Possible Effect of the Chlorine Oxide Dimer on Transient Ozone Loss in Rocket Plumes

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Preface

I want to thank Paul Zittel, Norm Cohen and John Edwards for sharing information and for many useful and interesting conversations.

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1. Introduction

Solid rocket boosters release HCl and Cl atoms directly into the stratosphere. This release may produce "local" transient effects or global, long-term effects on the ozone layer. In this report, we consider the special situation created locally by such a launch. For the purposes of calculation, we will consider the time scale of interest to be about a day, or 10^5 seconds.

This zero-dimensional, back-of-the-envelope calculation is not intended as a substitute for a computer model. We are assuming an isothermal plume at the local stratospheric temperature, and we are neglecting most HO_x and NO_x reactions. Mass transfer problems are also not considered, so there is an implicit assumption of uniform mixing with the surrounding stratosphere out to the scale of 30 km within a day. Nevertheless, the calculations given here are a necessary, but not sufficient, condition for the significance of the reactions, and computer modelers ignore such reactions at risk.

Work at The Aerospace Corporation and elsewhere has shown that afterburning in the rocket plume will convert a substantial fraction of the HCl to Cl_2 molecules, which, in turn, will photolyze to Cl atoms within a few minutes.[1] Conversion takes place because the afterburning produces high local concentrations of H and O atoms and OH radicals:

$$OH + HCl = H_2O + Cl$$
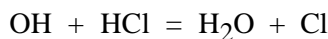
The chlorine atoms will react directly with ozone to cause local removal:

$$Cl + O_3 = ClO + O_2 \tag{1}$$

This is not a catalytic cycle, and the models to date for this process do not include the possible effects of further reactions on ozone loss. Because this reaction will greatly elevate the local concentration of ClO, it is important to explore the possibility of further reactions of this molecule. A likely reaction of interest is the formation of the chlorine oxide dimer:

$$2ClO = Cl_2O_2$$
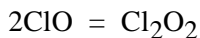
The chemistry of the chlorine oxide dimer has not been included in any of the plume models.[2-5] The reason this may be important is that this molecule introduces a new ozone destruction cycle that does not require the presence of atomic oxygen in order to operate.

2. Ozone Destruction Cycles

The "normal" ozone destruction cycle [Cycle I] at mid-latitudes is:

$$Cl + O_3 = ClO + O_2$$

$$ClO + O = Cl + O_2$$

$$\underline{}$$
$$O_3 + O = 2O_2$$
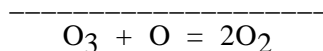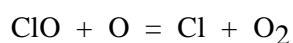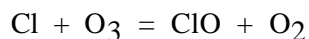
The requirement for atomic oxygen means that this cycle is essentially inoperative at low altitudes—say 20 km. The chlorine oxide dimer cycle, which is responsible for the Antarctic ozone hole, does not require atomic oxygen and, therefore, is allowed to operate at low altitudes [Cycle II]:

$$2[Cl + O_3 = ClO + O_2]$$
$$2ClO = Cl_2O_2$$
$$Cl_2O_2 + light = ClO_2 + Cl$$
$$ClO_2 = Cl + O_2$$

$$\underline{}$$
$$2O_3 = 3O_2$$
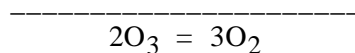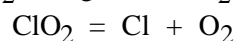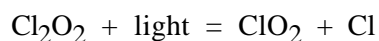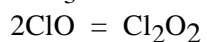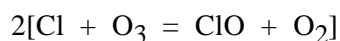
This cycle takes place in the Antarctic because the low temperatures favor the formation of the dimer. As we will show below, the elevated local chlorine concentrations in a plume will also favor the formation of the dimer, and an enhancement of the ozone destruction is anticipated.

3. Estimate of Significance

To begin an estimate of significance, we will need to present some numbers. Table 1 gives a set of concentrations in the present-day stratosphere, i.e., with 3.5 ppb of chlorine. The two altitudes chosen are 20 km, which is the peak ozone density, and 30 km, which is close to the peak ozone mixing ratio. These numbers are taken from three sources.[6,7,8] Given the variability with season, time of day, latitude, etc., the numbers are not meaningful to better than a factor of two.

Table 2 provides some necessary rate constants and equilibria computed at the two altitudes. We have chosen the U. S. Standard Atmosphere for the temperatures,[7] and the rate constant for the Cl + O_3 reaction from Hampson's compilation:[9]

$$k_1 = 2.8 \times 10^{-11} e^{-257/T}$$

Table 1. Concentrations of Pertinent Species, in Molecules/cc

Specie	20 km	30 km
Air	1.85×10^{18}	3.82×10^{17}
O_3	5.0×10^{12}	2.5×10^{12}
CH_4	3.0×10^{12}	2.1×10^{11}
HCl	1.1×10^9	5.0×10^8
$ClNO_3$	3.7×10^8	5.0×10^8
ClO	2.8×10^7	1.5×10^8
O	1.5×10^6	6×10^7
OH	6×10^5	1.8×10^6
Cl	8×10^2	2.1×10^4

Table 2. Kinetic and Equilibrium Data

Altitude, km	20	30
Temperature, K	217	227
k_1, $cm^3 molecule^{-1} s^{-1}$	8.57×10^{-12}	9.03×10^{-12}
k_p, Photolysis Rate Constant of Cl_2O_2, s^{-1}	1.3×10^{-3}	1.7×10^{-3}
K_1^*, $cm^3 molecule^{-1}$	2.52×10^{-10}	4.48×10^{-11}

The photolysis rate for the chlorine oxide dimer has been calculated by integrating the photon flux model of Ackerman[10] with cross sections from DeMore, et al.[11] The equilibrium constants were calculated from the expression of Cox and Hayman:[12]

$$K_p \text{ (atm}^{-1}) = K_1{}^* (RT)^{-1}$$

$$= (e^{-144/R})(e^{+72,500/RT}) \quad (R \text{ in J mol}^{-1} K^{-1})$$

$$K_1{}^* = [Cl_2O_2]/[ClO]^2 \quad (cm^3 molecule^{-1})$$

Photolysis of the chlorine oxide dimer to provide chlorine atoms has been confirmed experimentally by Molina, et al.[13]

The natural turnover rate of ozone in the stratosphere at steady state is quite slow. This time is given by the ozone concentration divided by the odd oxygen loss rate,[8] and is about 14 days at 30 km and 600 days at 20 km (turnover by chemical reaction only; mass transfer will be faster at this altitude). Thus, in order to create a local ozone depletion, it is not sufficient merely to compete with the natural turnover of ozone; it is necessary to remove ozone on a time scale of the physical and chemical dispersal of the rocket plume. Since we have chosen 10^5 s as the time scale of interest, it is necessary to find a process that will remove ozone on this time scale. Thus:

$$10^5 = [O_3]/\text{ozone loss rate}$$

We then back-calculate to get the amount of chlorine oxide loading required to do this. This is done in the following steps:

1. Calculate necessary ozone loss rate as shown above.

2. Calculate the chlorine atom concentration required to give this loss rate:

$$[Cl] = \text{ozone loss rate}/k_1[O_3]$$

3. Calculate the chlorine atom production rate required to get this steady-state concentration of chlorine atoms. This must come from photolysis of the chlorine oxide dimer, which ultimately yields two chlorine atoms per photolysis:

$$[Cl] = \text{production rate/loss rate} = 2k_p[Cl_2O_2]/k_1[O_3]$$

4. Step 3 gives the needed chlorine oxide dimer concentration. From this and the equilibrium constant, we can calculate the required chlorine oxide concentration:

$$[ClO] = \{[Cl_2O_2]/K_1{}^*\}^{1/2}$$

5. The sum of chlorine oxide and the dimer gives a required total chlorine concentration (for the short term). This and the rocket loading rate of active chlorine give an effective area within which this rate of ozone destruction takes place:

$$\text{Area in km}^2 \; = \; (\text{active chlorine loading in tons/km})/(\text{required chlorine in tons/km}^3)$$

From this, we can calculate an effective "hole" diameter due to the plume. A summary of the numbers in steps 1–4 for the two altitudes is shown in Table 3.

Table 3. Summary of Back-Calculation of Required Chlorine Loading

Altitude, km	20	30
Required Ozone Loss Rate, molecules $cm^{-3} s^{-1}$	5.0×10^7	2.5×10^7
Required [Cl], molecules cm^{-3}	1.17×10^6	1.11×10^6
Required Cl production rate, molecules $cm^{-3}s^{-1}$	1.00×10^8	2.6×10^7
Required [Cl_2O_2], molecules cm^{-3}	1.93×10^{10}	7.8×10^9
Required [ClO], molecules cm^{-3}	8.73×10^9	1.32×10^{10}

4. Rocket Chlorine Loading

Table 4 gives the loading rates for both the Space Shuttle and the Titan IV as a function of altitude. This was calculated from the total loading rates of Brady, et al.,[14] and the altitude profiles from an Aerodyne report.[15] The percent active chlorine is the fraction of total chlorine present as Cl or Cl_2, calculated by Zittel.[1] From the mass of active chlorine, we may estimate that the effective plume diameter with an average concentration of ClO_x sufficiently high to deplete ozone locally by 63% (1/e level) in one day is 17 km in diameter at 20 km altitude and 29 km in diameter at 30 km altitude. The considerations given below reduce the estimated size at 20 km altitude to about 12km, but will increase the size at 30 km altitude to about 49 km. This is substantially larger than the hole produced immediately by the Cl atoms released by afterburning in the plume.

Table 4. Stratospheric Loading of HCl from Launches in Tons

Altitude, km	Titan IV	% Active Chlorine (1)	Shuttle
15-20	10.2	21.2	22.0
20-25	9.8	35.8	17.2
25-30	9.0	65.7	13.9
30-35	8.4	65.7	11.3
35-40	6.8	75.7	9.0
40-45	2.9	75.7	4.0
45-50	1.0		1.5
Total in Stratosphere	**48.1**		**78.9**

	Tons per Kilometer		
	@20 km	**@ 30 km**	
Titan IV	2.0	1.8	
Shuttle	3.9	30	

5. Final Considerations

5.1 Persistence of the Effect

The excess local ClO_x will gradually convert to HCl because of reactions of the Cl atoms with H-containing species, including CH_4, H_2, HNO_3, HO_2, and H_2O_2. The time for this will be given by:

$$= \text{(characteristic time for Cl + RH reactions)}[ClO_x]/[Cl]$$

$$= (1/[RH]k_H)[ClO_x]/[Cl]$$

$$= 8.9 \text{ days @ 20 km, 16 days @ 30 km.}$$

Therefore, dissipation of the plume by mass transfer should take place faster than the decay of the chlorine oxide species.

5.2 Effect of Natural Methane and Hydrogen

The stratosphere at 20 km contains about 1.5 ppm of methane and 0.5 ppm of hydrogen, both from natural sources. At 30 km, these mixing ratios are reduced because of increasing loss of the methane and hydrogen through reactions with chlorine and OH. If the local ozone is completely removed by reaction with high concentrations of chlorine atoms, then these gases will scavenge chlorine also. Each methane molecule will remove at least one atom of chlorine, and each hydrogen molecule will remove two atoms of chlorine. Thus, at 20 km, the amount of chlorine removed by methane and hydrogen (total equivalent to 2.5 ppm) is roughly equal to the amount of ozone (2.7 ppm). This will reduce the amount of available ClO by a factor of roughly two, with a corresponding reduction in the hole size by the square root of two. This effect may be offset to an extent by the reaction sequence:

$$Cl + CH_4 = HCl + CH_3$$

$$CH_3 + O_2 = CH_3O_2$$

$$CH_3O_2 + Cl = CH_3O + ClO$$
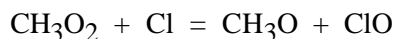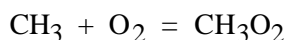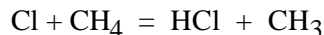
The third reaction above has never been studied, but it is thermodynamically allowed. By creating additional ClO, it can reduce the loss of active chlorine by up to half of the methane concentration (0.7 ppm).

The loss of active chlorine by reaction with the background methane and hydrogen leads to an additional consideration. The ratio of ozone to methane in the natural stratosphere is highly vari-

able,[7] and, therefore, the "hole" size may be expected to be highly variable also. Thus, a single event may not be sufficient to characterize the typical effect of launches on the local ozone layer.

5.3   Are Other Processes Rate Limiting?

The characteristic time for formation of the chlorine oxide dimer from the monomer is given by the three-body rate constant for:

$$ClO \; + \; ClO \; + M \; = \; Cl_2O_2 \; + \; M \qquad\qquad (2)$$

This has been given by DeMore, et al.[11,16] as:

$$k_2 = \; 1.9 \text{ x } 10^{-32} \, (300/T)^{3.9} \text{ cm}^6\text{molecule}^{-2}\text{s}^{-1} \qquad \text{(low pressure limit)}.$$

Applying this rate constant to the situation in the plume gives a pseudo-first-order characteristic time of 170 s at 20 km and 1600 s at 30 km. This is faster than the characteristic time for photolysis at 20 km (700 s), so the formation of the dimer will not be rate limiting at this altitude. At 30 km, the photolysis time is about 600 s, so the rate of dimerization will limit the rate of ozone destruction at this altitude, and the effective hole size due to Cycle II will be about 60% of the size calculated above. However, as we will show below, ozone destruction from Cycle I will dominate the transient ozone loss at 30 km, so a large hole is still predicted (see below).

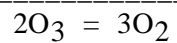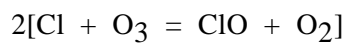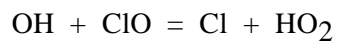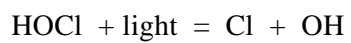Lastly, the rate for the decomposition of the photolyzed chlorine radical
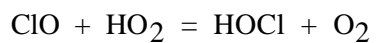
$$ClOO \; + \; M \; = \; Cl \; + \; O_2$$
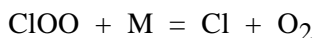
is very fast, with a lifetime of only 5 μs at 20 torr in laboratory experiments,[13] so this step should not be rate limiting under any circumstances in the stratosphere.

5.4   Are Other Cycles Important?

It is interesting to consider the effect of the "normal" ozone destruction cycle (Cycle I) as local chlorine is elevated. We can go through the same kind of analysis as in Table 3 to estimate how much ClO is required to destroy ozone on the required time scale, via the ClO + O reaction. Since atomic oxygen is not very abundant, about 850 ppb of ClO will be required at 20 km, and 26 ppb at 30 km. This means that a hole from this effect will be only about one-sixth as large as the hole due to Cycle II at 20 km, but at 30 km, Cycle I is more effective, and there should be about a 70% larger diameter hole (49-km diameter) than that caused by Cycle II. This effect, as before, will last as long as the excess ClO-to-HCl ratio lasts. Therefore, both ClO and its dimer will have to be considered. Heterogeneous chemistry can potentially change this picture by direct ozone destruction or possibly by the introduction of new reactions that convert ClO_x to Cl or Cl_2.

In view of the elevated ClO concentrations, we also considered the possible impact of "Cycle III", which was originally proposed by Solomon, et al.:[17]

$$ClO + HO_2 = HOCl + O_2$$

$$HOCl + light = Cl + OH$$

$$OH + ClO = Cl + HO_2$$

$$2[Cl + O_3 = ClO + O_2]$$
$$\overline{}$$
$$2O_3 = 3O_2$$

The photolytic lifetime of HOCl is about an hour at these altitudes. The slowest step in this cycle is the OH + ClO reaction, and about 1–2 ppm of ClO would be required to compete with Cycles I and II. Therefore, this does not appear to be an important cycle for transient ozone destruction.

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