

# On the Chain Length and Rate of Ozone Depletion in the Main Stratospheric Cycles

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## ABSTRACT

Algorithm for calculation of the chain length and rate of stratospheric ozone depletion in  $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $ClO_x$  and  $BrO_x$  cycles has been developed. The most important new element in the theory of stratospheric chain processes is the correct determination the propagation rate, taking into account all reactions involved rather than a single reaction, which has the lowest rate, as it was usually done before. The role of null chain processes in the cycles has been considered and shown that these processes play a decisive role in formation of families of the odd oxygen, nitrogen, chlorine and bromine in the daytime while at night they play no role. Using two-dimensional model Socrates, and algorithm developed correct rate of ozone depletion and chain length in the cycles above for model conditions of June 2020 at  $50^\circ N$  have been calculated.

**Keywords:** Ozone Depletion; Stratospheric Cycles; Chain Propagation; Chain Limitation; Limiting Step

## 1. Introduction

### 1.1. Short History of the Problem

For the first time the photochemical theory of stratospheric ozone was developed by the outstanding English geophysicist Sydney Chapman [1]. The theory was applied to model of ozone distribution in the atmosphere to explain ozone layer existence. An important consequence of the Chapman's finding was a conclusion that ozone in the stratosphere can be destroyed only by the depletion of odd oxygen (*i.e.* ozone molecules and atoms of oxygen) that today is a base of all known cycles of stratospheric ozone depletion. Forty years later, stratospheric ozone attracted an overall attention in connection with the threat of destruction of the ozone layer under action of anthropogenic chlorine-containing compounds found in the early 1970-ies by Molina and Rowland [2]. Among the works to precede this discovery (besides Chapman's one) it should be noted the paper by Hampson [3], where the first chain mechanism of the ozone depletion in reactions with hydrogen oxides, which amplifies an action of the Chapman mechanism, has been described. Intensive studies of stratosphere chemistry at that time has led to the discovery of catalytic cycles with participation of nitrogen oxides [4], chlorine oxides [5], bromine oxides [6,7] and iodine oxides [8]. In last year problems of stratosphere chemistry and processes of formation and decomposition of the stratosphere ozone have been examined in a number books [9-13], including the one by G.

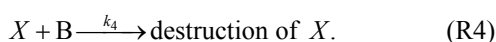
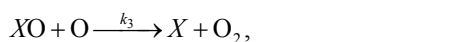
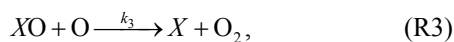
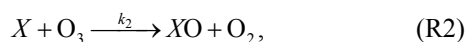
Brasseur and S. Solomon [14], that is most fully throwing light on all questions, connected with chemistry of ozone in the middle atmosphere. To the list of ozone references it should be added the work by Grenfell *et al.* [15], on chemical reaction pathways affecting stratospheric and mesospheric ozone and the one by D. J. Lary [16], which is probably the only one addressed the issue of the chain length in stratospheric ozone depletion cycles.

The chain length (in this case it's a number of molecules of ozone, destroyed by one active particle in its life time in the stratosphere) is one of the most important characteristics of chain process. Special importance this index has acquired in the contemporary conditions, when it was convincingly demonstrated, that because of the chain processes the anthropogenic factors proved to be capable of competing with the natural processes. Therefore it is important to understand, what a future potential participants of the chain stratospheric processes are danger for the ozone layer and what is their effectiveness in comparison with the chlorine components, having played the dominant role in the anthropogenic depletion of the ozone layer in the end of the past century. A definition of the chain length makes it possible to successfully solve the task as well as task of a comparison of the effectiveness of these cycles, similarly, as this is done with respect to various halogen-containing chemicals, for which an index of Ozone Depletion Potential is used (see, for example, [17]). In the present work we have considered some new conceptions of the stratospheric chain processes

theory, and also we have demonstrated how this theory can be used for description of the ozone depletion in  $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $ClO_x$  and  $BrO_x$  cycles which are considered now to be the main cycles of destruction of stratospheric ozone. New key points in our analysis are a correct determination of the rate of chain propagation and finding algorithm for the chain length calculations in the cycles mentioned above.

## 1.2. On Some Peculiarity of the Stratospheric Chain Processes

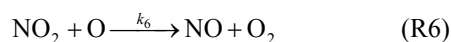
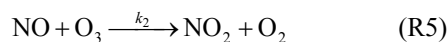
In the simplest case the chain process of the ozone depletion in the stratosphere can be written as follows [18]:



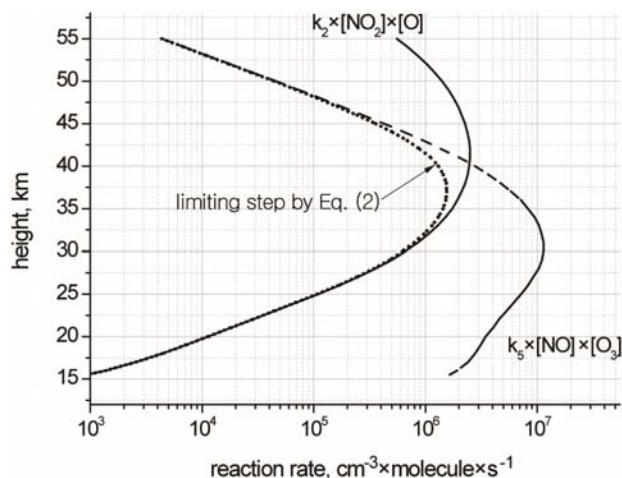
Here (R1) is a reaction of chain initiation, (R2), (R3) are the ones of chain propagation and (R4) is the one of chain termination. The length of chain,  $\nu$ , which in this case is a number of odd oxygen particles, destroyed by one active particle  $X$  in time of its stratospheric life, can be calculated using Equation (1):

$$\nu = \frac{\text{rate of chain propagation}}{\text{rate of chain termination}}. \quad (1)$$

If reactions (R2) and (R3) are unique processes of a mutual exchange between  $X$  and  $XO$ , their rates become identical already after several cycles. However, as a rule, besides reactions (R2) and (R3) other processes of exchange between  $X$  and  $XO$  run in the stratosphere. As a result, it does not lead to alignment of the reaction rates even at considerable chain length. But in any case because the reactions of chain propagation are consecutive ones, the rate of destruction of odd oxygen (*i.e.*  $O_3 + O$ ) are defined by the rate of so-called limiting step of the process. Usually the limiting step refers to the reaction with the lowest rate. But in most real situations in the stratosphere it is difficult to determine a true limiting step (as a single reaction) for all heights. For example, in the  $NO_x$  cycle the chain propagation reactions are



and reaction (R6) is considered to be a limiting step in  $NO_x$  cycle because it has a minimal rate in the stratosphere [12-14]. But as it seen from **Figure 1** near 40 km the rates of reactions (R6) and (R5) change places and at



**Figure 1. Reactions of chain propagation and the limiting step in  $NO_x$  cycle.**

more height reaction (R5) is getting slower than reaction (R6).

In addition, around 40 km reaction rates are the same and formally a limiting step here is missing.

To resolve the problem we offer a simple rule for calculating the rate of limiting step (=the rate propagation)—in case of two reactions of propagation, (R2) and (R3), the rate of the limiting step,  $W_{\text{lim}}(-O_3)$ , should be defined by Equation (2):

$$\frac{1}{W_{\text{lim}}(-O_3)} = \frac{1}{W_2} + \frac{1}{W_3} \text{ or } W_{\text{lim}}(-O_3) = \frac{W_2 \times W_3}{W_2 + W_3} \quad (2)$$

where  $W_2 = k_2 \times [X] \times [O_3]$ ,  $W_3 = k_3 \times [XO] \times [O]$ , and the rate of ozone depletion,  $W_p(-O_3)$ , should be defined by Equation (3):

$$W_p(-O_3) = 2 \times W_{\text{lim}}(-O_3), \quad (3)$$

where factor 2 appears as two particles of odd oxygen are destroyed in the chain process. Rate of limiting step by Equation (2) is shown in **Figure 1** (dotted curve). It's seen that Equation (2) allow one fully satisfy a concept of the lowest rate for limiting step at all stratospheric heights. Note also, that as it follows directly from Equation (2), at  $W_2 = W_3$  the rate of destruction of odd oxygen equals  $0.5 \times W_2$  or  $0.5 \times W_3$ . The last conclusion is a logical consequence of the fact that two successive steps require two times longer than one.

From here it is easy to conclude that under three reactions of chain propagation run with rates  $W_2$ ,  $W_3$  and  $W_4$ ,  $W_{\text{lim}}(-O_3)$  is expressed by Equation (4):

$$W_{\text{lim}}(-O_3) = \frac{W_2 \times W_3 \times W_4}{W_2 \times W_3 + W_2 \times W_4 + W_3 \times W_4}. \quad (4)$$

Similarly, it is possible to calculate the rate of a limiting step at any number of propagation reactions at any small differences in their rates that would represent a

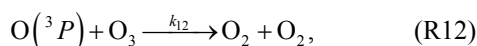
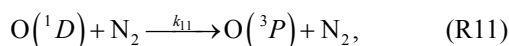
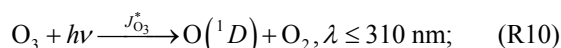
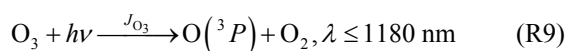
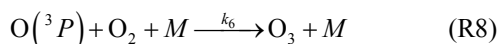
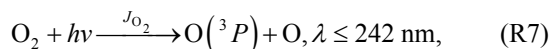
significant challenge for the limiting step in usual formulation. The concept of a limiting step of chain process introduced and its definition through inverse rates of chain propagation reactions is a basic new feature of stratospheric chain process, which was not considered till now at description of the chain stratospheric processes. We'll show how to use the new concept at consideration of main cycles of stratospheric ozone depletion in the next section.

## 2. Results and Discussion

This section presents the results of calculation of the chain lengths, as well as the rates of limiting steps and chain limitation in  $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $ClO_x$  and  $BrO_x$  cycles. The chain length has been determined by Equation (1). All numerical data have been obtained using 2D model Socrates [18] for conditions of June 2020 at the latitude  $50^\circ N$  and IPCC Scenarios for greenhouse gases [19,20]. By consideration of the chemistry of cycles only the reactions involved in the calculations specified above have been taken into account.

### 2.1. $O_x$ Cycle or Chapman's One

It's assumed that odd oxygen  $[O_x] = [O_3] + [O(^3P)] + [O(^1D)]$  where  $O(^3P)$  is atom O in the ground state and  $O(^1D)$  is the one in excited state with energy 1.96 eV. According [14] Chapman's cycle includes the reactions (R7)-(R12):

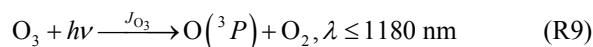
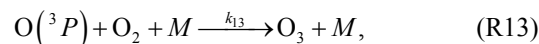


where  $M$  is molecules of air,  $J_{O_2}$ ,  $J_{O_3}$  and  $J_{O_3}^*$  are coefficients of photodissociation of  $O_2$  and  $O_3$ , respectively.

Since reaction (R11) converts  $O(^1D)$  to  $O(^3P)$ , it follows that the reaction (R12) determines the loss of all three component of odd oxygen, *i.e.* (R12) may be seen as a reaction of chain termination,  $W_d(-O_x)$ . On the other hand, reaction (R12) should be considered as a chain propagation reaction in  $O_x$  cycle because just this one does destroy odd oxygen. It follows that chain length in  $O_x$  cycle,  $\nu_{O_x}$ , is equal to 1 (see Equation (1)) and the rate of chain propagation,  $W_p(-O_x)$ , is:

$$W_p(-O_x) = k_{12} \times [O_3] \times [O(^3P)]. \quad (5)$$

It can be shown that stratospheric lifetime of  $O_x$ ,  $\tau(O_x)$ , is much more than  $\tau(O_3)$ ,  $\tau(O(^3P))$  and  $\tau(O(^1D))$  if the latter are defined through its individual ways of destruction. The situation is realized thank to so called  $O_x$  null cycle which doesn't destruct  $O_3$  or  $O(^3P)$ . The reactions of  $O_x$  null cycle are (R13) and (R9):



So using Equation (2) one can find that the rate of the limiting step in  $O_x$  null cycle

$$W_{\text{lim,null}}^{O_x} = \frac{W_{13} \times W_9}{W_{13} + W_9}, \quad (6)$$

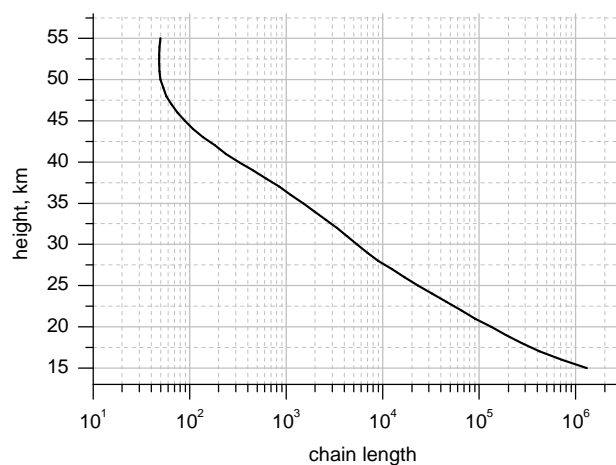
where  $W_{13} = k_{13} \times [O_3] \times [O_2] \times [M]$  and

$W_9 = J_{O_3} \times [O_3]$ . The rate of chain termination in null cycle is the same as in the main cycle, *i.e.*

$W_d(-O_x) = k_{12} \times [O_3] \times [O(^3P)]$ . So we obtain that

$$\nu_{O_x,\text{null}} = \frac{W_{\text{lim,null}}^{O_x}}{W_d(-O_x)}. \quad (7)$$

Height profile of  $\nu_{O_x,\text{null}}$  is shown in **Figure 2**. One can see that in the low stratosphere, chain length is about  $10^6$ , and at the altitude of 55 km it's about 50. In our case the chain length means a number of mutual conversion of  $O_x$  components occurring during stratospheric lifetime of  $O_x$ ,  $\tau(O_x)$ . So, a condition of  $\nu_{O_x,\text{null}} \gg 1$  means that mutual conversion of  $O_3$ ,  $O(^3P)$  and  $O(^1D)$  occur so fast in comparison with  $\tau(O_x)$  that they are getting chemically indistinguishable and one can consider lifetime of these components to be the same as  $\tau(O_x)$ . But it should be the case only for daytime conditions. At night  $J_{O_3}$ ,  $W_9$  and  $\nu_{O_x,\text{null}}$  are getting to zero,  $O_x$  family disappears and lifetime of  $O_3$ ,  $O(^3P)$  and  $O(^1D)$  are getting dependent on



**Figure 2.** Height profile of the chain length in  $O_x$  null cycle.

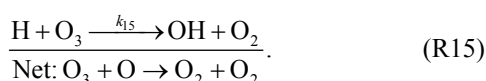
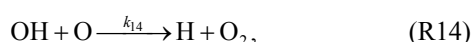
its individual loss processes.

Finally, let's underline that to understand a daytime chemistry of ozone it is possible only through a method of families. It is the only way to define correctly atmospheric lifetime of ozone as well as to show that a unique source of ozone in the stratosphere is photodissociation of  $O_2$ , and a unique sink is a reaction  $O_3$  with  $O(^3P)$ .

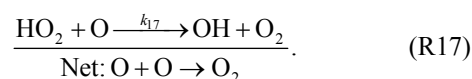
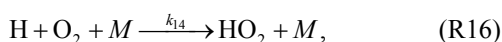
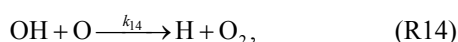
## 2.2. $HO_x$ Cycle

Family of odd hydrogen  $[HO_x] = [H] + [OH] + [HO_2]$ . Destruction of odd oxygen in  $HO_x$  cycle occurs through the following chain mechanisms.

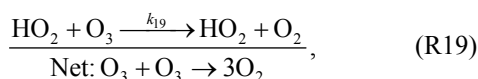
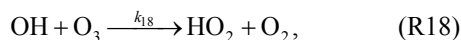
Cycle I:



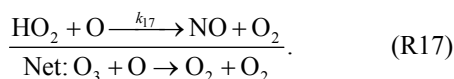
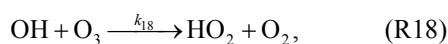
Cycle II:



Cycle III:



Cycle IV:



Rate of the limiting steps in Cycles I-IV is determined by Equations (8)-(11):

$$W_{\text{lim,I}}^{HO_x}(-O_3) = \frac{W_{14} \times W_{15}}{W_{14} + W_{15}}, \quad (8)$$

$$W_{\text{lim,II}}^{HO_x}(-O_3) = \frac{W_{14} \times W_{16} \times W_{17}}{W_{14} \times W_{16} + W_{14} \times W_{17} + W_{16} \times W_{17}}, \quad (9)$$

$$W_{\text{lim,III}}^{HO_x}(-O_3) = \frac{W_{18} \times W_{19}}{W_{18} + W_{19}}, \quad (10)$$

$$W_{\text{lim,IV}}^{HO_x}(-O_3) = \frac{W_{18} \times W_{17}}{W_{18} + W_{17}}, \quad (11)$$

where  $W_{\#}$  is the rate of reaction (R#). Height profiles of  $W_{\text{lim,I}}^{HO_x}(-O_3) - W_{\text{lim,IV}}^{HO_x}(-O_3)$  and their sum are shown in

**Figure 3.** Rate of destruction of odd oxygen in a hydrogen cycle,  $W_p^{HO_x}(-O_3)$ , one can define as a sum of  $W_{\text{lim},i}(-O_3)$  times factor 2,

$$W_p^{HO_x}(-O_3) = 2 \times \sum_{i=1}^{i=IV} W_{\text{lim},i}(-O_3). \quad (12)$$

Chain termination processes in  $HO_x$  cycle and their rates are shown in **Figure 4**. As it follows from **Figure 4** chain termination in  $HO_x$  cycle is due to the reaction (R20):

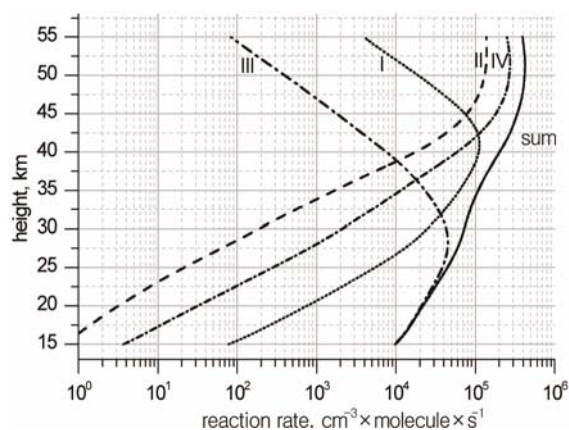


So the rate of chain termination in hydrogen cycle,  $W_d(HO_x)$ , can be written as Equation (13):

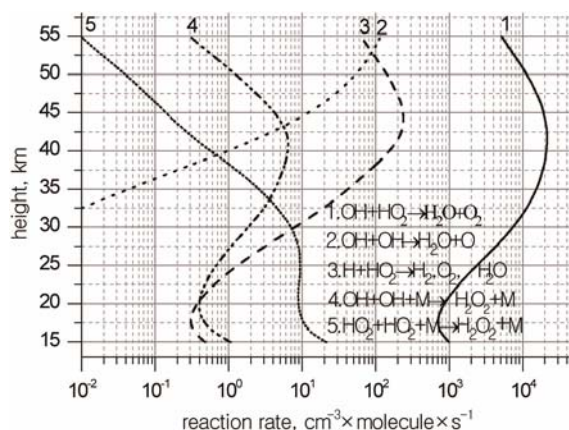
$$W_d(HO_x) = k_{20} \times [OH] \times [HO_2]. \quad (13)$$

Chain length in  $HO_x$  cycle one can find using Equation (14)

$$\nu_{HO_x} = \frac{W_p^{HO_x}(-O_3)}{W_d(HO_x)}. \quad (14)$$



**Figure 3.** Height profiles of  $W_{\text{lim,I}}(-O_3) - W_{\text{lim,IV}}(-O_3)$  and their sum in  $HO_x$  cycle.



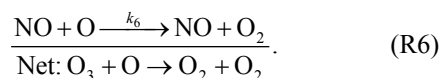
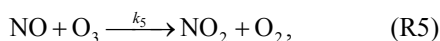
**Figure 4.** Chain termination processes in  $HO_x$  cycle and their rates.

In conclusion it should be noted that under description of ozone depletion in HO<sub>x</sub> cycle usually reactions with individual participation O<sub>3</sub> or O are taking into account (see [11,14]). In this connection it should be underlined that as it follows from Chapman's mechanism, ozone can be destructed only through depletion of the odd oxygen which requires at least two reaction of chain propagation. But in this case the rate of ozone depletion is expressed using limiting steps as it was done above. Using individual reaction with O<sub>3</sub> or O means, in fact, an ignoring chain mechanism of ozone depletion in the stratosphere.

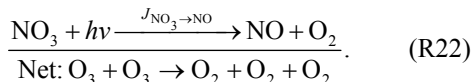
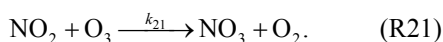
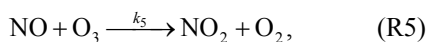
### 2.3. NO<sub>x</sub> Cycle

NO<sub>x</sub> family includes NO and NO<sub>2</sub>. Like HO<sub>x</sub>, cycle NO<sub>x</sub> includes three chain mechanisms

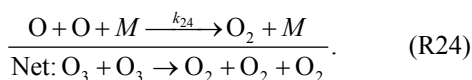
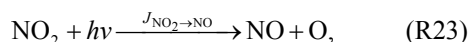
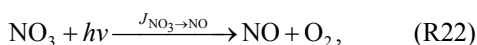
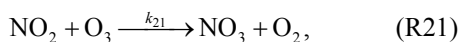
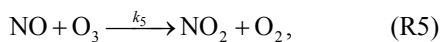
Cycle I:



Cycle II:



Cycle III:

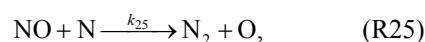


Height profiles of the rate of limiting steps in Cycles I-III are shown in **Figure 5**.

It's seen that the most important cycles in that case are Cycles I and II. So the rate of ozone depletion in total NO<sub>x</sub> cycle,  $W_p^{\text{NO}_x}(-\text{O}_3)$ , can be expressed by Equation (15):

$$W_p^{\text{NO}_x}(-\text{O}_3) = 2 \times \left\{ \frac{W_5 \times W_6}{W_5 + W_6} + \frac{W_5 \times W_{21} \times W_{22}}{W_5 \times W_{21} + W_5 \times W_{22} + W_{21} \times W_{22}} \right\}. \quad (15)$$

Chain limitation in NO<sub>x</sub> cycle occur through chemical conversion of NO in N<sub>2</sub>:



and physical process of the turbulent transport characterized by time  $\tau_d$  expressed by Equation (16):

$$\tau_d = \frac{H^2}{k_{zz}}. \quad (16)$$

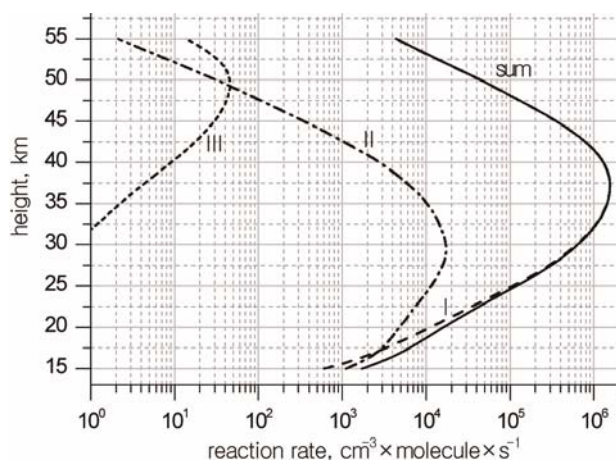
Here  $H$  is scale height,  $k_{zz}$  is a vertical coefficient of turbulent diffusion. So the rate of chain limitation in NO<sub>x</sub> cycle,  $W_d(\text{NO}_x)$ , can be expressed as

$$W_d(\text{NO}_x) = k_{25} \times [\text{NO}] \times [\text{N}] + \frac{[\text{NO}_x]}{\tau_d}. \quad (17)$$

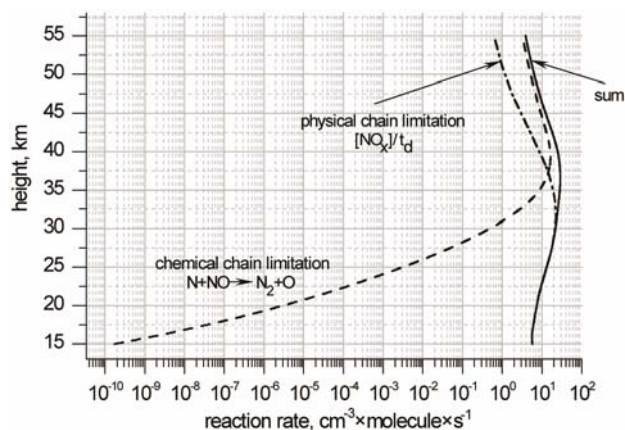
Height profiles of  $W_d(\text{NO}_x)$  are shown in **Figure 6**.

Knowledge of the rates of chain propagation and of chain limitation allows one to express a chain length in NO<sub>x</sub> cycle,  $\nu_{\text{NO}_x}$ :

$$\nu_{\text{NO}_x} = \frac{W_p^{\text{NO}_x}(-\text{O}_3)}{W_d(\text{NO}_x)} \quad (18)$$

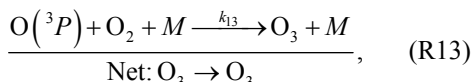
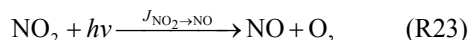
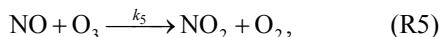


**Figure 5.** Height profiles of the limiting step rates of Cycles I-III in NO<sub>x</sub> cycle and their sum.



**Figure 6.** Height profiles of chain limitation rate in NO<sub>x</sub> cycle.

It should add that in the low and middle stratosphere NO<sub>x</sub> cycle runs mainly not destroying odd oxygen. It's explained by a null cycle, a chain length of which here is much higher than the one of main cycle determined by Equation (18). Reactions of the NO<sub>x</sub> null cycle are the following:



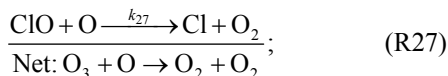
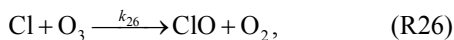
Limiting step of null cycle includes reactions (R5) and (R23) and its rate can be easily calculated by the same rules as above. Chain limitation is the same as in the main cycle (see Equation (17)). Let's remind, that the null cycle acts only in day conditions that provides a possibility of existence of NO<sub>x</sub> family. At night the rate of the reaction (R23) is getting to zero and NO<sub>x</sub> family disintegrates.

Figure 7 shows chain lengths of the main cycle (Equation (18)) and the null one in NO<sub>x</sub> cycle.

### 2.4. ClO<sub>x</sub> Cycle

Depletion of the odd oxygen in that case includes two cycles.

Cycle I:



Cycle II:

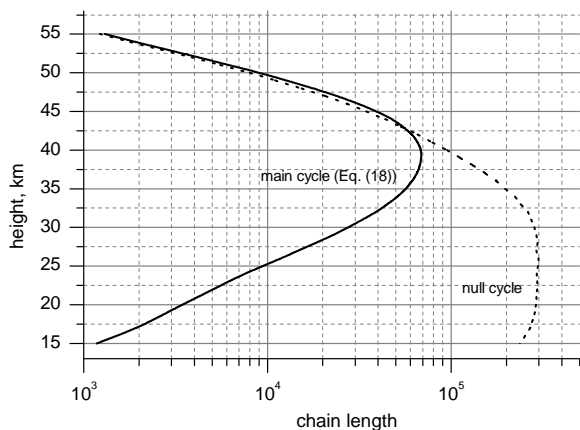
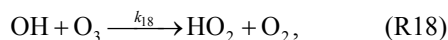
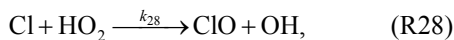
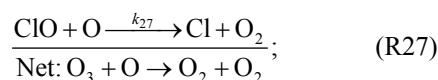


Figure 7. Chain lengths of the main cycle (Equation (18)) and the null one in NO<sub>x</sub> cycle.



Rates of the limiting step in Cycles I, II are calculated just as in case of a hydrogen cycle. The results of the calculations are shown in Figure 8.

It's seen from Figure 8 that one can neglect limiting step of Cycle II and express the rate of ozone depletion in ClO<sub>x</sub> cycle,  $W_p^{\text{ClO}_x}(-\text{O}_3)$ , as follows:

$$W_p^{\text{ClO}_x}(-\text{O}_3) = 2 \times W_{\text{lim,I}}^{\text{ClO}_x}. \quad (\text{19})$$

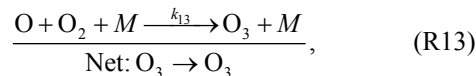
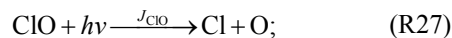
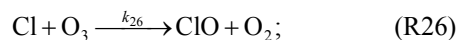
Chemical chain limitation in ClO<sub>x</sub> cycle occurs by reactions with formation of HCl, HOCl and ClONO<sub>2</sub>. However stratospheric lifetime of these species appears to be less than a transport time  $\tau_d$  (see Equation (16)). Consequently, the real chain limitation should be determined by the processes of turbulent transport, the rate of which is  $[\text{ClO}_x]/\tau_d$ . So one can consider that

$$W_d(\text{ClO}_x) = \frac{[\text{Cl}] + [\text{ClO}]}{\tau_d}. \quad (\text{20})$$

Respectively, ClO<sub>x</sub> chain length,  $\nu_{\text{ClO}_x}$ , one can find using Equation (21):

$$\nu_{\text{ClO}_x} = \frac{W_p^{\text{ClO}_x}(-\text{O}_3)}{W_d(\text{ClO}_x)}. \quad (\text{21})$$

Like NO<sub>x</sub> cycle, ClO<sub>x</sub> one has a null cycle as well which provides a mutual exchange of Cl and ClO:



It can be shown that like NO<sub>x</sub> cycle the null cycle of ClO<sub>x</sub> family appears to be faster than main ("working") cycle.

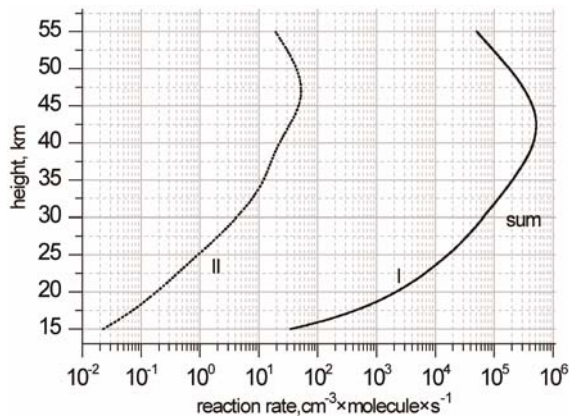
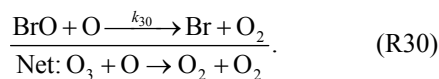
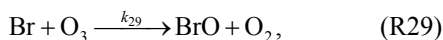


Figure 8. Height profiles of the limiting step rates of Cycles I and II in ClO<sub>x</sub> cycle and their sum.

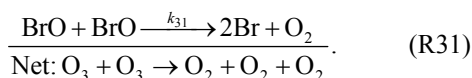
## 2.5. BrO<sub>x</sub> Cycle

First two BrO<sub>x</sub> cycles have been suggested by Wofsy *et al.* in 1975 [6].

Cycle I:

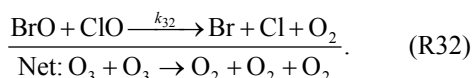
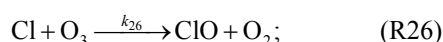
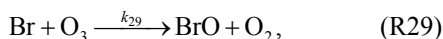


Cycle II:

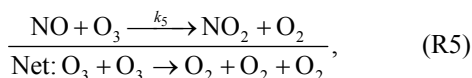
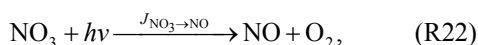
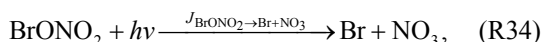
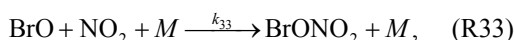
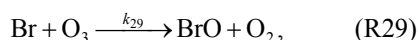


In 1980 Yung *et al.* [7] have added next four cycles.

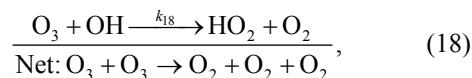
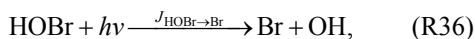
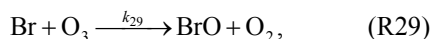
Cycle III:



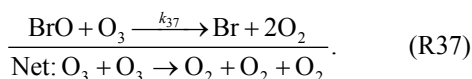
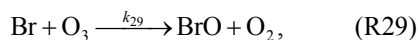
Cycle IV:



Cycle V:



Cycle VI:



The rates of limiting steps in Cycles I-VI can be found as above. They are shown in **Figure 9**.

So using Equation (22) one can get the rate of ozone

depletion in BrO<sub>x</sub> cycle:

$$W_p^{\text{BrO}_x}(-\text{O}_3) = 2 \times \sum_{i=1}^{i=\text{VI}} W_{\text{lim},i}^{\text{BrO}_x}(-\text{O}_3). \quad (22)$$

Formally chemical chain limitation in BrO<sub>x</sub> cycle run with formation HBr, HOBr and BrONO<sub>2</sub>. But it doesn't stop chain propagation because a stratospheric lifetime of these species is much less than τ<sub>d</sub>. So one can get for the real chain limitation in BrO<sub>x</sub> cycle the same expression as in case of ClO<sub>x</sub> cycle:

$$W_d(\text{BrO}_x) = \frac{[\text{Br}] + [\text{BrO}]}{\tau_d}. \quad (23)$$

From here follows, that chain length in BrO<sub>x</sub> cycle is:

$$\nu_{\text{BrO}_x} = \frac{2 \times \sum_{i=1}^{i=\text{VI}} W_{\text{lim},i}^{\text{BrO}_x}(-\text{O}_3)}{[\text{Br}] + [\text{BrO}]} \tau_d. \quad (24)$$

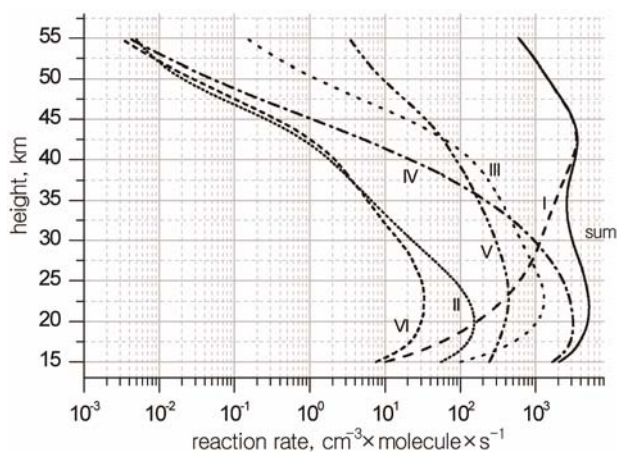
Chain length ν<sub>BrO<sub>x</sub></sub> as well as ones of all other cycles considered above are shown in **Figure 10**.

Finally, **Figures 11** and **12** show the absolute and relative contribution in ozone depletion all cycles for conditions specified above.

## 3. Conclusions

Algorithm for calculation of the limiting step rates in the chain propagation reactions of stratospheric ozone depletion has been developed. It allows one to calculate the rate of limiting steps with any number of propagation reactions and any arbitrarily small difference in the rates of these reactions. This provided the opportunity for the first time correctly to calculate the rate of ozone destruction in the main cycles of the stratospheric ozone depletion.

Using algorithm developed, 2D model Socrates and



**Figure 9.** Height profiles of the limiting step rates in BrO<sub>x</sub> cycle.

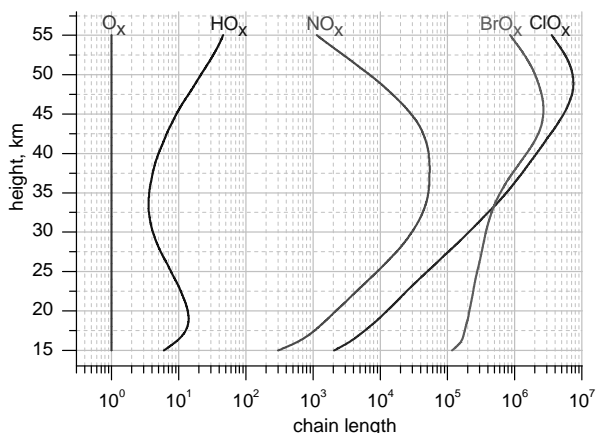


Figure 10. Height profiles of  $\nu_{O_x}$ ,  $\nu_{HO_x}$ ,  $\nu_{NO_x}$ ,  $\nu_{ClO_x}$  and  $\nu_{BrO_x}$  for June 2020 at latitude 50°N obtained using algorithm developed, 2D model Socrates and IPCC scenarios of greenhouse gases RCP 4.5.

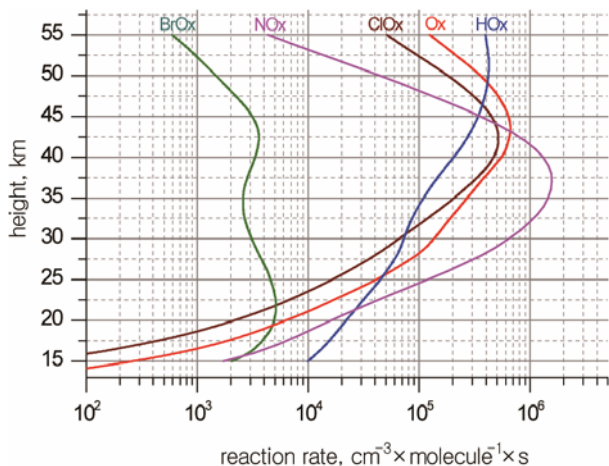


Figure 11. Rates of ozone depletion in  $O_x$ ,  $HO_x$ ,  $NO_x$ ,  $ClO_x$  and  $BrO_x$  cycles in the stratosphere for model conditions of June 2020 at 50°N.

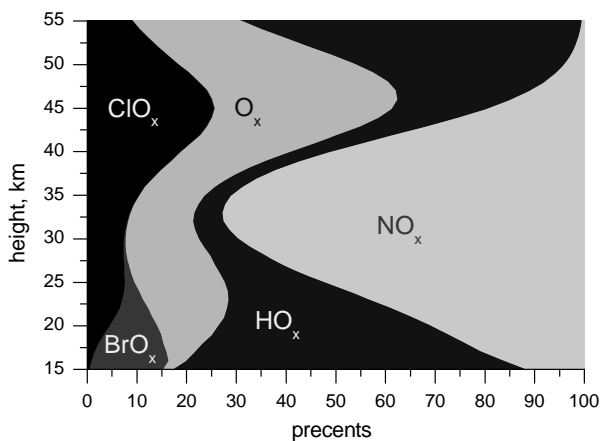


Figure 12. Relative contribution of main cycles into ozone depletion in the stratosphere for model conditions as in Figure 11.

other approaches chain lengths of the main stratospheric cycles have been calculated.

The role of the stratospheric null cycles has been considered. It has been shown that null cycles along with main cycles of ozone depletion provides a mutual exchange of the species participating in the chain processes and thereby does conditions of an existence of the stratospheric families such as  $O_x$ ,  $NO_x$ ,  $HO_x$ . It has also been shown that null cycles act only in daytime conditions. At night their action stops, families are disintegrating and their participants start to exist as individual species without any connection with a former family.

Finally, comparing the present results with data in [16], which also provides the chain lengths for major stratospheric cycles, shows that in case of  $HO_x$  cycle chain length in [16] slightly more than in this work. This is due to the fact that in [16] a single reaction (instead of pair) has been considered as limiting step, that has increased the rate of the chain propagation. In case of  $NO_x$ ,  $ClO_x$  and  $BrO_x$  cycles chain lengths in [16] were noticeably smaller than obtained here. This is due to the fact that in [16] chain limitation in these cycles is mistakenly attributed to the formation of reservoirs of  $HNO_3$ ,  $HCl$  and  $HBr$ . It can be shown that the atmospheric lifetime of these reservoirs much less than time of transport  $\tau_d$  and, therefore, a true chain limitation should be connected not with fast chemical reactions and slow transport processes, that significantly decreases the rate of limitation and increases the chain length.

#### 4. Acknowledgements

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