Effect of water vapor on the destruction of ozone in the stratosphere perturbed by ClX or NO(x) pollutants

Permalink
https://escholarship.org/uc/item/6md6t850

Journal
Journal of Geophysical Research, 81(18)

ISSN
0148-0227

Authors
Liu, SC
Donahue, TM
Cicerone, RJ
et al.

Publication Date
1976

DOI
10.1029/JC081i018p03111

License
CC BY 4.0

Peer reviewed
Effect of Water Vapor on the Destruction of Ozone in the Stratosphere Perturbed by CIX or NO\textsubscript{x} Pollutants

S. C. Liu, T. M. Donahue, R. J. Cicerone, and W. L. Chameides

Department of Atmospheric and Oceanic Science, Space Physics Research Laboratory, University of Michigan, Ann Arbor, Michigan 48109

We describe results of a self-consistent one-dimensional coupled flow calculation for O\textsubscript{3}, NO\textsubscript{x}, HO\textsubscript{x}, CIX, H\textsubscript{2}O, H\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O\textsubscript{2}, and N\textsubscript{2}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 CIX, NO\textsubscript{x}, and H\textsubscript{2}O independently in our model. We show that the effect of depletion of ozone by CIX 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\textsubscript{3} by CIX and also causes an increase in the rate of destruction of O\textsubscript{3} in the NO\textsubscript{x}-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 CIX (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 CIX or NO\textsubscript{x} (NO + NO\textsubscript{2} + HNO\textsubscript{3}) 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 \textit{Hunten}'s [1975] eddy diffusion coefficient. Originally, we were motivated to perform this exercise by realizing that in the presence of CIX from chlorocarbons, ozone is preferentially destroyed at high altitudes and the altitude of the peak O\textsubscript{3} concentration tends to be lowered. Thus the heating rate near the tropopause due to absorption by O\textsubscript{3} 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 [\textit{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\textsubscript{x} pollutants might decrease water vapor in the stratosphere. Since HO\textsubscript{x} (H + OH + HO\textsubscript{2}) plays such an important role in O\textsubscript{3} 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 CIX pollution because not only does HO\textsubscript{x} destroy O\textsubscript{3} catalytically in its own right but OH attacks HCl to release Cl and thus reinitiates the CIX catalytic chain reaction.

CALCULATION METHOD AND BOUNDARY CONDITIONS

In our calculation we have self-consistently treated O\textsubscript{3} (O + O), HO\textsubscript{x}, NO\textsubscript{x}, CIX, H\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}, H\textsubscript{2}O, and N\textsubscript{2}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\textsuperscript{-8} ppb vol/vol of CIX. 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 CIX mixing ratio could result from natural CH\textsubscript{3}Cl, first detected by Rasmussen (private communication, 1974) and Lovelock [1975]. In 1975, Rasmussen (private communication, 1975) measured 0.5 ppb CH\textsubscript{3}Cl in the troposphere, on average. Our standard model neglects this natural CIX background to emphasize the effects of added CIX. CIX perturbations are modeled by injecting Cl atoms between 25 and 35 km, as is approximately the case for photolysis of CF\textsubscript{2}Cl\textsubscript{2} and CFC\textsubscript{18} [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 CIX 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, 'CIX mixing ratio' means this high-altitude asymptote. (Recent measurements of HCl up to 30 km confirm this profile shape [\textit{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\textsubscript{3}, HO\textsubscript{x}, CIX, and NO\textsubscript{x} 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\textsubscript{3} at the value 0.06 cm\textsuperscript{-1}. A similar condition, with a ratio of 0.3 cm\textsuperscript{-1}, is imposed on H\textsubscript{2}O\textsubscript{2}, NO\textsubscript{x}, and CIX. Fixed mixing ratios are set for CH\textsubscript{4}, H\textsubscript{2}, H\textsubscript{2}O, and N\textsubscript{2}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\textsubscript{x} density at the lower boundary. We use the mid-latitude atmosphere (U.S. Standard Atmosphere Supplements, 1966) at equinocial 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 \(k_{18}\) for (R18),

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

by assuming in these calculations a 'high' value [Hochanadel et al., 1972], \(2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}\), and a 'low' value [Kaufman, 1975], \(2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}\), and analyzing in detail the sensitivity of our results to variations of this rate constant. Liu and Donahue [1974a] have shown that Anderson's [1971] measurements of OH densities can be reconciled with this range of values for \(k_{18}\) 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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate, s⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂ + hv → O + O</td>
<td>1.26 × 10⁻⁴</td>
<td>Hudson et al. [1969]</td>
</tr>
<tr>
<td>O₂ + hv → O₂ + O(D)</td>
<td>4.4 × 10⁻²</td>
<td>Ackerman [1970]</td>
</tr>
<tr>
<td>O₃ + hv → O₂ + O₂</td>
<td>2.1 × 10⁻⁷</td>
<td>Ackerman [1970]</td>
</tr>
<tr>
<td>H₂O + hv → H + OH</td>
<td>5.0 × 10⁻⁸</td>
<td>Thompson et al. [1963]</td>
</tr>
<tr>
<td>NO₂ + hv → NO + O₂</td>
<td>5 × 10⁻⁸</td>
<td>champagne et al. [1976]</td>
</tr>
<tr>
<td>HNO₃ + hv → OH + NO₂</td>
<td>8.6 × 10⁻⁸</td>
<td>Johnston and Graham [1973]</td>
</tr>
<tr>
<td>H₂O₂ + hv → OH + OH</td>
<td>5.3 × 10⁻⁸</td>
<td>Schumb et al. [1955]</td>
</tr>
<tr>
<td>N₂O + hv → N₂ + O</td>
<td>6.7 × 10⁻⁷</td>
<td>Johnston and Selwyn [1975]</td>
</tr>
<tr>
<td>H₂CO + hv → H₂ + CO</td>
<td>6.0 × 10⁻⁴</td>
<td>Calvert et al. [1972]</td>
</tr>
<tr>
<td>H₂CO + hv → HCO + H</td>
<td>4.1 × 10⁻⁸</td>
<td>Calvert et al. [1972]</td>
</tr>
<tr>
<td>HCl + hv → H + Cl</td>
<td>1.1 × 10⁻⁶</td>
<td>Myer and Samson [1970]</td>
</tr>
<tr>
<td>NO₂ + hv → NO + O₂</td>
<td>1 × 10⁻⁴</td>
<td>Schott and Davidson [1958]</td>
</tr>
</tbody>
</table>

Solar flux data are taken from Ackerman [1970].

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 × 10⁻² cm⁻², a quantity taken from the tables of

TABLE 2. Reactions and Rate Constants With References

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant, cm⁻³ s⁻¹</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CI + O₂ → ClO + O₂</td>
<td>2.4 × 10⁻¹² exp (−340/RT)</td>
<td>Zahniser et al. [1975]</td>
</tr>
<tr>
<td>ClO + CI → Cl + O₂</td>
<td>1.2 × 10⁻¹⁰ exp (−250/RT)</td>
<td>Bemandet al. [1973]</td>
</tr>
<tr>
<td>ClO + NO → Cl + NO₂</td>
<td>1.7 × 10⁻⁸</td>
<td>Cline and Watson [1974]</td>
</tr>
<tr>
<td>CI + CH₂ → Cl + CH₃</td>
<td>5.4 × 10⁻¹⁰ exp (−1125/RT)</td>
<td>Davis et al. [1975b]</td>
</tr>
<tr>
<td>HCl + OH → Cl + H₂O</td>
<td>2.0 × 10⁻⁸ exp (−310/RT)</td>
<td>Zahniser et al. [1974]</td>
</tr>
<tr>
<td>HCl + O → Cl + OH</td>
<td>2.0 × 10⁻⁸</td>
<td>Wong and Beller [1971]</td>
</tr>
<tr>
<td>HCl + H₂O → Cl + H₂O</td>
<td>6.0 × 10⁻⁸</td>
<td>Davis et al. [1975a]</td>
</tr>
<tr>
<td>H₂ + Cl → Cl₂ + H</td>
<td>8.0 × 10⁻⁸ exp (−2650/RT)</td>
<td>Benson et al. [1969]</td>
</tr>
<tr>
<td>H₂ + Cl → Cl₂ + H</td>
<td>1.0 × 10⁻⁸ exp (−1600/RT)</td>
<td>Benson et al. [1969]</td>
</tr>
<tr>
<td>H₂O₂ + O(‡D) → 2OH</td>
<td>3.5 × 10⁻⁶</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>CH₄ + O(‡D) → OH + CH₃</td>
<td>5.0 × 10⁻⁹</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>CH₄ + H₂O → H₂ + CH₃</td>
<td>2.95 × 10⁻⁹ exp (−1770/RT)</td>
<td>Davis et al. [1975a]</td>
</tr>
<tr>
<td>H₂ + O(‡D) → OH + H</td>
<td>2.9 × 10⁻⁹</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>H₂ + O → OH + H</td>
<td>3.0 × 10⁻⁹ exp (−4800/RT)</td>
<td>Baulch et al. [1973]</td>
</tr>
<tr>
<td>H₂ + O → OH + O</td>
<td>2.6 × 10⁻¹⁰</td>
<td>Hampson et al. [1973a]</td>
</tr>
<tr>
<td>H₂ + O → OH + M</td>
<td>6.0 × 10⁻¹⁰ exp (−320/RT)</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>H₂ + O → H₂O + O</td>
<td>4.2 × 10⁻⁸ exp (−350/RT)</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>H₂ + H₂O → H₂O + O</td>
<td>8.3 × 10⁻⁸ exp (−500/RT)</td>
<td>Lloyd [1973]</td>
</tr>
<tr>
<td>OH + O → H₂O + O</td>
<td>4.0 × 10⁻¹¹</td>
<td>Wilson [1973]</td>
</tr>
<tr>
<td>OH + H₂O → H₂O + O₃</td>
<td>see text</td>
<td>Anderson and Kaufman [1973]</td>
</tr>
<tr>
<td>OH + O → OH + O₂</td>
<td>1.3 × 10⁻¹⁰ exp (−950/RT)</td>
<td>Lloyd [1973]</td>
</tr>
<tr>
<td>H₂O + H₂O → OH + H₂O</td>
<td>8.0 × 10⁻¹⁰ exp (−500/RT)</td>
<td>Lloyd [1973]</td>
</tr>
<tr>
<td>H₂O + H₂O → OH + H₂O</td>
<td>1.1 × 10⁻¹⁰ exp (−1250/RT)</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>H₂O + H₂ → OH + H₂O</td>
<td>3.0 × 10⁻¹¹ exp (−500/RT)</td>
<td>Hampson et al. [1973a]</td>
</tr>
<tr>
<td>H₂O + H₂ → OH + H₂O</td>
<td>1.7 × 10⁻¹¹ exp (−910/RT)</td>
<td>Hampson et al. [1973a]</td>
</tr>
<tr>
<td>H₂O + NO → OH + NO₂</td>
<td>1.1 × 10⁻¹² exp (−1000/RT)</td>
<td>Davis et al. [1973]</td>
</tr>
<tr>
<td>N₂O + O(‡D) → 2NO</td>
<td>1.1 × 10⁻⁸</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>N₂O + O(‡D) → N₂ + O₂</td>
<td>1.1 × 10⁻¹⁰</td>
<td>Garvin and Hampson [1974]</td>
</tr>
<tr>
<td>NO + O₂ → NO₂ + O</td>
<td>9.0 × 10⁻¹² exp (−1200/RT)</td>
<td>Hampson et al. [1973a]</td>
</tr>
<tr>
<td>NO + O → NO₂ + O</td>
<td>7.0 × 10⁻⁸</td>
<td>Becker et al. [1973]</td>
</tr>
<tr>
<td>NO + O → NO₂ + M</td>
<td>1.7 × 10⁻¹¹ exp (−300/RT)</td>
<td>Baulch et al. [1973]</td>
</tr>
<tr>
<td>NO + O → NO₂ + M</td>
<td>1.0 × 10⁻¹² exp (−500/RT)</td>
<td>Andersen et al. [1974]</td>
</tr>
<tr>
<td>R₂₀</td>
<td>HNO₃ + OH → H₂O + NO₂</td>
<td>1.0 × 10⁻¹²/(3.5 × 10⁻⁷ T² + 25 [M])</td>
</tr>
<tr>
<td>R₂₁</td>
<td>NO₂ + NO → 2NO₂</td>
<td>9.0 × 10⁻¹⁸</td>
</tr>
<tr>
<td>R₂₂</td>
<td>NO₂ + O → NO₃</td>
<td>1.1 × 10⁻¹⁸ exp (−2450/RT)</td>
</tr>
<tr>
<td>R₂₃</td>
<td>NO₂ + O + M → NO₃ + M</td>
<td>1.0 × 10⁻¹⁸</td>
</tr>
<tr>
<td>R₂₄</td>
<td>O + O₃ + M → O₂ + M</td>
<td>1.0 × 10⁻¹⁸ exp (−2300/RT)</td>
</tr>
<tr>
<td>R₂₅</td>
<td>O + O₃ + M → O₂ + M</td>
<td>1.0 × 10⁻¹⁸ exp (−2100/RT)</td>
</tr>
</tbody>
</table>
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 NOx-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 $10^{-4}$ 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 at the tropopause would increase [Hunten and Strobel, 1974; Liu and Donahue, 1974a]. We show in Figure 3 the mixing ratio of hydrogen in the forms of CH₄, H₂O, and H₂ as a function of altitude for assumed mixing ratios of 0.5 ppm of H₂, 1.5 ppm of CH₄ at 10 km, and 3 ppm of H₂O in one case and $10^{-4}$ ppm of H₂O in the other. Plotted is the total hydrogen mixing ratio for each species, i.e., twice the H₂ and H₂O mixing ratios and 4 times the CH₄ mixing ratio. The total mixing ratio $(2[H₂O] + 2[H₂] + 4[CH₄])$ 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 H₂O near 50 km is essentially all produced from CH₄. Above 40 km, H₂ begins to be created as a result of the reaction (R16),

$$H + HO₂ → H₂ + O₂$$

In the case of 3 ppm H₂O at 10 km the H₂ 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 H₂O and CH₄. But with virtually no H₂O at 10 km the H₂ mixing ratio reaches only a little more than 3 ppm, since the increase comes only from the conversion of methane to H₂O and the subsequent production of odd hydrogen from H₂O.

Figure 2 also shows the effect of increasing the H₂O 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 H₂O for the sake of obtaining a clear separation of the curves.) Figures 4 and 5 show the percentage reduction in O₃ column abundances as CIX is added to the atmosphere and the H₂O 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),

$$Cl + O₃ ⇌ ClO + O₂$$

Fig. 1. Profiles of H₂O, CH₄, H₂, and H₂O 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 H₂O at the tropopause increased by a factor of 10 (open circles).

![Fig. 3. Mixing ratios of 2H₂O, 2H₂, and 4CH₄ 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 2H₂O, 4CH₄, and 2H₂, respectively. In the other model (dashed line) the corresponding mixing ratios are 2 × 10⁻⁴, 6, and 1 ppm.](image-url)
Fig. 4. Changes in O₃ column abundance as CIX mixing ratio increases. Results are shown for four mixing ratios of H₂O at the tropopause, 0.01 ppm (open triangles), 3 ppm (solid circles), 9 ppm (crosses), and 30 ppm (open circles), and for high k₈ (solid line) and low k₈ (dashed line).

newly measured by Davis et al. [1975a] and Zahniser et al. [1975], i.e., 2.4 × 10⁻¹¹ exp (-340/RT), and for the reaction (R4),

\[ \text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3 \]

where \( k_4 \) is 5.4 × 10⁻¹¹ exp (-1125/T) according to Davis et al. [1975b]. In early (pre-1975) studies of stratospheric CIX, \( k_4 \) was taken to be 4.3 × 10⁻¹¹ exp (-250/T) [see, e.g., Stolarski and Cicerone, 1974] based on Clyne and Watson's room temperature rate of 1.85 × 10⁻¹¹ [Watson, 1974]. Also, \( k_4 \) was taken to be 8.8 × 10⁻¹¹ exp (-1900/T) in the early studies, based on Davis et al. [1970]. The use of the new rates \( k_4 \) and \( k_5 \) in our model has significantly reduced the effect of a given amount of CIX on O₃ compared to that in previous models. In

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

Our results for the new rates \( k_4 \) and \( k_5 \), compared to those for the old \( k_4 \) and \( k_5 \), are that 1 ppb of CIX reduces the total amount of O₃ by 0.6% compared to 2.2%, 3 ppb of CIX reduces O₃ by 1.9% compared to 6.4%, and 5 ppb of CIX reduces O₃ by 3.6% compared to 10.4%. These comparisons are made for the larger value of \( k_5 \). In case the smaller value is more nearly correct the reduction in the integrated O₃ abundance for a given combination of CIX 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 CIX 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 \( k_5 \). Donahue et al. [1976] discuss this further. The 10% ozone destruction level is reached with less than 6 ppb of CIX if the low value of \( k_5 \) is correct.

Figures 4 and 5 also demonstrate the principal points that we wish to make in this paper. The effects produced by changing H₂O are significant. In particular, when the CIX pollution level is 1 ppb, the percentage ozone reduction goes from 0.6% to 2.9% if the amount of H₂O 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 \( k_5 \)). Again for the low value of \( k_5 \) a much more dramatic effect occurs, i.e., a 6.8% reduction for 1 ppb of CIX and 3 times normal H₂O and a 16.6% reduction for 10 times normal H₂O. 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 CH₄ in reaction (R4) is attached by OH (R5),

\[ \text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O} \]

thus reinitiating the CIX 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 \( k_5 \), where the influence of the enhanced destruction of CH₄ by OH when \( k_5 \) is low is apparent. Much

Fig. 6. Density distribution of methane for the standard atmosphere with high \( k_5 \) (solid line) and low \( k_5 \) (dashed line) and for atmosphere containing 8 ppb of CIX and low \( k_5 \) (dotted line).
more striking, however, is the rapid destruction of methane by Cl in the formation of HCl through reaction (R4) when 8 ppb of CIX 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 CIX. Tropospheric CH₄ is also affected by CIX-induced O₃ losses in the stratosphere, feeding back on the stratosphere [Chameides et al., 1976].

In Figure 7 the densities of HOx are plotted for the low value of k₈ in three cases: (1) the standard atmosphere, (2) with 8 ppb of CIX and normal H₂O, and (3) with 8 ppb of CIX and 3 times the normal H₂O. It is interesting that the presence of CIX increases the amount of HO₃ considerably below the ozone maximum and decreases it above. The reason is to be found in the preferential destruction of O₃ above the maximum by CIX released from chlorocarbons. This decrease in optical depth enhances O(¹D) production from O₃ at low altitudes, as is demonstrated by the curves showing the O(¹D) densities. Since O(¹D) interacting with H₂O and CH₄ is an important source of HO₃, the result is an increase in HO₃ at low altitudes. Conversely, above 40 km, where the atmosphere is optically thin for production of O(¹D), the O(¹D) density is lower because the O₃ density is lower. Thus the HO₂ density in the presence of CIX is reduced at higher altitudes. Figure 8 shows the CIX species as they are affected by the addition of water to the stratosphere: the conversion of HCl to Cl by OH can be easily detected below 40 km. Above 50 km, because the H₂O₂ 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 H₂O₂ with Cl.

In Figures 9 and 10 we show the major sinks of O₃ for the standard atmosphere with high and low values of k₈, respectively. These figures show that the odd hydrogen reactions dominate the loss of O₃ above 55 and below 20 km. The Chapman reaction (R35) between O₃ and O dominates only in a narrow range near 50 km, and the NO₂ 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 k₈ 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 k₈ is large but only from 43 to 47 km when k₈ is small. Figure 11 in turn, when compared with Figure 10, shows the changes in the dominant sinks of O₃ when 8 ppb of CIX is added. The ClO−O reaction rate in the CIX cycle at 40 km jumps from 3 × 10⁶ cm⁻³ s⁻¹ to more than 8 × 10⁶ cm⁻³ s⁻¹. The NO₂ + O rate is reduced when CIX becomes dominant because of the decreased amount of O₃ leading to less NO and less O₂. While the HO₂ + O reaction rate is not shown in Figure 11, its dependence upon the addition of CIX and water vapor is similar to that of OH + O₂.

Note that for low k₈ there is a significant amount of H₂O₂ near 25 km as a result of the large concentrations of HO₂.
The rate constants for the steps in the ozone-destroying reaction 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 CI is present and by an increasingly greater factor as the amount of CI increases.

**Effect of H$_2$O on NO$_2$-Perturbed Stratosphere**

We have also considered the effects of NO$_2$ and H$_2$O produced by the 'standard' SST models, at 20 km [Grobecker, 1974]. In Figure 12 we show our results for the globally averaged reduction in O$_8$ resulting from 100 SST's emitting $9 \times 10^4$ 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$_8$ in the hemisphere in which the NO$_2$ 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$_8$ reduction, no matter how little is added, whether $k_{18}$ is small or large. With normal or almost normal amounts of H$_2$O in the stratosphere the reduction in O$_8$ for a specified artificial source of NO$_2$ turns out to be greater when $k_{18}$ is large and the density of HO$_2$ 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$_2$ required to stay in balance with H$_2$O increases much more rapidly with the H$_2$O mixing ratio than when $k_{18}$ is large. For a small increase in the H$_2$O concentration the removal of O$_8$ by HO$_2$ becomes more important than the removal by the NO emitted from 100 SST's. This dominance by the HO$_2$ catalytic cycle causes the effect of added H$_2$O to be much more pronounced for the small value of $k_{18}$ than the large. The same effect is noticeable in Figure 5 for CI 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$_2$ destruction of O$_8$ dominates NO$_2$ destruction below 24 km and begins to compete seriously again above 40 km. It is the effect of HO$_2$ below 22 km that causes us to find that increasing the H$_2$O mixing ratio even by very small amounts causes the ozone column content to decrease, whereas others [McElroy et al., 1974; Crutzen, 1974a] found the opposite. McElroy et al. located their lower boundary at 28 km and multiplied the O$_8$ profile below that level by the change calculated at 28 km [Wofsy, 1974]. This exercise cannot duplicate the large effect of HO$_2$ on O$_8$ that we find below 24 km. Our disagreement with Crutzen [1974b] may be due to different reaction rate constants. We note that Rao-Vuppurti [1974] also finds that increased H$_2$O leads to decreased O$_8$.

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$_8$ and causes the temperature to rise below 25 km and fall above 25 km, will cause HO$_2$ to have different effects at high and low altitudes.

The rate constants for the steps in the ozone-destroying reactions:

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \\
\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2 \\
\text{HO}_2 + \text{O} \rightarrow \text{OH} + 2\text{O}_2
\]

increase with increasing temperature, while the rate constant for the reaction between HO$_2$ and NO$_2$ that produces the sink for NO$_2$:

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}
\]

decreases with increasing temperature. Thus as the temperature increases at low altitude, the destruction of ozone from HO$_2$ and from NO$_2$ 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.
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 H2O present in the stratosphere in the case of odd chlorine produced by photolysis of chlorocarbon because of the conversion of HCl to Cl by OH. The effects considered depend strongly on the value of the rate constant for the reaction of OH with H2O, 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 discussions 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 NGL-7187. We also acknowledge the National Center for Atmospheric Research (sponsored by NSF) for computer time.

REFERENCES


Thompson, B. A., F. Harteck, and R. R. Reeves, Jr., Ultraviolet absorption coefficients of \( \text{CO}_2, \text{CO}, \text{H}_2\text{O}, \text{H}_2\text{O}, \text{NH}_3, \text{NO}, \text{SO}_2, \text{and CH}_4 \) between 1800 and 4000 Å, J. Geophys. Res., 60, 6431–6446, 1963.


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