

The Potential Influence of ClO · O₂ on Stratospheric Ozone Depletion Chemistry

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Abstract. The inability to explain the observed oxygen suppression of chlorine photosensitized ozone loss remains a gap in our understanding of the photochemistry responsible for depletion of the stratospheric ozone layer. It has been suggested that the presence of a weakly bound ClO · O₂ complex could explain this effect. The existence of this complex would alter the chlorine budget of the stratosphere, perhaps reducing the chlorine available for catalytic ozone destruction. On the other hand, the chemistry of ClO · O₂ provides two new pathways for ClO dimer formation, which could increase the rate of catalytic ozone loss. In this paper, we constrain the kinetic rate system of ClO · O₂ to match the measured Cl_y budget. It is shown that ClO · O₂ cannot be both fairly stable and rapidly form the ClO dimer, or the resulting partitioning of chlorine becomes incompatible with observations of both ClO and total available chlorine. These constraints allow that either: (1) the ClO · O₂ is fairly stable, but does not significantly enhance ClO dimer formation and therefore has a negligible effect on ozone loss rates, or (2) the ClO · O₂ complex is only very weakly stable, but does rapidly form the ClO dimer, and therefore can influence stratospheric ozone depletion. Even at the ClO · O₂ mixing ratios allowed under the assumption of weak stability, 0.1 to 0.2 ppbv, significant ozone loss rate enhancements were calculated. Of course, the chlorine budget constraint also allows for a third possibility; that ClO · O₂ is neither very stable nor forms Cl₂O₂ very rapidly. Measured limits on the reaction rates for ClO · O₂ to form the ClO dimer would greatly aid the resolution of this issue. Since the uncertainties about ClO · O₂ chemistry are so large, a potential role for ClO · O₂ in stratospheric ozone loss cannot be ruled out at this time.

Key words: ozone depletion, stratosphere, chlorine chemistry.

1. Introduction

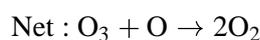
The catalytic destruction of ozone by chlorine is responsible for the majority of polar ozone depletion which creates the annual Antarctic ozone hole (e.g. Solomon, 1990), as well as playing a significant role in mid-latitude ozone loss over populated areas (World Meteorological Organization, 1994). In currently accepted chemistry, chlorine destroys polar ozone primarily through the ClO dimer catalytic cycle (Molina and Molina, 1987):





This catalytic cycle requires sunlight to proceed, and is limited under typical conditions found in the Antarctic springtime lower stratosphere by reaction 2, the rate of dimer formation.

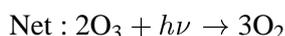
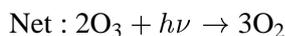
The 'standard' cycle, which may be important at mid-latitudes as well as playing a minor role in polar ozone depletion, is the following:



In both cycles, the rate of ozone loss is independent of the amount of oxygen present. It is therefore troubling that laboratory measurements have shown that oxygen in fact suppresses chlorine photosensitized ozone decomposition (Norrish and Neville, 1934; Wongdontri-Stuper *et al.*, 1979). A possible explanation was offered by Norrish and Neville (1934), and elaborated upon by Prasad (1980), who suggested that this Norrish–Neville effect could result from additional chemistry involving a $\text{ClO} \cdot \text{O}_2$ association complex if it were stable enough to exist in significant amounts. After ClO is formed following the irradiation of Cl_2 , the existence of the $\text{ClO} \cdot \text{O}_2$ complex would alter the branching ratios for the $\text{ClO} + \text{ClO}$ reaction to favor the formation of Cl_2 at the expense of Cl, leading to fewer free chlorine radicals which destroy ozone. The addition of oxygen would increase the amount of $\text{ClO} \cdot \text{O}_2$ formation, causing a reduction in the amount of chlorine radicals, and hence a reduction in the yield of ozone molecules depleted per photon absorbed by Cl_2 . A stable $\text{ClO} \cdot \text{O}_2$ complex could thus explain the Norrish–Neville effect.

Several recent laboratory chemical kinetics experiments (Ongstad and Birks, 1986; Sander *et al.*, 1989; Trolier *et al.*, 1990; DeMore, 1990; Nickolaisen *et al.*, 1994) have suggested that the 'current' $\text{ClO} + \text{ClO}$ branching ratios are in fact correct, although these experiments have set limits on the $\text{ClO} \cdot \text{O}_2$ reaction rates which still allow for the possibility that $\text{ClO} \cdot \text{O}_2$ may exist in significant amounts. Prasad and Lee (1994) have explicitly asserted that the laboratory experiments are inconclusive, and that the concentration ratio $[\text{ClO} \cdot \text{O}_2]/[\text{ClO}]$ may be as large as 0.75 within the polar vortex based on the laboratory upper limit for the equilibrium constant of the $\text{ClO} + \text{O}_2 \leftrightarrow \text{ClO} \cdot \text{O}_2$ reaction. A ratio this large could give $\text{ClO} \cdot \text{O}_2$ a major role in chlorine catalyzed ozone depletion chemistry. New catalytic cycles could take place via:





The formation of the ClO dimer could be enhanced through the two step process of formation of the ClO · O₂ complex, reaction (6), followed by either reaction (7) or (8), both of which form the ClO dimer. These steps could circumvent the rate limiting reaction (2) in the ClO dimer catalytic cycle given above, and increase the rate of chlorine catalyzed ozone depletion. Large amounts of ClO · O₂ could also indicate severe problems with current interpretation of ClO observations.

We examine here the implications of proposed ClO · O₂ chemistry, calculating the abundance of ClO · O₂ in equilibrium with typical measured values of enhanced ClO within the southern polar vortex. We show that a stable ClO · O₂ compound creates a significant chlorine reservoir, while fairly rapid dimer formation greatly increases the [Cl₂O₂]/[ClO] ratio. Forcing the resulting chlorine budget to be compatible with total chlorine, such that ClO + 2 × Cl₂O₂ + ClO · O₂ is constrained to be less than or equal to the total available chlorine (neglecting HCl and ClONO₂ at this point to set an upper limit on active chlorine), we show that one or both of the steps whereby ClO forms Cl₂O₂ via ClO · O₂ must proceed fairly slowly. Ozone depletion rates are then calculated based on these constraints.

2. The Chemical Model

The five chemical reactions involving ClO · O₂ are listed in Table I (reactions (6)–(10)), along with several other important chlorine reactions in the lower stratosphere. Reaction numbers follow those used in the catalytic cycles above. Rates are evaluated based on the rate constant parameters and photolysis cross

Table I. Chlorine reactions and their rate constants at $T = 197^\circ\text{K}$

#	Reaction	Rate constant
1	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	7.7×10^{-12}
2	$\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$	6.9×10^{-32}
3	$\text{Cl}_2\text{O}_2 + h\nu \rightarrow \text{Cl} + \text{ClOO}$	9.2×10^{-4}
4	$\text{ClOO} + \text{M} \rightarrow \text{Cl} + \text{O}_2 + \text{M}$	*
5	$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$	4.3×10^{-11}
6	$\text{ClO} + \text{O}_2 + \text{M} \rightarrow \text{ClO} \cdot \text{O}_2 + \text{M}$	2.1×10^{-32}
7	$\text{ClO} + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O}_2 + \text{O}_2$	1.0×10^{-12}
8	$\text{ClO} \cdot \text{O}_2 + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O}_2 + \text{O}_2 + \text{O}_2$	5.0×10^{-13}
9	$\text{ClO} \cdot \text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{O}_2 + \text{M}$	1.4×10^{-14}
10	$\text{Cl} + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O} + \text{O}_2$	1.0×10^{-10}
11	$\text{Cl} + \text{ClO} + \text{O}_2 \rightarrow \text{Cl}_2\text{O} + \text{O}_2$	2.7×10^{-12}
12	$\text{Cl} + \text{Cl}_2\text{O} \rightarrow \text{Cl}_2 + \text{ClO}$	9.8×10^{-11}
13	$\text{Cl} + \text{Cl}_2\text{O}_2 \rightarrow \text{Cl}_2 + \text{Cl} + \text{O}_2$	1.0×10^{-10}
14	$\text{Cl}_2\text{O}_2 + \text{M} \rightarrow \text{ClO} + \text{ClO} + \text{M}$	2.8×10^{-24}
15	$\text{Cl} + \text{OCIO} \rightarrow \text{ClO} + \text{ClO}$	7.7×10^{-11}
16	$\text{Cl}_2\text{O} + h\nu \rightarrow \text{Cl} + \text{ClO}$	5.5×10^{-4}
17	$\text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl}$	2.0×10^{-3}
18	$\text{OCIO} + h\nu \rightarrow \text{O} + \text{ClO}$	6.8×10^{-2}

Rate constants for reactions (6) and (9) are calculated using the upper limit for the equilibrium constant given in the text (with $\Delta H = 7$ kcal/mole) and the association reaction rate constants given in DeMore (1990). Rate constants for reactions (7), (8), (10), and (11) are taken from Prasad and Lee (1994), and for all other reactions from DeMore *et al.* (1994). Reaction (4) is so rapid that it is assumed to be instantaneous in these calculations. Photolysis rate constants are calculated using the cross sections of DeMore *et al.* (1994). Values given here are for midday, 78°S , 6 September conditions. Units are s^{-1} for photolysis reactions, $\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$ for bimolecular reactions, and $\text{cm}^6 \text{molec}^{-2} \text{s}^{-1}$ for three body reactions.

sections given in the NASA/JPL 1994 evaluation (DeMore *et al.*, 1994), or are taken from DeMore (1990) or Prasad and Lee (1994) as cited in the table.

The stability of the $\text{ClO} \cdot \text{O}_2$ complex is determined by reactions (6) and (9), the ratio of which is the equilibrium constant of this species. The equilibrium constant for the reaction $\text{ClO} + \text{O}_2 \leftrightarrow \text{ClO} \cdot \text{O}_2$ is given by the expression $k_{\text{eq}} = 2.9 \times 10^{-26} \exp(\Delta H/RT) \text{cm}^3$, where ΔH is the bond strength, R is the gas constant, and T is temperature in degrees Kelvin. An upper limit from recent laboratory measurements is a bond strength of ~ 7 kcal/mole (e.g. DeMore, 1990; Nikolaisen *et al.*, 1994), so that $k_{\text{eq}} = 2.9 \times 10^{-26} \exp(3500/T) \text{cm}^3$, which gives $k_{\text{eq}} = 1.5 \times 10^{-18} \text{cm}^3$ for $T = 197 \text{K}$ (the data evaluation of DeMore *et al.* (1994) suggests a conservative upper limit of $\Delta H/R < 3700$).

We also wish to consider the impact of $\text{ClO} \cdot \text{O}_2$ on ozone destruction, for which reactions (7) and (8) are also of primary importance, as shown in the catalytic

cycles above. Together, these reactions determine how rapidly $\text{ClO} \cdot \text{O}_2$ forms the ClO dimer, and could therefore enhance the chlorine catalyzed depletion of ozone by speeding up the rate limiting step of dimer formation. We begin our analysis using the current laboratory upper limit for the equilibrium constant, and the reaction rate constants proposed by Prasad and Lee (1994) given in the table for reactions (7) and (8), though we note that there is no experimental evidence for the latter two rate constants.

This reaction set has been used to calculate equilibrium mixing ratios of $\text{ClO} \cdot \text{O}_2$ and Cl_2O_2 for conditions appropriate to the polar springtime lower stratosphere at ~ 20 km (~ 39 mbars), when large amounts of ClO , ~ 1.7 – 1.9 parts per billion by volume (ppbv), have been observed (e.g. Waters *et al.*, 1993; de Zafra *et al.*, 1995). The photolysis calculations are performed using tridiagonal matrix inversion (Toon *et al.*, 1989) to find the radiation field in a spherical atmosphere, with radiative transfer within each layer calculated using the delta-Eddington method (Dvortsov *et al.*, 1992; Briegleb, 1992). Absorption due to molecular oxygen and ozone is calculated, with the ozone and pressure profiles taken from balloon measurements performed at McMurdo Station by the University of Wyoming (B. Johnson, personal communication, 1993), supplemented by MLS ozone above 35 km altitude (J. Waters, personal communication, 1994). Further details of the radiative transfer calculation can be found in Shindell and de Zafra (1996). For verification, the calculations were also performed using the full chemistry of the 1-dimensional model described in Shindell and de Zafra (1996), with the addition of the $\text{ClO} \cdot \text{O}_2$ and Cl_2O reactions (along with relatively unimportant reaction (13) for completeness). The solutions were virtually identical. Figure 1 shows the results of five such calculations. The first set of four bars show mixing ratios when $\text{ClO} \cdot \text{O}_2$ chemistry is excluded. The next two sets show mixing ratios calculated based on the $\text{ClO} \cdot \text{O}_2$ chemistry given in Table I, for the indicated temperatures.

3. Results

Using the recommended equilibrium constant, the calculated $[\text{ClO} \cdot \text{O}_2]/[\text{ClO}]$ ratio ranges from 0.5 to 1.2 for lower stratospheric vortex temperatures from 197° to 187°K respectively, at which large amounts of ClO have been observed. These values are in agreement with the results of Prasad and Lee (1994). The effect of the $\text{ClO} \cdot \text{O}_2$ chemistry on the $[\text{Cl}_2\text{O}_2]/[\text{ClO}]$ ratio is even more significant however. The two new pathways for Cl_2O_2 formation provided by the presence of $\text{ClO} \cdot \text{O}_2$, reactions (7) and (8) in Table I, increase the $[\text{Cl}_2\text{O}_2]/[\text{ClO}]$ ratio dramatically when the reaction rate constants suggested by Prasad and Lee are used. In this case, so much chlorine is sequestered in Cl_2O_2 and $\text{ClO} \cdot \text{O}_2$ that to accommodate an observed ClO level of 1.8 ppbv requires a total inorganic chlorine budget of 9 to 21 ppbv, for 197° and 187°K temperatures respectively, as shown in the second and third set of bars in Figure 1. These values are implausibly larger than the current total available inorganic chlorine of ~ 3.1 – 3.2 ppbv near 20 km altitude (von

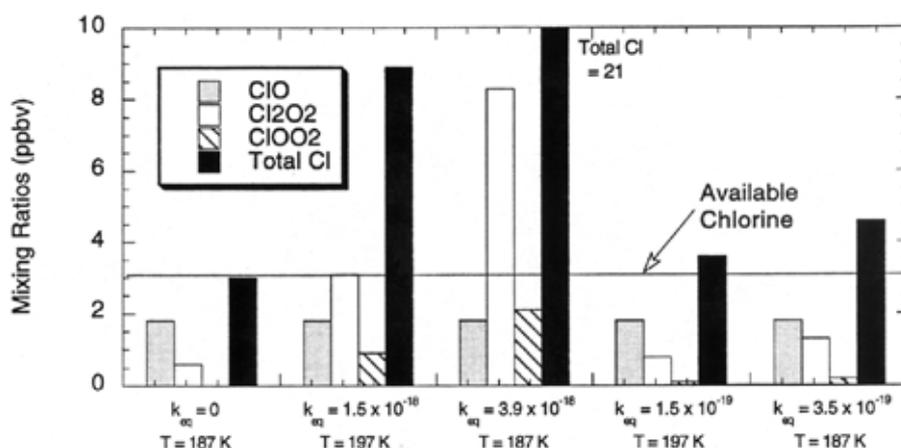


Figure 1. Calculated mixing ratios of active chlorine species at 20 km altitude (~ 39 mbars) based on an observed 1.8 ppbv CIO and using the indicated temperatures and equilibrium constants for the reaction $\text{CIO} + \text{O}_2 \rightarrow \text{CIO} \cdot \text{O}_2$ ($k_{eq} = 0$ represents 'standard' chlorine chemistry without $\text{CIO} \cdot \text{O}_2$). Photolysis calculations were performed for midday, 78°S , 6 September conditions, corresponding to a period when large CIO mixing ratios have been observed. Equilibrium constants given in $\text{cm}^3 \text{ molec}^{-1}$.

Clarmann *et al.*, 1995; Woodbridge *et al.*, 1995), which is shown as a horizontal line across Figure 1. While the presence of the $\text{CIO} \cdot \text{O}_2$ complex would likely influence the interpretation of some CIO observations, measurements of CIO using several techniques would all have to be too large by a factor of three or more to accommodate these $[\text{Cl}_2\text{O}_2]/[\text{CIO}]$ and $[\text{CIO} \cdot \text{O}_2]/[\text{CIO}]$ ratios. This does not seem believable, especially given that no rationale has been offered to explain how ground-based microwave measurements could be affected by $\text{CIO} \cdot \text{O}_2$. We conclude that when the proposed reaction rate constants for Cl_2O_2 formation from $\text{CIO} \cdot \text{O}_2$ are used, the $\text{CIO} \cdot \text{O}_2$ cannot be very stable.

Using the reaction rate constants suggested by Prasad and Lee for reactions (7) and (8), a bond strength of ~ 6.1 kcal/mole is the largest that can be reconciled with the available chlorine budget and measured active chlorine. The equilibrium constant is then approximately an order of magnitude lower ($k_{eq} = 1.5 \times 10^{-19} \text{ cm}^3$ at $T = 197^\circ \text{K}$). The total chlorine contained in observed CIO and calculated Cl_2O_2 and $\text{CIO} \cdot \text{O}_2$ becomes much closer to the total available inorganic chlorine with this equilibrium constant, though it is still larger, as shown in the two right-hand sets of bars in Figure 1. However, since the uncertainties in measurements of both CIO abundance and the CIO dimer reaction rates lead to an uncertainty of $\pm 48\%$ on inferred total chlorine (Shindell and de Zafra, 1995), this value is a reasonably conservative upper limit on the strength of the $\text{CIO}-\text{O}_2$ bond in the $\text{CIO} \cdot \text{O}_2$ complex and on the equilibrium constant derived from the bond strength. Again, this limit is valid when the proposed reaction rate constants for Cl_2O_2 formation from $\text{CIO} \cdot \text{O}_2$ are used. The maximum mixing ratio of the $\text{CIO} \cdot \text{O}_2$ complex that

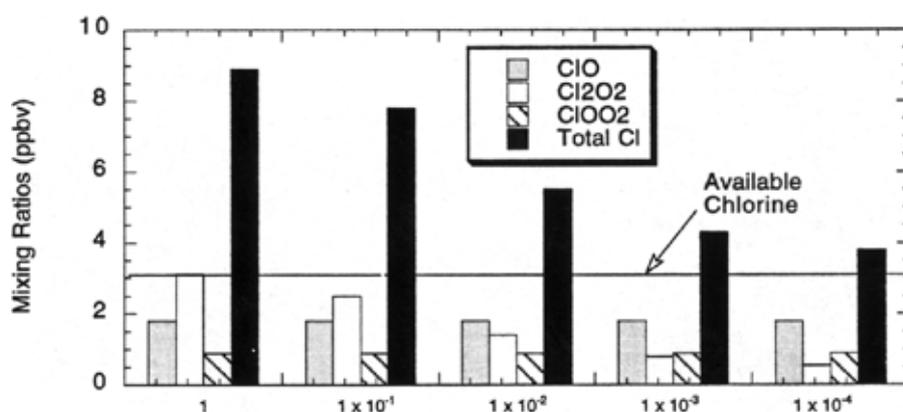


Figure 2. Calculated mixing ratios of active chlorine species as a function of the rapidity of ClO dimer formation from $\text{ClO} \cdot \text{O}_2$, based on 1.8 ppbv ClO and the upper limit of the $\text{ClO} \cdot \text{O}_2$ equilibrium constant. Both reactions that form Cl_2O_2 from $\text{ClO} \cdot \text{O}_2$, reactions (7) and (8), have been multiplied by the factor given under each set of bars.

could exist in the stratosphere for current chlorine loading is approximately 0.2 ppbv with this limit. The amount of $\text{ClO} \cdot \text{O}_2$ is strongly temperature dependent, falling from 0.19 ppbv at $T = 187^\circ\text{K}$ to 0.09 ppbv at $T = 197^\circ\text{K}$.

Another concern is that the rate constants for the new pathways to form Cl_2O_2 , reactions (7) and (8), have not been measured. If these rate constants were smaller than suggested, less Cl_2O_2 would be formed from $\text{ClO} \cdot \text{O}_2$. This raises the possibility that $\text{ClO} \cdot \text{O}_2$ could in fact be fairly stable, but not enhance ClO dimer formation as strongly, and so would not violate the chlorine budget in the manner shown above. To explore this possibility, we have reduced the reaction rate constants for both reactions (7) and (8) progressively by powers of ten. In Figure 2 we present the chlorine budget as a function of the rapidity of the $\text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O}_2$ reactions when the current recommendation for the upper limit of the $\text{ClO} \cdot \text{O}_2$ equilibrium constant is used. The rate constants were multiplied by the factors shown under each set of bars. Results for $T = 197^\circ\text{K}$ are shown. Clearly, the formation of the ClO dimer from $\text{ClO} \cdot \text{O}_2$ must be reduced by at least three orders of magnitude in order for the total chlorine budget to be in reasonable agreement with the available chlorine amount. The chlorine budget is even more constraining at 187°K , as colder temperatures would increase the stability of both Cl_2O_2 and $\text{ClO} \cdot \text{O}_2$, yielding roughly 30% more total chlorine for a given set of reaction rate constants. Based on the chlorine budget constraint, we conclude that $\text{ClO} \cdot \text{O}_2$ could in fact be fairly stable, but only if its presence does not greatly enhance ClO dimer formation. Even with a fairly stable $\text{ClO} \cdot \text{O}_2$ complex, the influence on the chlorine budget would be minimal in this scenario since it requires a compensating reduction in ClO dimer amounts in equilibrium with daytime ClO, as shown in Figure 2. Given that the abundance of the ClO dimer has never been measured, it is not currently possible to determine the veracity of this scenario.

A similar analysis has been performed at 16 km altitude (~ 78 mbars). Chlorine monoxide abundances of about 0.8 ppbv have been observed at these levels by several techniques (e.g. Toohey *et al.*, 1993; Waters *et al.*, 1993; de Zafra *et al.*, 1995). The higher pressure increases the rates of the three body reactions, increasing the $[\text{Cl}_2\text{O}_2]/[\text{ClO}]$ and the $[\text{ClO} \cdot \text{O}_2]/[\text{ClO}]$ ratios as compared to those found at lower pressures. At a temperature of 197 °K, the total chlorine contained in $\text{ClO} + 2 \times \text{Cl}_2\text{O}_2 + 2 \times \text{ClO} \cdot \text{O}_2$ is 9.4 ppbv using an equilibrium constant of $k_{\text{eq}} = 1.5 \times 10^{-18} \text{ cm}^3$, and 4.1 ppbv using $k_{\text{eq}} = 1.5 \times 10^{-19} \text{ cm}^3$, slightly larger than the 8.9 and 3.6 ppbv calculated at 39 mbars using the same equilibrium constants (shown in Figure 1). Despite the lower abundances of ClO typically observed at these levels, the pressure dependencies of the Cl_2O_2 and $\text{ClO} \cdot \text{O}_2$ formation reactions make these results slightly more constraining than those at lower pressures. Additionally, recently reported ground-based observations show ClO mixing ratios of 1.0–1.5 ppbv occurring at ~ 16 km late in the Antarctic springtime (de Zafra *et al.*, 1995). The vertical resolution of the ground-based instrument is fairly coarse (~ 6 km) however, so it is difficult to draw conclusions that are extremely pressure sensitive based solely on those data. Those measurements suggest that the $\text{ClO} \cdot \text{O}_2$ equilibrium constant may in fact be substantially smaller than the limit given here however.

Note also that the calculated ‘total’ chlorine amount used here includes only ClO, Cl_2O_2 , and $\text{ClO} \cdot \text{O}_2$, and that the presence of any chlorine in other species such as ClONO_2 or HCl would allow for even less of the $\text{ClO} \cdot \text{O}_2$ complex. Furthermore, the use of the recently measured Cl_2O_2 photolysis cross sections of Huder and DeMore (1995) would lead to approximately 80% more Cl_2O_2 in equilibrium with ClO and $\text{ClO} \cdot \text{O}_2$ (see Shindell and de Zafra (1995) for a detailed discussion of the chlorine budget with these new cross sections), making agreement with the available chlorine budget much worse.

4. Impact on Ozone Loss

Having established limits on the chemistry of $\text{ClO} \cdot \text{O}_2$, we can now examine whether the allowable amounts and reaction rates are capable of influencing chlorine catalyzed ozone depletion. As stated earlier, $\text{ClO} \cdot \text{O}_2$ forms the ClO dimer through either reaction (7) or (8), which we compare with the rate limiting reaction (2) in the ClO dimer catalytic cycle to assess the relative contributions to ozone loss. Reaction rates for these three pathways to form Cl_2O_2 are shown in Figure 3, along with the total ozone loss rate. Calculations were made for $\text{ClO} \cdot \text{O}_2$ chemistry with the $\text{ClO} \cdot \text{O}_2$ equilibrium constant upper limit and the lower value derived in the budget study, and using reactions (7) and (8) at both the suggested values and at the lower values used in the budget study. The case without $\text{ClO} \cdot \text{O}_2$ chemistry is also shown for comparison. Five sets of bars are shown for each temperature, with all calculations performed at 20 km altitude.

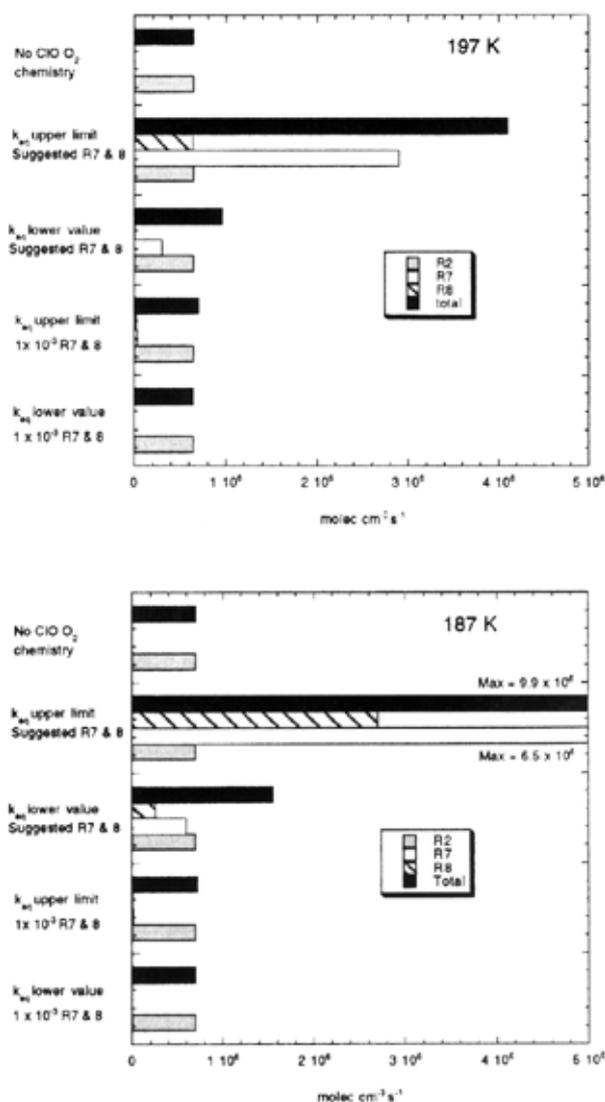


Figure 3. Ozone loss rates due to chlorine catalytic chemistry at the given temperatures with ClO set to observed values. The five sets of bars in each panel show loss rates for the indicated scenarios. K_{eq} refers to the equilibrium constant of $\text{ClO} \cdot \text{O}_2$. (R2) is the $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$ reaction, (R7) is the $\text{ClO} + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O}_2 + \text{O}_2$ reaction, and (R8) is the $\text{ClO} \cdot \text{O}_2 + \text{ClO} \cdot \text{O}_2 \rightarrow \text{Cl}_2\text{O}_2 + \text{O}_2 + \text{O}_2$ reaction, following the reaction numbers given in Table I.

In the control scenario, with no $\text{ClO} \cdot \text{O}_2$ chemistry, all dimer formation is obviously through reaction (2) only. When the upper limit for the $\text{ClO} \cdot \text{O}_2$ equilibrium constant is used along with the suggested rates for reactions (7) and (8) (second set of bars), there is a huge increase in the amount of ozone loss, with dimer formation

through reaction (7) proceeding several times faster than reaction (2), and reaction (8) going at approximately the same speed as reaction (2). As was shown in the second and third sets of bars in Figure 1 however, this scenario is unreasonable, as it results in total chlorine amounts far above those available. When we keep reaction rates (7) and (8) at the suggested values, so that dimer formation from $\text{ClO} \cdot \text{O}_2$ is comparatively rapid, but lower the $\text{ClO} \cdot \text{O}_2$ equilibrium constant to a value consistent with the total chlorine budget (third set of bars), we find an increase in ozone loss of $\sim 50\%$ at 197°K , and $\sim 70\%$ at 187°K . Though there is very little $\text{ClO} \cdot \text{O}_2$ in this case, as its stability is weak at the lower value of the equilibrium constant, the rapidity of reaction (7) still increases the dimer formation rate significantly. The last two sets of bars show results using the slower rates for reactions (7) and (8) that were shown in Figure 2 to give chlorine amounts in reasonable agreement with the budget constraint. When these rates are used, dimer formation is hardly enhanced at all, even with the upper limit of the $\text{ClO} \cdot \text{O}_2$ equilibrium constant. While the last three sets of bars are for scenarios which give chlorine amounts in reasonable agreement with the budget constraints, only the case with a weakly stable $\text{ClO} \cdot \text{O}_2$ complex but very rapid ClO dimer formation from $\text{ClO} \cdot \text{O}_2$ gives a large increase in ozone loss rates.

Ozone loss rates for the same set of reaction rates, but with Cl_y fixed at 3.2 ppbv and ClO allowed to vary are shown in Figure 4 for 197°K . When the $\text{ClO} \cdot \text{O}_2$ equilibrium constant upper limit is used, leading to a fairly stable $\text{ClO} \cdot \text{O}_2$ complex, there is a net reduction in ozone loss for a fixed amount of Cl_y since dividing chlorine between ClO and $\text{ClO} \cdot \text{O}_2$ decreases the efficiency of ozone destruction. In the case where the equilibrium constant lower limit is used, along with the suggested rates for reactions (7) and (8), ozone loss increases by 17% as little chlorine is sequestered in $\text{ClO} \cdot \text{O}_2$, so reaction (2) is still rapid, but the rate limiting reactions (7) and (8) in the additional catalytic cycles are also rapid enough to add significantly to total ozone destruction rates.

We find that if we decrease the stability of $\text{ClO} \cdot \text{O}_2$ even more, and increase the rates of ClO dimer formation from $\text{ClO} \cdot \text{O}_2$, we do not see an increase in ozone loss, as the amount of $\text{ClO} \cdot \text{O}_2$ becomes so small that it cannot contribute significantly. Thus the ozone loss increases here should be thought of as the upper limit of the possible effects of $\text{ClO} \cdot \text{O}_2$ chemistry. If reaction rates (7) and (8) were slower, a tighter chlorine budget was established, based on either some chlorine being sequestered in other species or on reduced uncertainties in inferred chlorine from ClO measurements, or the newer Cl_2O_2 photolysis cross sections were used, the influence of $\text{ClO} \cdot \text{O}_2$ on ozone loss would be less.

5. Summary

The importance of proposed $\text{ClO} \cdot \text{O}_2$ chemistry has been examined. It has been shown that both the stability of $\text{ClO} \cdot \text{O}_2$ and the degree to which $\text{ClO} \cdot \text{O}_2$ enhances formation of the ClO dimer are important for understanding potential impacts

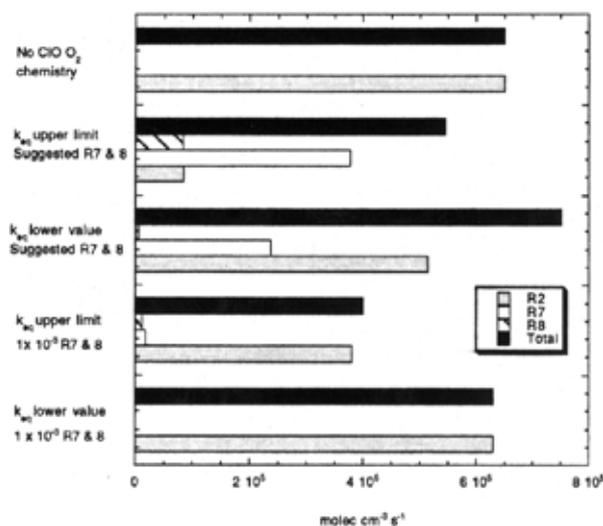


Figure 4. Ozone loss rates due to chlorine catalytic chemistry at 197 °K with Cl_y fixed at 3.2 ppbv. The five sets of bars in each panel show loss rates for the indicated scenarios as in Figure 3.

on ozone destruction. The stability of $\text{ClO} \cdot \text{O}_2$ is determined by its equilibrium constant. Use of the laboratory upper limit for this constant results in a fairly stable $\text{ClO} \cdot \text{O}_2$ complex, sequestering a significant amount of chlorine in $\text{ClO} \cdot \text{O}_2$. When the suggested reaction rates for dimer formation from $\text{ClO} \cdot \text{O}_2$ are used, there is a dramatic increase in the $[\text{Cl}_2\text{O}_2]/[\text{ClO}]$ ratio as well, so that active chlorine partitioning becomes incompatible with measurements of ClO and the total chlorine budget of the polar lower stratosphere. We can conclude that either the stability of the $\text{ClO} \cdot \text{O}_2$ complex must be less than the laboratory limit, or that the reaction rates for dimer formation from $\text{ClO} \cdot \text{O}_2$ must be slower than those suggested. These constraints greatly restrict the potential role of $\text{ClO} \cdot \text{O}_2$ in ozone depletion. However, our results indicate that even a very small amount of $\text{ClO} \cdot \text{O}_2$, 0.1 to 0.2 ppbv, can effectively contribute to ozone loss if $\text{ClO} \cdot \text{O}_2$ rapidly forms the ClO dimer. Laboratory measurements of the $\text{ClO} \cdot \text{O}_2$ to Cl_2O_2 reaction rates, or improved limits on the $\text{ClO} \cdot \text{O}_2$ equilibrium constant, are necessary to determine if this scenario could actually take place. Using rapid reaction rates for ClO dimer formation along with a weakly bound $\text{ClO} \cdot \text{O}_2$ complex, ozone loss rate increases of up to 20–70% were calculated while maintaining a plausible partitioning of chlorine, though at the upper limit of the total chlorine budget. Given the large uncertainties in the reaction rate constants of $\text{ClO} \cdot \text{O}_2$, it is not possible to say definitively if $\text{ClO} \cdot \text{O}_2$ effects ozone loss, but the potential cannot yet be ruled out.

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