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### Journal

Journal of Geophysical Research, 81(18)

### ISSN

0148-0227

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### Publication Date

1976-06-20

### DOI

10.1029/jc081i018p03111

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Peer reviewed

# Effect of Water Vapor on the Destruction of Ozone in the Stratosphere Perturbed by ClX or NO<sub>x</sub> Pollutants

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We describe results of a self-consistent one-dimensional coupled flow calculation for O<sub>3</sub>, NO<sub>x</sub>, HO<sub>2</sub>, ClX, H<sub>2</sub>O, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, and N<sub>2</sub>O densities between 10 and 120 km. Our results agree well with observations for the normal mid-latitude atmosphere over this altitude range. We have varied ClX, NO<sub>x</sub>, and H<sub>2</sub>O independently in our model. We show that the effect of depletion of ozone by ClX is to remove ozone preferentially above 30 km and to lower the altitude of maximum ozone density. This leads to enhanced solar heating of the lower stratosphere and tropopause and suggests the possibility of an increased flux of water into the stratosphere. We show that increasing water vapor in the stratosphere greatly enhances the rate of destruction of O<sub>3</sub> by ClX and also causes an increase in the rate of destruction of O<sub>3</sub> in the NO<sub>x</sub>-perturbed atmosphere.

## INTRODUCTION

Recently, a number of studies have been published showing the effect on the earth's ozone layer of increasing the concentration of odd chlorine, or ClX (Cl + ClO + HCl) in the stratosphere [Molina and Rowland, 1974; Cicerone et al., 1974; Crutzen, 1974a; Wofsy et al., 1975]. We wish to report here the result of calculations that show the influence of the amount of water vapor in the stratosphere on the effectiveness of a specific level of ClX or NO<sub>x</sub> (NO + NO<sub>2</sub> + HNO<sub>3</sub>) in ozone removal. Our calculations are for a steady state and cover the range 10–120 km. We employ a one-dimensional coupled flow calculation using *Hunten's* [1975] eddy diffusion coefficient. Originally, we were motivated to perform this exercise by realizing that in the presence of ClX from chlorocarbons, ozone is preferentially destroyed at high altitudes and the altitude of the peak O<sub>3</sub> concentration tends to be lowered. Thus the heating rate near the tropopause due to absorption by O<sub>3</sub> is thereby increased. This could lead to an increase in the temperature of the tropopause [Ramanathan et al., 1976] and thus decrease the 'cold trap' effect on water vapor [Stanford, 1973]. This in turn would increase the water vapor abundance in the stratosphere. On the other hand, a more uniform reduction of ozone such as by NO<sub>x</sub> pollutants might decrease water vapor in the stratosphere. Since HO<sub>2</sub> (H + OH + HO<sub>2</sub>) plays such an important role in O<sub>3</sub> chemistry, it seems to us important to assess the effect of changes in water concentration on the natural and the perturbed stratosphere. It is particularly significant in the case of ClX pollution because not only does HO<sub>2</sub> destroy O<sub>3</sub> catalytically in its own right but OH attacks HCl to release Cl and thus reinitiates the ClX catalytic chain reaction.

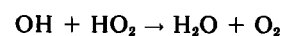
## CALCULATION METHOD AND BOUNDARY CONDITIONS

In our calculation we have self-consistently treated O<sub>3</sub> (O<sub>3</sub> + O), HO<sub>2</sub>, NO<sub>x</sub>, ClX, H<sub>2</sub>O, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O<sub>2</sub>, and N<sub>2</sub>O following the methods developed and described by *Liu and Donahue* [1974a, b, c, 1975a, 1976]. In the standard (i.e., 'unperturbed') atmosphere we have assumed a mixing ratio of 10<sup>-9</sup> ppb vol/vol of ClX. In reality there may be about 0.5 ppb odd chlorine due to natural sources in the middle and upper stratosphere as discussed by *Cicerone et al.* [1975]. Such a background ClX mixing ratio could result from natural CH<sub>3</sub>Cl, first detected by *Rasmussen* (private communication, 1974)

and *Lovelock* [1975]. In 1975, *Rasmussen* (private communication, 1975) measured 0.5 ppb CH<sub>3</sub>Cl in the troposphere, on average. Our standard model neglects this natural ClX background to emphasize the effects of added ClX. ClX perturbations are modeled by injecting Cl atoms between 25 and 35 km, as is approximately the case for photolysis of CF<sub>2</sub>Cl<sub>2</sub> and CFCI<sub>3</sub> [Molina and Rowland, 1974; Cicerone et al., 1974; Crutzen, 1974b; Rowland and Molina, 1975; Wofsy et al., 1975]. Steady injections of this kind lead to a characteristic ClX mixing ratio versus altitude [see, e.g., *Cicerone et al.*, 1974; *Wofsy et al.*, 1975]. The mixing ratio increases with altitude up to about 35 km, where a near-asymptotic value is attained; hereafter in this paper, 'ClX mixing ratio' means this high-altitude asymptote. (Recent measurements of HCl up to 30 km confirm this profile shape [Ackerman, 1976].)

The one-dimensional steady state continuity and diffusive flux equations are solved for the species mentioned above from 10 to 120 km. We use the now standard technique of treating O<sub>3</sub>, HO<sub>2</sub>, ClX, and NO<sub>x</sub> as single species and obtain individual species densities in each family from the photochemical equilibrium conditions. For upper boundary conditions we use the 'flux-to-density' relations described in detail by *Liu and Donahue* [1974a]. At the lower boundary (10 km) we fix the ratio of the flux to the density of O<sub>3</sub> at the value 0.06 cm s<sup>-1</sup>. A similar condition, with a ratio of 0.3 cm s<sup>-1</sup>, is imposed on H<sub>2</sub>O<sub>2</sub>, NO<sub>x</sub>, and ClX. Fixed mixing ratios are set for CH<sub>4</sub>, H<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>O at 10 km. In the standard atmosphere their values at 10 km are 1.5, 0.5, 3, and 0.25 ppm, respectively. Photochemical equilibrium is assumed in determining the HO<sub>2</sub> density at the lower boundary. We use the mid-latitude atmosphere (U.S. Standard Atmosphere Supplements, 1966) at equinoctial geometry in computing daily averaged rates of photolysis. The rates at 120 km are listed in Table 1.

The rate constants we used are tabulated in Table 2. We emphasize the importance of the value assumed for the rate constant *k*<sub>18</sub> for (R18),



by assuming in these calculations a 'high' value [*Hochanadel et al.*, 1972], 2 × 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>, and a 'low' value [*Kaufman*, 1975], 2 × 10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, and analyzing in detail the sensitivity of our results to variations of this rate constant. *Liu and Donahue* [1974c] have shown that *Anderson's* [1971] measurements of OH densities can be reconciled with this range of values for *k*<sub>18</sub> provided certain constraints are placed on a

TABLE 1. Daily Averaged Photodissociation Rates of Relevant Species at 120 km for Equinoctial Conditions at 30° Latitude

Reaction	Rate, s <sup>-1</sup>	Reference
O <sub>2</sub> + hν → O + O	1.26 × 10 <sup>-6</sup>	Hudson et al. [1969] Ditchburn and Young [1961] Metzger and Cook [1964]
O <sub>3</sub> + hν → O <sub>2</sub> + O( <sup>1</sup> D)	4.4 × 10 <sup>-8</sup>	Ackerman [1970] DeMore and Raper [1966]
O <sub>3</sub> + hν → O <sub>2</sub> + O( <sup>3</sup> P)	2.1 × 10 <sup>-4</sup>	Ackerman [1970]
H <sub>2</sub> O + hν → H + OH	5.0 × 10 <sup>-6</sup>	Thompson et al. [1963] Anderson [1971] Hampson et al. [1973b]
NO <sub>2</sub> + hν → NO + O	5 × 10 <sup>-8</sup>	Johnston and Graham [1973]
HNO <sub>3</sub> + hν → OH + NO <sub>2</sub>	8.6 × 10 <sup>-5</sup>	Schumb et al. [1955]
H <sub>2</sub> O <sub>2</sub> + hν → OH + OH	5.3 × 10 <sup>-8</sup>	Johnston and Selwyn [1975]
N <sub>2</sub> O + hν → N <sub>2</sub> + O	6.7 × 10 <sup>-7</sup>	Calvert et al. [1972]
H <sub>2</sub> CO + hν → H <sub>2</sub> + CO	6 × 10 <sup>-8</sup>	Calvert et al. [1972]
H <sub>2</sub> CO + hν → HCO + H	4.1 × 10 <sup>-8</sup>	Myer and Samson [1970]
HCl + hν → H + Cl	1.1 × 10 <sup>-6</sup>	Inn [1975] Schott and Davidson [1958]
NO <sub>3</sub> + hν → NO + O <sub>2</sub>	1 × 10 <sup>-2</sup>	

Solar flux data are taken from Ackerman [1970].

companion reaction destroying HO<sub>x</sub>, (R16) between H and HO<sub>2</sub>. The lower value of  $k_{18}$  usually calls for about 3 times as much HO<sub>x</sub> in the stratosphere for a given amount of water. There is, accordingly, less O<sub>3</sub> in models using the low value of

$k_{18}$ . The role of (R20), whose rate constant is also poorly known, is discussed by Donahue et al. [1976].

Below 10 km we have assumed the amount of ozone present to be  $0.54 \times 10^{18}$  cm<sup>-2</sup>, a quantity taken from the tables of

TABLE 2. Reactions and Rate Constants With References

Reaction	Rate Constant, cm <sup>3</sup> s <sup>-1</sup> , cm <sup>6</sup> s <sup>-1</sup>	Reference
R1 Cl + O <sub>3</sub> → ClO + O <sub>2</sub>	2.4 × 10 <sup>-11</sup> exp(-340/RT)	Zahniser et al. [1975]
R2 ClO + O → Cl + O <sub>2</sub>	1.2 × 10 <sup>-10</sup> exp(-250/T)	Bemand et al. [1973]
R3 ClO + NO → Cl + NO <sub>2</sub>	1.7 × 10 <sup>-11</sup>	Clyne and Watson [1974]
R4 Cl + CH <sub>4</sub> → HCl + CH <sub>3</sub>	5.4 × 10 <sup>-12</sup> exp(-1125/T)	Davis et al. [1975b]*
R5 HCl + OH → Cl + H <sub>2</sub> O	2 × 10 <sup>-12</sup> exp(-310/T)	Zahniser et al. [1974]
R6 HCl + O → Cl + OH	1.9 × 10 <sup>-11</sup> exp(-3600/T)	Wong and Belles [1971]
R7 Cl + HO <sub>2</sub> → HCl + O <sub>2</sub>	2 × 10 <sup>-11</sup>	estimated
R7a Cl + H <sub>2</sub> O <sub>2</sub> → HCl + HO <sub>2</sub>	6 × 10 <sup>-18</sup>	Davis et al. [1975a]
R8 H <sub>2</sub> + Cl → HCl + H	8 × 10 <sup>-11</sup> exp(-2650/T)	Benson et al. [1969]
R9 H + HCl → Cl + H <sub>2</sub>	1 × 10 <sup>-11</sup> exp(-1600/T)	Benson et al. [1969]
R10 H <sub>2</sub> O + O( <sup>1</sup> D) → 2OH	3.5 × 10 <sup>-10</sup>	Garvin and Hampson [1974]
R11 CH <sub>4</sub> + O( <sup>1</sup> D) → OH + CH <sub>3</sub>	4 × 10 <sup>-10</sup>	Garvin and Hampson [1974]*
R12 CH <sub>4</sub> + OH → H <sub>2</sub> O + CH <sub>3</sub>	2.95 × 10 <sup>-12</sup> exp(-1770/T)	Davis [1973]*
R13 H <sub>2</sub> + O( <sup>1</sup> D) → OH + H	2.9 × 10 <sup>-10</sup>	Garvin and Hampson [1974]
R13a H <sub>2</sub> + O → OH + H	3 × 10 <sup>-14</sup> T exp(-4480/T)	Baulch et al. [1973]
R14 H + O <sub>2</sub> → OH + O	2.6 × 10 <sup>-11</sup>	Hampson et al. [1973a]
R15 H + O <sub>3</sub> + M → HO <sub>2</sub> + M	6 × 10 <sup>-38</sup> exp(290/T)	Garvin and Hampson [1974]
R16a H + HO <sub>2</sub> → H <sub>2</sub> + O <sub>2</sub>	4.2 × 10 <sup>-11</sup> exp(-350/T)	Garvin and Hampson [1974]
R16b H + HO <sub>2</sub> → H <sub>2</sub> O + O	8.3 × 10 <sup>-11</sup> exp(-500/T)	Lloyd [1973]
R17 OH + O → H + O <sub>2</sub>	4 × 10 <sup>-11</sup>	Wilson [1973]
R18 OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	see text	
R19 OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	1.3 × 10 <sup>-12</sup> exp(-950/T)	Anderson and Kaufman [1973]
R20 HO <sub>2</sub> + O → OH + O <sub>2</sub>	8 × 10 <sup>-11</sup> exp(-500/T)	Lloyd [1973]
R21 HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	1 × 10 <sup>-18</sup> exp(-1250/T)	Garvin and Hampson [1974]
R22 HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	3 × 10 <sup>-11</sup> exp(-500/T)	Hampson et al. [1973a]
R23 H <sub>2</sub> O <sub>2</sub> + OH → HO <sub>2</sub> + H <sub>2</sub> O	1.7 × 10 <sup>-11</sup> exp(-910/T)	Hampson et al. [1973a]
R24 HO <sub>2</sub> + NO → OH + NO <sub>2</sub>	1.1 × 10 <sup>-11</sup> exp(-1000/T)	Davis et al. [1973]
R25 N <sub>2</sub> O + O( <sup>1</sup> D) → 2NO	1.1 × 10 <sup>-10</sup>	Garvin and Hampson [1974]
R25a N <sub>2</sub> O + O( <sup>1</sup> D) → N <sub>2</sub> + O <sub>2</sub>	1.1 × 10 <sup>-10</sup>	Garvin and Hampson [1974]
R26 NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	9 × 10 <sup>-18</sup> exp(-1200/T)	Hampson et al. [1973a]
R27 NO + O + M → NO <sub>2</sub> + M	7 × 10 <sup>-32</sup>	Becker et al. [1973]
R28 NO <sub>2</sub> + O → NO + O <sub>2</sub>	1.7 × 10 <sup>-11</sup> exp(-300/T)	Baulch et al. [1973]
R29 NO <sub>2</sub> + OH + M → HNO <sub>3</sub> + M	1 × 10 <sup>-11</sup> / (3.5 × 10 <sup>12</sup> T <sup>2.5</sup> + 2.5 [M])	Anderson et al. [1974]†
R30 HNO <sub>3</sub> + OH → H <sub>2</sub> O + NO <sub>2</sub>	0.89 × 10 <sup>-18</sup>	Margitan et al. [1975]
R31 NO <sub>3</sub> + NO → 2NO <sub>2</sub>	8.7 × 10 <sup>-12</sup>	Harker and Johnston [1973]
R32 NO <sub>2</sub> + O <sub>3</sub> → NO <sub>3</sub> + O <sub>2</sub>	1.1 × 10 <sup>-18</sup> exp(-2450/T)	Garvin and Hampson [1974]
R33 NO <sub>2</sub> + O + M → NO <sub>3</sub> + M	1 × 10 <sup>-31</sup>	Hampson et al. [1973b]
R34 O + O <sub>2</sub> + M → O <sub>3</sub> + M	10.0 × 10 <sup>-36</sup> exp(510/T)	Garvin and Hampson [1974]
R35 O + O <sub>3</sub> → 2O <sub>2</sub>	1.9 × 10 <sup>-11</sup> exp(-2300/T)	Hampson et al. [1973a]
R36 O + O + M → O <sub>2</sub> + M	2.76 × 10 <sup>-34</sup> exp(710/T)	Campbell and Thrush [1967]

\*Methane oxidation chain of Chameides and Walker [1973] is adopted.

† Best fit to the results of Anderson et al. [1974] and Tsang [1973].

Hering and Borden [1967] as appropriate to the equinoxes. This quantity is added to the integrated amounts obtained above 10 km in calculating the total column ozone abundance for all of our models.

#### RESULTS: STANDARD AND CIX-PERTURBED ATMOSPHERE

In Figure 1 we show some of the profiles of species obtained from our calculations for standard conditions and, where appropriate, for high and low values of  $k_{18}$ . Figure 2 shows standard ozone profiles for both values of  $k_{18}$ . Also shown in Figure 2 is the effect of adding 8 ppb CIX on the ozone densities. The preferential removal of ozone at high altitude is obvious. As a result of this perturbation, the altitude of the ozone maximum is decreased, leading to an increase in the solar and infrared heating rates below the ozone maximum [Ramanathan *et al.*, 1976]. For example, when  $k_{18}$  is high and 15 ppb of CIX is present, the ozone maximum is lowered from 24 to 22 km, and the solar heating rate at 10, 15, and 20 km is 13%, 16%, and 19% larger, respectively. Ramanathan *et al.* [1976] have indicated that this kind of change in the ozone distribution might increase the temperature at the tropopause by several degrees. The saturation vapor pressure doubles for a 4°K rise in tropopause temperature and increases by an order of magnitude for a 15°K rise. Thus in the presence of CIX the water vapor concentration at the tropopause would increase [Stanford, 1973]. In the  $\text{NO}_x$ -perturbed stratosphere, however, the ozone density profile is affected more uniformly [McElroy *et al.*, 1974] and thus could lead to a decrease of water vapor concentration at the tropopause [Ramanathan *et al.*, 1976].

To assess the effect of changing the amount of water vapor in the stratosphere on the ozone distribution, we have repeated the steady state calculations for water vapor mixing ratios at 10 km ranging from  $10^{-2}$  to 30 ppm. When the water vapor mixing ratio at the tropopause is lower than about 1 ppm, the water vapor present in the stratosphere will be produced mostly from methane because oxidation of methane is an important source of water vapor above the tropopause [Hunten and Strobel, 1974; Liu and Donahue, 1974a]. We show in Figure 3 the mixing ratio of hydrogen in the forms of  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$  as a function of altitude for assumed mixing ratios of 0.5 ppb of  $\text{H}_2$ , 1.5 ppm of  $\text{CH}_4$  at 10 km, and 3 ppm of  $\text{H}_2\text{O}$  in one case and  $10^{-2}$  ppm of  $\text{H}_2\text{O}$  in the other. Plotted is the total hydrogen mixing ratio for each species, i.e., twice the  $\text{H}_2$  and  $\text{H}_2\text{O}$  mixing ratios and 4 times the  $\text{CH}_4$  mixing ratio. The total mixing ratio ( $2[\text{H}_2\text{O}] + 2[\text{H}_2] + 4[\text{CH}_4]$ ) must be almost constant with altitude, or a very large flux compared to the escape flux of hydrogen would result [Hunten, 1973]. When there is almost no water at 10 km, the 2.8 ppm of  $\text{H}_2\text{O}$  near 50

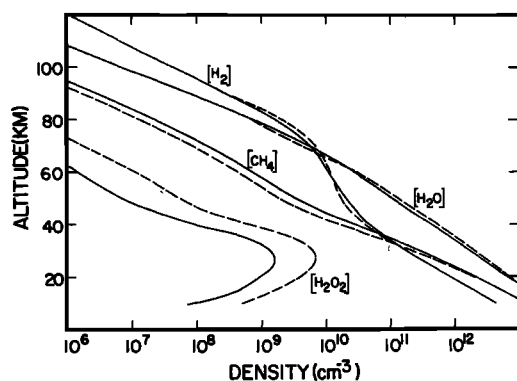


Fig. 1. Profiles of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}_2$  for high  $k_{18}$  (solid line) and low  $k_{18}$  (dashed line).

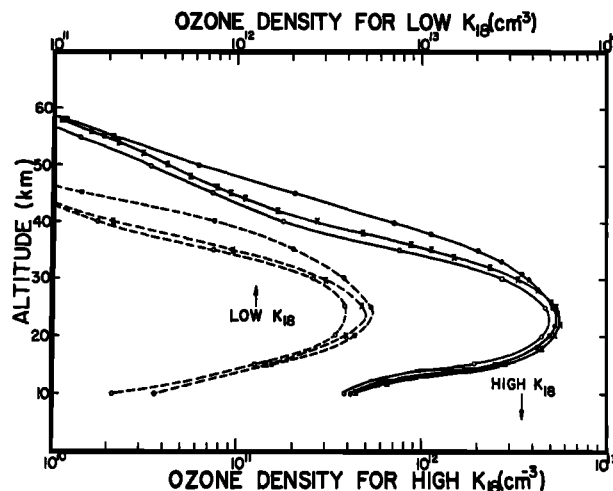
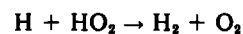


Fig. 2. Ozone profiles for high  $k_{18}$  (solid line) and low  $k_{18}$  (dashed line) for the standard equinoctial atmosphere at mid-latitudes (solid circles), for this atmosphere with 8 ppb of CIX (crosses), and with  $\text{H}_2\text{O}$  at the tropopause increased by a factor of 10 (open circles).

km is essentially all produced from  $\text{CH}_4$ . Above 40 km,  $\text{H}_2$  begins to be created as a result of the reaction (R16),



In the case of 3 ppm  $\text{H}_2\text{O}$  at 10 km the  $\text{H}_2$  mixing ratio will grow from 0.5 ppm at 10 km to more than 4 ppm at 90 km as a result of conversion of  $\text{H}_2\text{O}$  and  $\text{CH}_4$ . But with virtually no  $\text{H}_2\text{O}$  at 10 km the  $\text{H}_2$  mixing ratio reaches only a little more than 3 ppm, since the increase comes only from the conversion of methane to  $\text{H}_2\text{O}$  and the subsequent production of odd hydrogen from  $\text{H}_2\text{O}$ .

Figure 2 also shows the effect of increasing the  $\text{H}_2\text{O}$  mixing ratio to 30 ppm on the ozone distribution already modified by the presence of 8 ppb CIX. (We plot profiles for large increases in CIX and  $\text{H}_2\text{O}$  for the sake of obtaining a clear separation of the curves.) Figures 4 and 5 show the percentage reduction in  $\text{O}_3$  column abundances as CIX is added to the atmosphere and the  $\text{H}_2\text{O}$  mixing ratio at 10 km is varied. Again, results are shown for two choices of  $k_{18}$ .

Before discussing the effects of varying the water vapor source, we call attention to rate constants for the reaction (R1),

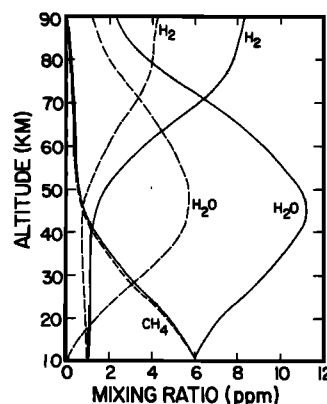
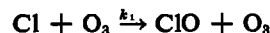


Fig. 3. Mixing ratios of  $2\text{H}_2\text{O}$ ,  $2\text{H}_2$ , and  $4\text{CH}_4$  as functions of altitude for two atmosphere models with different water vapor mixing ratios at the tropopause. In the standard model (solid line) the mixing ratios at the tropopause are 6, 6, and 1 ppm for  $2\text{H}_2\text{O}$ ,  $4\text{CH}_4$ , and  $2\text{H}_2$ , respectively. In the other model (dashed line) the corresponding mixing ratios are  $2 \times 10^{-3}$ , 6, and 1 ppm.

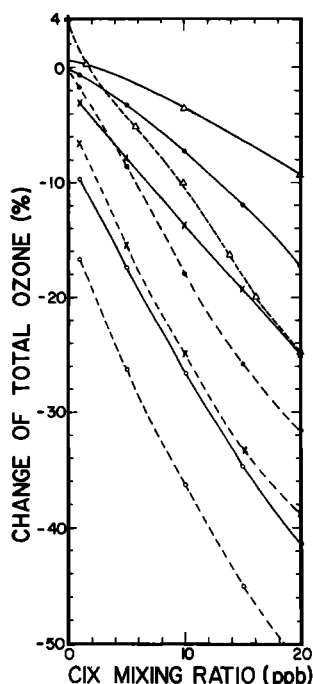
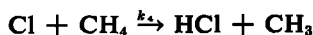


Fig. 4. Changes in  $O_3$  column abundance as CIX mixing ratio increases. Results are shown for four mixing ratios of  $H_2O$  at the tropopause, 0.01 ppm (open triangles), 3 ppm (solid circles), 9 ppm (crosses), and 30 ppm (open circles), and for high  $k_{18}$  (solid line) and low  $k_{18}$  (dashed line).

newly measured by *Davis et al.* [1975a] and *Zahniser et al.* [1975], i.e.,  $2.4 \times 10^{-11} \exp(-340/RT)$ , and for the reaction (R4),



where  $k_4$  is  $5.4 \times 10^{-12} \exp(-1125/T)$  according to *Davis et al.* [1975b]. In early (pre-1975) studies of stratospheric ClX,  $k_1$  was taken to be  $4.3 \times 10^{-11} \exp(-250/T)$  [see, e.g., *Stolarski and Cicerone*, 1974] based on Clyne and Watson's room temperature rate of  $1.85 \times 10^{-11}$  [*Watson*, 1974]. Also,  $k_4$  was taken to be  $8.8 \times 10^{-11} \exp(-1900/T)$  in the early studies, based on *Davis et al.* [1970]. The use of the new rates  $k_1$  and  $k_4$  in our model has significantly reduced the effect of a given amount of ClX on  $O_3$  compared to that in previous models. In

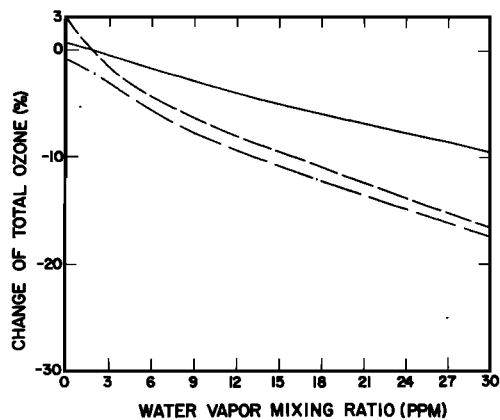


Fig. 5. Changes in  $O_3$  column abundance as the  $H_2O$  mixing ratio at the tropopause is changed. Results are as shown for high  $k_{18}$  with 1 ppb of ClX (solid line), low  $k_{18}$  with 1 ppb of ClX (dashed line), high  $k_{18}$  with 5 ppb of ClX (dash-dotted line), and low  $k_{18}$  with 5 ppb of ClX (dotted line).

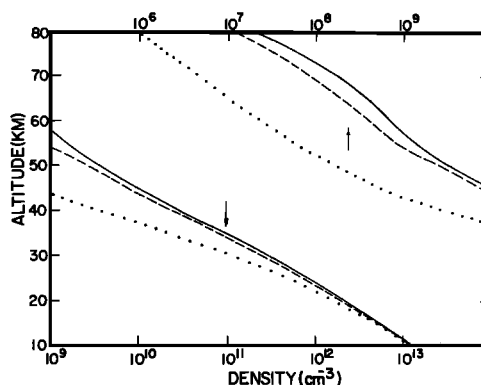


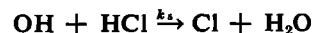
Fig. 6. Density distribution of methane for the standard atmosphere with high  $k_{18}$  (solid line) and low  $k_{18}$  (dashed line) and for atmosphere containing 8 ppb of ClX and low  $k_{18}$  (dotted line).

this result we agree with *Crutzen* as quoted by *Hammond* [1975] and with *Wofsy and McElroy* [1975].

Our results for the new rates  $k_1$  and  $k_4$ , compared to those for the old  $k_1$  and  $k_4$ , are that 1 ppb of ClX reduces the total amount of  $O_3$  by 0.6% compared to 2.2%, 3 ppb of ClX reduces  $O_3$  by 1.9% compared to 6.4%, and 5 ppb of ClX reduces  $O_3$  by 3.6% compared to 10.4%. These comparisons are made for the larger value of  $k_{18}$ . In case the smaller value is more nearly correct the reduction in the integrated  $O_3$  abundance for a given combination of ClX and water vapor concentrations could be much greater, as can be seen in Figures 2, 4, and 5. Thus unless the amount of water vapor in the stratosphere were to change significantly from its present value, the time scale for a specified amount of ozone destruction by ClX could be appreciably greater than first calculated [*Cicerone et al.*, 1974; *Crutzen*, 1974a; *Wofsy et al.*, 1975]. Even this conclusion is dangerous, however, based as it is on the assumed high value of  $k_{18}$ . *Donahue et al.* [1976] discuss this further. The 10% ozone destruction level is reached with less than 6 ppb of ClX if the low value of  $k_{18}$  is correct.

Figures 4 and 5 also demonstrate the principal points that we wish to make in this paper. The effects produced by changing  $H_2O$  are significant. In particular, when the ClX pollution level is 1 ppb, the percentage ozone reduction goes from 0.6% to 2.9% if the amount of  $H_2O$  is tripled (9 ppm at 10 km) and to 9.7% if it is increased by a factor of 10 (for the high value of  $k_{18}$ ). Again for the low value of  $k_{18}$  a much more dramatic effect occurs, i.e., a 6.8% reduction for 1 ppb of ClX and 3 times normal  $H_2O$  and a 16.6% reduction for 10 times normal  $H_2O$ . Of course if the stratosphere were to dry out for some reason, the changes would occur in the opposite sense.

The reason that water vapor has such a great influence is that it is converted by reaction with  $O(^1D)$  into odd hydrogen in the stratosphere. All forms of odd hydrogen destroy ozone catalytically in their own right, but in addition to this direct effect there is a special indirect effect on ozone destruction. The HCl produced by reactions of Cl with  $CH_4$  in reaction (R4) is attached by OH (R5),



thus reinitiating the ClX catalytic chain. Figures 7, 8, 10, and 11 quantitatively demonstrate the nature of the effects just described. Figure 6 shows the methane distribution as a function of altitude for the standard atmosphere with high and low values of  $k_{18}$ , where the influence of the enhanced destruction of  $CH_4$  by OH when  $k_{18}$  is low is apparent. Much

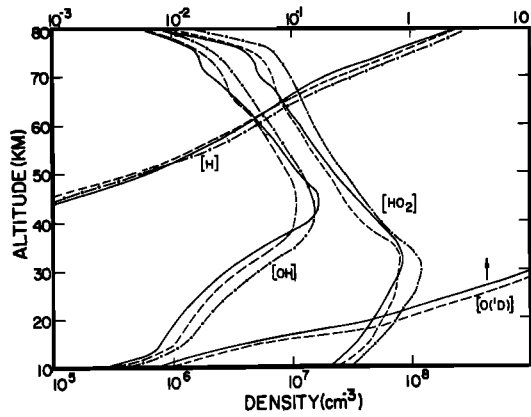


Fig. 7. Profiles of odd hydrogens and O(<sup>1</sup>D) for the standard atmosphere (solid line), with 8 ppb of ClX added and normal H<sub>2</sub>O (dashed line) and with 8 ppb of ClX and 3 times H<sub>2</sub>O at the tropopause (dash-dotted line). Low value of  $k_{18}$  is used here.

more striking, however, is the rapid destruction of methane by Cl in the formation of HCl through reaction (R4) when 8 ppb of ClX is present. At 45 km the methane density has been cut by an order of magnitude compared to the normal value as a result of the presence of ClX. Tropospheric CH<sub>4</sub> is also affected by ClX-induced O<sub>3</sub> losses in the stratosphere, feeding back on the stratosphere [Chameides et al., 1976].

In Figure 7 the densities of HO<sub>x</sub> are plotted for the low value of  $k_{18}$  in three cases: (1) the standard atmosphere, (2) with 8 ppb of ClX and normal H<sub>2</sub>O, and (3) with 8 ppb of ClX and 3 times the normal H<sub>2</sub>O. It is interesting that the presence of ClX increases the amount of HO<sub>x</sub> considerably below the ozone maximum and decreases it above. The reason is to be found in the preferential destruction of O<sub>3</sub> above the maximum by ClX released from chlorocarbons. This decrease in optical depth enhances O(<sup>1</sup>D) production from O<sub>3</sub> at low altitudes, as is demonstrated by the curves showing the O(<sup>1</sup>D) densities. Since O(<sup>1</sup>D) interacting with H<sub>2</sub>O and CH<sub>4</sub> is an important source of HO<sub>x</sub>, the result is an increase in HO<sub>x</sub> at low altitudes. Conversely, above 40 km, where the atmosphere is optically thin for production of O(<sup>1</sup>D), the O(<sup>1</sup>D) density is lower because the O<sub>3</sub> density is lower. Thus the HO<sub>x</sub> density in the presence of ClX is reduced at higher altitudes. Figure 8 shows the ClX species as they are affected by the addition of water to the stratosphere: the conversion of HCl to Cl by OH can be easily

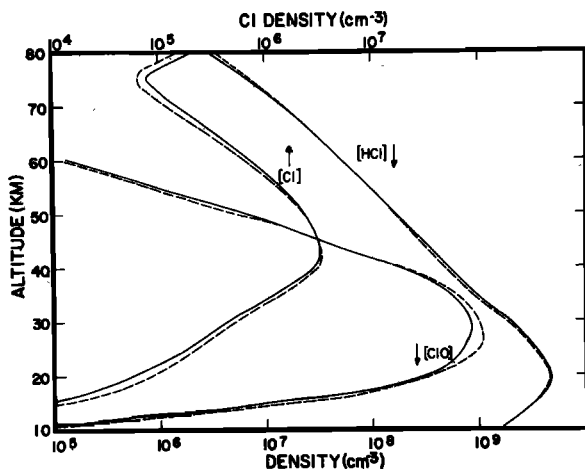


Fig. 8. Profiles of Cl, ClO, and HCl for atmosphere with 8 ppb of ClX and normal H<sub>2</sub>O (solid line) and for atmosphere with 8 ppb of ClX and 3 times H<sub>2</sub>O (dashed line). Low value of  $k_{18}$  is used here.

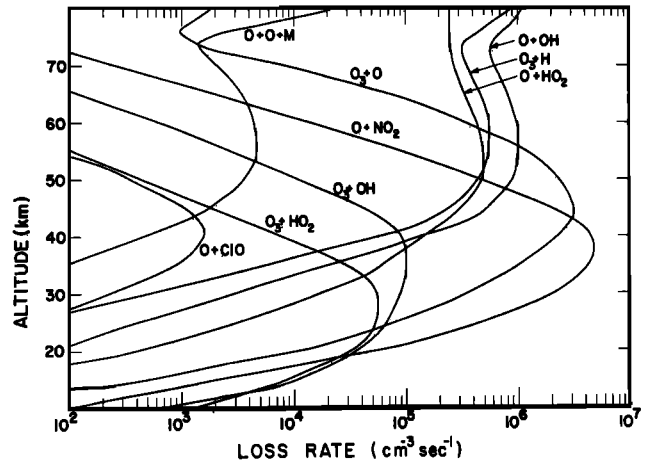


Fig. 9. Sinks of O<sub>3</sub> for the standard atmosphere with high  $k_{18}$ .

detected below 40 km. Above 50 km, because the H<sub>2</sub>O<sub>2</sub> density increases by a larger factor than does the OH density for a given increase in water vapor concentration, Cl is preferentially converted to HCl by the reaction of H<sub>2</sub>O<sub>2</sub> with Cl.

In Figures 9 and 10 we show the major sinks of O<sub>3</sub> for the standard atmosphere with high and low values of  $k_{18}$ , respectively. These figures show that the odd hydrogen reactions dominate the loss of O<sub>3</sub> above 55 and below 20 km. The Chapman reaction (R35) between O<sub>3</sub> and O dominates only in a narrow range near 50 km, and the NO<sub>x</sub> catalytic cycle is in control from 20 to about 40 km, where the ozone density is largest. The effect of increasing the odd hydrogen density by reducing  $k_{18}$  is apparent in a comparison of Figures 9 and 10, particularly in the region where the Chapman reaction prevails. This region stretches from 43 to 56 km when  $k_{18}$  is large but only from 43 to 47 km when  $k_{18}$  is small. Figure 11 in turn, when compared with Figure 10, shows the changes in the dominant sinks of O<sub>3</sub> when 8 ppb of ClX is added. The ClO+O reaction rate in the ClX cycle at 40 km jumps from  $3 \times 10^8$  cm<sup>-3</sup> s<sup>-1</sup> to more than  $8 \times 10^8$  cm<sup>-3</sup> s<sup>-1</sup>. The NO<sub>2</sub> + O rate is reduced when ClX becomes dominant because of the decreased amount of O<sub>3</sub> leading to less NO<sub>2</sub> and less O. While the HO<sub>2</sub> + O<sub>3</sub> reaction rate is not shown in Figure 11, its dependence upon the addition of ClX and water vapor is similar to that of OH + O<sub>3</sub>.

Note that for low  $k_{18}$  there is a significant amount of H<sub>2</sub>O<sub>2</sub> near 25 km as a result of the large concentrations of HO<sub>2</sub>

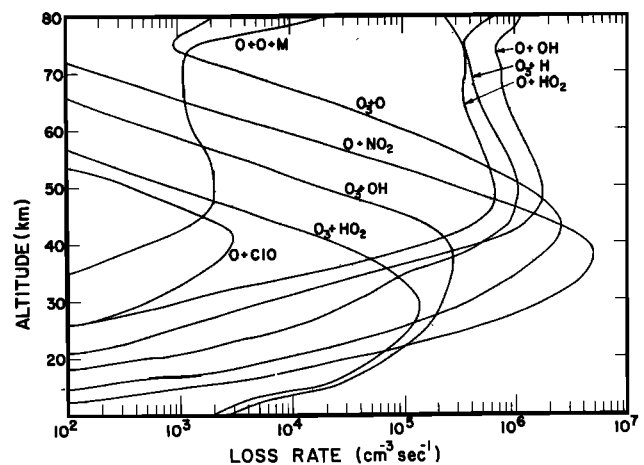


Fig. 10. Same as Figure 9 but with low  $k_{18}$ .

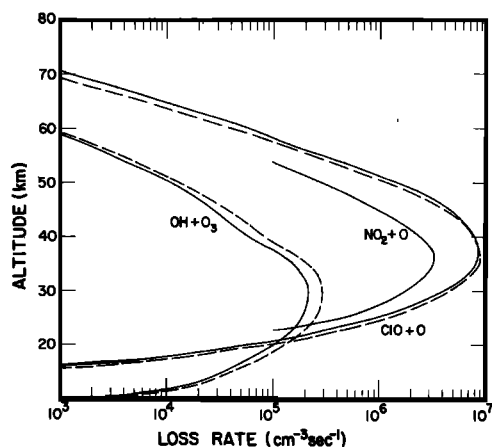
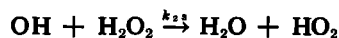
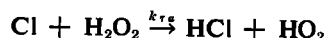


Fig. 11. Three important sinks of  $O_3$  for atmosphere with 8 ppb of ClX and normal  $H_2O$  (solid line) and for atmosphere with 8 ppb of ClX and 3 times  $H_2O$  (dashed line). Low value of  $k_{18}$  is used here.

(Figure 1). The reaction (R23)



then becomes an important sink of  $HO_x$  and results in about 10% more ozone in the standard atmosphere than would be the case if  $k_{23}$  were not included. Even the reaction (R7a)



must be taken into account when  $k_{18}$  is small despite the relatively small rate constant recently obtained by Davis *et al.* [1975a]. Without the inclusion of this reaction in the chemical scheme the destruction of ozone would be overestimated by a factor of 1.3 when 1 ppb of ClX is present and by an increasingly greater factor as the amount of ClX increases.

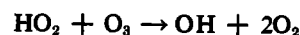
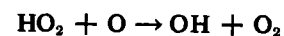
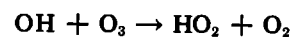
#### EFFECT OF $H_2O$ ON $NO_x$ -PERTURBED STRATOSPHERE

We have also considered the effects of  $NO_x$  and  $H_2O$  produced by the 'standard' SST models, at 20 km [Grobeck, 1974]. In Figure 12 we show our results for the globally averaged reduction in  $O_3$  resulting from 100 SST's emitting  $9 \times 10^6$   $NO$   $cm^{-2} s^{-1}$  between 19 and 21 km. If the stratosphere contains 3 ppm of water vapor, the reduction is 1.22% for the high value of  $k_{18}$  and 0.66% for the low value. This means 1.83% and 1% reduction of  $O_3$  in the hemisphere in which the  $NO_x$  is dominantly emitted, a result that agrees well with previous calculations (summarized in the publication by the *National Academy of Sciences* [1975]). Note, however, that adding water vapor to the stratosphere causes an enhancement in  $O_3$  reduction, no matter how little is added, whether  $k_{18}$  is small or large. With normal or almost normal amounts of  $H_2O$  in the stratosphere the reduction in  $O_3$  for a specified artificial source of  $NO_x$  turns out to be greater when  $k_{18}$  is large and the density of  $HO_x$  is small because of the less effective formation of  $HNO_3$  from OH and  $NO_2$ . However, when  $k_{18}$  is small, the amount of  $HO_x$  required to stay in balance with  $H_2O$  increases much more rapidly with the  $H_2O$  mixing ratio than when  $k_{18}$  is large. For a small increase in the  $H_2O$  concentration the removal of  $O_3$  by  $HO_x$  becomes more important than the removal by the NO emitted from 100 SST's. This dominance by the  $HO_x$  catalytic cycle causes the effect of added  $H_2O$  to be much more pronounced for the small value of  $k_{18}$  than the large. The same effect is noticeable in Figure 5 for ClX catalysis.

The decrease in ozone density caused by an increase in the

water vapor content of the stratosphere in our model occurs predominantly below about 22 km and above about 45 km.  $HO_x$  destruction of  $O_3$  dominates  $NO_x$  destruction below 24 km and begins to compete seriously again above 40 km. It is the effect of  $HO_x$  below 22 km that causes us to find that increasing the  $H_2O$  mixing ratio even by very small amounts causes the ozone column content to decrease, whereas others [McElroy *et al.*, 1974; Crutzen, 1974b] found the opposite. McElroy *et al.* located their lower boundary at 28 km and multiplied the  $O_3$  profile below that level by the change calculated at 28 km [Wofsy, 1974]. This exercise cannot duplicate the large effect of  $HO_x$  on  $O_3$  that we find below 24 km. Our disagreement with Crutzen [1974b] may be due to different reaction rate constants. We note that Rao-Vupputuri [1974] also finds that increased  $H_2O$  leads to decreased  $O_3$ .

In a sense, our result is disturbing because it suggests that the ozone layer is necessarily unstable against runaway destruction from perturbations (even natural ones that may have occurred in the past) allowing water into the stratosphere. Such a conclusion is not warranted, however, for the nature of the perturbation, the exact nature and location of the change in ozone density, the changes in temperature accompanying the perturbation, and the temperature dependences of all important rate constants must all be considered. Thus a perturbation like the one we describe here resulting from chlorocarbons, which removes the top of the layer of  $O_3$  and causes the temperature to rise below 25 km and fall above 25 km, will cause  $HO_x$  to have different effects at high and low altitudes. The rate constants for the steps in the ozone-destroying reactions,



increase with increasing temperature, while the rate constant for the reaction between  $HO_x$  and  $NO_x$  that produces the sink for  $NO_x$ ,



decreases with increasing temperature. Thus as the temperature increases at low altitude, the destruction of ozone from  $HO_x$  and from  $NO_x$  tends to be augmented, but the opposite is true at high altitude. As a consequence, the ozone will tend to recover and the opacity to grow at high altitude, leading to a decrease in temperature below. Effects such as these certainly must be taken into account in a complete time-dependent theory of the phenomena we are describing in this note.

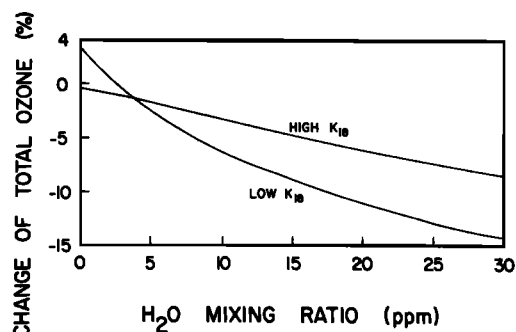


Fig. 12. Changes in  $O_3$  column abundance in the atmosphere with 100 SST's when the  $H_2O$  mixing ratio at the tropopause is changed.

## CONCLUSION

This paper draws attention to the very large influence of water vapor in the stratosphere on the catalytic destruction of ozone, particularly by odd chlorine originating from photolysis of chlorocarbon. A change in water vapor concentration, either an increase or a decrease, could conceivably result from changes in the environment affecting the so-called cold trap for water vapor, the production of methane, or both. The destruction of ozone by pollutants is particularly sensitive to the amount of H<sub>2</sub>O present in the stratosphere in the case of odd chlorine produced by photolysis of chlorocarbon because of the reconversion of HCl to Cl by OH. The effects considered depend strongly on the value of the rate constant for the reaction of OH with HO<sub>2</sub> producing water vapor, because it determines the amount of odd hydrogen in equilibrium with a given amount of water vapor.

**Acknowledgments.** This work has greatly benefited from discussion with J. G. Anderson and W. R. Kuhn. The research was supported in part by the Atmospheric Sciences Section, National Science Foundation (NSF) grants DES 74-21598 and DES 74-11478 and by NASA grant NSG-7187. We also acknowledge the National Center for Atmospheric Research (sponsored by NSF) for computer time.

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(Received October 14, 1975;  
revised February 10, 1976;  
accepted February 10, 1976.)