introduction

The importance of atmospheric catalytic cycles was first recognised by *Bates and Nicolet* [1950]. Since then, it has become well established that the concentration of stratospheric ozone is controlled by the balance between its production, and its destruction, and that the destruction of ozone is mainly due to catalytic cycles involving nitrogen, hydrogen, chlorine, and bromine species. A comprehensive introduction to these cycles is presented by, for example, *Johnston and Podolske* [1978], *Brasseur and Solomon* [1986], *Wayne* [1991] and the reports of the *World Meteorological Organization (WMO)* [1986, 1990, 1992, 1994]. One of several useful historical overviews has been presented by *Schmidt* [1988].

The recent WMO assessments [*WMO*, 1992, 1994] reported that for the first time there are statistically significant decreases in ozone in all seasons in both the northern and southern hemispheres at mid and high latitudes during the 1980s, and that most of this decrease is occurring in the lower stratosphere. This has also been supported by trends derived from ozone sondes [*Logan*, 1994].

The effectiveness of catalytic cycles in destroying ozone is controlled by two factors, the chain length of the catalytic cycles and the abundance of the radical which is the chain center. The chain length is the number of times the catalytic cyclic is executed before the reactive radical involved, the chain center, is destroyed. To date, the chain length of catalytic ozone destruction cycles has received relatively little attention, with emphasis being placed almost exclusively on the abundance of the chain centers involved. It is therefore valuable to systematically consider the effectiveness of the ozone destruction cycles in the stratosphere. This study examines the chain length and the rate of catalytic cycles for the conditions typically encountered in the stratosphere.

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Chain Length and Effectiveness

The chain length of catalytic cycles is limited by termination steps which destroy the chain center (radical) involved in the cycle. The chain length $\mathcal{N}$ is usually defined as the rate of propagation (ρ) divided by the rate of termination. The rate of propagation is the rate of the rate limiting step. The rate of termination is the rate of production or destruction (δ) of the chain center.

$$\mathcal{N} = \frac{\rho}{\delta} \tag{1}$$

If a particular radical is involved in a catalytic cycle which has a very long chain length but is present in only small concentrations, the effectiveness of the cycle will be limited. It is therefore useful for us to define a chain effectiveness $\aleph$. This is particularly useful when comparing different cycles involving radicals present in very different amounts, for example, when comparing HO_x, ClO_x, BrO_x, and NO_x catalytic cycles which destroy O_3.

$$\aleph = \mathcal{N}\,\rho \tag{2}$$

Care needs to be taken when δ becomes very small as then very long chain lengths are calculated, which in turn can lead to a large chain effectiveness even if the rate of propagation ρ is tiny.

The following sections consider the chain length and chain effectiveness of the various atmospheric catalytic cycles as a function of altitude and latitude. The numerical model used was the AUTOCHEM model described by *Lary et al.* [1995, 1996], *Lary* [1996], and *Fisher and Lary* [1995]. The version of the model used in this study contains a total of 81 species. Of these, 74 species are integrated, namely: $O(^1D)$, $O(^3P)$, O_3, N, NO, NO_2, NO_3, N_2O_5, HONO, HNO_3, HO_2NO_2,

CN, NCO, HCN, Cl, Cl_2, ClO, ClOO, OClO, Cl_2O_2, $ClNO_2$, $ClONO_2$, HCl, HOCl, CH_3OCl, Br, Br_2, BrO, $BrONO_2$, BrONO, HBr, HOBr, MeOBr, BrCl, H_2, H, OH, HO_2, H_2O_2, CH_3, CH_3O, CH_3O_2, CH_3OOH, CH_3ONO_2, $CH_3O_2NO_2$, HCO, HCHO, CF_3, CF_3O, CF_3O_2, CF_3OOCl, CF_3OH, CF_3OOH, CF_3OONO_2, F, F_2, FO, FO_2, F_2O_2, COF_2, FCO, FCOO, FCOOH, $FC(O)O_2$, FNO, FONO, FO_2NO_2, HF, CH_4, CHF_3, CH_3Br, CF_2Cl_2, N_2O, and CO. The remaining seven species are not integrated and not in photochemical equilibrium, namely: CO_2, H_2O, O_2, N_2, $HCl_{(S)}$, $H_2O_{(S)}$, and $HNO_{3(S)}$. The model contains a total of 438 reactions, 287 bimolecular reactions, 43 trimolecular reactions, 65 photolysis processes, and 43 heterogeneous reactions.

Hydrogen Catalytic Cycles

One of the early landmarks in the atmospheric chemistry of odd hydrogen radicals occurred in 1964 when J. Hampson highlighted the fact that $O(^1D)$ produced by O_3 photolysis at wavelengths <310 nm led to the formation of hydroxyl radicals due to the reaction of $O(^1D)$ with water vapor. This led to the socalled "wet theory" of stratospheric ozone. In 1965, E. Hesstvedt and P.L. Roney published the first papers which included the effects of odd hydrogen radicals on the photochemistry of ozone. In 1969, P.J. Crutzen published a further paper which considered the effect of odd hydrogen radicals on ozone loss.

Figure 1 schematically shows the main HO_x ozone loss catalytic cycles. Catalytic cycles involving HO_2 are very important in the lower stratosphere. The fastest of these cycles is

OH/HO_2, HO_x cycle 1

$$OH + O_3 \longrightarrow HO_2 + 2O_2 \quad (3)$$

$$HO_2 + O_3 \longrightarrow OH + O_2 \quad (4)$$

$$\text{Net} : 2O_3 \longrightarrow 2O_2$$

This cycle has a rate of between 10^4 and 10^5 molecules cm^{-3} s^{-1} between 10 and 35 km and a chain length of between 1 and 40 in the midlatitude lower stratosphere (Figure 2). At midlatitudes it has a peak chain effectiveness of 10^6 molecules cm^{-3} s^{-1} at around 20 km (Figure 2). However, the cycle is also effective at destroying ozone in the winter polar lower stratosphere (Figure 3). At approximately 15 km and above the rate limiting step is the reaction of O_3 with HO_2 (i.e., the rate of propagation is given by $\rho = k_4[O_3][HO_2]$). Below approximately 15 km the rate limiting step is the reaction of OH with O_3 ($\rho = k_3[O_3][OH]$). However, both reactions (3) and (4) are fast.

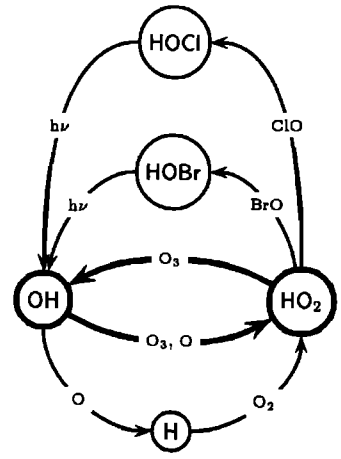

Figure 1. A schematic of the main HO_x ozone loss catalytic cycles.

The HO_2 cycle involving ClO is also important.

HO_2/ClO, HO_x cycle 2

$$ClO + HO_2 \longrightarrow HOCl + O_2 \quad (5)$$

$$HOCl + h\nu \longrightarrow Cl + OH \quad (6)$$

$$Cl + O_3 \longrightarrow ClO + O_2 \quad (7)$$

$$OH + O_3 \longrightarrow HO_2 + 2O_2$$

$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

At midlatitudes this cycle has a peak rate of 10^4 molecules cm^{-3} s^{-1} and a chain length of between 1 and 25 in the lower stratosphere (Figure 2). It has a peak chain effectiveness of 10^6 molecules cm^{-3} s^{-1} at around 25 km (Figure 2). The cycle is very effective at destroying ozone in the midlatitude lower stratosphere and also plays a role in the sunlit polar lower stratosphere (Figure 3). The cycle is not effective in the dark as throughout the stratosphere the rate limiting step is the photolysis of HOCl ($\rho = j_{HOCl}$ [HOCl]). The cycle forms an important link between chlorine and odd-hydrogen chemistry.

HO_2/BrO, HO_x cycle 3

$$BrO + HO_2 \longrightarrow HOBr + O_2 \quad (8)$$

$$HOBr + h\nu \longrightarrow Br + OH \quad (9)$$

$$Br + O_3 \longrightarrow BrO + O_2 \quad (10)$$

$$OH + O_3 \longrightarrow HO_2 + 2O_2$$

$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

This cycle has a peak rate of 10^4 molecules cm^{-3} s^{-1} and a chain length of between 1 and over 1000 in the stratosphere (Figure 2). It has a peak chain effectiveness of almost 10^7 molecules cm^{-3} s^{-1} at around 20 km (Figures 2 and 3). Throughout the stratosphere the rate limiting step is the photolysis of HOBr ($\rho =$

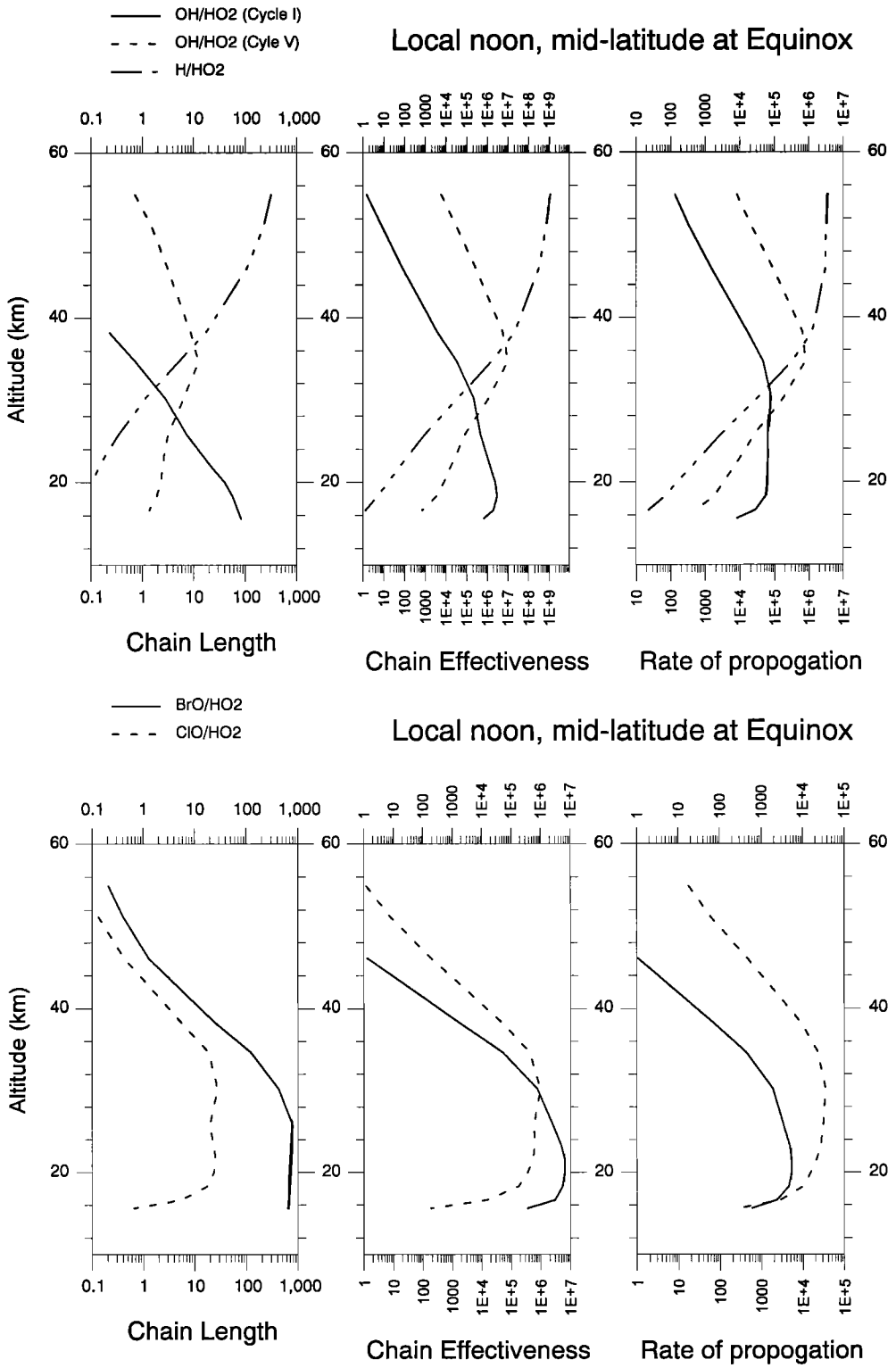

Figure 2. The calculated chain effectiveness, rate, and chain length of various HO_x ozone loss catalytic cycles for local noon at midlatitudes at equinox.

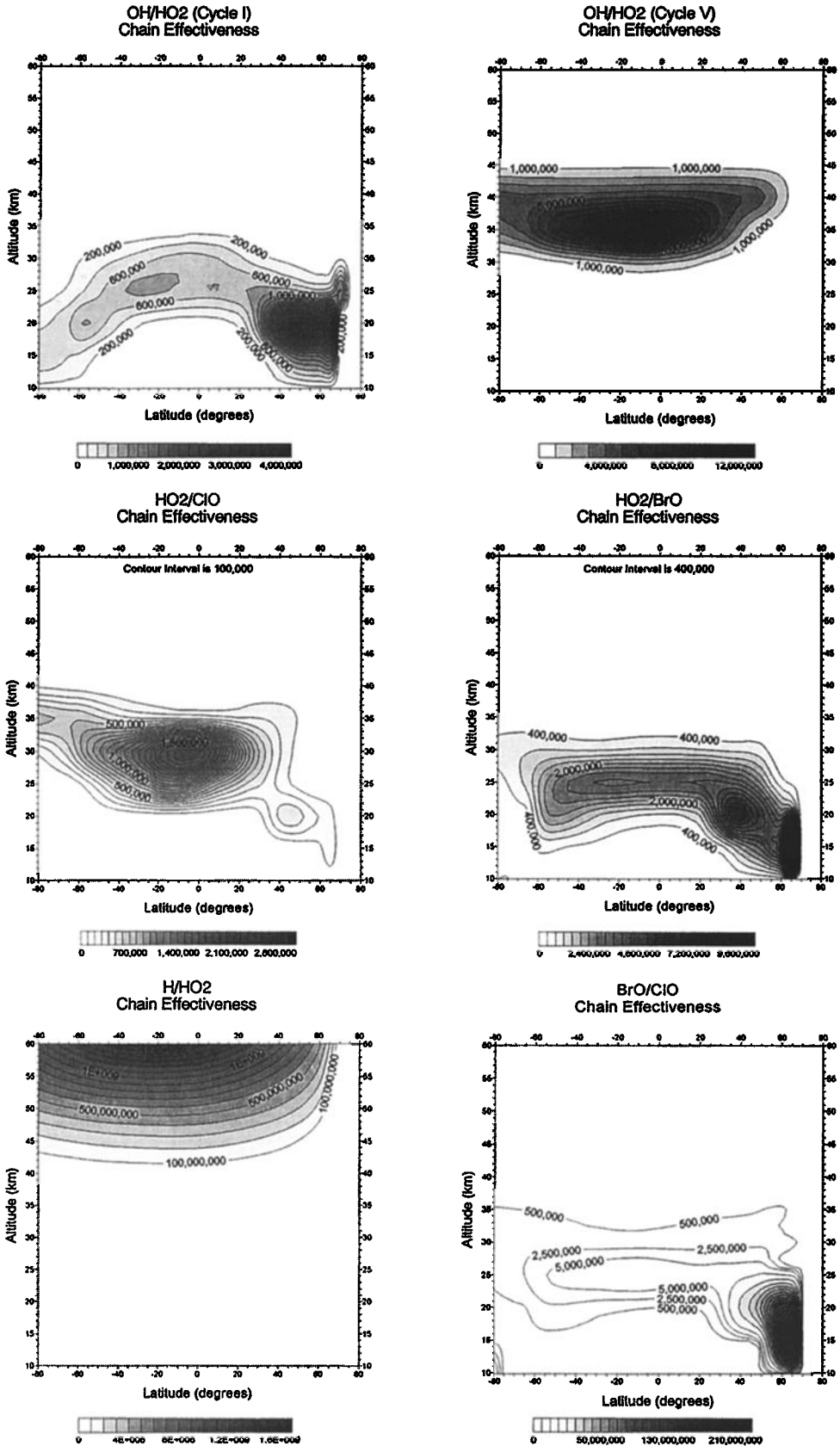

Figure 3. The calculated variation in the chain effectiveness of various cycles for the winter solstice as a function of altitude and latitude.

j_{HOBr} [HOBr]). The cycle forms an important link between bromine and hydrogen chemistry and is particularly effective at destroying ozone in the sunlit part of the winter polar lower stratosphere (Figure 3).

H/OH/HO_2, HO_x cycle 4

$$H + O_2 \xrightarrow{M} HO_2 \quad (11)$$
$$HO_2 + O(^3P) \longrightarrow OH + O_2 \quad (12)$$
$$OH + O(^3P) \longrightarrow H + O_2 \quad (13)$$
$$\text{Net}: 2O(^3P) \longrightarrow O_2$$

This is one of the most effective ozone loss cycles in the upper stratosphere (Figures 2 and 3). This cycle has a peak rate of 10^6 molecules cm^{-3} s^{-1} and a chain length of between 1 and a few hundred in the stratosphere. It has a peak chain effectiveness of 10^9 molecules cm^{-3} s^{-1} at between 50 and 70 km (Figure 2). Below approximately 35 km the rate limiting step is the reaction of $O(^3P)$ with OH, reaction (13) ($\rho = k_{13}[O(^3P)][OH]$). All three reactions involved in this cycle are fast in the upper stratosphere. Above approximately 35 km the rate limiting step is either the reaction of $O(^3P)$ with HO_2, reaction (12) ($\rho = k_{12}[O(^3P)][HO_2]$), or the reaction of H with O_2 ($\rho = k_{11}[O_2][H]$), reaction (11).

There is another OH/HO_2 cycle which is effective in the mid to upper stratosphere but which is not as fast HO_x Cycle 1.

OH/HO_2, HO_x Cycle 5

$$OH + O_3 \longrightarrow HO_2 + 2O_2$$
$$HO_2 + O(^3P) \longrightarrow OH + O_2$$
$$\text{Net}: O(^3P) + O_3 \longrightarrow 2O_2$$

This cycle has a peak rate of approximately 10^6 molecules cm^{-3} s^{-1} between 30 and 40 km where it has a chain length of between 1 and 12 (Figure 2). It has a peak chain effectiveness of approximately 10^7 molecules cm^{-3} s^{-1} at between 35 and 40 km (Figure 2). At 35 km and above the rate limiting step is the reaction of O_3 with OH ($\rho = k_3[O_3][OH]$); below this it is the reaction of HO_2 with $O(^3P)$ ($\rho = k_{12}[O(^3P)][HO_2]$).

For all of the reactive hydrogen catalytic cycles just considered the rate of destruction of the chain center has been taken as the rate of formation of H_2 and H_2O; namely, δ = k[H][HO2] + k[OH]^2 + k[OH][HO_2]. Let us now turn our attention to some chlorine cycles.

Chlorine Catalytic Cycles

The early landmark in the atmospheric chemistry of reactive chlorine radicals occurred when *Molina and Rowland* [1974] published their famous paper which showed that the stratosphere was the only sink for chlorofluoromethanes, and that ozone destruction would result as a consequence of the chlorine released. This was closely followed by the work of *Stolarski and Cicerone* [1974] and *Rowland and Molina* [1975]. Then *Farman et al.* [1985] discovered the ozone hole and suggested that it was due to the interaction of atmospheric chlorine and nitrogen.

Figure 4 schematically shows the main ClO_x ozone loss catalytic cycles.

Cl/ClO, ClO_x cycle 1

$$ClO + O(^3P) \longrightarrow Cl + O_2 \quad (14)$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$\text{Net}: O(^3P) + O_3 \longrightarrow 2O_2$$

Between approximately 40 and 50 km this is one of the most effective ozone loss cycles (Figures 5 and 6). At midlatitudes it has a peak rate of 10^6 molecules cm^{-3} s^{-1} and a chain length of greater than 10 throughout most of the stratosphere and of approximately 10^3 in the upper stratosphere (Figures 5 and 6). It has a peak chain effectiveness of approximately 10^8 molecules cm^{-3} s^{-1} at between 35 and 45 km (Figure 5). The rate limiting step is the reaction of $O(^3P)$ with ClO ($\rho = k_{14}[O(^3P)][ClO]$).

ClO/ClO, ClO_x cycle 2

$$ClO + ClO \xrightarrow{M} Cl_2O_2 \quad (15)$$
$$Cl_2O_2 + h\nu \longrightarrow Cl + ClOO \quad (16)$$
$$ClOO \xrightarrow{M} Cl + O_2 \quad (17)$$
$$2 \text{ x } (Cl + O_3 \longrightarrow ClO + O_2)$$
$$\text{Net}: 2O_3 \longrightarrow 3O_2$$

In the midlatitude lower stratosphere between approximately 20 and 25 km this cycle has a peak rate of 10^4 molecules cm^{-3} s^{-1} (Figure 5). However, when

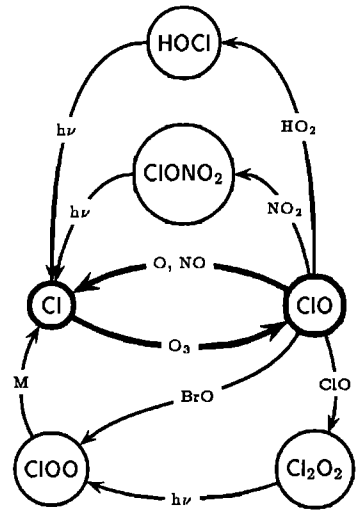

Figure 4. A schematic of the main ClO_x ozone loss catalytic cycles.

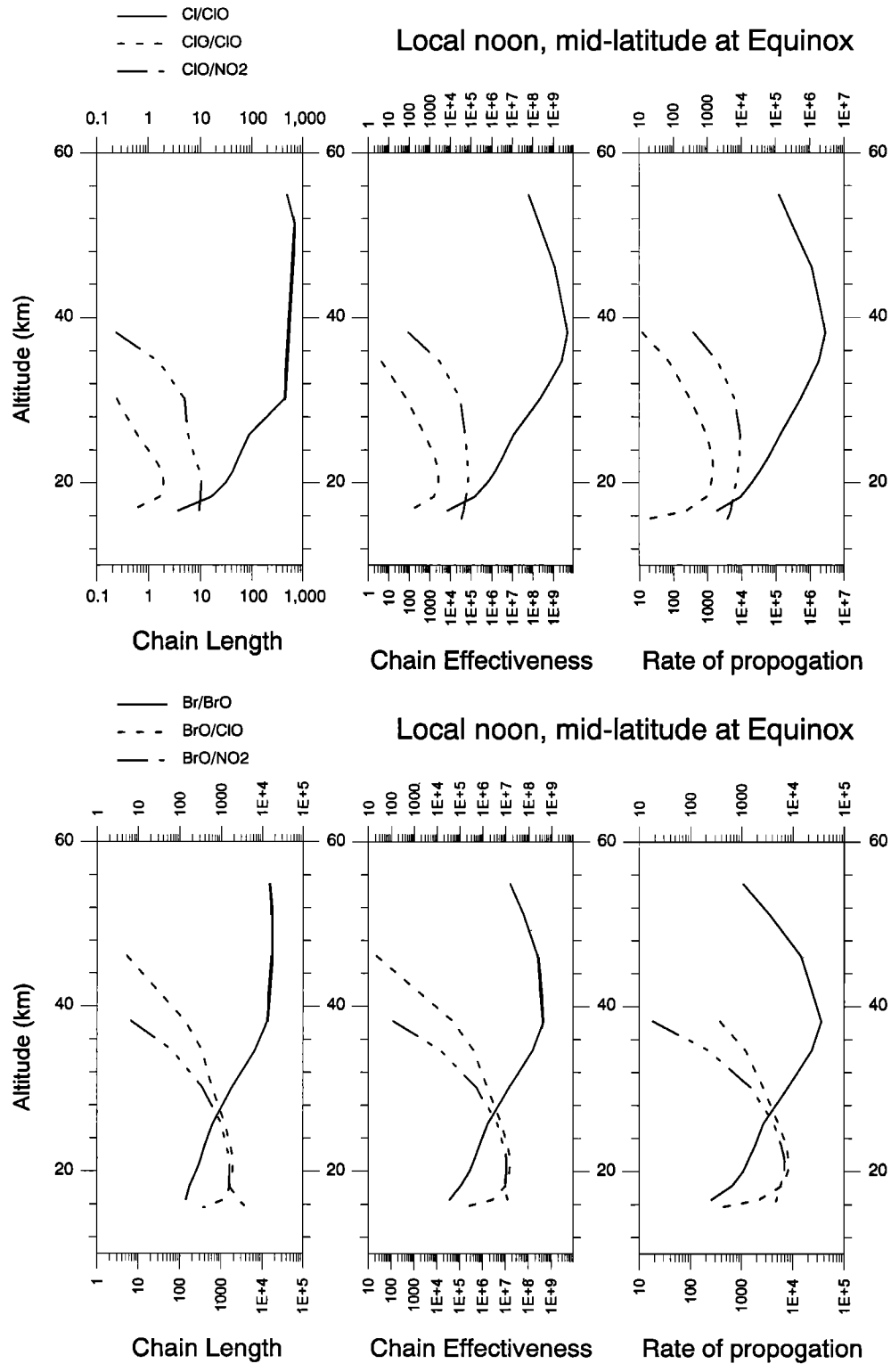

Figure 5. The calculated chain effectiveness, rate, and chain length of various chlorine and bromine ozone loss catalytic cycles for local noon at midlatitudes at equinox.

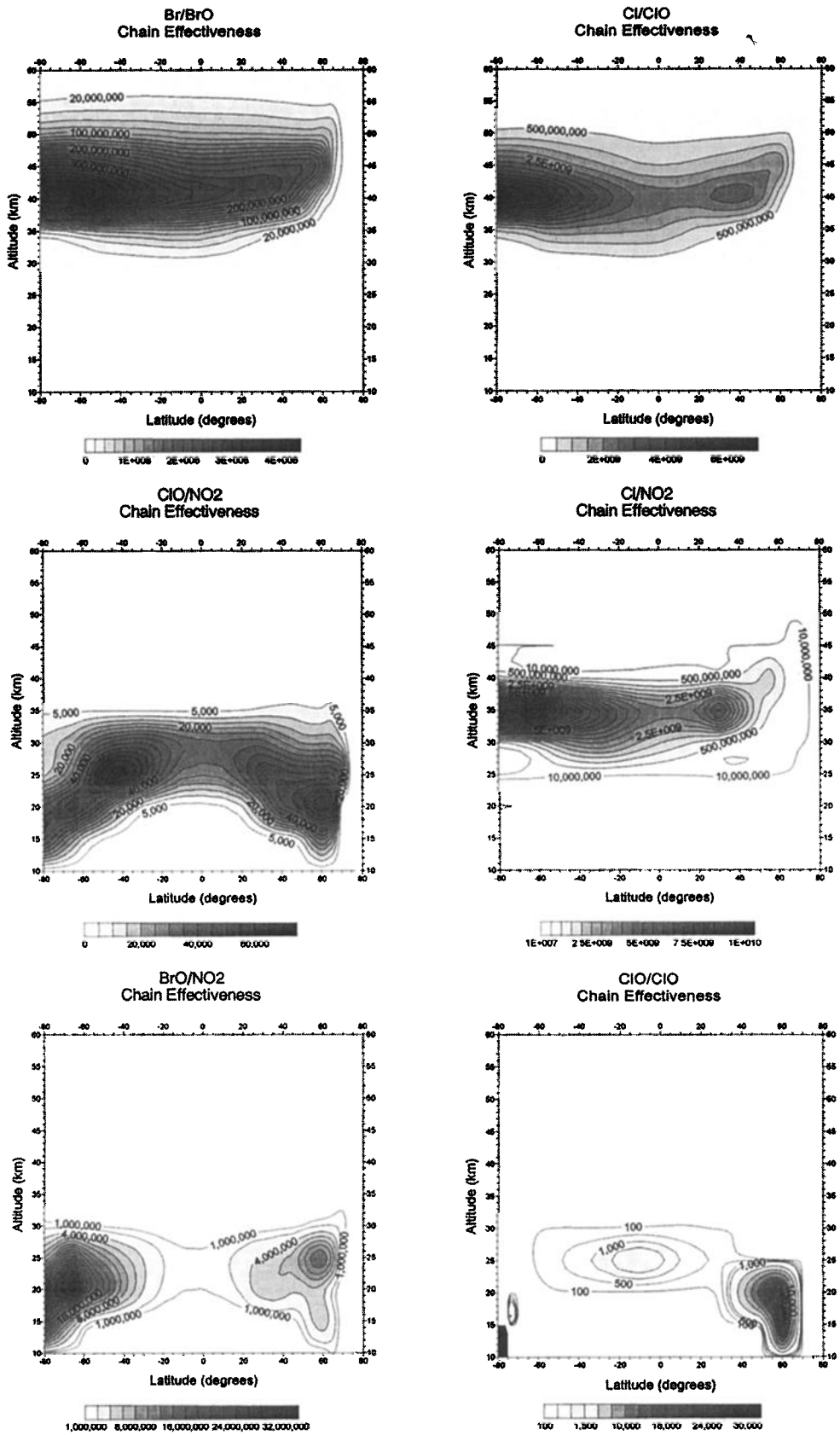

Figure 6. The calculated variation in the chain effectiveness of various cycles for the winter solstice as a function of altitude and latitude.

cold aerosols and polar stratospheric clouds (PSCs) are absent, it is barely catalytic in this region (Figures 5 and 6). At midlatitudes it has a peak chain effectiveness of approximately 10^3 molecules cm^{-3} s^{-1} at between 20 and 25 km (Figure 5) increasing to $2x10^4$ molecules cm^{-3} s^{-1} in the polar lower stratosphere. In the stratosphere the rate limiting step is the photolysis of Cl_2O_2 ($\rho = j_{Cl_2O_2}$ $[Cl_2O_2]$).

Cl/NO_2, ClO_x cycle 3

$$ClO + NO \longrightarrow Cl + NO_2 \quad (18)$$
$$NO_2 + O(^3P) \longrightarrow NO + O_2 \quad (19)$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$\text{Net} : O(^3P) + O_3 \longrightarrow 2O_2$$

This is the cycle that *Farman et al.* [1985] suggested was involved with the formation of the ozone hole. Although it is an effective ozone loss cycle over a large altitude range, namely, between 15 and 50 km (Figure 10), it is most effective at midlattitudes and in the summer midstratosphere. It is not as effective in the spring polar lower stratosphere (Figure 6), whereas the next cycle, the ClO/NO_2 cycle is. It has a peak rate of 10^6 molecules cm^{-3} s^{-1} between 30 and 40 km. The cycle has a chain length of greater than 1 throughout the stratosphere reaching approximately 1000 at around 30 km. At midlatitudes it has a peak chain effectiveness of approximately 10^9 molecules cm^{-3} s^{-1} at between 30 and 40 km (Figure 10), but reaches 10^{10} molecules cm^{-3} s^{-1} at high latitudes in summer (Figure 6). At approximately 25 km and above the rate limiting step is the reaction of ClO with NO ($\rho = k_{18}[ClO][NO]$). Below this it is the reaction of $O(^3P)$ with NO_2 ($\rho = k_{19}[O(^3P)][NO_2]$).

ClO/NO_2, ClO_x cycle 4

$$ClO + NO_2 \xrightarrow{M} ClONO_2 \quad (20)$$
$$ClONO_2 + h\nu \longrightarrow Cl + NO_3 \quad (21)$$

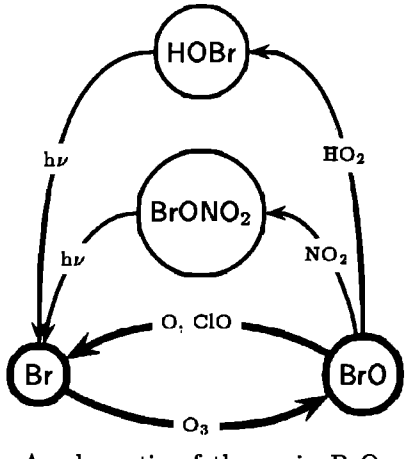

Figure 7. A schematic of the main BrO_x ozone loss catalytic cycles.

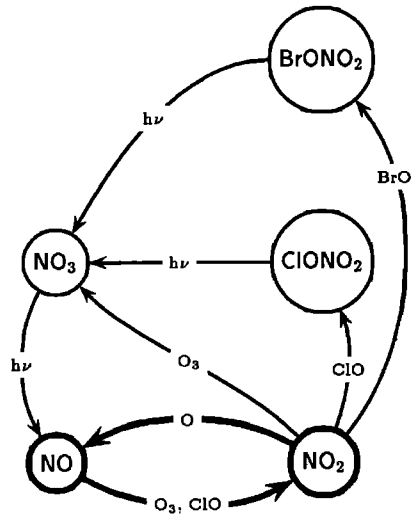

Figure 8. A schematic of the main NO_x ozone loss catalytic cycles.

$$NO_3 + h\nu \longrightarrow NO + O_2 \quad (22)$$
$$NO + O_3 \longrightarrow NO_2 + O_2$$
$$Cl + O_3 \longrightarrow ClO + O_2$$
$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

Between 15 and 40 km the ClO/NO_2 cycle is an effective ozone loss cycle (Figure 5). It has a peak rate of 10^4 molecules cm^{-3} s^{-1} between 20 and 25 km and a chain length of between 1 and 10 between 15 and 35 km (Figures 5 and 6). It has a peak chain effectiveness of approximately 10^5 molecules cm^{-3} s^{-1} at 20 km (Figure 5). Between approximately 45 and 10 km the rate limiting step is the photolysis of NO_3 ($\rho = j_{NO_3}$ $[NO_3]$). For most of the region above 45 km the rate limiting step is the reaction of ClO with NO_2 ($\rho = k_{20}[ClO][NO_2]$).

For all of the reactive chlorine catalytic cycles just considered the rate of destruction of the chain center has been taken as the rate of formation of HCl; namely, $\delta = k[Cl][H_2] + k[Cl][CH4] + k[Cl][H_2O] + k[Cl][HO_2] + k[Cl][HCHO] + k[Cl][CH_3OOH]$.

Let us now turn our attention to some bromine catalytic cycles.

Bromine Catalytic Cycles

The atmospheric chemistry of bromine and its synergy with chlorine was first studied in detail by *Wofsy et al.* [1975] and *Yung et al.* [1980]. *Lary* [1996] and *Lary et al.* [1996] present a review of the atmospheric gas phase and heterogeneous chemistry of bromine. Figure 7 schematically shows the main BrO_x ozone loss catalytic cycles.

Br/BrO, BrO_x cycle 1

$$BrO + O(^3P) \longrightarrow Br + O_2 \quad (23)$$

$$\begin{aligned} Br + O_3 &\longrightarrow BrO + O_2 \quad (24)\\ \text{Net}: O(^3P) + O_3 &\longrightarrow 2O_2 \end{aligned}$$

This cycle has a peak rate of 10^4 molecules cm^{-3} s^{-1} at between 35 and 45 km and a chain length of greater than 50 throughout the stratosphere (Figures 5 and 6), with a chain length of greater than 10^4 at 40 km. The cycle has a peak chain effectiveness of approximately 10^8 molecules cm^{-3} s^{-1} at between 35 and 45 km (Figure 5). At all altitudes the rate limiting step is the reaction of $O(^3P)$ with BrO ($\rho = k_{23}[O(^3P)][BrO]$). However, both reactions (23) and (10) are fast.

BrO/ClO, BrO_x cycle 2

$$\begin{aligned} BrO + ClO &\longrightarrow Br + ClOO \quad (25)\\ ClOO &\xrightarrow{M} Cl + O_2\\ Cl + O_3 &\longrightarrow ClO + O_2\\ Br + O_3 &\longrightarrow BrO + O_2\\ \text{Net}: 2O_3 &\longrightarrow 3O_2. \end{aligned}$$

Of all the bromine cycles this is the most important for high-latitude, lower-stratosphere ozone loss with a chain effectiveness which reaches 10^8 molecules cm^{-3} s^{-1} in the polar lower stratosphere (Figure 3).

The reaction of BrO with ClO has several channels. The most effective ozone loss channel is the one yielding ClOO. This cycle has a peak rate of almost 10^4 molecules cm^{-3} s^{-1} at between 20 and 25 km and a chain length of greater than 1 between 15 and 45 km and is approximately 10^3 in the lower stratosphere (Figure 5). Between 20 and 25 km the chain length approaches 2000. At midlatitudes the cycle has a peak chain effectiveness of approximately 10^7 molecules cm^{-3} s^{-1} at between 20 and 25 km (Figure 5). At all altitudes the rate limiting step is the reaction of BrO with ClO ($\rho = k_{25}[BrO][ClO]$).

BrO/NO_2, BrO_x cycle 3

$$\begin{aligned} BrO + NO_2 &\xrightarrow{M} BrONO_2 \quad (26)\\ BrONO_2 + h\nu &\longrightarrow Br + NO_3 \quad (27)\\ NO_3 + h\nu &\longrightarrow NO + O_2\\ NO + O_3 &\longrightarrow NO_2 + O_2\\ Br + O_3 &\longrightarrow BrO + O_2\\ \text{Net}: 2O_3 &\longrightarrow 3O_2 \end{aligned}$$

This cycle will only be effective if $BrONO_2$ photolyses to give NO_3 [*Lary et al.*, 1996]. If it does, as has been assumed here, then this cycle has a peak rate of almost 10^4 molecules cm^{-3} s^{-1} at 20 km and a chain length of greater than 10 between 10 and 40 km (Figure 5). The cycle has a peak chain length of greater than 1000 between 15 and 25 km (Figure 5). Between 15 and 35 km the rate limiting step is the photolysis of $BrONO_2$, and below this it is the photolysis of NO_3 ($\rho = j_{NO_3}[NO_3]$). At 35 km and above, the rate limiting step is the reaction of BrO with NO_2 ($\rho = k_{26}[BrO][NO_2]$).

For all of the reactive bromine catalytic cycles just considered the rate of destruction of the chain center has been taken as the rate of formation of HBr; namely, $\delta = k[Br][H_2] + k[Br][HCHO] + k[Cl][H_2O_2]$.

Let us now turn our attention to the most important nitrogen catalytic cycle.

Nitrogen Catalytic Cycle

In 1967 Bates and Hays published a paper on the concentrations, sources and sinks for N_2O in the atmosphere. Then in 1970 and 1971 Crutzen and Johnston introduced the consideration of the NO_x radical into the photochemical theory of stratospheric ozone. In 1971 Nicolet published a paper of the N_2O-$O(^1D)$-NO-NO_2 mechanism and Johnston pointed to the danger of NO_x emissions from stratospheric aircraft for stratospheric ozone. Figure 8 schematically shows the main NO_x ozone loss catalytic cycles.

NO/NO_2, NO_x cycle 1

$$\begin{aligned} NO + O_3 &\longrightarrow NO_2 + O_2 \quad (28)\\ NO_2 + O(^3P) &\longrightarrow NO + O_2 \quad (29)\\ \text{Net}: O(^3P) + O_3 &\longrightarrow 2O_2 \end{aligned}$$

This cycle has a peak rate of 10^6 molecules cm^{-3} s^{-1} between 30 and 40 km and a chain length of greater than 1 throughout the stratosphere reaching 10^5 in the upper stratosphere (Figure 10). The cycle has a chain effectiveness of greater than 10^4 molecules cm^{-3} s^{-1} throughout the stratosphere reaching a peak of greater than 10^9 molecules cm^{-3} s^{-1} at 45 km (Figures 9 and 10). At 50 km and above, the rate limiting step is the reaction of NO with O_3 ($\rho = k_{28}[NO][O_3]$).

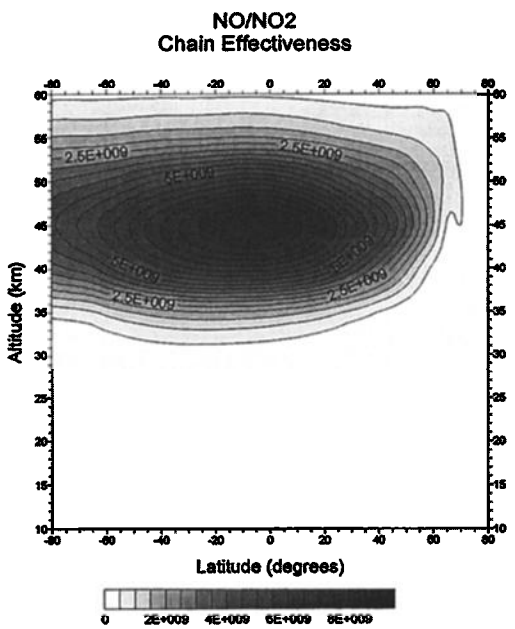

Figure 9. The calculated variation in the chain effectiveness of the NO/NO_2 cycle for the winter solstice as a function of altitude and latitude.

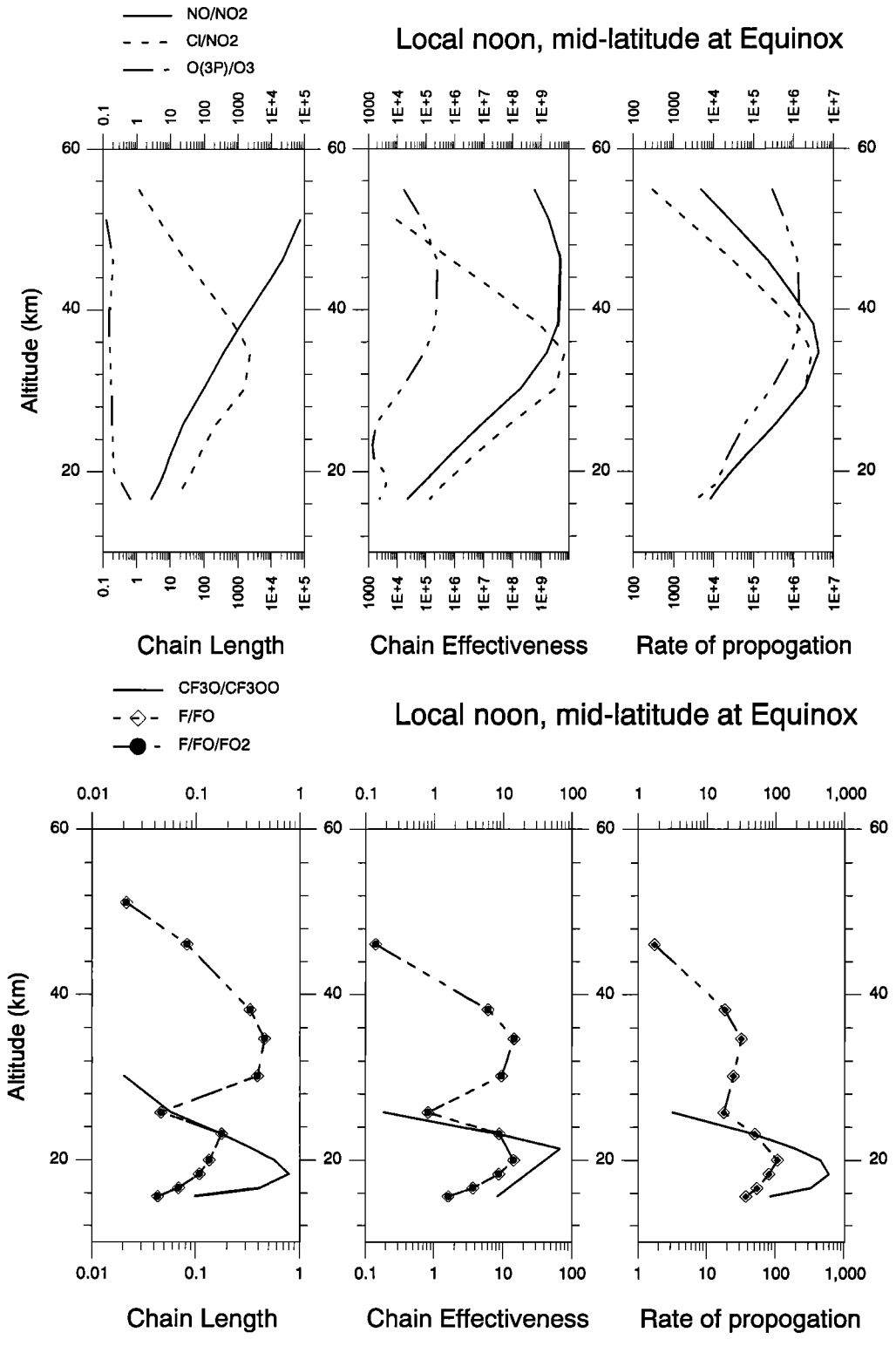

Figure 10. The calculated chain effectiveness, rate, and chain length of various nitrogen and fluorine ozone loss catalytic cycles for local noon at midlatitudes at equinox.

Below 50 km the rate limiting step is the reaction of NO_2 with $O(^3P)$ ($\rho = k_{29}[O(^3P)][NO_2]$).

For the reactive nitrogen catalytic cycles the rate of destruction of the chain center has been taken as the rate of formation of HNO_3; namely, $\delta = k[OH][NO_2] + k[H_2O][N_2O_5] + k[H_2O][ClONO_2]$. The last two terms are the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$.

Finally, let us consider some fluorine catalytic cycles.

Fluorine Catalytic Cycles

In 1975 Zander, Roland and Delboville found an absorption line of HF in a solar spectrum which was due to stratospheric absorption of HF. In 1978 Sze supported their findings with model calculations.

There are two sets of catalytic ozone loss cycle involving fluorine: those involving the CF_3 group which

are terminated by the production of COF_2 and those involving F, FO, and FO_2 which are terminated by the formation of HF. This section examines the chain length of the fastest of these cycles.

The fastest of all the fluorine catalytic cycles and the only fluorine cycle considered to have a chain length of greater than 1 is

CF_3O/CF_3OO, CF_3O_x cycle 1

$$O_3 + CF_3OO \longrightarrow CF_3O + 2O_2 \quad (30)$$
$$O_3 + CF_3O \longrightarrow CF_3OO + O_2 \quad (31)$$
$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

Even so, under normal conditions in the midlatitude lower stratosphere, this cycle is barely catalytic, having a peak chain length of 2 at 20 km; that is the cycle is only executed once before the CF_3 group is destroyed by the formation of COF_2 (i.e., $\delta = k[NO][CF_3O]$). In these calculations it has been assumed that as much fluorine is in the atmosphere as chlorine. Even with this assumption, the cycle proceeds at a maximum rate of only 10^3 molecules cm^{-3} s^{-1} (Figure 10).

As examined by D. J. Lary et al. (Atmospheric fluorine photochemistry, submitted to the Journal of Geophysical Research, 1996), the rate of termination by the formation of COF_2 due to the reaction of CF_3O with NO slows down as the temperature is increased as it has a negative activation energy. In contrast, the reaction of O_3 with CF_3O has a large positive activation energy and is therefore faster at warmer temperatures. In addition, for high sulphate aerosol loadings less, NO will be present in the atmosphere further slowing down the rate of formation of COF_2. Consequently, this can lead to a longer chain length of approximately 40 for temperatures around 240 K and sulphate aerosol loadings of greater than 5 $\mu m^2 cm^{-3}$.

The fastest $F/FO/FO_2$ catalytic cycles are

F/FO, FO_x cycle 1

$$O_3 + F \longrightarrow FO + O_2 \quad (32)$$
$$O_3 + FO \longrightarrow F + 2O_2 \quad (33)$$
$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

$F/FO/FO_2$, FO_x cycle 2

$$O_3 + F \longrightarrow FO + O_2$$
$$O_3 + FO \longrightarrow FO_2 + O_2$$
$$FO_2 \xrightarrow{M} F + O_2 \quad (34)$$
$$\text{Net} : 2O_3 \longrightarrow 3O_2$$

Even so, in the calculations performed here, both of these cycles are never catalytic, having a peak chain length of 0.4 between approximately 30 and 40 km; that is the cycle cannot proceed more than once as HF is formed so rapidly by the reaction of F with CH_4, H_2O, and H_2 ($\delta = k[F][H_2] + k[F][CH_4] + k[F][H_2O]$). The cycles proceed at a rate of approximately 70 molecules cm^{-3} s^{-1} (Figure 10). For both of these cycles the rate limiting step is the reaction of FO with O_3 ($\rho = k[FO][O_3]$), so both cycles have the same chain length.

Summary

Table 1 tabulates the approximate altitude at which the rate of each cycle reaches a maximum. In line with earlier work, such as that of *Johnston and Podolske* [1978], *Brasseur and Solomon* [1986], *Wayne et al.* [1991] and the reports of the *WMO* [1986, 1990, 1992, 1994], a few obvious points can be made in conclusion.

1. In the upper stratosphere, where the abundance of O_3 is relatively low, the most effective catalytic cycles are those whose net reaction is $2O(^3P) \rightarrow O_2$.
2. In the mid stratosphere the most effective catalytic cycles are those whose net reaction is $O(^3P) + O_3 \rightarrow 2O_2$.
3. In the lower stratosphere, where the abundance of $O(^3P)$ is relatively low, the most effective catalytic cycles are those whose net reaction is $2O_3 \rightarrow 3O_2$.
4. Examining the rate limiting step alone does not give any idea as to how many *times* a cycle can proceed. Consequently, calculating the cycle's chain length is valuable. This is particularly true when comparing cycles which involve chain cen-

Table 1. Summary Table Showing the Approximate Altitude in Kilometres at Which the Various Catalytic Cycles are Fastest for Midlatitudes At Equinox. For this Altitude the Approximate Chain Length, $\mathcal{N}$, is Also Given

Z (km)	ρ_{max}	$\mathcal{N}$	Cycle	
65	$8x10^6$	10^3	$H/OH/HO_2$	HO_x cycle 4
40	$2x10^6$	10^3	Cl/ClO	ClO_x cycle 1
	$1x10^6$	10^6	O/O_3	
	$2x10^4$	10^4	Br/BrO	BrO_x cycle 1
35	$4x10^6$	10^5	NO/NO_2	NO_x cycle 1
	$3x10^6$	10^3	Cl/NO_2	ClO_x cycle 3
	$8x10^5$	10	OH/HO_2	HO_x cycle 5
30	$8x10^4$	80	OH/HO_2	HO_x cycle 1
	$3x10^4$	10	HO_2/ClO	HO_x cycle 2
25	$9x10^4$	10	ClO/NO_2	ClO_x cycle 4
22	$1x10^4$	10^3	BrO/ClO	BrO_x cycle 2
	$6x10^3$	10^3	BrO/NO_2	BrO_x cycle 3
	$2x10^3$	2	ClO/ClO	ClO_x cycle 2
20	$5x10^3$	10^3	HO_2/BrO	HO_x cycle 3
	10	.1	CF_3O/CF_3OO	CF_3O_x cycle 1
	$1x10^2$	.4	F/FO	FO_x cycle 1
	$1x10^2$	.4	$F/FO/FO_2$	FO_x cycle 2

ters of very different abundance, such as the chlorine and bromine cycles. In general, although bromine is less abundant than chlorine, it is still very effective in destroying ozone as the bromine cycles tend to have very long chain lengths. In this context, the chain effectiveness is useful as it is the product of the cycle's rate and chain length. A cycle with a chain effectiveness greater than 10^8 molecules cm^{-3} s^{-1} is likely to be an effective ozone loss cycle.

5. In the low stratosphere the cycles involving HO_2 are important [e.g. *Brasseur and Solomon*, 1986]. What has only relatively recently become apparent is that the cycles involving HO_2 and halogens are particularly important. With increasing levels of atmospheric bromine the HO_2/BrO will assume a greater role in lower stratospheric and upper tropspheric ozone loss.

6. The most important ozone loss cycles in the polar lower stratosphere in their approximate order of importance are the BrO/ClO, HO_2/BrO, and OH/HO_2 cycles, with chain effectivenesses reaching $2x10^8$, $9x10^6$, and $4x10^6$ molecules cm^{-3} s^{-1}, respectively, with the ClO dimer cycle having a much lower chain effectiveness of around $3x10^4$ molecules cm^{-3} s^{-1}.

7. The currently known fluorine cycles are barely catalytic and experience rapid termination. They are therefore not effective at destroying ozone.

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