Stratospheric Chlorine: a Possible Sink for Ozone

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This study proposes that the oxides of chlorine, ClO_x, may constitute an important sink for stratospheric ozone. A photochemical scheme is devised which includes two catalytic cycles through which ClO_x destroys odd oxygen. The individual ClX constituents (HCl, Cl, ClO, and OClO) perform analogously to the respective constituents (HNO$_3$, NO, NO$_2$, and NO$_3$) in the NO_x catalytic cycles, but the ozone destruction efficiency is higher for ClO_x. Our photochemical scheme predicts that ClO is the dominant chlorine constituent in the lower and middle stratosphere and HCl dominates in the upper stratosphere. Sample calculations are performed for several ClX altitude profiles: an assumed 1 p.p.b. volume mixing ratio, a ground level source, and direct injection by volcanic explosions. Finally we discuss certain limitations of the present model: uncertainty in stratospheric OH concentrations, the possibility that ClOO exists, the need to couple ClO_x cycles with NO_x and HO_x cycles, and possible heterogeneous reactions.

Cette étude suggère que les oxydes de chlore, ClO_x, peuvent être une raison importante de la diminution de l'ozone stratosphérique. Un schéma photochimique est élaboré, lequel inclut deux cycles catalytiques par l'intermédiaire desquels ClO_x détruit l'oxygène impair. Les constituants individuels ClX (HCl, Cl, ClO et OClO) agissent de façon analogue aux constituants respectifs (HNO$_3$, NO, NO$_2$ et NO$_3$) dans les cycles catalytiques des NO_x, mais la destruction de l'ozone est plus efficace pour ClO_x. Notre schéma photochimique laisse prévoir que ClO est le constituant chlore dominant dans la basse et moyenne stratosphère et que HCl domine dans la haute stratosphère. Des calculs types sont effectués pour plusieurs profils d'altitude des ClX: un rapport de mélange en volume de 1 p.p.b. est considéré, une source au niveau du terrain et des injections directes par des explosions volcaniques. Finalement nous discutons certaines limitations du modèle présent: incertitude des concentrations en OH dans la stratosphère, la possibilité de l'existence de ClOO, le besoin de réunir les cycles de ClO_x avec ceux des NO_x et HO_x et des réactions hétérogènes possibles. [Traduit par le journal]

Introduction

Recent studies have pointed out the crucial effect of catalytic cycles in stratospheric ozone chemistry (*e.g.*, refs. 1–3). Extensive work has been done on the cycles of the nitrogen oxides, NO_x, and the hydrogen oxides, HO_x. Both are potential ozone destroyers through their cyclic reactions with ozone and atomic oxygen. It is likely that there are numerous other catalytic cycles potentially capable of influencing stratospheric chemistry. Here we focus attention on one possibility, previously neglected, involving the oxides of chlorine, ClO_x, and propose a chemical reaction scheme for gas-phase chlorine in the stratosphere which is analogous to the NO_x catalytic cycle, but even more efficient for ozone destruction.

Chlorine from ground level sources can diffuse upward through the troposphere into the stratosphere. Likely sources are industry, sea salt spray, and fumaroles. Also explosive volcanic eruptions and solid fuel rockets may directly inject chlorine into the stratosphere.

We will show from source estimates that reasonable ClO_x levels can yield ozone destruction rates comparable to those for NO_x. In reality, ozone destruction by ClO_x depends on all the complexities of stratospheric chemistry, e.g., interaction with NO_x and HO_x cycles.

Gas-phase Chlorine Reactions

Gas-phase chlorine injected or transported into the stratosphere forms a number of different molecules the most important of which are HCl, Cl, ClO, OClO, ClOO, and Cl_2. We shall define the sum of all of these as ClX. Reaction rates for transfer amongst the various ClX species are rapid and local steady-state chemistry may be used to calculate the ratio of each chlorine species to ClX independent of transport. Figure

TABLE 1. Chlorine reactions in the stratosphere

| Reaction	Rate (cm^3 molecule^{-1} s^{-1})*
[1] $hv + HCl \rightarrow H + Cl$	Slow, see text
[2] $hv + Cl_2 \rightarrow Cl + Cl$	Fast, see text
[3] $Cl + O_3 \rightarrow ClO + O_2$	$4.3 \times 10^{-11} \exp(-500/RT)$
[4] $ClO + O \rightarrow Cl + O_2$	$1.2 \times 10^{-10} \exp(-500/RT)$
[5] $ClO + O_3 \rightarrow OClO + O_2$	$\leq 5 \times 10^{-15}$
[6] $Cl + ClO \rightarrow Cl_2 + O$	5×10^{-11}
[7] $OClO + O \rightarrow ClO + O_2$	5×10^{-13}
[8] $hv + ClO \rightarrow Cl + O$	Slow, see text
[9] $hv + OClO \rightarrow O + ClO$	See text
[10] $Cl + CH_4 \rightarrow HCl + CH_3$	$8.8 \times 10^{-11} \exp(-3800/RT)$
[11] $OH + HCl \rightarrow H_2O + Cl$	$1.8 \times 10^{-11} \exp(-2000/RT)$
[12] $Cl + O_2 + M \rightarrow ClOO + M$ ⎫ $K = (k_{12}/k_{13}) = 3.6 \times 10^{-21}$ cm^3
[13] $ClOO + M \rightarrow Cl + O_2 + M$ ⎬
[14] $HCl + O \rightarrow OH + Cl$	$6.8 \times 10^{-12} \exp(-5100/RT)$
[15] $ClO + NO \rightarrow Cl + NO_2$	1.7×10^{-11}
[16] $Cl + NH_3 \rightarrow HCl + NH_2$	1×10^{-12}

*See text for rate references.

1 shows our proposed ClX reaction scheme and Table 1 lists the reactions and their rates. The major ozone destroying catalytic cycle is the set of reactions

[3] $Cl + O_3 \rightarrow ClO + O_2$

[4] $ClO + O \rightarrow Cl + O_2$

net $O_3 + O \rightarrow 2O_2$
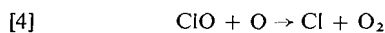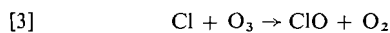
The rate of [3] has been measured recently at room temperature by Watson[1] to be 1.85×10^{-11} cm^3 molecule^{-1} s^{-1}. Its maximum activation energy is 1 kcal mol^{-1} and we have assumed 0.5 kcal mol^{-1}. Rate [4] has been measured by Bemand et al. (4) as 5.3×10^{-11} cm^3 molecule^{-1} s^{-1} at room temperature and again we have assumed an activation energy of 0.5 kcal mol^{-1}. ClO is photodissociated in the ultraviolet by [8]. We used the cross section of Johnston et al. (5) and the solar intensities of Brinkmann et al. (6) to determine that [8] is 10 times slower than [4] at all altitudes. It has therefore been neglected.
    A second catalytic cycle is initiated by [5]

[5] $ClO + O_3 \rightarrow OClO + O_2$

[7] $OClO + O \rightarrow ClO + O_2$

net $O + O_3 \rightarrow 2O_2$
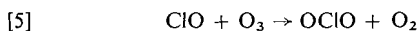
Reaction 5 forms OClO, chlorine dioxide, distinct from the peroxy radical ClOO discussed later. The effect of this cycle is to lower the net ozone destruction because a fraction of the total available ClX is diverted to OClO and [7] is
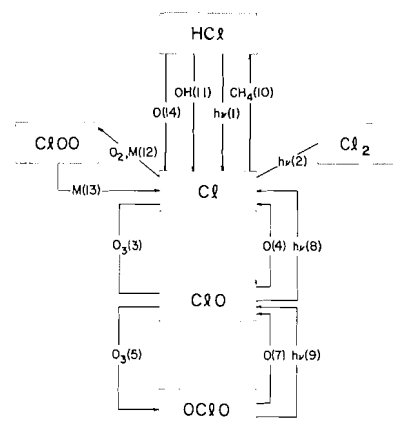

FIG. 1. Chemical reaction scheme for gas-phase chlorine.

two orders of magnitude slower than [4]. Even if 90% of the total ClX were OClO the odd oxygen destruction rate of the Cl–ClO cycle would be larger than that of the ClO–OClO cycle. Reaction 5 is slow with an upper limit rate (7) of 5×10^{-15} cm^3 molecule^{-1} s^{-1}. Photodissociation of OClO [9] is probably faster than [7] and provides a return to ClO which gives no net destruction of ozone. Although we have performed some calculations including the ClO–OClO cycle we show here only calculations for which $k_5 = 0$.
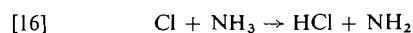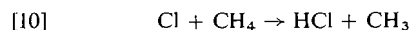   Cl may also react with CH_4 and NH_3 to form HCl

[10] $Cl + CH_4 \rightarrow HCl + CH_3$

[16] $Cl + NH_3 \rightarrow HCl + NH_2$

[1]R. T. Watson, personal communication, 1973.

TABLE 2.   Input data*

Altitude	T (°K)	[O]	[O$_3$]	[CH$_4$]	High [OH]	Low [OH]
5	270	3(3)	3.3(11)	2(13)	8(5)	8(5)
10	238	6.5(3)	4.3(11)	1(13)	6(5)	4(5)
15	218	2.2(4)	6.5(11)	5(12)	3(5)	5(4)
20	212	3.0(5)	1.8(12)	2.5(12)	1(6)	1.7(5)
25	220	6.0(6)	4.3(12)	1.2(12)	2(6)	9(5)
30	232	2.7(7)	3.5(12)	5(11)	5(6)	2.5(6)
35	243	1.2(8)	1.7(12)	1.5(11)	1(7)	3.5(6)
40	255	3.8(6)	5.0(11)	4(10)	1.2(7)	3(6)
45	265	1.2(9)	1.5(11)	1(10)	1.3(7)	4(6)
50	272	2.5(9)	5.0(10)	2(9)	1(7)	4(6)
55	269	4.4(9)	1.8(10)	1(9)	8(6)	3(6)
60	255	7.0(9)	6.3(9)	4(8)	6(6)	2(6)

*Concentrations are per cm³. Numbers in parentheses are powers of 10.

Reaction 10 has been measured at room temperature by Davis *et al.* (8) to have a rate of 1.7×10^{-13} cm³ molecule^{-1} s^{-1}. Its activation energy is 3.8 kcal mol^{-1} (9). Kondratiev (10) gives an estimated rate for [16] of $\sim 10^{-12}$ cm³ molecule^{-1} s^{-1}. Since ammonia concentrations in the stratosphere are small (11) we have chosen to neglect [16] in our calculation. HCl is returned to Cl by reaction with O and OH

[11]   HCl + OH → Cl + H$_2$O

[14]   HCl + O → OH + Cl
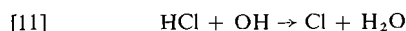
Reaction 11 measured by Takacs and Glass (12) is by far more important than [14] which has been measured by Balakhnin *et al.* (13). At altitudes of 50–60 km the rates of [11] and [14] become comparable. HCl acts as a temporary storage tank for ClO$_x$ analogous to HNO$_3$ for NO$_x$.

The three-body reaction 12, has been studied by Johnston *et al.* (5). They give an equilibrium constant of 3.64×10^{-21} cm³. This implies a [ClOO]/[Cl] ratio of $< 10^{-3}$ at stratospheric pressures and indicates that [12] is unimportant. When one uses more recent values of thermodynamic constants one finds $K_{12} \sim 4 \times 10^{-19}$ at 300 K and 8×10^{-21} at 220 K.[2] This indicates that ClOO could possibly be important if it is as reactive as Cl, but this is not likely.

The only ClX compound not yet mentioned is Cl$_2$ which is rapidly photodissociated via [2] to 2Cl in the visible and near ultraviolet. Seery and Britton's (14) cross section implies a lifetime for Cl$_2$ of ~ 400 s. Thus, concentrations will be low.

Under all of the above assumptions, ratios of individual constituents to total ClX can be calculated for local, steady-state chemistry. They are

$$[17] \qquad \frac{[ClO]}{[ClX]} = \frac{1}{1 + \dfrac{k_4}{k_3}\dfrac{[O]}{[O_3]}\left(1 + \dfrac{k_{10}[CH_4]}{k_{11}[OH] + k_{14}[O]}\right) + \dfrac{k_5[O_3]}{J_9 + k_7[O]}}$$

$$[18] \qquad \frac{[HCl]}{[ClX]} = \frac{k_4}{k_3}\frac{[O]}{[O_3]}\left(\frac{k_{10}[CH_4]}{k_{11}[OH] + k_{14}[O]}\right)\frac{[ClO]}{[ClX]}$$

$$[19] \qquad \frac{[Cl]}{[ClX]} = \frac{k_4[O]}{k_3[O_3]}\frac{[ClO]}{[ClX]}$$

$$[20] \qquad \frac{[OClO]}{[ClX]} = \frac{k_5[O_3]}{J_9 + k_7[O]}\frac{[ClO]}{[ClX]}$$

[2]D. Garvin, personal communication, 1973.

TABLE 3.   Ratios of chlorine compounds to ClX

	High OH ratios			Low OH ratios		
Altitude	$\dfrac{[ClO]}{[ClX]}$	$\dfrac{[HCl]}{[ClX]}$	$\dfrac{[Cl]}{[ClX]}$	$\dfrac{[ClO]}{[ClX]}$	$\dfrac{[HCl]}{[ClX]}$	$\dfrac{[Cl]}{[ClX]}$
5	0.90	0.10	2.3($-$8)	0.90	0.10	2.6($-$7)
10	0.93	0.075	4.0($-$8)	0.98	0.11	5.0($-$7)
15	0.89	0.11	8.6($-$8)	0.57	0.43	9.8($-$7)
20	0.92	0.078	4.4($-$7)	0.67	0.33	1.5($-$5)
25	0.84	0.16	3.4($-$6)	0.70	0.30	3.3($-$4)
30	0.82	0.18	1.8($-$5)	0.69	0.31	1.6($-$3)
35	0.73	0.27	1.5($-$4)	0.50	0.50	5.2($-$3)
40	0.50	0.50	1.1($-$3)	0.21	0.79	7.4($-$3)
45	0.27	0.72	6.3($-$3)	0.12	0.87	0.014
50	0.20	0.77	0.028	0.12	0.86	0.030
55	0.093	0.84	0.065	0.061	0.90	0.026
60	0.052	0.78	0.17	0.037	0.84	0.024

Reactions 3 and 4 control the ratio of Cl to ClO at altitudes greater than $\sim$35 km. At lower altitudes reaction 15 meshes the ClO_x cycle with the NO_x cycle[3]

[3] $Cl + O_3 \rightarrow ClO + O_2$

[15] $ClO + NO \rightarrow Cl + NO_2$

          $NO_2 + O \rightarrow NO + O_2$
          ────────────────────────
net $O + O_3 \rightarrow 2O_2$
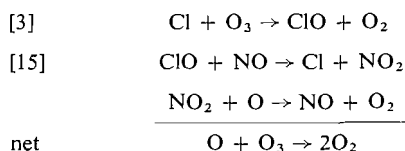
Since [15] ties chlorine to the complex, incompletely understood NO_x cycle it will be neglected in this paper. Reaction 15 is fast[4] and will tend to convert ClO to Cl leading back to HCl. Thus the ratios in Table 3 would show higher fractions of HCl at low altitudes. The last section of the paper will discuss the implications of neglect of interactions with NO_x, HO_x, CO_x, etc.

Table 2 lists the input data used in the ratio calculation and Table 3 shows the ratios for two cases, high OH and low OH, corresponding to the extremes of the OH model calculations of Wofsy et al. (15). The OH concentration is very important because of its role in returning chlorine from its storage tank, HCl, to the catalytic cycle of Cl–ClO. Another important factor governing the amount of chlorine in the HCl tank is [14] which is unusually slow for an O atom reaction. If this rate were significantly increased HCl would be rapidly converted to Cl. Reaction 15 below 30 km will convert ClO to Cl more rapidly and tends to make more Cl available for forming HCl by [10].

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[3]D. Garvin, personal communication, 1973.
[4]D. Garvin, personal communication, 1973.

Ozone Destruction Rates

Figure 2 shows calculated odd oxygen destruction rates vs. altitude for an assumed constant ClX mixing ratio of 1 p.p.b. Destruction rates for any other value of ClX can be linearly scaled. Also shown in Fig. 2 are the destruction rates for the Chapman mechanism reaction

[21] $O + O_3 \rightarrow 2O_2$

and the two catalytic cycles of NO_x; the NO–NO_2 cycle and the NO_2–NO_3 cycle. All of these were calculated using the rates and NO_x profiles of McConnell and McElroy (3). The chlorine cycle, according to the present calculations, is not the dominant loss mechanism for odd oxygen but it is significant if ClX concentrations are near the 1 p.p.b. range. It should be noted that the NO_x profiles used here represented mixing
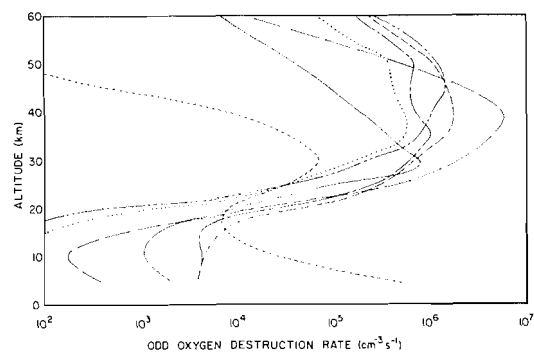

FIG. 2.   Odd oxygen destruction rates vs. altitude. (-··-) NO–NO_2 cycle; (---) NO_2–NO_3 cycle; (————) Chapman mechanism; (. . .) ClO_x volcanic source; (— —) ClO_x 1 p.p.b. high OH; (— - —) ClO_x 1 p.p.b. low OH; (——) ClO_x ground level source.

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ratios of more than 10 p.p.b. in the altitude region (>20 km) most important for ozone destruction. Thus Fig. 2 illustrates the fact that ClO_x is more efficient for ozone destruction than NO_x. In Table 4 we show the column-integrated odd oxygen destruction rates for each of the seven mechanisms graphed in Fig. 2. The calculations for stratospheric ozone destruction due to direct injection by volcanic explosions are described in the next section.

Sources of Chlorine and Model Calculations

A number of ground level chlorine sources exist. Fumaroles emit gaseous Cl_2 and HCl (16). Sea salt spray contributes chlorine-containing particles (17), some of which lead to gaseous chlorine. Industrial processes emit chlorine in many forms, particularly HCl (18). All of these contribute directly to the tropospheric chlorine budget and indirectly to the stratosphere via transport upward through the troposphere. Junge (19) has measured the gaseous chlorine content at sea level to be ∼1 p.p.b. This concentration will vary with altitude in the troposphere because of loss through rainout of HCl but indicates that the assumed value for Fig. 3 is reasonable.

Other potential sources of stratospheric chlorine are direct injections by volcanic explosions (20, 21) and solid fuel rockets. Data on gaseous contents of eruptions are very sparse. Those explosive events which penetrate the tropopause are likely to involve large amounts of chlorine because they are often associated with intrusions of sea water (16). It is not known whether the chlorine will be in the gas phase or associated with ash cloud particles. Odd oxygen destruction rates were calculated for a volcanic injection source estimated in the following way. The data of Eaton (20) and Cronin (21) were
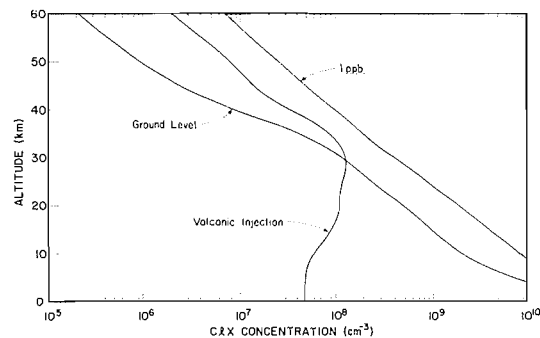

FIG. 3. Total gaseous chlorine (ClX) vs. altitude. The profiles due to ground level sources and direct injection into the stratosphere by volcanoes were computed as described in the text. A profile corresponding to an assumed 1 p.p.b. mixing ratio is also shown.

used to estimate a global and time averaged volcanic injection source strength of ∼10^{11} g/year. The injection rate certainly falls off rapidly with altitude and we guessed an exponential falloff with an e-folding height of 7 km. This is not unlike an observed ash cloud-top height distribution (20). Although the source strength is not very large and the statistics are very uncertain, the potential importance of this source is the direct injection of chlorine to stratospheric altitudes where ozone destruction occurs. Large volcanic eruptions which penetrate to the middle or upper stratosphere where most of the ozone destruction occurs could leave a noticeable local ozone hole.

In order to evaluate the destruction rate for this volcanic injection profile we used steady-state results from a one-dimensional eddy diffusion model for ClX. The diffusion equation was solved by an implicit technique with 2 km altitude steps and 5 day time steps. Tests were run with 12 h time steps with no change in results. The eddy diffusion coefficient was the seasonal average of Hays and Olivero (22). The density was taken as zero at 120 km and the flux to the ground was proportional to the density at the ground. The proportionality constant is the diffusion velocity near the ground which we took as 0.007 cm/s (23). Loss due to rainout with a 30 day period was included in the troposphere (24). This model was also used to evaluate a ground level source. These results were scaled to Junge's (19) measurement at the ground and the resulting ozone destruction rates are shown in Fig. 2. The ClX profile is given in Fig. 3 along with the ClX profile for the volcanic source described above

TABLE 4. Column-integrated odd oxygen destruction rates (molecules $cm^{-2} s^{-1}$)

Chapman mechanism	3×10^{12}
NO–NO$_2$ cycle	7.5×10^{12}
NO$_2$–NO$_3$ cycle	3.1×10^{11}
ClO$_x$ cycle, 1 p.p.b.	
High OH	3.9×10^{12}
Low OH	2.3×10^{12}
ClO$_x$ cycle	
Ground level source	4.4×10^{11}
Volcanic source	1.2×10^{12}

and a 1 p.p.b. constant mixing ratio. Figure 2 shows the corresponding odd oxygen destruction rates.

Summary

We have proposed a chemical scheme for gas-phase chlorine reactions in the stratosphere. We have shown that total ClX concentrations of ~ 1 p.p.b. give significant ozone destruction rates. A ClX concentration of 1 p.p.b. at 16 km implies about 0.1 p.p.b. of HCl. This is equal to the upper limit set by Farmer's (25) measurement. Indications are, therefore, that Fig. 2 gives an upper limit to the ClO_x ozone destruction. More precise statements cannot be made until the details of the interaction of chlorine chemistry with nitrogen, hydrogen, and carbon chemistry are investigated. Reaction 15 tying the ClO_x and NO_x cycles together tends to diminish the ozone destruction capacity of ClO_x. However, it converts NO to NO_2, thereby increasing the destruction of ozone by NO_x. Cl reactions with carbon compounds have been discussed by Prinn (26) in relation to the CO_2 stability problem on Venus and should be considered in a more detailed evaluation of stratospheric Cl chemistry. Finally, the next stage of stratospheric chlorine calculations should include a careful reevaluation of all possible chlorine sources and possible sinks such as adsorption on aerosols.

NOTE ADDED IN PROOF: The role of chlorine oxides in the stratosphere has also been discussed by M. J. Molina and F. S. Rowland in a paper submitted to Nature and is further elaborated by P. Crutzen and by S. Wofsy and M. McElroy in this issue.

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