

Ozone Calculations With Large Nitrous Oxide and Chlorine Changes

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The purpose of this study is broadly to reinvestigate $\text{NO}_x\text{-Cl}_x$ interactions relative to ozone control in the stratosphere, using the long-established Lawrence Livermore National Laboratory one-dimensional model. To obtain perspective on reasonably expected atmospheric perturbations, this study includes unrealistic conditions in the calculations, and several interesting or unexpected features are found. (1) By varying both NO_x and Cl_x over wide ranges, regions are found where ozone column reduction is linear and nonlinear in added chlorine or in added nitrogen oxides. (2) If the stratosphere had much less NO_x than the natural amount, small chlorine increases would cause large reductions of ozone. (3) At high Cl_x , a region of $\text{NO}_x\text{-Cl}_x$ space is found where added NO_x (at constant Cl_x) increases the ozone column, but no region was found where added chlorine (at constant nitrous oxide boundary condition) increases the ozone column. (4) The solar self-healing effect in response to ozone reduction by increasing Cl_x is much greater than that associated with ozone reduction by increasing nitrous oxide. (5) For any fixed amount of Cl_x , the amount of chlorine nitrate in the stratosphere is decreased by added NO_x , and an explanation for this effect is presented. (6) Any increase of stratospheric Cl_x shrinks the rate profile of ozone destruction by NO_x , and any increase of nitrous oxide shrinks the rate profile of ozone destruction by Cl_x . (7) Total ozone changes linearly with Cl_x until the rate of $\text{ClO} + \text{O}$ exceeds that of $\text{NO}_2 + \text{O}$ below about 30 km, and then it becomes nonlinear with downward curvature. (8) Removal of all Cl_x and all HO_x from the stratosphere has only a slight effect on the magnitude and shape of the altitude profile of the rate of ozone destruction by NO_x . (9) The NO_x and HO_x families almost completely suppress the effect of 1 parts per billion by volume (ppbv) chlorine on ozone; but in the absence of NO_x and HO_x , even 1 ppbv chlorine is a powerful ozone-destroying catalyst from the bottom to the top of the stratosphere. (10) In its altitude flexibility, Cl_x destruction of ozone is qualitatively different from NO_x and HO_x destruction of ozone.

1. INTRODUCTION

In this study we used the standard Lawrence Livermore National Laboratory (LLNL) one-dimensional chemical-radiative-transport model of the troposphere and stratosphere [Luther et al., 1979; Wuebbles, 1981; Wuebbles et al., 1983; Connell and Wuebbles, 1986]. Calculations were made including large changes of NO_x , Cl_x , and HO_x . The object was to see if any interesting or unexpected effects could be found, and this article is a one-by-one presentation of what we regard as such effects. The examples listed in the abstract are associated with individual figures in this paper as follows: example 1, Figure 2; example 2, Figure 2b; example 3, Figure 3; example 4, Figure 4; example 5, Figures 5, 6, 7, and 8; example 6, Figure 9; example 7, Figures 9 and 2a; example 8, Figure 11; example 9, Figures 10, 11d, and 12; example 10, Figures 11d, 12, 11b, 11c, 1b, and 1c.

There have been many model studies of how stratospheric ozone is affected by NO_x and Cl_x , both acting individually and taken together [for example, Chang and Duewer, 1979; World Meteorological Organization (WMO), 1981, 1985; Callis et al., 1983; Cicerone et al., 1983; Crutzen and Schmailzl, 1983; Wuebbles, 1983; Wuebbles et al., 1983; Prather et al., 1984; Herman and McQuillan, 1985; Brasseur et al., 1985; Owens et al., 1985; Isaksen and Stordal, 1986; Stolarski and Douglass, 1986]. As is well known, stratospheric chlorine is increasing

from the release of chlorofluorocarbons (CFCs) [WMO, 1985].

To obtain a new perspective on the effect of possible atmospheric perturbations, this study includes unrealistic conditions. The nitrous oxide boundary value is varied from 1/4 to 8 times the reference (1960) value of 300 parts per billion by volume (ppbv). Stratospheric Cl_x is varied from 0 to 22 ppbv [WMO, 1985, chap. 3; Quinn et al., 1985]. Special atmospheres are considered in which all HO_x , NO_x , Cl_x , or combinations of these are omitted from the reference atmosphere.

2. ATMOSPHERIC MODEL

The LLNL one-dimensional chemical-radiative-transport model of the troposphere and stratosphere is used in this study. The details of this model have been presented previously [Luther et al., 1979; Wuebbles, 1981; Wuebbles et al., 1983; Connell and Wuebbles, 1986]. Briefly, the one-dimensional model calculates the vertical distribution of 37 species as a function of boundary conditions and time. There are 119 chemical reactions and 46 photochemical reactions included in the model. The chemical and photochemical rate constants are based on those recommended by the NASA Panel for Data Evaluation [DeMore et al., 1985]. The one-dimensional model atmosphere is divided up into 44 vertical layers, which extend from the surface up to 56 km. Transport of trace species is controlled by an empirically based eddy diffusion representation.

Luther et al. [1979, p. 135] described a diurnally averaged model that is consistent with their full diurnal model. The diurnal model is used to generate species profiles for compari-

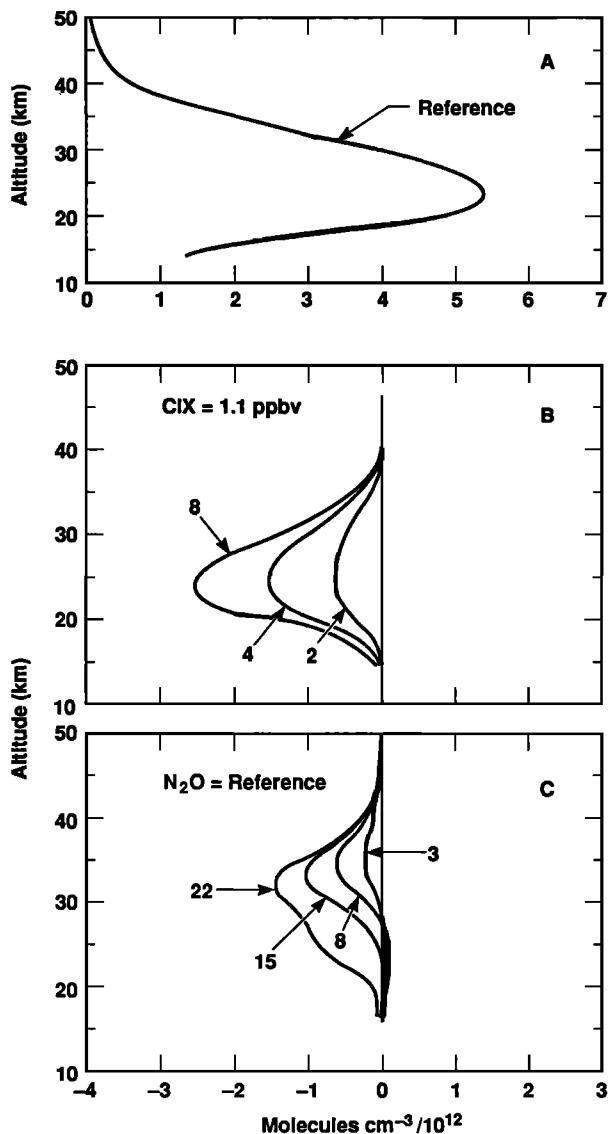


Fig. 1. (a) Calculated ozone vertical profile based on the reference model, Cl_x = 1.1 ppbv, N₂O = 300 ppbv. (b) Calculated changes in the ozone vertical profile for Cl_x = 1.1 ppbv and for N₂O at 2, 4, and 8 times the reference value. (c) Calculated changes in the ozone vertical profile for reference boundary value of N₂O and for 3, 8, 15, and 22 ppbv of Cl_x. The same concentration scale is used on all three panels.

son with measurements and for short-time perturbations (such as solar eclipse), and the diurnal-average model is used for perturbation and sensitivity studies involving long-time integrations. For each reaction rate and altitude, diurnal weighting factors α_{mn} and β_{mn} are defined as

$$k_{mn} \overline{C_m C_n} = \alpha_{mn} k_{mn} \overline{C_m C_n}, \quad \overline{j_m C_m} = \beta_{mn} \overline{j_m C_m}$$

where averages are for 24 hours, using the diurnal model with closely spaced time steps. These factors depend primarily on the shape of concentrations, as they vary over 24 hours and not on the absolute values of concentrations. These factors change slowly under perturbed atmospheric conditions.

Another necessary feature in handling large diurnal changes in photochemical reactions is illustrated by chlorine nitrate photolysis and its product NO₃. Chlorine nitrate is slowly photolyzed to produce NO₃, which is rapidly photolyzed to

give NO₂ + O and NO + O₂. In the model, photolysis products of ClONO₂ are taken to be NO₂ + O and NO + O₂. The NO₃ produced by chemical reactions is treated with diurnal factors in the usual way.

In this study we tested the stability of the diurnal factors by calculating the ozone column change for a very large perturbation, namely, a fourfold increase of nitrous oxide, in two ways: (1) A set of diurnal-weighting factors was derived from the reference atmosphere and was used to calculate the ozone change (−24.3%), and (2) the factors were updated using the full diurnal model at steady state ($\Delta O_3 = -22.8\%$). This difference is unimportant considering the purpose of these studies. Associated relative differences for smaller perturbations would be much less.

2.1. The Reference Atmosphere

The reference atmosphere is designed to represent the pre-chlorofluorocarbon atmosphere, perhaps that of about 1960. It is made up of the following families of atmospheric species: the oxygen species in the Chapman model, NO_x, HO_x, and Cl_x.

1. The "Chapman model" atmosphere includes only the chemistry of O₂, O, O₃, and O¹D) [Chapman 1930a, b, c].

2. The nitrogen oxides family, NO_x, is defined here as NO_x = N + NO + NO₂ + NO₃ + 2N₂O₅ + (HNO₃ + HNO₄ + ClONO₂ + CINO₂). The primary members are NO and NO₂, and the interaction species with the HO_x and Cl_x families are enclosed in parentheses. Its sources are the reaction in the stratosphere of singlet atomic oxygen with N₂O that rises from the troposphere, lightning, and cosmic rays [WMO 1985, chap. 3, pp. 85–88].

3. The free radicals derived from water and their important reservoir species are here called HO_x: HO_x = H + HO + HO₂ + 2H₂O₂ + (HNO₃ + HNO₄ + HCl + HOCl + CHO_x). Water is specified by a tropopause boundary condition, and methane is transported from the troposphere. The sources of the HO_x free radicals are the reaction of H₂O with singlet atomic oxygen, photolysis of H₂O, and the reaction of CH₄ with singlet oxygen, with atomic chlorine, and with HO [WMO, 1985, chap. 3, pp. 88–100]. Methane and its derivatives (CHO_x) are included in the HO_x family in all cases, except where noted to the contrary.

4. The active chlorine family is represented as Cl_x, where Cl_x = Cl + ClO + (HCl + HOCl + ClONO₂ + CINO₂). The maximum value of Cl_x is 1.1 ppb at 55 km. In the reference model the source is tropospheric CH₃Cl and CCl₄ [WMO, 1985, chap. 3]. Cl_x perturbations are based on increases of CCl₄, CFCl₃, CF₂Cl₂, and CH₃CCl₃.

The vertical profile (10–55 km) of ozone concentration, calculated with the reference atmosphere, is shown in Figure 1a. The profile, like most others in this paper, is given as concentration in molecules per cubic centimeter versus altitude, both with a linear scale. The ozone profile calculated from the reference atmosphere agrees reasonably well with the standard observed profile [WMO, 1985], and the calculated distributions of other species generally compare satisfactorily with observations [Wuebbles, 1983].

3. SEQUENCES OF LARGE NO_x AND Cl_x CHANGES

The reference (1960) background of stratospheric chlorine is taken to be 1.1 ppbv. The 1988 level of stratospheric chlorine is about 3 ppbv [WMO, 1985, chap. 3]. If the rate of CFC

production and release continues indefinitely at the present rate, stratospheric chlorine will reach about 8 ppbv by the middle of the next century. Assuming worldwide growth of the CFC industry, an increase of stratospheric chlorine to about 15 ppbv is regarded as possible [Quinn *et al.*, 1985]. In a search for nonlinear trends, an increase of stratospheric chlorine to about 22 ppbv is considered. The unrealistically large Cl_x increase assumed here is about 50% greater than the plausible extreme scenario. In this study this targeted range of round numbers comes out to be 1.1, 3.1, 7.9, 14.7, and 21.4 ppbv of stratospheric chlorine, respectively, although at times these are referred to as the nominal values of 1, 3, 8, 15, and 22 ppbv.

Natural stratospheric NO_x is largely derived from tropospheric nitrous oxide, N₂O, which is broken down to NO, O₂, and N₂ in the stratosphere [Crutzen, 1971; Weiss, 1981; Prather, 1985]. A wide range of nitrous oxide was included in these model calculations: 1/4, 1/2, 1, 2, 4, and 8 times the reference amount of N₂O. The reference boundary value is 300 ppbv, occurring at 37.5 km. Extrapolation of the current increasing trend in nitrous oxide indicates that it might increase by about 40% over the next century [Weiss, 1981; Prather, 1985; WMO, 1985, chap. 3, p. 84]. Large increases of stratospheric nitrogen oxides from stratospheric aircraft or nuclear bombs are conceivable, and these large changes of nitrous oxide provide some background for thinking about these perturbations.

4. RESULTS OF MODEL CALCULATIONS FOR N₂O AND Cl_x CHANGES

Many results of this study are summarized in Table 1 and in Figures 1, 2, and 3. Figure 1a gives the calculated ozone vertical profile for the reference model; on the same linear scale, Figure 1b shows the changes of ozone as the boundary value of nitrous oxide is increased by factors of 2, 4, and 8, and Figure 1c shows the changes of ozone from the reference model as stratospheric Cl_x is increased from 1 to 3, 8, 15, and 22 ppbv. As N₂O increases in Figure 1b, the successive curves show quantitatively increased ozone reductions, and they all show the same slightly asymmetrical bell-shape profile, centered at about 22 km. As Cl_x increases (with other boundary values of the reference model held constant), the ozone-change profiles show different qualitative features as well as quantitative changes. For small Cl_x increases, ozone reduction occurs over a narrow band between 35 and 45 km and increases weakly in the 25- to 35-km range. For large Cl_x increases, the ozone decrease spreads downward, spanning the range from 25 to 45 km (Figure 1c).

The changes of the ozone column as a joint function of varied N₂O and Cl_x are shown by Figure 2.

Figure 2a shows the percentage ozone column change plotted against stratospheric Cl_x for various fixed boundary values of nitrous oxide. The pattern of these curves is varied and complex.

1. For the reference value of N₂O (300 ppbv), ozone decreases linearly, with Cl_x up to about 10 ppbv, but above 15 ppbv it decreases in a nonlinear, accelerating manner. At 22 ppbv Cl_x the ozone reduction is 23%.

2. At 1 ppbv Cl_x and for large amounts of NO_x (2, 4, and 8 times the reference boundary condition of N₂O), there are large ozone reductions caused by NO_x. For these large

TABLE 1. Calculated Ozone Vertical Column for Wide Range of Assumed N₂O Boundary Values and for Five Values of Stratospheric Cl_x

Cl _x , ppbv	N ₂ O, (reference)	O ₃ Column ($\div 10^{18}$)	Percent Difference	Maximum NO _x , ppbv	Maximum Altitude, km
0.0	0	10.99	+18.9	0	
1.1	0	9.535	+3.1	1.9*	31
3.1	0	7.756	-16.1	1.9*	32
7.9	0	4.919	-46.8	1.9*	32
1.1	1/4	9.936	+7.5	7.8	40.0
3.1	1/4	9.235	-0.1	7.6	37.5
7.9	1/4	7.351	-20.5	7.3	37.5
14.7	1/4	4.352	-52.9	6.6	37.5
21.4	1/4	3.436	-62.8	6.3	37.5
1.1	1/2	9.770	+5.7	12.3	37.5
3.1	1/2	9.417	+1.9	12.3	37.5
7.9	1/2	8.544	-7.6	12.3	37.5
14.7	1/2	7.114	-23.0	12.3	37.5
21.4	1/2	4.016	-56.6	10.9	37.5
1.1	1	9.244	+0.0	19.4	37.5
3.1	1	9.116	-1.4	20.0	35
7.9	1	8.775	-5.1	20.7	35
14.7	1	8.121	-12.2	22.3	35
21.4	1	7.055	-23.6	22.9	35
1.1	2	8.282	-10.4	30.5	35
3.1	2	8.238	-10.9	31.2	35
7.9	2	8.097	-12.4	33.8	34
14.7	2	7.882	-14.7	37.8	34
21.4	2	7.684	-16.9	41.0	34
1.1	4	6.994	-24.3	47.1	33
3.1	4	6.954	-24.8	48.8	33
7.9	4	6.813	-26.3	53.6	33
14.7	4	6.615	-28.4	61.8	33
21.4	4	6.464	-30.1	67.6	33
1.1	8	5.660	-38.8	72.2	31
3.1	8	5.613	-39.3	74.8	31
7.9	8	5.455	-41.0	82.6	31
14.7	8	5.232	-43.4	95.1	31
21.4	8	5.077	-45.1	105.	31

The reference conditions are 1.1 ppbv Cl_x at 50 km, and $7.645 \times 10^{12} \text{ cm}^{-3} \text{ N}_2\text{O}$ (300 ppbv) at the surface. The maximum NO_x mixing ratio occurs at altitudes between 31 and 37.5 km; in this discussion, NO_x includes all forms: N, NO, NO₂, NO₃, 2N₂O₅, HNO₃, ClNO₂, etc., and Cl_x includes all forms: Cl, ClO, HCl, HOCl, and ClONO₂.

*From lightning and cosmic rays.

amounts of NO_x, as Cl_x is increased to 3, 8, 15, and 22 ppbv, ozone decreases slowly and linearly.

3. For the hypothetical case of one-half the reference value of N₂O and thus low NO_x, the decrease of ozone with increasing Cl_x is much faster and more nonlinear than for the case of reference N₂O, reaching "56%" ozone reduction at 22 ppbv Cl_x. For one-quarter the reference boundary value of N₂O, the ozone decrease with increasing Cl_x is even faster, becoming "53%" at 15 ppbv Cl_x. With all NO_x removed from the model atmosphere, merely 8 ppbv Cl_x is calculated to reduce ozone by "48%." (These very large ozone reductions are put in quotation marks to acknowledge that such large perturbations would affect stratospheric temperature and dynamics; quantitative significance should not be ascribed to these numbers, but the trends should be noted). In no case does the ozone column increase with an increase of chlorine at constant boundary values of nitrous oxide (even though local ozone increases in some cases with increasing Cl_x, see Figure 1c).

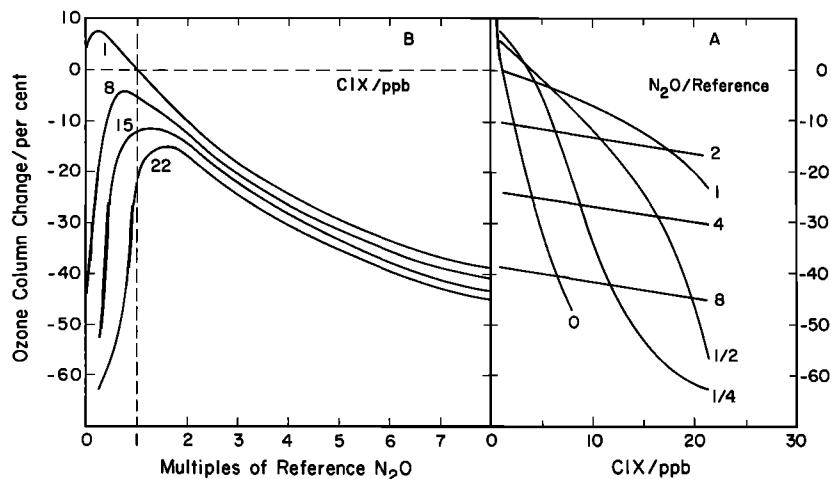


Fig. 2. (a) Steady state ozone column changes by increasing stratospheric chlorine for various assumed values of the nitrous oxide boundary values, spanning the range of 0, 1/4, 1/2, 1, 2, 4, and 8 times the reference amount, which is 300 ppbv. The stratospheric NO_x associated with these multiples of the reference boundary value of N_2O is 1/4, 7.6 ppbv; 1/2, 12 ppbv; 1, 20 ppbv; 2, 31 ppbv; 4, 47 ppbv; and 8, 72 ppbv. For large amounts of NO_x , ozone decreases linearly with increasing stratospheric chlorine; for small amounts of NO_x , ozone changes very rapidly and nonlinearly with increasing chlorine. (b) Steady state ozone column changes by increasing tropospheric nitrous oxide for various fixed values of stratospheric Cl_x .

Figure 2b shows the percentage ozone column change plotted against N_2O boundary values from zero to 8 times reference N_2O , at various values of fixed stratospheric Cl_x . The curves all show the same general shape. For a fixed amount of Cl_x , the ozone column is a maximum at a finite value of nitrous oxide, decreasing both for less and for more nitrous oxide. When nitrous oxide is low, increasing nitrous oxide increases the ozone column, the degree of which depends on the amount of Cl_x .

The results shown in Figure 2 are reexpressed in Figure 3,

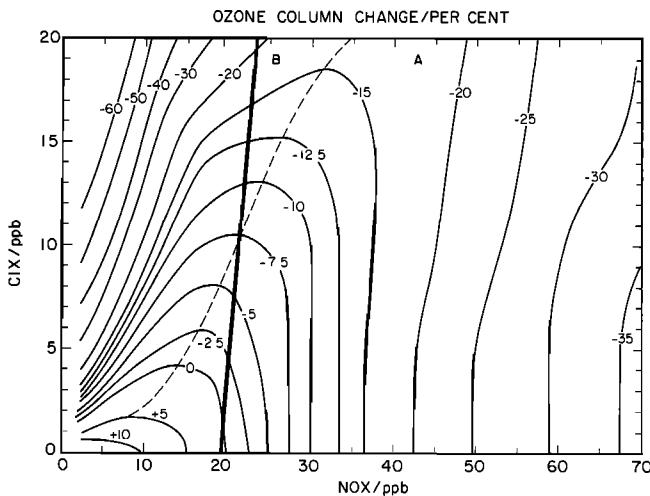


Fig. 3. Contour plot of percentage ozone column change (relative to reference atmosphere) as a function of stratospheric Cl_x and maximum stratospheric NO_x (which occurs between 30 and 35 km; see Table 1). Figure 3 uses maximum stratospheric NO_x as an independent variable. The region to the left of the almost vertical line contains less NO_x than the reference atmosphere. If ozone has reached steady state with respect to chlorine species, added NO_x increases ozone in region B and further decreases ozone in region A. The region to the left of the dashed line and to the right of the solid line represents possible future conditions where added NO_x would increase the ozone column.

with the independent variable taken to be the maximum mixing ratio of NO_x , which occurs between 35 and 40 km, instead of the multiple of the reference nitrous oxide. These values are included in Table 1. These data are expressed as a contour plot of the percentage change of the ozone vertical column (relative to the reference model) as a joint function of stratospheric NO_x and Cl_x mixing ratios. The values of NO_x for the reference boundary value of N_2O are indicated by an almost vertical solid line across Figure 3; this value increases slowly with increasing Cl_x . As Cl_x increases along the constant NO_x reference line, the ozone column decreases. Points on the contour lines where the tangent is parallel to the NO_x axis are connected by a dashed line to divide the contour plot into two regions, A and B. Anywhere in region B of Figure 3 (including the region to the left of the reference nitrous oxide line), an increase of NO_x at constant Cl_x reduces the ozone reduction, thus increasing ozone. Anywhere in region A, an increase of NO_x at constant Cl_x decreases ozone, in addition to the reduction caused by chlorine. The A/B boundary line intersects the reference nitrous oxide line at about 10 ppbv Cl_x , where the ozone column reduction is about 7%; a small increase of stratospheric NO_x decreases ozone at lower amounts of Cl_x and increases ozone at larger amounts of Cl_x .

The contour map in Figure 3 is constructed from a relatively small number of points. The data for the fitting program have been extended by reading points off hand-drawn curves similar to Figure 2. One should not expect Figure 3 to give quantitative results for all possible cuts through the figure.

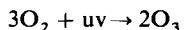
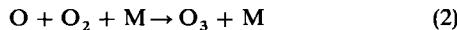
A surprising feature of Figures 2 and 3 is that if the stratosphere had much less NO_x than the natural amount, a very small chlorine increase would cause a large reduction of ozone. An interesting feature is the region of high Cl_x , where increasing NO_x in the stratosphere would increase the ozone column.

5 INTERACTION MECHANISMS BETWEEN NO_x AND Cl_x

Figures 1–3 show strong interactions between Cl_x and NO_x , so far as ozone reduction is concerned. Some of these interactions can be identified, and such cases are given below.

5.1. Photochemical Self-Healing of Ozone

Ozone formation occurs through the reactions



and for the Chapman reactions the ozone destruction mechanism is

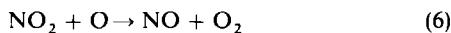


In the stratosphere, solar radiation below 244 nm can either dissociate molecular oxygen to make two ozone molecules (equations (1) and (2)) or dissociate ozone

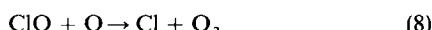


which with rare exceptions is followed by (2), leading to no net chemical reaction. Ozone and oxygen compete for the same limited supply of radiation below 244 nm. In this way a reduction of the mixing ratio of ozone in a volume of air increases ozone production from (1) and (2) relative to the null cycle (equations (4) and (2)), which partially cancels the ozone reduction. This feedback is called the "self-healing effect." In the Chapman atmosphere, ozone destruction occurs primarily by the sequence (4), (3).

For NO_x and Cl_x the predominant ozone-destroying catalytic cycles are, respectively,



and



for which (6) and (8) are the rate-determining steps.

Increasing stratospheric Cl_x up to 22 ppbv (at constant reference N₂O boundary value) decreases the column of ozone up to 21% (Figure 2a), which increases the photolysis rate of molecular oxygen and thus increases the rate of ozone production, Figure 4a. Increasing nitrous oxide up to 8 times the reference value (with Cl_x constant at 8 ppbv, for example) decreases the column of ozone by "40%" (Figure 2b), which increases the photolysis rate of molecular oxygen and thus increases the rate of production of ozone, Figure 4b.

Although the ozone column reduction by NO_x is almost twice as great as that caused by added Cl_x, the self-healing effect with increased Cl_x is much larger than that associated with NO_x (compare Figure 4a with Figure 4b). This difference is general. For both NO_x and Cl_x this "self-healing effect" extends weakly down to 20 km.

5.2. Chlorine Nitrate

A strong interaction between the Cl_x and NO_x systems is the formation of chlorine nitrate [Rowland *et al.*, 1976; WMO, 1985].

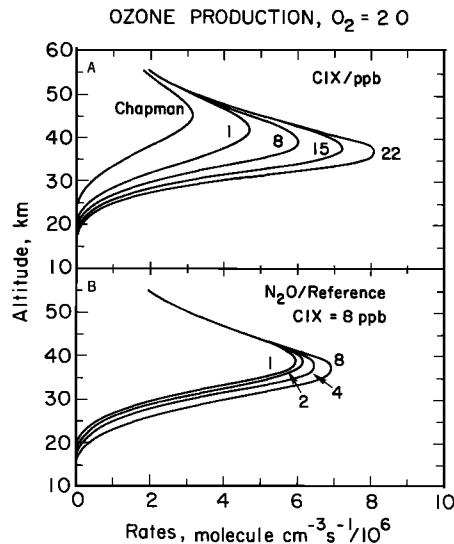


Fig. 4. Profiles of the rate of production of atomic oxygen and thus ozone from the photolysis of molecular oxygen. (a) The first profile is for the Chapman model, the second is the reference atmosphere, including 1.1 ppbv of Cl_x, and the other curves are the reference atmosphere plus CFC to give stratospheric Cl_x of 8, 15, and 22 ppbv. (b) With stratospheric Cl_x = 8 ppbv, this panel gives the rate of ozone production from oxygen photolysis, with tropospheric N₂O multiplied by factors of 1, 2, 4, and 8.

By this process the species occurring in the rate-determining step of both the Cl_x catalytic cycle (8) and the NO_x catalytic cycle (6) are tied up in a "reservoir species," chlorine nitrate. Vertical profiles of diurnally averaged concentrations of chlorine nitrate are shown in Figure 5. At a rate slightly faster than linearly, increasing Cl_x increases chlorine nitrate, Figure 5a. However, as NO_x increases in a model of fixed Cl_x (8 parts per million by volume (ppmv), for example) the surprising result is that chlorine nitrate decreases, Figure 5b. (This effect is general, observed for all levels of Cl_x from 1.1 to 21.4 ppbv and for all amounts of N₂O equal to or greater than the reference model). The components of chlorine nitrate are ClO and NO₂. The vertical profiles of ClO concentration show the same relation as chlorine nitrate (Figure 6). Increasing Cl_x increases ClO, but increasing N₂O decreases ClO. The vertical profiles of nitrogen dioxide are more complex than that for chlorine oxide (Figure 7). NO₂ is increased in the upper stratosphere by increasing Cl_x, but it is decreased in the lower stratosphere by increasing Cl_x. Nitrogen dioxide increases slightly faster than linearly with increasing NO_x, Figure 7b.

5.3. Mechanism to Explain Some Major NO_x-Cl_x Interactions

The major features of Figures 5-7 are explained in terms of a simplified 10-reaction mechanism given in Table 2. The steady state approximation is made for the rapidly changing species (NO, NO₂, Cl, ClO, and ClONO₂), and a small additive term is neglected in one case. Five relations are derived and given in the upper part of Table 2, and the relations of ClO to Cl_x and of NO₂ to NO_x are given in the footnote. For algebraic simplicity in Table 2, total Cl_x is approximated by the sum of the three species, HCl, ClO, and ClONO₂, and NO_x is approximated by NO + NO₂ + HNO₃ + ClONO₂; model calculations include all members of each family.

Chlorine nitrate (Figure 6) is formed by the third-body de-

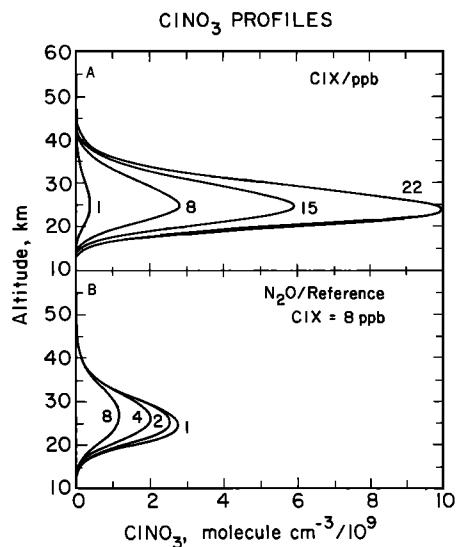
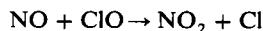


Fig. 5. Profiles of the concentration of chlorine nitrate for the same model atmospheres as those in Figure 4. Note the expected increase of chlorine nitrate with increasing Cl_x, but unexpected decrease of chlorine nitrate with increasing nitrogen oxides.

pendent reaction (g_M), ClO + NO₂, and destroyed by photolysis (h). The steady state concentration of chlorine nitrate is

$$[\text{ClONO}_2] = g_M[\text{ClO}][\text{NO}_2]/h \quad (10)$$

From this relation we had assumed that chlorine nitrate increased with NO_x, but Figure 5 shows it to be otherwise. By virtue of reaction (d) between nitric oxide and chlorine oxide



the concentration of chlorine oxide is reduced by nitric oxide. As given in Table 2, ClO is approximately proportional to Cl_x and inversely proportional to NO in the lower stratosphere

$$[\text{ClO}] = C_1[\text{Cl}_x]/[\text{NO}] \quad (11)$$

The "constant" C_1 depends weakly on the concentrations of

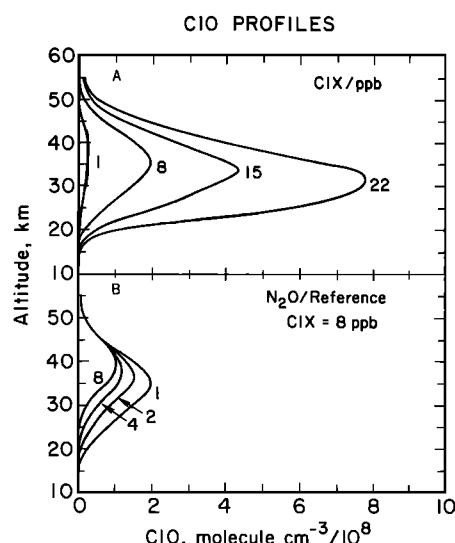


Fig. 6. Profiles of the concentration of chlorine monoxide for the same model atmospheres as those in Figure 4. Note the decrease of ClO with increasing nitrogen oxides in Figure 6b.

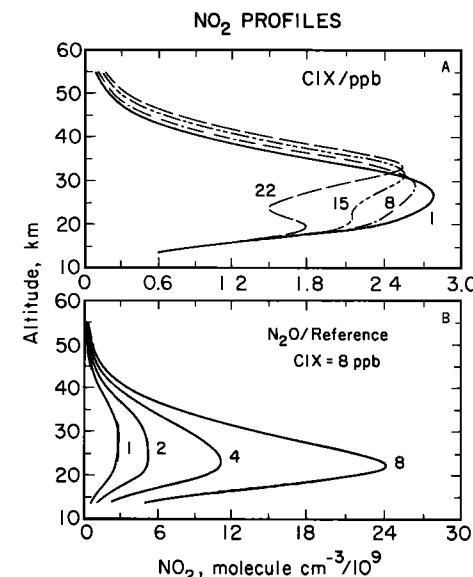


Fig. 7. Profiles of the concentration of nitrogen dioxide for the same model atmospheres as those in Figure 4. (a) NO₂ decreases between 20 and 30 km but increases above 30 km upon increasing Cl_x. (b) NO₂ increases with increasing nitrous oxide.

ozone, hydroxyl radicals, and methane (Table 2). Substitution of (11) into (10) gives the concentration of chlorine nitrate as

$$[\text{ClONO}_2] = (C_1 g_M/h)[\text{Cl}_x][\text{NO}_2]/[\text{NO}] \quad (12)$$

With NO₂ in the numerator and nitric oxide in the denominator of (12), it would appear that chlorine nitrate should be independent of NO_x. However, the ratio of nitrogen dioxide to nitric oxide depends on the concentration of ozone. In the lower half of the stratosphere where chlorine nitrate is impor-

TABLE 2. Abbreviated Mechanism for Major Interactions Between Active NO_x and Cl_x Species, Used for the Interpretation of Figures 5-8

Reaction	Rate Constant	Approximate Steady Relation
Cl + CH ₄ → HCl + CH ₃ HO + HCl → H ₂ O + Cl	<i>a</i> <i>b</i>	<i>a</i> [Cl][CH ₄] = <i>b</i> [HO][HCl]
Cl + O ₃ → ClO + O ₂ ClO + NO → Cl + NO ₂	<i>c</i> <i>d</i>	<i>c</i> [Cl][O ₃] = <i>d</i> [ClO][NO]
NO + O ₃ → NO ₂ + O ₂ NO ₂ + hν → NO + O	<i>e</i> <i>f</i>	<i>f</i> [NO ₂] = (<i>d</i> [ClO] + <i>e</i> [O ₃])[NO]
NO ₂ + ClO → ClONO ₂ ClONO ₂ + hν → Cl + NO ₂ + O	<i>g_M</i> <i>h</i>	<i>g_M</i> [NO ₂][ClO] = <i>h</i> [ClONO ₂]
HO + NO ₂ → HNO ₃ HNO ₃ + hν → HO + NO ₂	<i>i_M</i> <i>j</i>	<i>i_M</i> [HO][NO ₂] = <i>j</i> [HNO ₃]

$[\text{ClO}] \approx C_1[\text{Cl}_x]/[\text{NO}]$ and $[\text{NO}_2] \approx C_2[\text{NO}_x]$, where $[\text{Cl}_x]/[\text{ClO}] = ad[\text{CH}_4]/bc[\text{HO}][\text{O}_3] + (g[\text{ClO}] + e[\text{O}_3])[\text{NO}]/f + 1 = [\text{NO}]/C_1 \rightarrow ad[\text{CH}_4]/bc[\text{HO}][\text{O}_3] + ge[\text{O}_3]/f)[\text{NO}]$, low stratosphere; $[\text{NO}_x]/[\text{NO}_2] = \{1 + f/(e[\text{O}_3] + d[\text{ClO}]) + i_M[\text{HO}]/j + g_M[\text{ClO}]/h\} = 1/C_2 \rightarrow \{1 + f/e[\text{O}_3] + i_M[\text{HO}]/j + g_M[\text{ClO}]/h\}$, low stratosphere $\rightarrow \{1 + f/d[\text{ClO}] + i_M[\text{HO}]/j\}$, high stratosphere.

tant, the ratio of nitrogen dioxide to nitric oxide is approximately

$$[\text{NO}_2]/[\text{NO}] = e[\text{O}_3]/f \quad (13)$$

and the final expression for chlorine nitrate from this simplified mechanism is

$$[\text{ClONO}_2] = (C_1 g_M e/hf)[\text{Cl}_x][\text{O}_3] \quad (14)$$

This expression agrees with and explains Figure 5. At constant (reference) N₂O boundary conditions, chlorine nitrate increases approximately linearly with [Cl_x] (Figure 5a). At constant Cl_x (for example, 8 ppbv in Figure 5b, but also for any other value of Cl_x), as nitrous oxide increases ozone decreases in the lower stratosphere (Figure 1), the ratio of [NO₂]/[NO] decreases (13) and chlorine nitrate decreases (12).

Profiles of chlorine oxide are given in Figure 6, and these follow the main features of the mechanism in Table 2. As indicated by (11), ClO increases with Cl_x at constant N₂O boundary condition (Figure 6a). At constant Cl_x (8 ppbv, for example), chlorine oxide decreases with increasing nitric oxide, which increases with increasing N₂O (Figure 6b).

Profiles of nitrogen dioxide are given in Figure 7. According to the simplified mechanism of Table 2, the ratio of nitrogen dioxide to total NO_x is the somewhat complicated expression C₂, which, however, takes on relatively simple forms in the upper and in the lower stratosphere. In the upper stratosphere the reaction rate of nitric oxide with chlorine oxide (d) is very fast (Figure 8a), becoming faster than the rate of nitric oxide with ozone (e). The increase of NO₂ with increasing Cl_x, seen above 30 km in Figure 7a, is a result of reaction (d), as approximately given by the high stratosphere limit of C₂ in Table 2. The effect of reaction (d) falls off very rapidly below 30 km (Figure 8a), and the rate of the reaction of ozone with nitric oxide dominates in the region of maximum ozone concentration. The erosion of the NO₂ profile between 20 and 30 km with increasing Cl_x, shown in Figure 7a, is caused by the formation of chlorine nitrate, the term g_M[ClO] in the low-altitude form of C₂ in Table 2.

The rate of chlorine nitrate formation (Figure 8b) reflects the trends of NO₂ concentrations above 30 km (Figure 7a) and the trends of chlorine oxide concentrations below 30 km (Figure 6b).

The explanations given above do not include the effect of atmospheric motions on the local concentrations of chemical species, and thus are not expected to be and are not fully quantitative. However, the simple mechanism of Table 2 does give a definite, semiquantitative explanation of the major features of Figures 5-8.

5.4. Ozone Loss Rate Profiles Over a Wide Range of NO_x and Cl_x

Reaction rate profiles for reaction (6), NO₂ + O, and for reaction (8), ClO + O, are given for a wide range of NO_x and Cl_x in Figure 9. These reaction rate profiles should be studied in conjunction with Figure 2b. From top to bottom, the three strips in Figure 9 correspond to the curves marked 1/2, 1, and 2, in Figure 2b, for which the changes of ozone column with increasing Cl_x from 1 to 22 ppbv are linear, slightly nonlinear, and extremely nonlinear, with strong downward curvature, respectively.

Nitrous oxide is given its reference value, and Cl_x changes from 1 to 22 ppbv across the center strip of Figure 9. At 1

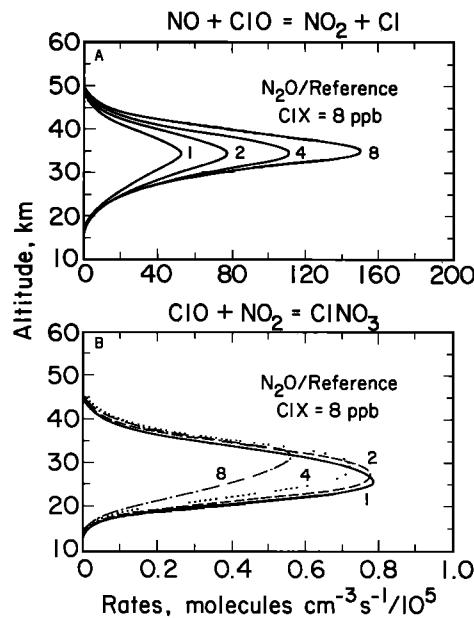
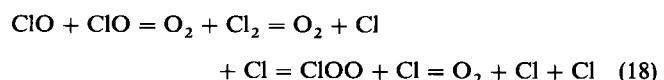
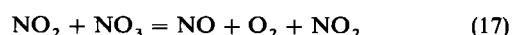
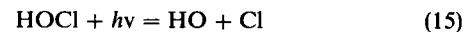


Fig. 8. Profiles of rates of reaction for the same model atmospheres as those in Figure 4b. (a) At fixed Cl_x the fast reaction shown here between nitric oxide and chlorine monoxide reduces ClO upon increasing NO_x. (b) At fixed Cl_x the rate of formation of chlorine nitrate decreases with increasing NO_x.

ppbv Cl_x, ozone destruction by NO_x (6) is much faster than ozone destruction by Cl_x (8) at all altitudes; 8 ppbv Cl_x has overtaken NO_x at all altitudes above 35 km, 15 ppbv Cl_x has overtaken NO_x at all altitudes (note that curve of ozone reduction versus Cl_x is distinctly nonlinear at and above this point in Figure 2b), and 22 ppbv Cl_x dominates ozone destruction from 20 to 55 km.

When the boundary value of N₂O is twice the reference value (bottom strip of Figure 9), the NO_x ozone-destroying curve exceeds that for Cl_x at altitudes below about 30 km in all panels, and the reduction of the ozone column is linear in increasing Cl_x, Figure 2b. The top strip of Figure 9 is based on the hypothetical scenario of one-half the reference value of nitrous oxide. In this case, ozone destruction is dominated by NO_x at 1 ppbv Cl_x, 8 ppbv or more Cl_x overwhelms NO_x, and total ozone changes nonlinearly with added chlorine at and above 8 ppbv (Figure 2b). These three cases suggest that total ozone changes linearly with Cl_x until the rate of ClO + O exceeds that of NO₂ + O below about 30 km, and then it becomes nonlinear, with downward curvature.

Objections can be raised to this statement, including inquiries about other ozone-destroying processes, such as catalytic cycles closed by the reactions



The rates of (15) and (16) are significant relative to (8) and (6) only in the lowest stratosphere, where all of these rates are vanishingly slow. Even at the high values of NO_x or Cl_x, the

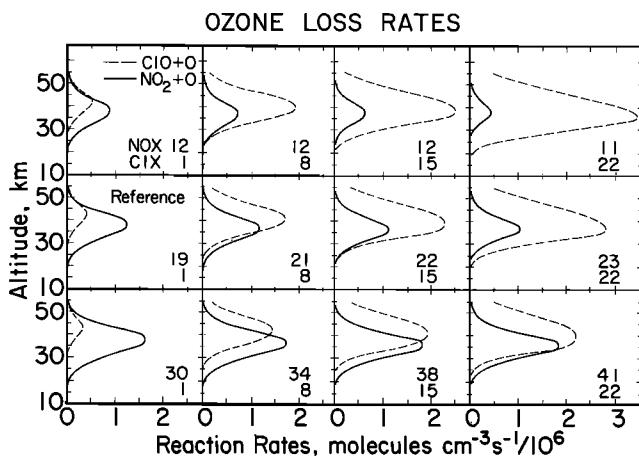


Fig. 9. Profiles of ozone loss rates due to NO_x (NO_x + O → NO + O₂) and to Cl_x (ClO + O → Cl + O₂) for a wide range of hypothetical atmospheres: (N₂O/reference = 0.5, 1, 2; Cl_x/ppbv = 1, 8, 15, 22). From top to bottom, the rows correspond to the cases in Figure 2a where ozone reduction is highly nonlinear, slightly nonlinear, and linear, respectively, with increasing Cl_x. The onset of nonlinearity in Figure 2a occurs when stratospheric Cl_x has increased to the degree that the rate of ClO + O exceeds that of NO_x + O below about 35 km: panel 12, 8 in the first row; panel 22, 15 in the second row, and 41, 22 in the last row.

rates that are bimolecular in radicals, (17) and (18), are very slow compared to (6) and (8), respectively, at altitudes where the rates of (6) or (8) are important. Reactions (17) and (18) are not included in the model, and these statements are based on spot calculations.

For each of the horizontal strips of Figure 9, which represents a constant nitrous oxide boundary condition, as Cl_x increases from 1 to 22 ppbv, the entire rate profile of (6), O + NO_x, decreases. Likewise, reading down any vertical column in Figure 9, one sees that the rate profile of (8), O + ClO, for constant ppbv Cl_x decreases as NO_x increases. Throughout this wide range of conditions, any increase of stratospheric Cl_x tends to shrink the rate profile of ozone destruction by NO_x, and any increase of nitrous oxide tends to shrink the rate profile of ozone destruction by Cl_x.

Another interesting aspect of this study concerns the vertical spread of the rates of ozone destruction by the NO_x and Cl_x reactions. The "spread" of the plots of reaction-rate profiles in Figure 9 is defined as full altitude difference between the two points where the rate is half the maximum value. Over the 12 individual panels in Figure 9, the spread of the NO_x profiles covers the narrow range of 11–13 km, but the spread of the Cl_x profiles varies from 9 to 18 km.

6. SPECIAL ATMOSPHERES

6.1. Reason for Considering Special Atmospheres

The calculations reported above concern large variations of NO_x and Cl_x, but no variation of HO_x was carried out, since a three-dimensional variation of parameters would involve a prohibitive amount of computer time. To explore the effects of large changes of HO_x, calculations are given for "special atmospheres" with various inclusions and exclusions of the entire families, NO_x, HO_x, and Cl_x, from the model (Table 3).

TABLE 3a. Special Atmospheres: Effect of Adding One Family of Ozone-Destroying Catalysts at a Time to the Chapman or O_x Only Atmosphere

O _x	NO _x	Cl _x	HO _x	HC	Column Ozone (÷ 10 ¹⁸)	Percent Difference Relative to Reference Atmosphere	Percent Difference Relative to Chapman Model
X	0	0	0	0	14.72	+59.2	+0.0
X	X	0	0	0	7.425	-19.7	-49.6
X	0	X	0	0	8.442	-8.4	-42.6
X	0	0	X	0	10.99	+18.9	-25.3
X	0	0	0	X	10.57	+14.3	-28.2
X	X	X	X	X	9.244	+0.0	-37.2

Effect is measured in terms of the percentage ozone column change (in molecules per square centimeter) relative to the Chapman model and to the reference model: 1.1 ppbv Cl_x at 50 km, as generated by CH₃Cl and CCl₄, and with other species corresponding to values appropriate to 1960. The reference atmosphere includes HNO₃, HOONO₂, HOCl, ClONO₂, etc. In this table, a cross indicates that the species is present; a zero indicates that it is absent. O_x = O(³P) + O(¹D) + O₃; NO_x = N + NO + NO₂ + N₂O + NO₃ + 2N₂O₅; Cl_x = Cl + ClO + CCl₄ + CH₃Cl + HCl. HO_x = H + HO + HO₂ + H₂O₂ + H₂ + H₂O. HC = CH₄ + HCO + CH₂O + CH₃OOH + CH₃O + CH₃O₂ + CO + CH₃.

6.2. Ozone Profiles Calculated With Different Model Atmospheres

Figure 10a gives the ozone vertical profiles calculated by the reference model and the ozone profile calculated from the Chapman model. The Chapman model gives an ozone column 59% greater than the reference model.

The effects of deleting the individual NO_x, HO_x, and Cl_x families, one at a time, from the reference atmosphere are given in Table 3b and are shown in Figure 10c. In terms of the 1985 model, removal of all chlorine species from the reference atmosphere has almost no effect on the ozone column or the altitude of the ozone profile, and thus the curve marked -Cl may be regarded as the ozone profile of the reference atmosphere. Removal of all NO_x, leaving hydrogen species and 1.1 ppbv Cl_x, gives a 19.4% ozone reduction and a substantial increase in the altitude of the ozone profile (Figure 10c), relative to the reference model. Removal of all hydrogen species

TABLE 3b. Special Atmospheres: Effect of Removing One Family of Ozone-Destroying Catalysts at a Time From the Reference (1960) Model Atmosphere

Chapman Model	NO _x	Cl _x	HO _x	HC	Column Ozone (÷ 10 ¹⁸)	Percent Difference Relative to Reference Atmosphere	Percent Difference Relative to Chapman Model
X	X	X	X	X	9.244	+0.0	-37.2
X	0	X ^a	X ^a	X ^a	7.449	-19.7	-49.4
X	X ^b	0	X ^b	X ^b	9.348	+1.1	-36.5
X	X ^c	X ^c	0	X ^c	7.416	-19.7	-49.6
X	0	0	0	0	14.72	+59.2	+0.0

Effect is measured in terms of percentage ozone column change (in molecules per square centimeter) relative to the Chapman model and to the reference model (see footnotes to Table 3a).

^aIncludes CH₃Cl, HCl, and HOCl.

^bIncludes HONO₂, HO₂NO₂, and HONO.

^cIncludes ClONO₂ and CINO₂.

gives a 19.8% ozone reduction with little change in the ozone-profile altitude, relative to the reference atmosphere.

Using the 1985 atmospheric model, the effect of adding just the HO_x reactions (including methane) to the O_x reactions is given by Figure 10b and in Table 3a. The ozone column is reduced 28% relative to the Chapman value (increased 14% relative to the reference atmosphere); with the exclusion of methane and its derivatives, the reduction is 25% relative to the Chapman model. Adding only NO_x to the O_x family, the calculated ozone column is given in Figure 10b and Table 3a. The ozone column is reduced 50% relative to the Chapman mechanism, it is about 20% lower than the reference column, and the calculated profile is similar in shape and in peak altitude compared to the observed ozone profile. In 1960 the amount of stratospheric chlorine, Cl_x, was about 1.1 ppbv. When this small amount is added to the Chapman model (with no NO_x or HO_x), the calculated ozone column is reduced 43% below the O_x model, the column is 8% less than that of the reference atmosphere (Table 3a), and the ozone profile (Figure 10b) is similar to, but slightly broader than, that of the reference model. This calculation shows that chlorine in the absence of HO_x and NO_x is an extremely powerful destroyer of ozone. Similar calculations using then current stratospheric chemistry were made by *Chang and Duewer* [1979]; aside from some quantitative differences, similar results were obtained in 1979 and in this study.

Adding 1.1 ppbv of Cl_x to the Chapman model reduces the ozone column by 43% relative to the O_x-only atmosphere (Table 3a, Figure 10b), but removing all (1.1 ppbv) chlorine from the reference model has virtually no effect on the ozone vertical column nor on the ozone vertical profile (Table 3b, Figure 10c). The contrast between the effect of 1.1 ppbv in Figure 10c and Figure 10b shows that the NO_x and HO_x families almost completely suppress the effect of 1 ppbv chlorine on ozone; but in the absence of NO_x and HO_x, even 1 ppbv chlorine is a powerful ozone-destroying catalyst.

6.3. Ozone Destruction Rates in the Special Atmospheres

6.3.1. Ozone destruction by the reaction $O + O_3 \rightarrow 2O_2$. Vertical profiles of the rates of ozone destruction are given by Figure 11. In the Chapman model, essentially the only chemical process that destroys ozone is (3), O + O₃, and this rate of odd oxygen destruction for the Chapman model is given in Figure 11a. In the reference model the ozone-destroying catalysts supplant this reaction, reducing its peak value by a factor of 3 (Figure 11a). When HO_x is removed from the reference model, rate (3) increases, especially above 45 km, the region previously dominated by HO_x. When NO_x is removed from the reference model, the rate, O + O₃, increases, especially in the 35- to 45-km range. Removal of Cl_x from the reference model produces a very small increase in (3) between 40 and 45 km (not shown in Figure 11a).

6.3.2. Ozone destruction by the reaction $O + HO_2 \rightarrow HO + O_2$. There are at least five ozone-destroying catalytic cycles based on the free radicals derived from water. The principal ozone-destroying HO_x reaction in the middle and upper stratosphere is

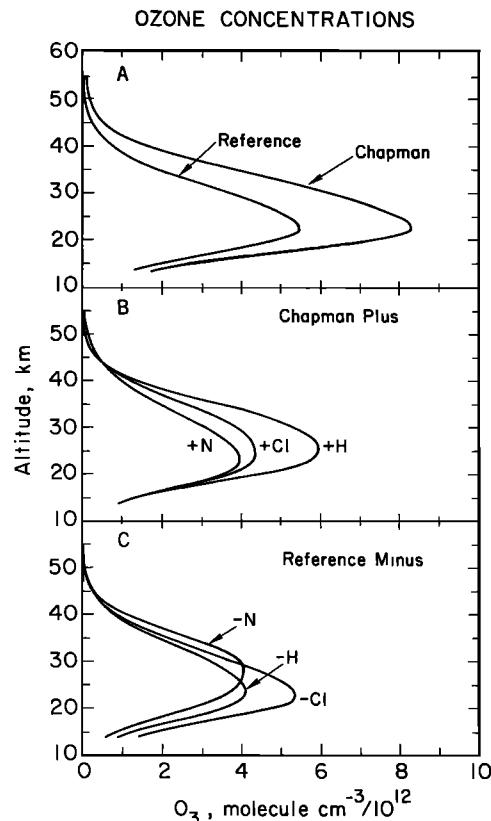
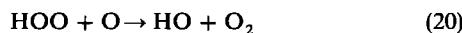
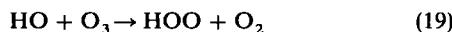


Fig. 10. Calculated ozone vertical profiles for various special atmospheres. (a) Chapman or O_x model, with only O₂, O, and O₃ as reactive species; the reference atmosphere, presumably that existing in 1960, including 1.1 ppbv Cl_x and the amounts of NO_x, HO_x, and methane derivatives as given in Table 3. (b) The Chapman model plus either the NO_x family, the HO_x family, or the Cl_x family. (c) The reference model with the complete removal of either the NO_x family, the HO_x family, or the Cl_x family. The profile with all chlorine removed is almost identical with the reference profile of Figure 10a.

for which the rate-determining step is (20), O + HOO. The rate of (20) is shown as a function of altitude in Figure 11b. Relative to the reference atmosphere, its rate is slightly increased between 25 and 50 km omission of NO_x (about 19 ppbv), and it is slightly increased between 40 and 50 km by removal of Cl_x (1.1 ppbv) (see Figure 11b). The principal feature of Figure 11b is that the rate profile of (20) is only slightly changed by total removal of NO_x or Cl_x.

6.3.3. Ozone destruction by the reaction $O + NO_2 \rightarrow NO + O_2$. The dominant ozone-destroying mechanism in the reference model is the NO_x catalytic cycle, (5), (6), with (6) as rate-determining step. The rates of ozone destruction by NO_x for the reference atmosphere and for the reference atmosphere minus all hydrogen-containing species are shown in Figure 11c. Removal of Cl_x from the reference atmosphere has no detectable effect on the rate profile of (6), and it is not shown as a separate curve. Although removal of HO_x from the reference model causes a small increase of the rate of O + NO₂ below 34 km and above 45 km; it has little effect on the magnitude or altitude of this rate profile as a whole. This result is unexpected, since large amounts of nitrogen dioxide are tied up as nitric acid in the lower stratosphere and elimination of HO_x releases the NO₂ from nitric acid and is expected to increase the rate of (6). When HO_x is omitted, ni-

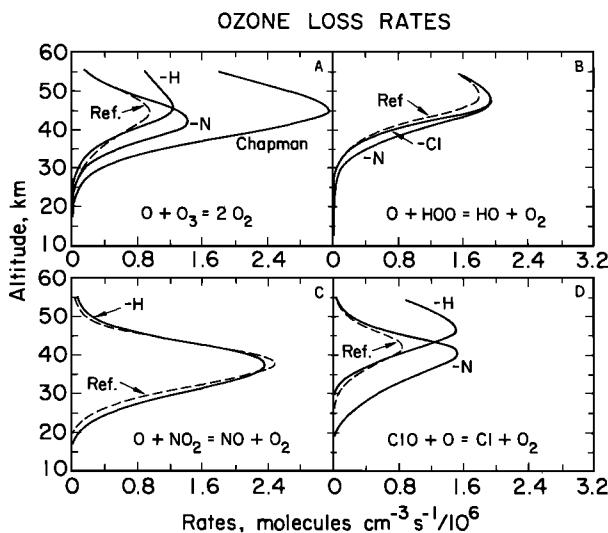


Fig. 11. Profiles of ozone loss rates as caused by various chemical reactions and for various special atmospheres whose ozone profiles are given by Figures 10a and 10c. (a) Reaction $O + O_3 = 2 O_2$, as influenced by the presence or absence of H, N, or Cl species. (b) Reaction $O + HOO \rightarrow HO + O_2$, as influenced by the presence or absence of N or Cl species. (c) Reaction $O + NO_2 = NO + O_2$, as influenced by the presence or absence of H or Cl species. (d) Reaction $ClO + O = Cl + O_2$, as influenced by the presence or absence of H or N species. The ozone loss rates given in Figure 11 are twice the rate of these reactions.

trogen dioxide does increase, but ozone (Figure 10c) and thus atomic oxygen decrease in the lower stratosphere. This increase of nitrogen dioxide and decrease of atomic oxygen very nearly balance, and there is no major change in the rate profile of (6). Figure 11c shows that the vertical profile of ozone destruction by NO_x is largely unmoved by total elimination of HO_x or Cl_x .

6.3.4. *Ozone destruction by the reaction $O + ClO \rightarrow Cl + O_2$.* The reactions that destroy ozone in the chlorine system are primarily (7) and (8), the rate of ozone destruction being twice the rate of (8), $O + ClO$. In the reference model with 1.1 ppbv Cl_x , its rate of ozone destruction is much less than that for HO_x or NO_x (compare Figure 11d with Figures 11b and 11c), but it does have significant values between 35 and 50 km (Figure 11d). Upon removal of NO_x , the rate of $O + ClO$ increases throughout the region where NO_x had been dominant, and it becomes an important ozone-destroying mechanism between 25 and 45 km (Figure 11d). Upon removal of HO_x , chlorine reactions take over ozone destruction in the uppermost stratosphere, where HO_x had been dominant (Figure 11d).

The strong increase in ozone destruction by Cl_x upon removal of HO_x and NO_x is examined in more detail in Figure 12. (Figure 12 gives the rate of the reaction, $ClO + O$; Figure 11d gives the rate of ozone destruction by this reaction, which is a factor of 2 greater). The role of 1.1 ppbv of stratospheric Cl_x is relatively small and vertically constrained in the reference model (Figure 11d). Upon removal of NO_x , the upper boundary of the Cl_x ozone-destroying profile remains at about the same altitude, but Cl_x ozone destruction moves down into the stratosphere, where NO_x had been dominant (Figure 12). Upon removal of NO_x and HO_x from the model, chlorine destruction of ozone becomes important from 18 km to the top of the stratosphere.

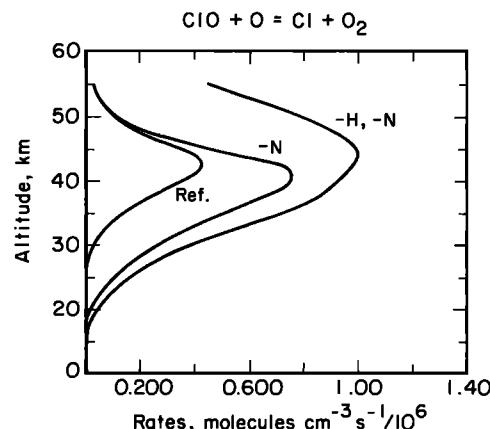


Fig. 12. Increase in the reaction rate, $ClO + O \rightarrow Cl + O_2$, upon the assumed complete removal of all nitrogen species from the atmosphere and from the removal of both HO_x and NO_x species from the atmosphere (compare Figure 11d). In Figure 12 the rate is that of the named reaction, not the rate of ozone loss, which is twice as great.

From studying model calculations for realistic scenarios, one may get the impression that the altitude region for ozone reduction by Cl_x is largely in the 35- to 50-km range, but if NO_x or HO_x should be unexpectedly low in some region, ozone would undergo a large destruction by chlorine (via equation (8)) from 20 km to well above 55 km (Figure 12). Figure 9 gives another aspect to this situation: even in the presence of HO_x and NO_x , at high Cl_x levels the rate of ozone destruction by the reaction, $O + ClO$, is important from 20 km to well above 55 km. In its altitude flexibility, chlorine destruction of ozone is qualitatively different from NO_x and HO_x destruction of ozone.

7. CONCLUSIONS

For some cases (4, 5, 6, 7, and 10 in the abstract), effects present in the reference atmosphere or in mildly perturbed atmospheres are amplified by the unrealistic conditions included in this study, so that they become clearly visible on graphs. These effects should not be dismissed simply because unrealistic conditions are used to point them out. For other cases (1, 2, 3, 8, and 9, in the abstract) the effects reported are properties of the large perturbations. They may be of interest to studies of primitive atmospheres, and perhaps in some cases they may be important at some latitudes in two-dimensional models. In any case, they are interesting in giving perspective to the real atmosphere.

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