DERIVING A LINEARISED OZONE CHEMISTRY SCHEME FOR A 3-D CHEMICAL TRANSPORT MODEL OF THE MIDDLE ATMOSPHERE

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ABSTRACT

A simple but computer efficient parameterized ozone chemistry is developed to account for updates in reaction rate recommendations, and also completely assess the contributions of the individual catalytic cycles to the ozone budget in the entire stratosphere. Two conceptual approaches, namely total time approach and rate limiting step approach, have been used to improve upon an existing comprehensive stratospheric chemistry model to calculate the coefficient of linearised ozone chemistry scheme. The total time approach is accurate in calculating for the coefficients of the ozone chemistry scheme whiles the rate limiting step approach is effective in assessing the contributions of the individual catalytic cycles to the ozone budget. The catalytic cycle with the rate limiting step of NO_2/O is very prominent in altitudes between 15 and 48 km, and peaks at 30 km with ozone loss percentage contribution of about 75%. HO_2/O rate limiting step dominates above 40 km and peaks around 58 km with about 90% loss contribution to the ozone budget. Rate limiting steps involving BrO were the least ozone loss reactions in the set at the chosen mid-latitude June condition, and they concentrate at the lower stratosphere.

INTRODUCTION

Computing time and computing space are two important and fundamental factors to be considered in the development of any computer model. Particularly in 3-D atmospheric chemical transport model which usually deals with large numbers of grid points, there is the need to limit the number of chemical tracers without necessarily deviating from the exact results. The limitation is necessary so that the detailed rigid chemical mechanisms as well as the large computer space required for storage could be reduced. Thus to be able to run global 3-D chemical transport models for a long period of time, parameterized chemistry will have an obvious advantage.

Linearised ozone chemistry is the parameterization of ozone chemistry in the stratosphere. The fundamental term in the linearised chemistry is the ozone tendency. The ozone tendency describes the balance between the ozone production rates and the ozone loss rates at any given location in the atmosphere. In the linearised chemistry, the ozone tendency is linearised about the local ozone mixing ratio, temperature, and overhead column ozone density using first-order Taylor expansion.

The linearised ozone chemistry has at least four advantages: 1. It requires only a single tracer (ozone) with negligible central processing unit requirements for the chemistry, 2. It is suitable for coupling with general circulation models for long-term climate simulations, 3. It can readily be incorporated into tropospheric chemical transport models, 4. It is a simplified form of stratospheric ozone simulation.

The idea of linearized ozone (LINOZ) chemistry scheme was conceived and firstly developed by Cariolle and Deque. They used it in a stratospheric 3-D chemical transport model (Cariolle and Deque, 1986). Since its development, this scheme has been used in a number of studies and publications (Hadjinicolaou *et al.*, 1997; Cariolle *et al.*, 1990)

McLinden *et al.* (2000) followed this basic parameterization and offered a detailed description of the formation of linearised ozone chemistry (LINOZ). They also made available, upon request, seven sets of tabulated coefficients calculated at 25 pressure altitudes and 18 latitudes for 12 months. The calculations of these sets of coefficients were based on 1997 Jet Propulsion Laboratory (JPL) recommendation for rate coefficients and photochemical cross sections. These sets were used by Sinnhuber *et al.* (2003a) to study total ozone during the unusual Antarctic Winter of 2002. The present paper here only attempts to supplement work done earlier on by other scientists.

In this work two different conceptual approaches have been used to derive the sets of coefficients in the linearised ozone chemistry scheme. The first approach which is called total time approach derives the ozone tendency of the linearised chemistry directly from the model iterations. The second approach which is termed rate-limiting step approach calculates the ozone tendency by summing up together the rate limiting steps of all the reactions that directly produce and destroy ozone in the model. An existing standard 1-D stratospheric photochemical model was developed to implement the two approaches. The development was done such that the model can easily be used to calculate the sets of coefficients of the linearised chemistry for any reaction rate recommendation. The standard model uses the chemical code of the Single Layer Isentropic Model of Chemistry and Transport (SLIMCAT) (Chipperfield, 1999).

The main objectives of this work are to develop a set of catalytic cycles that could effectively describe the ozone budget in the entire stratosphere, and develop a standard model that can be used to calculate coefficients of linearised chemistry from any updated reaction rate recommendation.

CONCEPTUAL APPROACHES

Total/Chain Time Approach

In any given chain cycle involving elementary steps, the rate of the cycle is given as the reciprocal of the total time required to pass through each step in the cycle (Benson, 1976). Consider for example the catalytic reaction below:

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\textbf{Net:}\quad O_3 + O \rightarrow 2O_2$$

where the pairs O/XO could be H/HO, OH/HO_2, NO/NO_2, Cl/ClO, and Br/BrO.

The rate of a species to react is given as:

$$\frac{d[X]}{dt} = -k[X][O_3] \qquad (1)$$

where the square brackets denote concentration of the reactants and k is the reaction rate coefficient.

The mean time required for an atom X to react, τ_n, is given by:

$$\tau_n = \frac{[X]}{\left(\frac{d[X]}{dt}\right)} \qquad (2)$$

where negligible contribution by the reverse reaction is assumed. Multiplying equation (1) by equation (2), and rearranging, we obtain

$$\tau_n = \frac{1}{k[O_3]} \qquad (3)$$

$$\tau_n = \tau_1 + \tau_2 + \tau_3 + \ldots + \tau_n \tag{4}$$

Equation (4) defines the total time approach which is one of the two conceptual approaches used in this work. Thus in the chain time approach, the total time required to derive the rate of a reaction is obtained by adding up the mean time of each elementary step in the cycle. This approach has an advantage in that it uses the true time for the process. However, the contribution of each cycle to the entire process cannot be assessed directly.

Using the chain time approach, the following mathematical formulation is used to derive the ozone tendency *(P – L)*:

$$\frac{df}{dt} \approx \frac{f(z, t_{i+1}) - f(z, t_i)}{\Delta t} \tag{5}$$

where $f(z, t_i)$ is the ozone mixing ratio at height z and current time t_i, $f(z, t_{i+1})$ is the modeled ozone mixing ratio at height z and the next time t_{i+1}, and Δt is the time step in the model.

Averaging over N number of iterations, we have:

$$\frac{df}{dt} = \frac{1}{N}\sum_{i=i}^{N} \frac{f(z, ti+1) - f(z, t_i)}{\Delta t} \tag{6}$$

$$\frac{df}{dt} = \frac{1}{N}\sum_{i=i}^{N} \frac{f(z, t_{i+1})}{\Delta t} - \frac{1}{N}\sum_{i=i}^{N} \frac{f(z, t_i)}{\Delta t} \tag{7}$$

However, in this work, the ozone mixing ratio at each time step is always replaced with the ozone climatology (f^{o}) which is taken from observations (Fortuin and Kelder, 1998). This ensures that the climatological value of the chemical ozone tendency $(P - L)^{o}$ is calculated at ozone climatology (f^{o}) and not for some other ozone mixing ratio (f).

Thus:

$$\frac{df}{dt} = \frac{f^1 - f^0}{\Delta t} = (P - L)^0 \tag{8}$$

where $f(z,t_i) = f^{o}$ and f^{1} is the averaged calculated ozone mixing ratio after a model time step $f(z, t_{i+1})$.

Rate Limiting Step Approach

In order to study the contributions of each individual cycle to the overall ozone budget, the rate limiting step approach is used. If competition occurs in any given cycle, then the mean time (τ_k) for a step k which is significantly slower than the rest of the steps could be approximated to the chain time τ_n.

This defines the rate limiting step which is the reaction rate in a cycle with the slowest overall reaction rate (or reaction flux). The rate limiting step approach has an advantage in that it permits an explicit evaluation of the contribution of each cycle to the entire process. However, this approach is not applicable in a purely cyclic process where all the steps occur with the same rate (Brasseur *et al.*, 1999). In addition, this approach breaks down when the time contributions from other steps become comparable to the selected rate limiting step.

In this research, a set of 13 reactions are used to estimate the ozone budget (see Table 1). The set basically involves the ozone production by oxygen photolysis and ozone loss by reactions with NO_x, BrO_x, ClO_x and HO_x families**.** Each reaction cycle listed below accounts for either the production or loss of two molecules of odd oxygen hence the net rate are determined by doubling the diurnally averaged rate of the rate limiting step.

METHODS

The efficiency and quality of a model is ascertained from the kinds of numerical schemes used, as well as from different processes taken into account in the development of the model. In this work, we used the stratospheric chemical one-dimensional model described in (Chipperfield 1996; 1999). This model has been used in a number of studies and publications (e.g., Millard *et al.*, 2002; Hadjinicolaou and Pyle, 2004). For the purpose of comparison with the LINOZ parameterization (McLinden *et al.*, 2000), pressure altitudes and latitudes in the model were linearly interpolated onto that of

Table 1: Rate limiting steps used to derive the ozone budget of the stratosphere

	Rate Limiting Step	Rate Equation
1.	$ClOOCl + hv \rightarrow Cl + ClOO$	$2j_1[ClOOCl]$
2.	$ClO + O \rightarrow Cl + O_2$	$2k_2[ClO][O]$
3.	$NO_2 + O \rightarrow NO + O_2$	$2\,k_3\,[NO_2][O]$
4.	$HO_2 + O_3 \rightarrow OH + 2O_2$	$2\,k_4\,[HO_2]\,[O_3]$
5.	$BrO + O \rightarrow Br + O_2$	$2\,k_5\,[BrO]\,[O]$
6.	$BrO + ClO \rightarrow Br + ClOO$	$2\,k_6\,[BrO][ClO]$
7.	$ClO + BrO \rightarrow BrCl + O_2$	$2\,k_7\,[ClO][BrO]$
8.	$ClO + HO_2 \rightarrow HOCl + O_2$	$2\,k_8\,[HO_2][ClO]$
9.	$BrO + HO_2 \rightarrow HOBr + O_2$	$2\,k_9\,[HO_2][BrO]$
10.	$O + O_3 \rightarrow 2O_2$	$2\,k_{10}\,[O][O_3]$
11.	$HO_2 + O \rightarrow HO + O_2$	$2\,k_{11}\,[HO_2][O]$
12.	$NO_3 + hv \rightarrow NO + O_2$	$2\,j_{12}\,[NO_3]$
13.	$O_2 + hv \rightarrow O + O$	$2\,j_{13}[O_2]$

LINOZ which consists of 25 pressure altitudes (z^o=10 to 58 km at 2 km increments) and 18 latitudes from 85°S to 85°N in the step of 5°. The model was initialized with a 2-D model output in which ozone and temperature have been replaced with an observed climatology.

During each model run, the ozone climatology for the given altitude, latitude, and month were fixed during the integration period. The model was integrated for 30 days using mid-month solar conditions. To take care of spin-up periods in the model, the first 15 days were excluded from the averaging. The ozone tendency calculations were performed by the two conceptual approaches described in section 2. The linearization terms (i.e. the partial derivatives) were determined by perturbing the local ozone, temperature, and column ozone separately and recalculating radicals and the diurnally averaged tendency. The perturbations were +5% in local ozone, +4 K in temperature, and +5% in column ozone (McLinden *et al*., 2000).

For the purpose of comparison with LINOZ, the model was run for different months and latitudes using 1997 JPL recommendation and in each case the ozone tendencies as well as the derivatives were calculated. In order to study the contributions of the ozone loss catalytic cycles and how they change with the changes in the JPL recommendations, the model was run separately using three JPL recommendations (JPL 1997, JPL 2000, JPL 2002) (DeMore *et al*., 1997; Sander *et al*., 2000; 2002). The model run for northern hemisphere middle latitude conditions in June was taken as representative for other conditions. This was done because most other conditions showed similar results except polar conditions in both hemispheres. In addition, under this condition, the effect of heterogeneous chemistry on polar stratospheric clouds (PSCs) has no effect on the model results due to the warm temperatures associated with this condition. With very low temperatures (~ -80 °C) formation of PSCs is facilitated leading to enhanced chemical destruction of ozone by man-made halogens (mostly chlorine and bromine) compounds.

RESULTS AND DISCUSSION

Validation of Results

The results of (McLincen *et al,* 2000) are used to validate this work in terms of ozone tendency, the rate of change of ozone tendency with respect to ozone, ozone lifetime, and the steady state ozone.

The JPL 1997 photochemical data and the total time approach were used since the result in

LINOZ (McLinden *et al*., 2000) was obtained with the same approach. The results in summer mid-latitude conditions in the northern hemisphere (i.e. June, latitude 45°N) were used as a representative for the other months and latitudes. The overall agreement between these results and LINOZ was generally good especially in the lower stratosphere.

The two results were obtained from two different models which might vary in terms of details of processes and parameterizations. It was therefore expected that there would be some discrepancies between the two results.

The differences between the two models are summarized in table 2.

Mid-latitude summer conditions (June, latitude 45° N) were selected to avoid discrepancy which may arise from the heterogeneous reactions on polar stratospheric clouds (PSC) and ternary aerosols.

The odd oxygen family ($O_x=O(^1D) + O(^3P) + O_3$) used in the model has an advantage that it allows longer time step which saves computer time and memory, and it also reduces the cost of calculation of species in the solution to the continuity equation. The family approach is effective in partitioning the species involved only when photochemical equilibrium is established. However, the use of family approach is an approximation, and thus some discrepancies would be expected, in particular at high altitudes.

Other potential source of differences can come from the climatologies used to initialize the 1–D model. There are limited observed climatologies for many trace gases in the stratosphere. Thus mostly, stratospheric models are initialized with climatologies either derived from 2–D models or through empirical tracer correlations with the few observations available. The fact that the two models were not initialized with the same source gas climatologies can be a potential source of discrepancy. For example, if there are differences in the Cl_y (chlorine) and Br_y (bromine) loading, or in water vapor which is the main source of HO_x, then obviously there will be differences in the ozone tendency and its derivatives. In this work, much effort was made to reduce this type of discrepancy by replacing both the ozone and the temperature climatologies in the 2–D model output with the same observed climatologies as used by McLinden *et al*, 2000.

Comparison of Parameters used in LINOZ

In this section, the ozone tendency, the derivative of ozone tendency with respect to ozone, and the ozone lifetime in this work are compared with the standard results.

Comparing Ozone Tendency (*P* - *L*)

The ozone tendency gives information about the time rate of the differences between ozone production and loss at any given location in the atmosphere. Positive ozone tendency at any given location means ozone production rates

Table 2: Difference between the two models used for this study and LINOZ adopted from McLinden *et al*., 2000.

Model for this work	Model for LINOZ
Family approach for odd oxygen was used.	Non–family approach for odd oxygen as used.
Polar stratospheric clouds and ternary aerosols inside the polar vortex were considered.	Polar stratospheric clouds and ternary aerosols inside the polar vortex were not considered.
N_2O and CFC were included in the radical balance.	N_2O and CFC were not included in the radical balance.
Fifty-three chemical species were included in the model.	Forty-three chemical species were included in the model.

exceed ozone loss rate, and negative ozone tendency means ozone loss rate exceeds ozone production rate.

The general agreement between the two curves (Fig. 1.0) particularly in the lower stratosphere is good. The ozone tendency is negatively high in the upper stratosphere and it becomes more positive as altitude decreases. The high negative values in the upper stratosphere are due to the high amount of solar radiation which causes the photolysis of both the limited oxygen molecules available in the upper stratosphere and the ozone produced in this region. However, oxygen molecules are needed in the formation of ozone. Furthermore, the catalysts that destroy ozone, especially hydroxyl radical (OH) compete with oxygen molecules for the oxygen atoms thus enhancing the loss of ozone.

The ozone production in the middle stratosphere is more enhanced because of the abundance of oxygen molecules and also enough energetic solar radiation to facilitate the photochemical production of ozone. In the lower stratosphere, however, the values of the ozone tendency are negative. This is because the ozone layer limits the amount of energetic solar radiation needed for photochemical processes, even though there is abundance of oxygen molecule. In addition the odd oxygen suffers from catalytic destruction particularly by NO_2 and HO_2.

The curve for these results, Fig. 1.0, is more positive than the curve for the standard result in the upper stratosphere. One possible reason for this observation could be the use of family approach for odd oxygen in the model used for these results and the use of non-family approach for odd oxygen in the model used for the standard results. The use of family approach for odd oxygen implies photochemical stationary state for ozone and oxygen atom, and this works effectively during the day when there is much sunlight. However, during and after sunset, it takes some time before equilibrium between ozone and oxygen atoms is reached. The time to reach equilibrium is so slow that it might be reached only during polar night. Thus

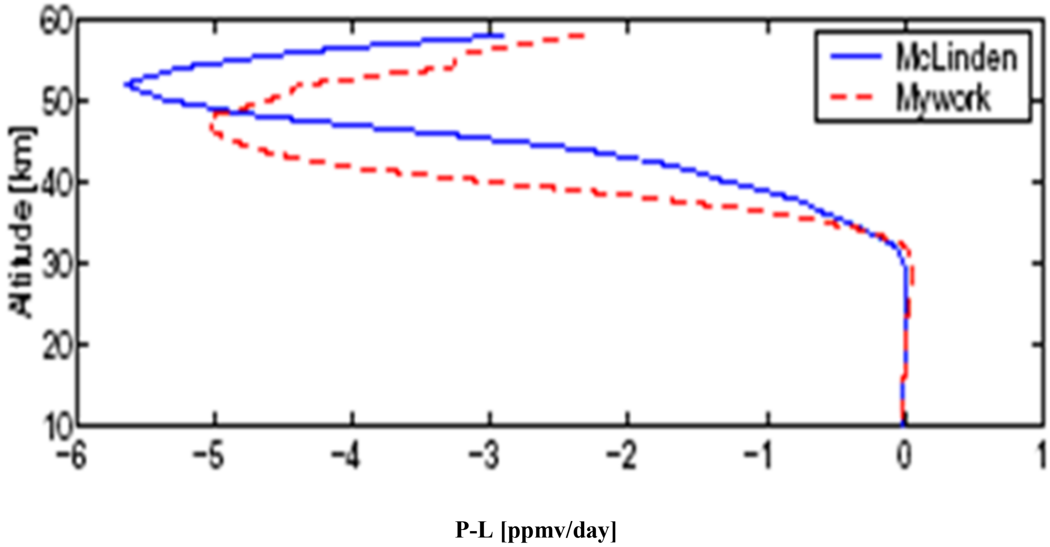

Fig. 1.0 Comparison of ozone tendency derived from the standard set and the set in this work in June, latitude 45° N. McLinden is the curve for the standard results and Mywork is the curve for the results of this work

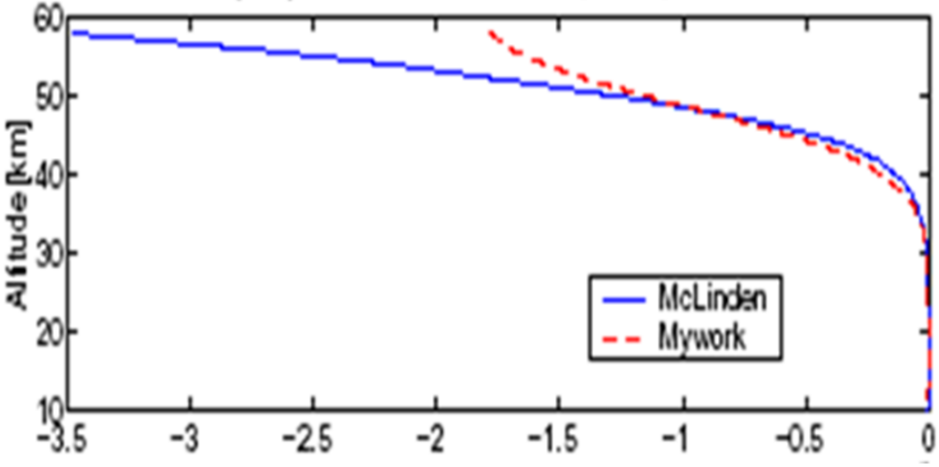

Fig. 2.0: Shows the derivative of ozone tendency with respect to ozone. McLinden is the curve for the standard results and Mywork is the curve for the results of this work.

the family approach, in this case, over estimate the amount of ozone produced. This is especially true for altitudes greater than 50 km; below, photochemical equilibrium within the O_x family is a good estimate. There is also a shift (ranging between 2 km and 10 km) between the two curves in altitudes above 35 km where the curve of these results is always below that of the standard results. One possible reason for the observed shift could be that the model used in this work uses a solar flux different from that of McLinden's model, however, this needs further investigation.

The main ozone production cycle in this result involves the photolysis of molecular oxygen. The photolysis of molecular oxygen increases with increasing altitude due to the availability of energetic photons to photolyse the oxygen molecule. Between 10 and 16 km, both curves show negative ozone tendency indication that ozone losses exceed ozone production. The losses in this range are mainly due to the dominance of HO_2 reactions with O_3 and ClO. The two reactions together contributed about 80% to ozone catalytic losses in this range. In this altitude range these values are greater than the standard values, and the maximum difference is about 0.002 ppmv/day. Between 18 and 28 km, both curves show positive ozone tendency meaning ozone production exceeds the losses. The main catalytic loss cycles here are O/O_3, NO_2/O, O_3/HO_2, and ClO/O. The values in this range are still greater than the standard values with the maximum difference of about 0.053 ppmv/day. Between 36 and 48 km, the losses in these results are greater than that of the standard results with a maximum difference of about 2.43 ppmv/day occurring at an altitude of 42 km. The major contributing catalytic loss cycles are O/O_3, NO_2/O, and ClO/O. Between 48 and 58 km, the losses in the standard results exceed these results with a maximum difference of 1.9 ppmv/day occurring at the altitude of 52 km. The major catalytic loss cycles are O/HO_2, and O/O_3.

In absolute terms, the results obtained in this work are not so different from the standard results (McLinden *et al.*, 2000; Millard *et al.*, 2002).This is confirmed by comparing the ozone lifetime (Fig. 3.0) and the ozone tendency (Fig. 4.0).

Comparing Derivative of Ozone Tendency with Respect to Ozone

The derivative of ozone tendency with respect to ozone, $d(P–L)/dO_3$, describes the effect of ozone on chemistry. If this parameter is high in any given region then less energetic solar radiation would penetrate through the region, and hence photochemistry would be reduced. This quantity is in the orders of 10^4 to 10^7 per day. The high values make this quantity relatively very important in the stratosphere. This quantity is also very useful in estimating the lifetime of ozone. This is because the lifetime is given by the negative reciprocal of $d(P–L)/dO_3$.

The two curves in Fig. 2.0 show negative values throughout the stratosphere, and the negative values increases with increasing altitude. This could be explained in terms of perturbation of the ozone in the model. By increasing the ozone concentration by 5%, the ozone tendency is reduced in the stratosphere so that the difference between the perturbed ozone and the unperturbed ozone is always negative. There is a horizontal shift between the two curves in the uppermost stratosphere. These results are about a factor of 2.5 greater than the standard results at about 58 km altitude. These observed differences could be attributed to the use of family approach for odd oxygen in the model for these result, and non-family approach in the standard result. The family approach favors ozone in the lower and the middle stratosphere. As a result, below about 50 km, the results indicate more decreasing values than the standard results.

Comparing Ozone Lifetime

The abundance of ozone in any given locality in the stratosphere depends on two processes namely chemistry and transport. In the regions where the ozone chemical lifetime is very short, chemistry dominates the contribution to the amount of ozone present. On the other hand when the lifetime is very long then transport processes dominate the contribution to the amount of ozone present. From Fig. 3.0, the lifetime of ozone is short (in the order of hours for both curves) in the upper stratosphere. This indicates that ozone abundance in the upper stratosphere is mainly contributed by chemistry. The ozone lifetime increases with decreasing altitude as shown in Fig. 3.0; thus in the middle stratosphere where ozone lifetime ranges between days and a few months, the abundance of ozone is contributed by both transport and chemistry. The ozone lifetime is

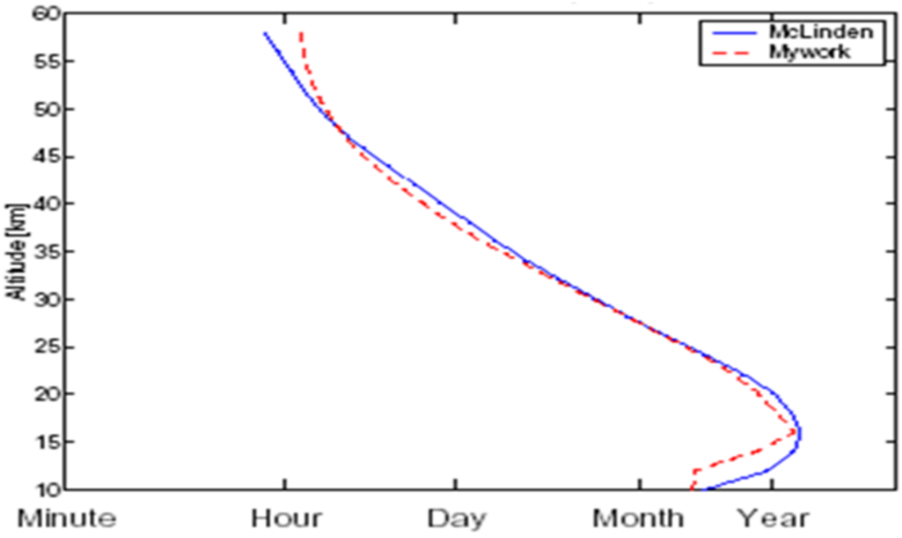

Fig. 3.0: **Comparison of ozone chemical lifetime in the stratosphere for the standard results and the results of this work**

longest in the lower stratosphere. The transport processes dominate in the abundance of ozone in this region.

Comparing Sets of Rate Limiting Steps for the Ozone Budget of the Stratosphere

In an effort to ascertain the effective contributions of the various ozone destructive cycles in the stratosphere, two sets namely standard set (RLS _Millard), following Millard *et al*, 2002, and the set in this work (RLS_Mywork) were examined. The standard set was earlier on used in this work but it was realized that there was unreasonably negative ozone tendency in the upper stratosphere. Upon investigation, it was found that the problem was associated with the partitioning of the HO_x family especially in the upper stratosphere. There was therefore the need to describe the HO_x mechanism in one cycle (Wayne, 2000) instead of two cycles as used in the standard set (Millard *et al*., 2002). The results from this set and the standard set were compared with the result from the total time approach (INT) derived from the complete chemistry in the 1–D model. Thus the results of INT serve as the reference for the ozone tendency results in this set and the standard set. The underlying assumption was that if the correct set of the rate limiting steps was used then the results should be comparable to INT since they were all derived from the same chemistry. From Fig. 4.0, the three ozone tendencies agree very well in the altitude below about 35 km as expected. In this range of altitudes, the reactions with oxygen atoms are less important since the concentration of oxygen atoms is very low due to lack of sufficient energetic solar radiation to photolyse the abundant oxygen molecules. Above about 35 km, however, the reactions of HO_x (H, OH, HO_2) with odd oxygen become significant. The large difference between the rate limiting step in this work (RLS_Mywork) and the rate limiting step obtained by Millard *et al*. (2002) (RLS_Millard) comes from the partitioning between the members of the HO_x family especially OH and HO_2 as mentioned earlier on. In this set, the reaction between oxygen atom and HO_x family is described in one cycle (Wayne, 2000) as:

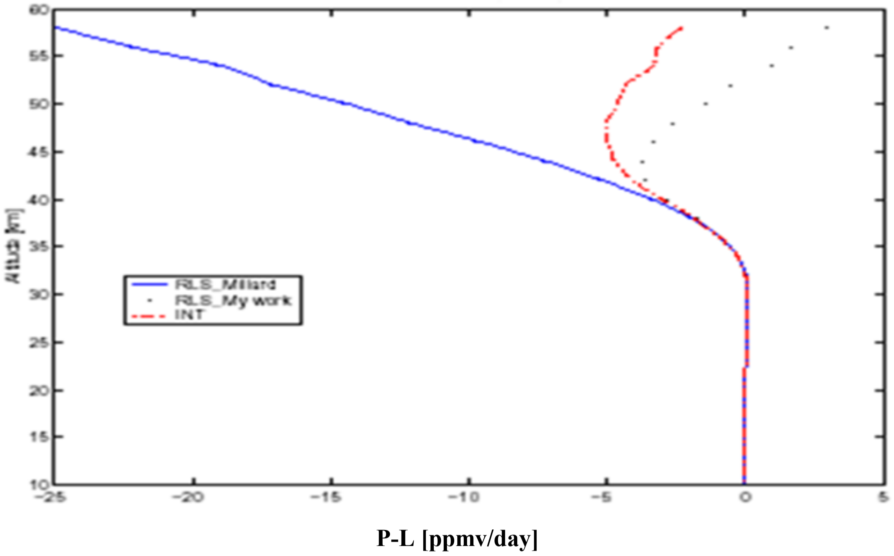

Fig. 4.0 Comparing the ozone tendency derived from the total time approach (INT) with that derived from the rate limiting step-approach using the standard set (RLS Millard), and the set in this work (RLS Mywork).

$$\begin{aligned} &OH + O \rightarrow H + O_2 \\ &H + O_2 + M \rightarrow HO_2 + M \\ &HO_2 + O \rightarrow OH + O_2 \\ \text{Net: } &O + O \rightarrow O_2 \end{aligned}$$

where the HO_2/O reaction is selected as the rate limiting step because of its relatively long mean time. However in the standard set, the reaction between oxygen atoms and the HO_x family is described in terms of two catalytic cycles as:

$$\begin{aligned} &HO_2 + O \rightarrow OH + O_2 \\ &OH + O_3 \rightarrow HO_2 + O_2 \\ \text{Net: } &O_3 + O \rightarrow 2O_2 \end{aligned}$$

Where the HO_2/O reaction is selected as the limiting step, and

$$\begin{aligned} &H + O_3 \rightarrow OH + O_2 \\ &OH + O \rightarrow H + O_2 \\ \text{Net: } &O_3 + O \rightarrow 2O_2 \end{aligned}$$

where the HO/O reaction is selected as the limiting step. It was earlier on checked how the contributions from HO/O and HO_2/O reactions as independent rate limiting steps would be. It was found out that they together contributed about 95% to the ozone destruction at 58 km altitude, and their contribution decreases with decreasing altitude. It was also observed that the contributions of HO_2/O cycle were always higher than that of HO/O by about 9% between about 45 km and 58 km, and these differences also decrease with decreasing altitude up to about 42 km where HO/O dominates over HO_2/O. The maximum percentage contribution of about 10% was observed for the two cycles together below about 40 km. These contributions below 40 km were mostly by the HO/O cycles. Thus using the set in this work would mean a maximum loss of about 4% in the HO_x contribution below 40 km. Thus from these analyses it is clear that the standard set was appropriate for the studies in the lower stratosphere. However for the entire stratosphere, this would mean doubling the effect of HO_x catalytic destruction in ozone especially in the upper stratosphere. Therefore the set in this work is more appropriate for the ozone budget in the entire stratosphere. The increase in difference between the rate limiting step approach and the total time approach in the range between 50 and 58 km could be explained in terms of the mean time of HO/O and HO_2/O. The mean time of HO/O becomes more comparable to the mean time of the selected rate limited step (HO_2/O). Even under this condition the shapes of the two plots are similar and hence the set in this work could be conveniently used in the assessment of the contributions of the individual catalytic destruction to ozone in the entire stratosphere.

Percentage Contributions of Catalytic Cycles to Ozone Loss: JPL 1997, 2000, 2002

The availability of species in a given reaction may depend on at least four main factors namely the abundance of the source gas, conditions necessary for the release of the reactive species, the coupling processes between the species in question and other species in the system, and partitioning processes between species in the same family.

The altitude of dominance by the catalytic cycles depends on the availability of species involved in the rate limiting step and the rate coefficient. This could also provide information about the strength of bonds present in the source gases, as well as the intensity of radiation needed in the process of photolysis.

The effect of each catalytic cycle to the ozone loss depends on the rate of the limiting step. If the rate is high then destruction of ozone by that reaction will be great, and vice versa. In general, the rate of any given reaction is given by the product of the rate coefficient, and the concentration of the individual species in that reaction. Thus a change in either the rate coefficient or the concentration of the species will either increase or decrease the rate, or keep the rate constant. In a situation where both rate coefficient and concentration of the reaction are increased, there will be an increase in the rate of the reaction and hence more destruction of ozone by that reaction. However, if any one of the two: rate coefficient or concentration is reduced and the other is increased, then the rate will increase, decrease or remain the same. From the individual plots in figures Fig. 5.0, Fig. 6.0, Fig. 7.0, we observe changes in the individual curves that indicate that there have been changes in the JPL recommendation. Even if there is no change in the data for a particular reaction, it is possible to observe changes in the percentage contribution. The reason is that coupling processes occur between different families so that the concentration is either increase or decreased. (Portmann *et al*., 1999) reported that increase in NO_x abundance up to 40% led to reduction in the abundance of HO_x (10 – 30%) and ClO_x (20 – 40%). The increase in NO_x abundance was due to changes in rate coefficients for the reactions: O/NO_2, OH/HNO_3, and OH/NO_2. In addition, partitioning processes occur between species in the same family that may change the concentration.

In order to find out how our knowledge and understanding of the chemistry of the stratosphere is improving, we compare the contributions of the various catalytic loss cycles in the three most recent JPL recommendations (1997, 2000, 2002). For most of the conditions considered in this study, each cycle maintains its characteristic shape under all conditions (seasons and latitudes) except under polar conditions. However, the contributions of each cycle to the ozone budget may differ from one condition to the other. This is because the contributions depend, among other factors, on the abundance of the species in the cycle, and this may not be the same under all conditions.

NO_2/O cycle (Fig. 5.0) is one of the most important catalytic cycles to ozone destruction under the summer mid-latitude condition. It is effective between 16 and 46 km where the minimum contribution is about 22%. The NO_2/O cycles peaks around 32 km altitude with a maximum percentage contribution between 66 and 72%. It is very active in the middle stratosphere (between 25 and 40 km) where it contributes at least 50% to ozone destruction. It is at least a factor of two more effective than any of the catalytic cycles in the middle strato-

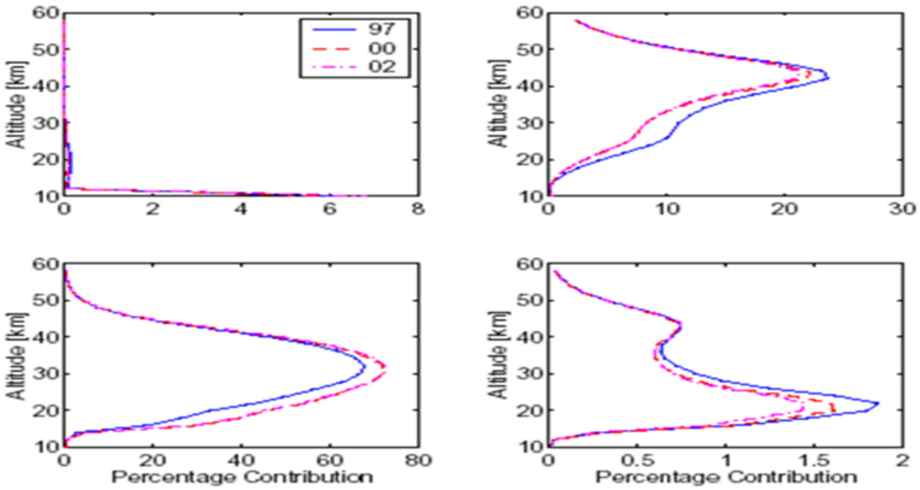

Fig. 5.0: Percentage contributions of Cl_2O_2 cycle (top left), ClO/O cycle (top right), NO_2/O cycle (bottom left) and BrO/O cycle (bottom right) to the ozone loss rate for June, latitude 45° N. The legend 97, 00, and 02 represent JPL recommendations 1997, 2000, and 2002 respectively.

sphere. A possible reason for the great contribution in the middle stratosphere could be the increase in abundance of the NO_y species and also significant amount of oxygen atoms available (Brasseur *et al*., 1999). The two most recent recommendations (JPL 2000 and 2002) indicate a general increase in percentage contribution of NO_2/O cycle.

The *ClO/O* cycle (Fig. 5.0) generally spreads in the stratosphere even though the percentage contribution in most part of the stratosphere is relatively small. It is quite active between 26 and 50 km, and it peaks at about 44 km with a maximum of about 22%. One of the reasons for the peak is the abundance of oxygen atoms in this altitude. There is an observed reduction trend in the percentage contribution from JPL 97 to JPL 2002. However, there is no change in the rate coefficient for this reaction since 1997. The observed changes are likely to originate from the change in the NO_x which couples with *ClO/O* as reported by Portmann *et al*., 1999.

The O/HO_2 cycle (Fig.6.0) is the single most important catalytic cycle to ozone destruction in the upper stratosphere, an observation also reported by Sinnhuber *et al*., 2003b. The contributions of this cycle increases with increasing altitude and get the maximum contribution of about 90% at 58 km altitude. The observed nature of curve for O/HO_2 cycle could be explained in terms of the abundance of oxygen atoms and HO_2 molecules in the stratosphere. The trend is partly due to increase in the source gas for the reactive hydrogen (i.e. water vapor) with increasing altitude in the stratosphere. The tropopause serves as a cold trap to the moist air lifted from the troposphere in the tropics thus limiting the amount of water vapor found in the lower stratosphere. However, methane could enter into the stratosphere without any hindrance by the cold temperatures of the tropopause. Methane in the stratosphere is oxidized by hydroxyl radical (*OH*) thus producing water vapor which then generates the reactive hydrogen species (*OH*, HO_2) in the stratosphere. Furthermore, the increase in concentrations of O_x and HO_x at mid-latitudes beginning after sunlight, due respectively to the onset of molecular oxygen photolysis (primarily in the Schumann–Range bands) and water vapour photolysis (primarily at Lymann–α) (Marsh *et al*., 2001). The 3 curves for this reaction cycle

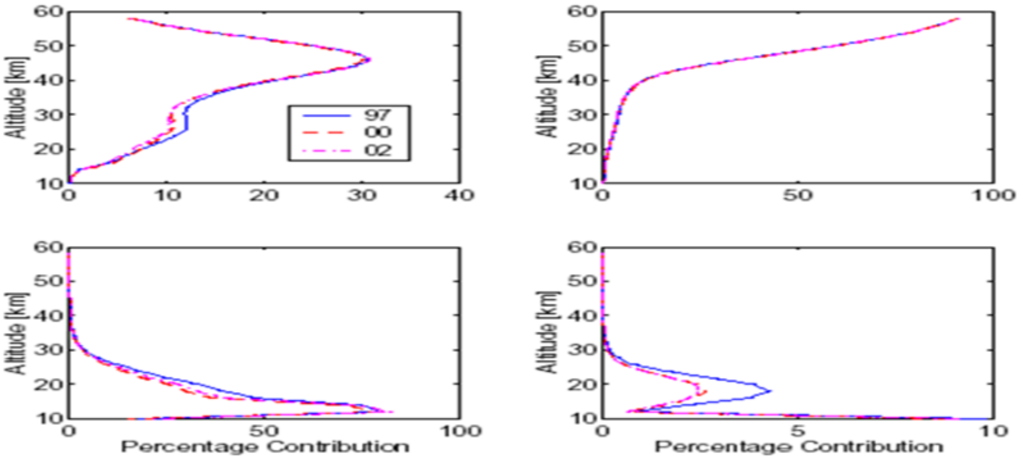

Fig. 6.0: Percentage contributions of O/O_3 cycle (top left), O/HO_2 cycle (top right), O_3/HO_2 cycle (bottom left), and *ClO/BrOb* cycle (bottom right) to the ozone loss rate for June, latitude 45^o N. The legend 97, 00, and 02 represent JPL recommendations 1997, 2000, and 2002 respectively.

agree very well in the whole stratosphere. The reason for this observation is that there have not been any changes in the JPL recommendations since that of JPL 1997.

The O_3/HO_2 cycle (Fig. 6.0) is an important cycle in the lower stratosphere where it peaks around 12 km with a percentage range between 79 and 82%. The effectiveness of the cycle generally decreases with increasing altitude. A possible explanation to this observation can be the low value of the ratio of the concentration of oxygen atom to that of ozone. This low ratio favors cycles with net effect of destroying 2 molecules of ozone and yielding 3 molecules of oxygen (Wayne, 2000). There are observed variations in the curves for the 3 JPL recommendations. The agreement between the JPL 97 and JPL 2002 seems to be better than the agreement between JPL 2000 and JPL 2002. There are changes in all the 3 JPL recommendations.

The O/O_3 cycle (Fig. 6.0) is an important ozone loss cycle in the upper stratosphere during summer mid-latitude conditions. Percentage contribution is significant between 26 and 54 km where the contributions are in the range of 24 and 30%. The observations can be due to high ratio of concentration of oxygen atoms to that of ozone. There are little changes in the percentage contributions from JPL 2002 and JPL 2000. The change in the percentage contributions of either JPL 2002 or JPL 2000 from the JPL 1997 is quite significant especially between 20 and 30 km. This may be due to changes in the photolysis of O_3 and in the partitioning of $O/O(^1\Delta)$ formed. Another possible explanation could be the changes in the quantum yield of the photolysis that might affect the O/O_3 cycle as it affects the concentration of O (Sander *et al*., 2000; 2002).

The percentage contributions to the ozone loss by the reactions with the halogens (ClO/BrO cycle, HO_2/BrO cycle, HO_2/ClO cycle) shown in Fig. 7.0 during the summer mid-latitude conditions are generally low. The maximum of these reactions is mostly in the lower stratosphere extending a little into the middle strato-

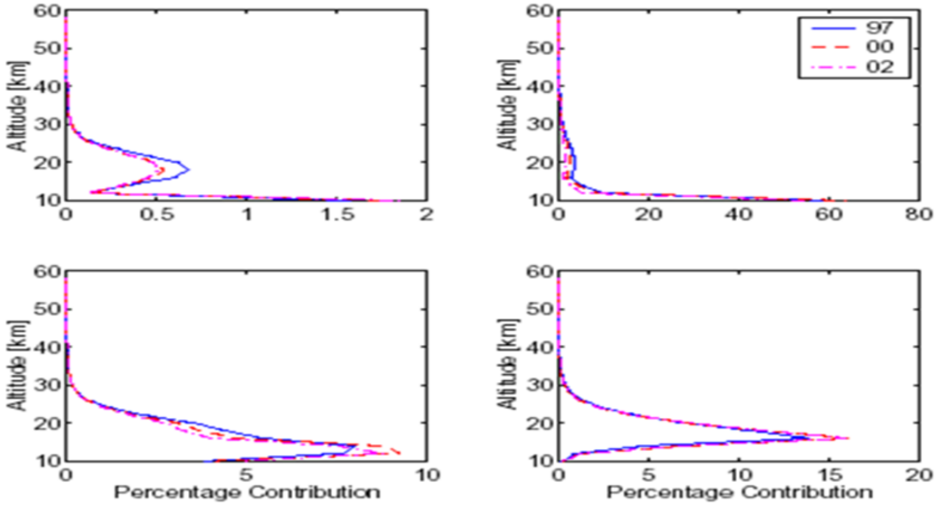

Fig.7.0: Percentage contributions *$ClO/BrOc$* cycle (top left), *HO_2/ClO* cycle (top right), *HO_2/BrO* cycle (bottom left), and *NO_3* cycle (bottom right) to the ozone loss rate for June, latitude 45° N. The legend 97, 00, and 02 represent JPL recommendations 1997, 2000, and 2002 respectively.

sphere. The percentage contributions of the halogens are sensitive to temperature, and aerosol surface area, varies with season, and has a maximum in spring (Portmann *et al*., 1999). Like most of the cycles, the contributions of these cycles for the three JPL recommendations are not the same.

During the day nitrate free radical, NO_3, is rapidly photolyzed so that its concentration is negligible. However during the night when there is no solar radiation for photolytic reactions, NO_3 is produced by destruction of O_3. The NO_3 cycle (Fig. 7.0) is of minor importance during summer mid-latitude conditions such as mid-latitude spring in the northern hemisphere. The major contribution of the NO_3 cycle occurs between 16 and 18 km with a maximum of less than 17% for any of the three JPL recommendations. There are observed uncertainties between 12 and 18 km that is attributed to measurement of the concentration of NO_3 (Sander *et al*., 2002). There is an observed increase in NO_3 contributions to the ozone budget in the two most recent JPL recommendations. The agreement between the contributions from the JPL 2000 and 2002 is good.

Impact of JPL Recommendations on Steady State Ozone

The net variation of the photochemical data for the cycles is summarized in the plot of the steady state ozone for the three JPL recommendations, Fig.8.0. There are observed maximum variations occurring between 22 km and 32 km. These are mainly attributed to some uncertainties in the major catalytic cycles NO_2/O, and O_3/HO_2 in this region as described by Portmann *et.al* 1999.

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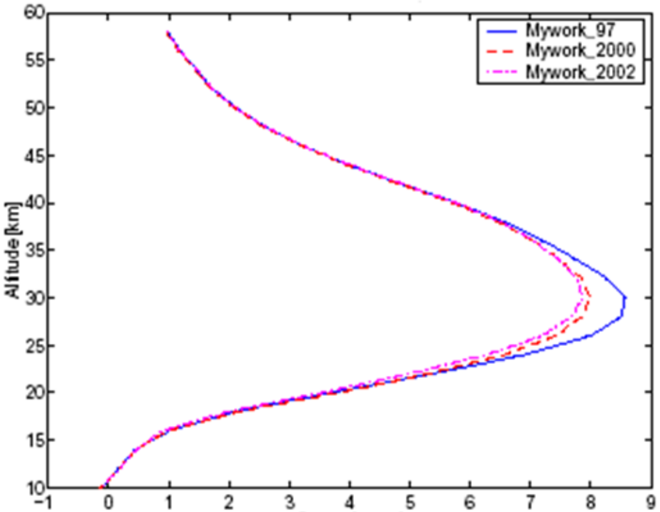

Fig. 8.0: **Comparing steady state ozone for the three most recent JPL recommendations: Mywork 97, Mywork 2000, Mywork 2002 for JPL 1997, 2000 and 2002 respectively.**

The trend is partly due to increase in the source gas for the reactive hydrogen (i.e. water vapor) with increasing altitude in the stratosphere. The tropopause serves as a cold trap to the moist air lifted from the troposphere in the tropics thus limiting the amount of water vapor found in the lower stratosphere. However, methane could enter into the stratosphere without any hindrance by the cold temperatures of the tropopause. Methane in the stratosphere is oxidized by hydroxyl radical (OH) thus producing water vapor which then generates the reactive hydrogen species (OH, HO_2) in the stratosphere. Furthermore, the increase in concentrations of O_x and HO_x at mid-latitudes beginning after sunlight, due respectively to the onset of molecular oxygen photolysis (primarily in the Schumann–Range bands) and water vapour photolysis (primarily at Lymann–α) (Marsh *et al*., 2001). The 3 curves for this reaction cycle agree very well in the whole stratosphere. The reason for this observation is that there have not been any changes in the JPL recommendations since that of JPL 1997.

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CONCLUSION

In this work, a standard 1–D stratospheric model was used as an important diagnostic tool. This model was used to derive a set of coefficients of a linearised ozone chemistry scheme, to be used in a 3–D chemical transport model. Two different conceptual approaches to the linearised ozone chemistry scheme (LINOZ) were carefully formulated. A set of catalytic cycles which could describe the ozone budget in the entire stratosphere was developed. Using the 1–D model as a diagnostic tool and the two conceptual approaches as means for effective analysis, the coefficients of LINOZ chemistry were derived. The derived coefficients in this work compared favorably with the standard set except in the upper stratosphere where there is some discrepancies. The observed discrepancies in the upper stratosphere could be due to the use of the family approach in the model for these results.

Among the four terms in the linearised ozone chemistry scheme, the derivative of ozone tendency with respect to ozone ($d(P–L)/dO_3$) is the major term. The $d(P–L)/dO_3$ has relatively larger contributions than any other term in the linearised ozone chemistry scheme. Furthermore, the $d(P–L)/dO_3$ can easily be used to estimate the lifetime of ozone in the stratosphere.

Concerning the contributions of the various catalytic cycles to the loss of ozone in the stratosphere, the following cycles dominated the loss processes in the upper stratosphere for all the three JPL recommendations: ClO/O, O/O_3 and O/HO_2. The NO_2/O cycle dominated in the ozone loss processes in most part of the middle and the lower stratosphere. The O_3/HO_2, NO_3/ClO and HO_2/BrO were the dominant cycles in the lower stratosphere.

The set of catalytic cycles developed in this work could serve several purposes. It could be used to describe the chemistry in the simulated ozone throughout the stratosphere. In other words, the key processes in the chemistry could be ascertained using the set developed in this research. The set could also be used to study how measurements leading to changes in JPL recommendation are converging. This is important because it could deepen our knowledge and understanding about the chemistry in the stratosphere.

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