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Nonlinear Response of Stratospheric Ozone Column to Chlorine Injections

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With a reasonably complete and up-to-date photochemical model of the stratosphere, we find that the calculated stratospheric ozone-column response to chlorine injections is highly nonlinear. The model calculations assume that the background inorganic (or odd) chlorine, CIX, is due to CH3Cl and CCl3. Additional CIX is added to the stratosphere by varying input fluxes of CCl2F2 and CCl3F. The sensitivity, ΔO3/ΔCIX, of the stratospheric O3 column to added CIX is relatively small for CIX ≤ 3 ppb or ACIX ≤ 2 ppb; slight ozone increases with CIX are possible over a limited range of CIX if the formation of chlorine nitrate proceeds rapidly. This may have important implications for total ozone-column trend assessment. As CIX increases beyond 3 ppb, the stratospheric O3 column decreases with CIX increasingly rapidly. This marked departure from the linearity calculated in past years is largely due to presently accepted faster rates of reaction of OH with HNO3, HNO2, HO2, and HO2. If stratospheric CIX increases to about 9 ppb due to continued usage of CCl2F2, CCl3F, and CH3CCl3, the stratospheric O3 column depletion is calculated to be 6.7–9.0%. Principal uncertainties in these calculations, including the rate of formation of chlorine nitrate, the products of its photolysis, and the present day mixing ratio of CIX are discussed. Calculated ozone decreases due to increased N2O concentrations are also presented.

1. INTRODUCTION

The identification of human activities that can affect global-scale atmospheric chemistry has led to an intensification of research aimed at understanding both the natural and perturbed systems. Man's potential impact on stratospheric ozone, on the entire stratospheric photochemical system, and indirectly on climate has been recognized to involve a rich variety of coupled chemical and physical phenomena. Accordingly, efforts to understand the future impact of continued usage of chlorofluoromethanes (CFM), CH3CCl3, and of nitrous oxide have broadened in scope to consider the coupled effects of increasing atmospheric CO2 and CFM concentrations [Luther et al., 1977; Haigh and Pyle, 1979] and of stratospheric dynamics and chemistry [Harwood and Pyle, 1977; Garcia and Solomon, 1983]. Recently documented trends in atmospheric CH4 levels [Rasmussen and Khalil, 1981; Blake et al., 1982] have been shown [Owens et al., 1982] to be capable of influencing stratospheric response to CFMs. Further, the potential interactions of simultaneous increases in N2O and CFMs were investigated by Logan et al. [1978] even before the convincing documentation of an upward secular trend in N2O concentrations appeared in print [Weiss, 1981]. Further, Logan et al. [1978] demonstrated the potential effects of combustion-produced gases on tropospheric O3 and OH and through these OH changes, the effects on stratospheric chlorine and ozone concentrations. The more speculative but plausible increases in tropospheric ozone due to commercial aircraft operations [Liu et al., 1980; Derwent, 1982] would necessitate a still broader view of atmospheric ozone perturbations, especially from the point of view of trend assessment in ground-based total ozone-column measurements. Simultaneous variations in CFMs, N2O, CH4, and tropospheric NOx were investigated by Wuebbles et al. [1983].

Since 1974 when the CFM-O3 problem was identified by Molina and Rowland [1974], there have been many attempts to calculate future changes in stratospheric O3. Although more emphasis has been placed on potential decreases in the total ozone column (both in one- and two-dimensional models) the potential redistribution of ozone (large decreases at high altitudes and small changes or increases at altitudes below 30 km) is also of great scientific interest and possibly important to climate [Cruzen, 1974; Ramanathan and Dickinson, 1979]). During the 8-year period 1974–1982, the estimated sensitivity of total stratospheric ozone to CFM injections has varied [see, e.g., NAS/NRC, 1982] as model parameterizations and laboratory photochemistry and kinetics data improved. However, three features of the CFM-O3 problem remained in updated calculations as originally estimated: (1) large O3 decreases were projected near 40 km altitude; (2) as CFMs were added to the atmosphere, the total O3 column diminished; and (3) an essentially linear response was observed between total O3 column and the amount of added CFM, or equivalently stratospheric odd chlorine, CIX. For a representative statement on the linearity of the response, see Miller et al. [1978].

In this paper, we show that an updated photochemical model of the stratosphere now predicts a highly nonlinear response of total stratospheric ozone to CIX increments. It is shown further that a change in the sign of the response might occur, at least over a limited range of CIX increments. Before presenting these results in section 3 and discussing them in section 4, we describe essential features of the model in section 2.

2. THE PRESENT MODEL

Despite its obvious meteorological shortcomings, the one-dimensional eddy-diffusion/photochemical model of atmospheric chemistry has been proven to be useful especially to...
Table 1. Atmospheric Model Input Data

| Altitude (km) | N (cm⁻³) | T (°K) | K₁ (cm² s⁻¹) | K₂ (cm² s⁻¹) |
|--------------|---------|-------|-------------|-------------|
| 10           | 8.60(18)| 223   | 9.4(4)      | 9.4(4)      |
| 12           | 6.49(18)| 218   | 2.1(4)      | 2.1(4)      |
| 14           | 4.74(18)| 217   | 4.0(3)      | 3.8(3)      |
| 16           | 3.46(18)| 216   | 5.4(3)      | 4.3(3)      |
| 18           | 2.53(18)| 216   | 6.6(3)      | 5.0(3)      |
| 20           | 1.85(18)| 217   | 8.4(3)      | 6.0(3)      |
| 22           | 1.34(18)| 218   | 1.0(4)      | 7.8(3)      |
| 24           | 0.97(17)| 220   | 1.34(4)     | 1.0(4)      |
| 26           | 0.71(17)| 222   | 1.6(4)      | 1.2(4)      |
| 28           | 0.52(17)| 224   | 2.2(4)      | 1.8(4)      |
| 30           | 0.38(17)| 226   | 3.1(4)      | 2.6(4)      |
| 32           | 0.28(17)| 230   | 4.2(4)      | 3.4(4)      |
| 34           | 0.20(17)| 234   | 5.7(4)      | 4.8(4)      |
| 36           | 0.15(17)| 239   | 7.8(4)      | 6.2(4)      |
| 38           | 0.12(17)| 245   | 1.1(5)      | 9.2(4)      |
| 40           | 0.83(16)| 250   | 1.5(5)      | 1.3(5)      |
| 42           | 0.62(16)| 256   | 2.0(5)      | 1.8(5)      |
| 44           | 0.47(16)| 262   | 2.7(5)      | 2.4(5)      |
| 46           | 0.35(16)| 266   | 3.7(5)      | 3.4(5)      |
| 48           | 0.27(16)| 270   | 5.1(5)      | 4.7(5)      |
| 50           | 0.21(16)| 271   | 7.0(5)      | 6.0(5)      |
| 52           | 0.17(16)| 273   | 7.7(5)      | 7.0(5)      |
| 54           | 0.13(16)| 276   | 8.4(5)      | 7.9(5)      |
| 56           | 0.10(16)| 280   | 9.3(5)      | 8.9(5)      |
| 58           | 0.08(15)| 286   | 1.0(6)      | 9.7(5)      |
| 60           | 0.06(15)| 290   | 1.1(6)      | 1.0(6)      |
| 62           | 0.05(15)| 295   | 1.2(6)      | 1.2(6)      |
| 64           | 0.04(15)| 300   | 1.4(6)      | 1.4(6)      |
| 66           | 0.03(15)| 305   | 1.5(6)      | 1.5(6)      |
| 68           | 0.03(15)| 310   | 1.6(6)      | 1.6(6)      |
| 70           | 0.02(15)| 315   | 1.7(6)      | 1.7(6)      |
| 72           | 0.02(15)| 320   | 1.7(6)      | 1.7(6)      |
| 74           | 0.01(15)| 325   | 1.7(6)      | 1.7(6)      |
| 76           | 0.01(15)| 330   | 1.8(6)      | 1.8(6)      |
| 78           | 0.01(15)| 335   | 1.9(6)      | 1.9(6)      |
| 80           | 0.01(15)| 340   | 2.0(6)      | 2.0(6)      |

K₁(z) is an altitude-dependent, eddy-diffusion coefficient that is essentially 2x the value of the 1975 Hunten coefficient [see, e.g., Massie and Hunten, 1981] below 30 km but larger above 30 km. K₂(z) has been constructed to provide better agreement between calculated and measured values of stratospheric ozone-layer photochemistry. Most of the photodissociation reactions included in this model are listed in Table 2 along with the reaction products adopted for standard-case calculations; nonstandard-case assumptions are discussed later and in Table 4. Table 3 lists the chemical kinetic reactions, rates, and products included explicitly in the present study's standard-case calculations; deviations from this set are discussed later and are shown in Table 4. The present model does not follow a chemical-family grouping. Instead, a mass-conservation equation is solved for each individual chemical species, and, thus, assumptions of chemical equilibrium are avoided. In our steady state model, a proper 24-hour averaging is constructed to provide better agreement between calculated and measured vertical profiles of CH₄, N₂O, CF₂Cl₂, and CFCl₃. N(z) is the total atmospheric number density versus altitude, and T is temperature. 8.6(18) is 8.6 x 10⁻¹⁸.

K₂(z) is not more than 28% lower than K₁(z) and is closer to K(z) at most altitudes.

Table 3 and 4 will show that this chemical reaction scheme includes all reactions presently believed to be significant in stratospheric ozone-layer photochemistry. The present model does not follow a chemical-family grouping. Instead, a mass-conservation equation is solved for each individual chemical species, and, thus, assumptions of chemical equilibrium are avoided. In particular, for steady state calculations, solutions are calculated for 32 species, and as discussed in the appendix a flux-divergence term is included in each individual species equation. These are H₂O, H₂, CH₄, CO, N₂O, CH₃Cl, CCl₃, CFC₁₃, CF₂Cl₂, O₃, O, N₂(S), NO, NO₂, NO₃, N₂O₅, HNO₃, HNO₄, H, OH, HO₂, H₂O₂, Cl, ClO, ClO₂, H₂O₂, H₂O, and CH₃OOH. For O(¹D), HCO, and CIOO photochemical equilibrium is assumed, i.e., no flux-divergence term is carried in the equations. In our time-dependent calculations, 23 species are calculated as per the appendix, and the first nine species of the 32 listed above are held fixed at specified self-consistent initial conditions.

In our steady state model, a proper 24-hour averaging is included according to the procedure of Turco and Whitten [1978] wherein a completely time-dependent calculation is performed and diurnal factors are determined. These factors are then employed in the steady state model, new solutions are computed, and these become new initial conditions for the time-dependent diurnal model. After iterating twice we have found that this approach yields daily averaged values from the steady state code that are within 1% of those from the nearly exact time-dependent code. In this way, potential problems with radical-radical reactions [Johnston and Whitten, 1975; Turco and Whitten, 1978] are avoided.
As noted in the appendix, two distinct types of boundary conditions are employed for the chemical species. In the steady state model at 10 km fixed-flux boundary conditions (as opposed to fixed densities) are used for N2O, CH3Cl, CCl4, CF2Cl2, and CFC3. The exact flux values are adjusted to yield volume mixing ratios at 10 km as follows: N2O (0.30 ppm), CH3Cl (0.68 ppb), CCl4 (0.125 ppb). As model parameters such as chemical reaction rates are varied, the input fluxes of these species must be readjusted to yield the stated mixing ratios. A fixed mixing ratio of 1.6 ppm is used for CH4 at 10 km except as noted in Table 4. Assuming a constant flux for species like CH4Cl (with appreciable tropospheric loss) is not an essential procedure; one might select a constant mixing ratio instead. Fluxes for CF2Cl2 and CFC3 are varied to produce variable amounts of stratospheric inorganic (or odd) chlorine, ClX. Other boundary conditions for the remaining species and for time-dependent calculations have been tested carefully and are displayed in the appendix.

Certain model calculations reported below were compared with those of a second model. The latter model is essentially that of Liu et al. [1976] but with updated and fuller chemical reaction schemes. The two models gave excellent agreement in the essential nonlinear character of O3-ClX perturbations reported below. Because the Liu et al. model solves equations for grouped chemical families, it can be stated that our results do not depend on family grouping or on assumptions of chemical equilibrium, or the lack of both.

3. Results of Model Calculations

Table 4 describes fourteen different configurations of the photochemical models that we used to calculate the response of stratospheric ozone to chlorine injections. Except as noted in Table 4, the reaction rates listed in Table 3 and the photochemical data of Table 2 were employed. For example, models A-K used k12 (the rate of formation of ClONO2) equal to one-half the faster rate listed in NASA/JPL [1982] while models L and M used the fast rate and model N used the NASA/JPL [1982] slow rate (about 25% of the fast rate). Similarly, models K, M, and N employed a new faster rate for HCl + OH → H2O + Cl, i.e., \( k_{67} = 4.6 \times 10^{-12} \exp \left( -500/T \right) \) (M. J. Molina, private communication, 1982), approximately 1.2 times the value listed in Table 3. All models used \( k_{52} (\text{e}) \) from Table 1 except for model H. Finally, an important recent adjustment to the rate of photolysis of N2O5, namely, a temperature-dependent photoabsorption cross section [Yao et al., 1982] was incorporated into our calculations. Although the Yao et al., results are exactly those recommended in NASA/JPL [1982] we used the older temperature-independent cross sections [see, e.g., Hudson and Reed, 1979] for models A-D. Further, in models F and G we assumed that the products of N2O5 photolysis are 2NO2 + O, contrary to recent data (H. S. Johnston, private communication, 1982).

Because of the remaining uncertainties in laboratory kinetic data for \( k_{52} \) and \( k_{67} \), it is not completely clear as to which of the models of Table 4 are to be preferred. Models A, B, C, D, F, G, H, and I are not defensible based on available data; they were employed to study sensitivities. Further, model J, while possible, is hard to defend as available evidence suggests that ClONO2 + hv → Cl + NO3, not ClO + NO2. Models E, K, L, M, N are most likely, but \( k_{12} \) is probably not the intermediate, standard value adopted in Table 3 and models E and K; it is either the NASA/JPL [1982] fast rate or the slow rate. Assuming that \( k_{52} \) is best chosen as the new, faster rate, our preferred models are M and N. Note once again that the rate, \( k_{72} \), of formation of chlorine nitrate is four times faster in model M than in model N.

### Table 2. Photodissociation Reactions and Products Included in the Model and References for Photoabsorption Coefficients

| Photolysis | Rate | Reference |
|------------|------|-----------|
| O2 + hv → O + O | \( J_1 \) | 175 < \( \lambda \) < 205 nm: Hudson and Mahle [1972] |
| O3 + hv → O2 + O | \( J_2 \) | 205 < \( \lambda \) < 242 nm: see text Hudson and Kiefer [1975] |
| NO2 + hv → NO + O | \( J_4 \) | |
| N2O + hv → N2 + O(\text{D}) | \( J_5 \) | |
| HNO2 + hv → OH + NO2 | \( J_6 \) | |
| H2O2 + hv → OH + OH | \( J_7 \) | |
| NO3 + hv → NO + O2 | \( J_8 \) | |
| H2CO + hv → H + HCO | \( J_9 \) | |
| CFCl3 + hv → Cl + CF2Cl | \( J_{10} \) | |
| CFCF3 + hv → Cl + CFCF | \( J_{11} \) | Marinelli and Johnston [1982] |
| ClO2 + hv → Cl + NO3 | \( J_{12} \) | |
| HCl + hv → H + Cl | \( J_{14} \) | |
| HOCI + hv → OH + Cl | \( J_{15} \) | |
| N2O2 + hv → NO2 + NO2 | \( J_{16} \) | |
| CH3OOH + hv → OH + CH2O | \( J_{17} \) | Kan et al. [1979] |
| CCl4 + hv → Cl + CCl3 | \( J_{18} \) | Nicolet [1979] |
| HNO2 + hv → HO2 + NO2 | \( J_{19} \) | |
| CH2O + hv → CH2 + O2 | \( J_{20} \) | Sun and Weissler [1955] |
| NO + hv → N + O | \( J_{21} \) | |
| NO2 + hv → NO2 + O | \( J_{22} \) | |
| CH3 + hv → H + CH4 | \( J_{23} \) | |
| H2O + hv → H + OH | \( J_{24} \) | Hudson and Kiefer [1975] |

Where no reference is shown, the critical review recommendations from NASA/JPL [1982] were adopted. Deviations from these standard rates and photodissociation products in certain of our calculations are noted in Table 4.
### TABLE 3. Chemical Reactions, Rates, and Products Included in the Present Model

| Reactions                                                                 | Rate                        | Reference |
|----------------------------------------------------------------------------|-----------------------------|-----------|
| $O + O_2 + M \rightarrow O_3 + M$                                         | $k_1 = 1.50E-11 \exp (-2220/T)$ | b         |
| $O + O_3 + O_2$                                                            |                             |           |
| $O_3 + M \rightarrow O_3 + O_2$                                            |                             |           |
| $O + O + M \rightarrow O_2 + M$                                            |                             |           |
| $O(D) + N_2 + O + N_2$                                                     | $k_2 = 1.80E-11 \exp (107/T)$ | a         |
| $O(D) + O_3 + O + O_2$                                                     | $k_3 = 3.20E-11 \exp (67/T)$ | a         |
| $O(D) + O_2 + O_2$                                                         | $k_6 = 1.20E-10$            | a         |
| $O(D) + O_2 + O + O_2$                                                     | $k_7 = 1.20E-10$            | a         |
| $O(D) + N_2O \rightarrow NO + NO_2$                                        | $k_{10} = 2.30E-12 \exp (-1450/T)$ | a       |
| $N + O_2 + NO + O_2$                                                       | $k_{11} = 9.30E-12$         | a         |
| $N + O_2 + NO + O$                                                         | $k_{12} = 5.00E-16$         | a         |
| $NO_2 + O + NO_2 + O_2$                                                    | $k_{13} = 4.40E-12 \exp (-3220/T)$ | a      |
| $NO + NO_2 + NO_2 + NO_2$                                                  | $k_{14} = 1.20E-13 \exp (-2450/T)$ | a       |
| $NO + O + M \rightarrow NO_2 + M$                                          | $k_{15} = 2.00E-11$         | a         |
| $NO_2 + NO_2 + M$                                                          |                             |           |
| $N_2O_5 + M \rightarrow NO_3 + NO_2 + M$                                   |                             |           |
| $N + NO \rightarrow N_2 + O$                                              | $k_{18} = \text{formula from reference f}$ | f         |
| $O + NO_2 + N_2 + O$                                                       | $k_{19} = 3.40E-11$         | a         |
| $O(D) + H_2O \rightarrow OH + OH$                                         | $k_{21} = 2.20E-10$         | a         |
| $O(D) + CH_3 + H_2O \rightarrow OH + CH_3$                                 | $k_{22} = 1.40E-10$         | a         |
| $O(D) + H_2 + H_2O \rightarrow OH + H$                                     | $k_{24} = 9.90E-11$         | a         |
| $H + O_2 + NO \rightarrow H_2O + M$                                       | $k_{25} = 1.40E-10 \exp (-470/T)$ | a       |
| $OH + O + CH_3 + H_2O \rightarrow NO_2 + CH_3 + O_2$                      | $k_{26} = 1.60E-12 \exp (-940/T)$ | a       |
| $OH + OH + CH_3 + NO_2 + O_2$                                              | $k_{27} = 1.10E-14 \exp (-580/T)$ | a*      |
| $OH + O_2 + O_3 + O_2$                                                     | $k_{28} = 2.30E-11 \exp (110/T)$ | a         |
| $OH + O + O_2 + O_2$                                                       | $k_{29} = 4.00E-11$         | a         |
| $H_2O_2 + O_2 \rightarrow OH + H_2O$                                      | $k_{30} = 2.80E-12 \exp (-2125/T)$ | a*      |
| $OH + CH_3 + H_2O + CH_3 + O_2$                                           | $k_{32} = 2.36E-12 \exp (-1710/T)$ | a*      |
| $OH + NO \rightarrow O + NO_2 + O$                                        | $k_{33} = 3.50E-12 \exp (-250/T)$ | a*      |
| $OH + CO + CO_2 + H$                                                       | $k_{34} = 1.35E-13 \exp (1 + p)$ | a         |
| $OH + H_2 + H_2O + H$                                                     | $k_{35} = 1.20E-11 \exp (-2220/T)$ | g       |
| $OH + NO + M \rightarrow HNO_3 + M$                                       | $k_{37} = 1.52E-14 \exp (650/T)$ | h         |
| $OH + HNO_3 + H_2O + NO_3$                                                 | $k_{38} = 2.70E-12 \exp (-145/T)$ | a*      |
| $OH + NO_2 + H_2O + O_2$                                                   | $k_{39} = 8.00E-11$         | a*       |
| $OH + OH + H_2O + O_2$                                                     | $k_{40} = 4.50E-12 \exp (-275/T)$ | a*      |
| $OH + H_2O_2 + H_2O + HCO$                                                 | $k_{41} = 1.00E-11$         | a         |
| $OH + OH + CH_3 + O_2$                                                     | $k_{42} = 7.40E-12$         | k         |
| $H + O_2 + H_2 + O_3$                                                      | $k_{43} = 2.22E-12$         | k         |
| $H + HO_2 + H_2O + O$                                                     | $k_{44} = 6.44E-11$         | k         |
| $HCO + O + OH + HCO$                                                       | $k_{45} = 3.00E-11 \exp (-1550/T)$ | a       |
| $CH_2 + O_2 + M \rightarrow CH_2O_2 + M$                                  | $k_{46} = 7.40E-12$         | b         |
| $CH_3 + O_2 + M \rightarrow CH_2O_2 + M$                                  |                             |           |
| $CH_3 + O_2 + NO + CH_2O + O_2$                                            | $k_{47} = 7.40E-12$         | a         |
| $CH_2O + HO_2 + CH_3 + CH_2 + O_2$                                         | $k_{48} = 7.70E-14 \exp (1300/T)$ | a       |
| $CH_2O + HO_2 + CH_3 + CH_2 + O_2$                                         | $k_{49} = 2.01E-12 \exp (-150/T)$ | a*      |
| $CH_3 + O _2 + HCO + HO_2$                                                 | $k_{50} = 9.20E-13 \exp (-2200/T)$ | g       |
| $CICO + O_2 + CO + HO_2$                                                   | $k_{51} = 5.00E-12$         | a*       |
| $O(D) + CF_2Cl_2 \rightarrow CICO + CF_2Cl$                                | $k_{52} = 1.40E-10$         | a*       |
| $O(D) + CF_2Cl_2 \rightarrow CICO + CF_2Cl$                                | $k_{53} = 2.20E-10$         | a*       |
| $O(D) + CF_2Cl_2 \rightarrow CICO + CF_2Cl$                                | $k_{54} = 1.00E-10$         | estimate |
| $OH + H_2O_2 + H_2O_2 + M$                                                 | $k_{55} = 1.80E-12 \exp (-1110/T)$ | a       |
| $H + NO_2 + H + O_3$                                                       | $k_{56} = 2.80E-11 \exp (-257/T)$ | a         |
| $Cl + O_3 + ClO + O_2$                                                     | $k_{57} = 2.90E-11 \exp (-130/T)$ | a         |
| $ClO + O + Cl + O_2$                                                       | $k_{58} = 6.50E-12 \exp (280/T)$ | a         |
| $ClO + NO + Cl + NO_2$                                                     |                             |           |
| $O(D) + HCl + Cl + O_2$                                                    | $k_{59} = 1.40E-10$         | a         |
| $Cl + CH_4 + HCl + CH_3$                                                   | $k_{60} = 9.60E-12 \exp (-1350/T)$ | a       |
| $Cl + HO_2 + HCl + CH_3$                                                   | $k_{61} = 4.80E-11$         | a*       |
| $Cl + H_2 + HCl + H$                                                       | $k_{62} = 3.50E-11 \exp (-2290/T)$ | a*      |
| $HCl + H + Cl + H_2$                                                       | $k_{63} = 4.70E-11 \exp (-2340/T)$ | a         |
| $Cl + H_2O_2 + HCl + HO_2$                                                 | $k_{64} = 1.10E-11 \exp (-980/T)$ | a         |
| $OH + HCl + Cl + H_2O$                                                     | $k_{65} = 2.80E-12 \exp (-425/T)$ | a         |
| $Cl + O_2 + M \rightarrow ClO + M$                                        |                             |           |
| $ClO + M \rightarrow Cl + O_2 + M$                                        |                             |           |
| $H_2O + ClO + HOCl + O_2$                                                  | $k_{70} = 4.60E-13 \exp (710/T)$ | a         |
| $H + ClO + OH + Cl$                                                        | $k_{71} = 3.00E-11$         | estimate  |
### Table 3. (continued)

| Reactions                                      | Rate                        | Reference |
|------------------------------------------------|-----------------------------|-----------|
| $\text{CIO} + \text{NO}_2 + \text{M} \rightarrow \text{CIONO}_2 + \text{M}$ | $k_{13} = 3.00 \times 10^{-12} \exp \left(-808/T\right)$ | c         |
| $\text{CIONO}_2 + \text{O} \rightarrow \text{CIO} + \text{NO} + \text{O}_2$ | $k_{14} = 1.20 \times 10^{-12} \exp \left(-333/T\right)$ | a         |
| $\text{H}_2\text{CO} + \text{Cl} \rightarrow \text{HCl} + \text{HCO}$ | $k_{15} = 9.20 \times 10^{-11} \exp \left(-68/T\right)$ | a\*       |
| $\text{H}_2 + \text{O} \rightarrow \text{OH} + \text{H}$ | $k_{16} = 8.80 \times 10^{-12} \exp \left(-4200/T\right)$ | i         |
| $\text{OH} + \text{HOCI} \rightarrow \text{CIO} + \text{H}_2\text{O}$ | $k_{17} = 3.50 \times 10^{-10}$ | a\*       |
| $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ | $k_{18} = 3.00 \times 10^{-12} \exp \left(-150/T\right)$ | a         |
| $\text{HNO}_3 + \text{M} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{M}$ | $k_{61} = 6.00 \times 10^{-13} \exp \left(650/T\right)$ | d         |

Except as specified in Table 4, these standard values were those employed in the calculations. References for these selections are as follows:

- a, NASA/JPL [1982].
- b, all three-body reaction rates are calculated from the generalized expression and species-specific data given in NASA/JPL [1982].
- c, for $k_{13}$, NASA/JPL [1982] gives two possible rate constants, one fast and one slow. At stratospheric conditions they differ by about a factor of 4. We adopted the NASA/JPL [1982] fast rate divided by two as the standard rate here.
- d, Smith et al. [1982].
- e, Campbell and Gray [1973].
- f, Connell and Johnston [1979].
- g, NASA/JPL [1981].
- h, Wine et al. [1981].
- i, Dubinsky and McKenney [1975].
- j, Graham et al. [1978].
- k, Sridharan et al. [1982].

An asterisk after a reference (e.g., a*) indicates that the adopted rate constant or reaction product is within the range of that recommended by reference a.

### Table 4. Distinguishing Characteristics of Models A–N

| Model | Kinetic Parameters | Temperature-Dependent $\alpha\text{N}_2\text{O}_5$? | Other Characteristics |
|-------|-------------------|-----------------------------------------------|-----------------------|
| A     | $k_{37}/4, k_{81}/10$ | no                                           | no fixed CH$_4$ flux at 10 km |
| B     | $k_{39}/2, k_{81}/10$ | no                                           |                       |
| C     | $k_{39}/2, k_{81}/10$ | no                                           |                       |
| D     | $k_{39}/2, k_{81}/10$ | yes                                          |                       |
| E     | $\text{N}_2\text{O}_5 + \text{hv} \rightarrow 2 \text{NO}_2 + \text{O}$ | yes                                          |                       |
| F     | $k_{37}/4, k_{39}/2, k_{81}/10$ | yes                                          |                       |
| G     | $\text{N}_2\text{O}_5 + \text{hv} \rightarrow 2 \text{NO}_2 + \text{O}$ | yes                                          |                       |
| H     | $k_{37}/4, k_{39}/2, k_{81}/10$ | yes                                          |                       |
| I     | $k_{10}/10$ | yes                                          | $K_i(z)$ (see Table 1) |
| J     | $\text{CIONO}_2 + \text{hv} \rightarrow \text{ClO} + \text{NO}_2$ | yes                                          |                       |
| K     | $k_{72} = 4.6 \times 10^{-12} \exp \left(-500/T\right)$ | yes                                          |                       |
| L     | $k_{72} = \text{NASA/JPL fast rate}$ | yes                                          |                       |
| M     | $k_{72} = \text{NASA/JPL fast rate}$ | yes                                          |                       |
| N     | $k_{72} = \text{NASA/JPL slow rate}$ | yes                                          |                       |

Standard rates and products of kinetic and photochemical reactions are shown in Tables 3 and 2; differences from standard choices are indicated here. Standard eddy-mixing coefficient is $K_i(z)$ (see Table 1) except for model H. Methane was held at 1.60 ppm by volume at 10 km except in model D, where a fixed flux of $7.4 \times 10^6 \text{cm}^{-2} \text{s}^{-1}$ was used. In models K, M, and N the rate for $\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$, i.e., $k_{67}$ is from M. J. Molina (private communication, 1982).
### Table 5. Calculated Response of Stratospheric Ozone Column, $f_{30}^{o}$O$_x$ $dz$, versus inorganic (or odd) chlorine, ClX

| ClX (ppb) | $f_{30}^{o}$O$_x$ $dz$ (10$^{-18}$ cm$^{-2}$) | $-\Delta f_{30}^{o}$O$_x$ $dz$ (%) | $-\Delta f_{30}^{o}$O$_x$ $dz$ ($\%$/ppb) |
|-----------|---------------------------------|---------------------------------|---------------------------------|
| **Model A** | | | |
| 1.14 | 9.460 | 0.10 | 0.077 |
| 2.52 | 9.450 | 0.99 | 0.230 |
| 5.42 | 9.566 | 4.35 | 0.530 |
| **Model B** | | | |
| 1.01 | 9.745 | 2.12 | 1.56 |
| 2.37 | 9.538 | 2.12 | 1.56 |
| 5.21 | 9.012 | 7.52 | 1.79 |
| 8.94 | 8.049 | 17.40 | 2.19 |
| **Model C** | | | |
| 0.96 | 9.730 | 1.74 | 1.27 |
| 2.33 | 9.561 | 6.53 | 1.56 |
| 5.15 | 9.095 | 15.92 | 1.79 |
| 8.85 | 8.181 | | |
| **Model D** | | | |
| 0.98 | 9.721 | 1.81 | 1.33 |
| 2.34 | 9.545 | 7.06 | 1.69 |
| 5.16 | 9.035 | 18.10 | 2.33 |
| 8.75 | 7.959 | | |
| **Model E** | | | |
| 1.16 | 9.666 | 0.23 | 0.165 |
| 2.54 | 9.644 | 1.63 | 0.380 |
| 5.45 | 9.508 | 6.51 | 0.80 |
| 9.34 | 9.037 | | |
| **Model F** | | | |
| 1.15 | 9.582 | 0.03 | 0.045 |
| 1.84 | 9.579 | 0.12 | 0.09 |
| 5.44 | 9.470 | 1.17 | 0.27 |
| 9.36 | 9.089 | 5.15 | 0.63 |
| **Model G** | | | |
| 0.94 | 9.724 | 1.56 | 2.29 |
| 1.62 | 9.572 | 3.21 | 2.38 |
| 2.29 | 9.412 | 10.62 | 2.57 |
| 5.07 | 8.691 | 23.05 | 2.98 |
| **Model H** | | | |
| 1.14 | 10.05 | 0.10 | 0.15 |
| 1.82 | 10.04 | 0.20 | 0.15 |
| 2.49 | 10.03 | 1.22 | 0.35 |
| 4.64 | 9.927 | 4.43 | 0.65 |
| **Model I** | | | |
| 1.16 | 9.672 | 0.12 | 0.09 |
| 2.54 | 9.660 | 4.93 | 0.60 |
| **Model J** | | | |
| 1.16 | 9.635 | 0.20 | 0.29 |
| 1.84 | 9.616 | 0.47 | 0.34 |
| 2.53 | 9.590 | 1.98 | 0.46 |
| 5.43 | 9.444 | 5.28 | 0.64 |
| **Model K** | | | |
| 1.16 | 9.665 | 0.09 | 0.13 |
| 1.85 | 9.635 | 0.31 | 0.23 |
| 2.53 | 9.463 | 2.09 | 0.49 |
| 9.23 | 8.874 | 8.18 | 1.01 |
| **Model L** | | | |
| 1.16 | 9.711 | | |
| 1.86 | 9.728 | -0.18 | -0.26 |
| 2.56 | 9.737 | -0.27 | -0.19 |

The ClX mixing ratio (ppb) is the high altitude asymptote of the ClX vertical profile [see Figure 1 of Cicerone, 1981]. The lowest value of ClX in each model group (e.g., 1.14 ppb in model A) resulted from the input fluxes of CH$_3$Cl and CC$_4$ discussed in the text and no CF$_2$Cl$_2$ or CFC$_1$. The highest ClX value in each model group (e.g., 9.36 ppb in model A) resulted from adding input fluxes of 1.5 x 10$^7$ cm$^{-2}$ s$^{-1}$ for CF$_2$Cl$_2$ and 10$^7$ cm$^{-2}$ s$^{-1}$ for CFC$_1$. Ozone changes were calculated by comparing the calculated ozone columns with zero and nonzero CF$_2$Cl$_2$ and CFC$_1$ inputs. The last column to the right is calculated by dividing the total ozone change by the change in ClX starting from zero CF$_2$Cl$_2$ and zero CFC$_1$. If the total-ozone response were linear the entries in the right-hand column within each model group would be equal regardless of ClX. 

ClX, i.e., the value of ClX in that row of the table minus the minimum value for the model group. The lowest value of ClX in each model group resulted from fixed-flux inputs of CH$_3$Cl and CC$_4$ and zero CF$_2$Cl$_2$ and CFC$_1$. Highest values of ClX in each model group, e.g., 9.36 ppb in model A, resulted from full fluxes for CF$_2$Cl$_2$ and CFC$_1$, 1.5 x 10$^7$ and 10$^7$ cm$^{-2}$ s$^{-1}$ for CFC$_1$. Ozone changes were calculated by comparing the calculated ozone columns with zero and nonzero CF$_2$Cl$_2$ and CFC$_1$ inputs. The lowest value of ClX in each model group resulted from fixed-flux inputs of CH$_3$Cl and CC$_4$ and zero CF$_2$Cl$_2$ and CFC$_1$. Intermediate ClX values resulted from portions of these CFC fluxes. Within each model group, fluxes of CH$_3$Cl, CC$_4$, and N$_2$O were held fixed at the value that yielded the desired mixing ratios (listed above) when no CF$_2$Cl$_2$ or CFC$_1$ was present.

If the response of total ozone to added ClX were linear the slopes in the right-hand column of Table 5 would be constant within each model group. Instead, the slopes are functions of ClX, often strong functions varying by factors of 5 or more or even changing sign in models L and M. Figure 2 shows the calculated ozone changes versus ClX for five different models. The responses are all nonlinear. Indeed, model M shows a net column ozone increase for AC1X less than about 3 ppb. The most nearly linear responses are found for models B, C, D, and G (see Table 5), all of which models are characterized by lower (and presently unaccepted) reaction rates for OH (i.e., not the standard rates of Table 3). O$_3$ is reduced at all altitudes for models B, C, D, and G. For model J wherein an altered product distribution (ClX + NO$_2$) is assumed in photolysis of ClXONO$_2$, the ozone response is moderately nonlinear (slope changes by about 100%) for AC1X between 1 and 8 ppb and O$_3$ is reduced above 24 km but increased below 24 km when AC1X = 8.23 ppb. Recently, Marinelli and Johnston [1982]...
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Fig. 1a

Fig. 1b

Fig. 1. Ozone densities (cm⁻³) versus altitude calculated for background stratospheres, Figure 1a (ClX due only to CH₃Cl and CCl₄ inputs) and for ClX-perturbed stratospheres, Figure 1b. The added ClX resulted from steady state input fluxes of CCl₂F₂ and CCl₃F of 1.5 × 10⁻⁷ and 10⁻⁸ cm⁻² s⁻¹, respectively. In Figure 1b, model B, note that O₃ is decreased at all altitudes; model E, O₃ is decreased above 25 km and increased below there and in model M, O₃ is decreased above 24 km but increased below 24 km. See also Figure 3. See Table 4 for distinguishing characteristics of these models.

have presented new evidence that the principal products (over 55%) are Cl and NO₃ in chlorine nitrate photolysis.

Let us look more closely at the effects of adding chlorine to the stratosphere by focusing on two models, one (B) that is nearly linear in its response of column ozone to ClX and model M which is highly nonlinear. Figures 3a and 3b show the calculated change in O₃ versus altitude for these models for three different levels of ClX. The linear scale (i.e., ΔO₃ in units of 10¹¹ cm⁻³) allows one to see that the calculated nonlinear response of the stratospheric ozone column arises from the increase of ozone that appears below about 26 km. Qualitatively, the sequence of events that occur as ClX is increased is clear. First, the decrease in O₃ above 30 km allows more UV light to penetrate to altitudes below 30 km, Wavelengths below 240 nm dissociate O₂, and the ozone production rates increase. Larger UV fluxes (λ < 310 nm) also lead to elevated levels of O(¹D) and thus increased OH and the ratio of HCl/ClO decreases. Further, the higher concentrations of ClO (elevated both by increased ClX and by the OH effect) allow more ClONO₂ to form, thus sequestering more NO₂. Higher ClO also increases the ratio NO₃/NO through reaction No. 60. Many other chemical feedbacks also begin, e.g., CF₂Cl₂, N₂O, etc., are photodissociated more rapidly. Also, as the shape of the O₃ profile changes, vertical fluxes of O₃ change. Accordingly, the extent of ozone healing (increases below 26 or 28 km) must depend on a number of factors.

To see more clearly how the nonlinearities arise requires more detailed analysis. We have examined ozone production and loss processes at several key altitudes. A term-by-term analysis of ozone production and loss terms at 26 km appears in Table 6 for models B and M. Recall from Table 5 that model B gave a nearly linear response and model M was highly nonlinear. Table 6 lists, for four ClX levels in model B and seven ClX levels in model M, the values of the terms 2J₃[O₂], 2k₉₈[ClO][O], 2k₁₁[NO₃][O], 2k₈₈[O][O₃], 2k₂₉[HO₂][O₃], 2J₃₈[HOCI], and 2J₃₉[ClONO₂]/9. The latter two terms represent ozone volume destruction rates (cm⁻³ s⁻¹) due to the catalytic cycles [Wuebbles and Chang, 1981]

\[
\text{OH} + O₃ \rightarrow HO₂ + O₂ \\
\text{Cl} + O₃ \rightarrow ClO + O₂ \\
\text{HO₂} + ClO \rightarrow HOCI + O₂ \\
\text{HOCI} + hv \rightarrow OH + Cl \\
\text{net:} \ 2O₃ + hv \rightarrow 3O₂
\]

and

\[
\text{Cl} + O₃ \rightarrow ClO + O₂ \\
\text{NO} + O₃ \rightarrow NO₂ + O₂ \\
\text{ClO} + NO₂ + M \rightarrow ClONO₂ + M \\
\text{ClONO₂} + hv \rightarrow Cl + NO₃ \\
\text{NO₃} + hv \rightarrow NO + O₂ \\
\text{net:} \ 2O₃ + 2hv \rightarrow 3O₂
\]

The factor 1/9 multiplying 2J₃₉[ClONO₂] arises from the fact that NO₃ photolysis yields NO only 1/9 of the time and NO₂ 8/9 of the time [Magnotta and Johnston, 1980]. The analysis of the seven terms shown in Table 6 is purely diagnostic because

Fig. 2. Calculated percentage decreases in the vertical ozone column between 10 and 80 km for five of the models listed in Table 4, as functions of added ClX. Note that model M shows an ozone increase for ΔClX < 3 ppb and that the ozone decreases shown for model B are half the computed values for convenience of display. Aside from model B, all response curves are markedly nonlinear; see also Table 5.
Models B and M use the standard photochemical and kinetic data of Tables 2 and 3 except as noted in Table 4. Model B (outdated kinetic data) gave a nearly linear response of total stratospheric O₃ to added C1X while model M was highly nonlinear.

Several features of Table 6 should be noted. First, the C1X-induced increase in the O₃ production rate, 2Jl[-Oe-I , is pronounced at 26 km. Second, the reaction NOe + O slows as C1X is added, largely due to the formation of additional C1ONOe. Also, the rates of the ozone-destroying reactions C10 + O and HOC1 + hv increase with C1X but at rates that are more than simple proportionality with C1X would predict. C10 and HOC1 densities increase for several reasons: (a) C1X increases, (b) NOe decreases as more of it is sequestered in C1ONOe, and (c) the increased penetration of UV light to 26 km leads to increased OH, thereby increasing the C10/C1X ratio, and to increased HOe. The increased HOe and C10 lead to increased HOC1 and to HOCI/C1X.

This chain of events occurs in both B and M and similar net changes occur in ozone-production minus ozone-loss terms. For models B and M at 26 km, photochemical production (P) of O₃ exceeds losses (L) for all C1X values. Indeed, P-L increases with C1X in model B and in model M except for the last increase of C1X in model M. While this term-by-term analysis is incomplete because some less important terms have been omitted (e.g., 2k3o[-HO2][O] and 2Jal-NO3[Johnson and Podolske, 1978] it does indicate that an analysis of photochemical terms at a single altitude is not capable of explaining why model B differs from model M and how the nonlinear response of total column ozone originates. An analysis similar to that in Table 6 has been performed including those latter two loss terms for altitudes of 28 and 30 km. For models B and M (P-L) > 0 at all C1X concentrations and P-L increases with C1X.

A clearer view is obtained by considering ozone vertical fluxes. The need for considering the effects of transport should not be surprising because the chemical time constant, τc, for ozone is about 2 weeks at 30 km [McElroy et al., 1974; Prinn et
In model B (wherein O₃ decreases at all altitudes as CIX increases; see Figures 1b and 3a) the flux of O₃ reaching each of these altitudes from above with increasing CIX is 4.0 x 10⁻⁸ cm⁻² s⁻¹ (for about 3 months) at 25 km in an unperturbed stratosphere. These values of τᵥ can be compared with an approximate time constant τᵥ for vertical transport to move air between model grid points (2 km), i.e., τᵥ ≈ 2AZK/K where K may be taken from Table 1. At 28 km τᵥ ≈ 3.6 x 10⁶ s so τᵥ < τᵥ, a situation that suggests a nonlocal analysis. Table 7 presents downward ozone fluxes (10⁻¹⁰ cm⁻² s⁻¹) through the altitudes 29, 27, 25, and 23 km calculated in models B and M. Note that the downward ozone flux increases with decreasing altitude for any CIX concentration in either model (except for model M at 23 km with 1.16 ppb CIX). For comparison, Mahlin et al. [1980] computed a globally averaged downward flux of 5 x 10⁻¹⁰ cm⁻² s⁻¹ at the tropopause. More relevant to the task at hand is the way these calculated fluxes change as CIX increases. In model B, the downward O₃ flux decreases at each altitude as CIX increases, just as O₃ densities behave (see Figures 1b and 3b). In model M the downward O₃ flux at 29 km decreases as CIX increases. At 27 km the downward O₃ flux decreases as CIX increases, but more slowly than at 29 km. At 25 and 23 km, the downward O₃ flux increases as CIX increases from 1.16 to 5.49 ppb, then it decreases with further increases of CIX. This pattern in the downward O₃ flux mirrors that displayed by ozone changes for model M; see Figures 1b and 3b and Table 5.

TABLE 7. Ozone Fluxes (10⁻¹⁰ cm⁻² s⁻¹, downward) Through Four Discrete Altitudes Calculated for Various Values of Stratospheric CIX in Models B and M

| Altitude (km) | Model B, CIX at 50 km (ppb) | Model M, CIX at 50 km (ppb) |
|--------------|-----------------------------|----------------------------|
| 29           | 2.59                        | 2.57                       |
| 27           | 3.28                        | 3.32                       |
| 25           | 3.67                        | 3.71                       |
| 23           | 3.72                        | 3.73                       |

In Table 6, τᵥ = [O₂] / 2J₁[O₃] = about 7.5 x 10⁶ s (or about 3 months) at 25 km in an unperturbed stratosphere. These values of τᵥ can be compared with an approximate time constant τᵥ for vertical transport to move air between model grid points (2 km), i.e., τᵥ ≈ 2AZK/K where K may be taken from Table 1. At 28 km τᵥ ≈ 3.6 x 10⁶ s so τᵥ < τᵥ, a situation that suggests a nonlocal analysis. Table 7 presents downward ozone fluxes (10⁻¹⁰ cm⁻² s⁻¹) through the altitudes 29, 27, 25, and 23 km calculated in models B and M. Note that the downward ozone flux increases with decreasing altitude for any CIX concentration in either model (except for model M at 23 km with 1.16 ppb CIX). For comparison, Mahlin et al. [1980] computed a globally averaged downward flux of 5 x 10⁻¹⁰ cm⁻² s⁻¹ at the tropopause. More relevant to the task at hand is the way these calculated fluxes change as CIX increases. In model B, the downward O₃ flux decreases at each altitude as CIX increases, just as O₃ densities behave (see Figures 1b and 3b). In model M the downward O₃ flux at 29 km decreases as CIX increases. At 27 km the downward O₃ flux decreases as CIX increases, but more slowly than at 29 km. At 25 and 23 km, the downward O₃ flux increases as CIX increases from 1.16 to 5.49 ppb, then it decreases with further increases of CIX. This pattern in the downward O₃ flux mirrors that displayed by ozone changes for model M; see Figures 1b and 3b and Table 5.

As noted above, no such complicated pattern arises in Model B where the downward O₃ flux decreases with added CIX at all altitudes, there is less incoming O₃ at all altitudes below 29 km (see Table 7) and O₃ concentrations are decreased there (see Figures 1b and 3a). In our model M, O₃ is decreased above 30 km as one adds CIX and O₃ decreases below there (first (see Figure 3b) largely due to the behavior of the downward O₃ flux (Table 7). As CIX increases further, the crossover altitude where ΔO₃ = 0 moves downward. The downward movement of this crossover altitude is largely explained, at least in a one-dimensional (1-D) model, by the sign of the change in the downward O₃ flux (see Table 7) at each altitude as CIX increases.

The possibility of a strongly nonlinear response of the stratospheric ozone column to added chlorine has important consequences for ozone trend detection. In Figure 4, we plot the calculated change in [O₃] dz for the years 1970–2140. The calculated ozone column changes arise from predicted CIX values published previously by Logan et al. [1978] (and extrapolated here beyond A.D. 2100). In particular, we adopted case B2 of Logan et al. wherein future CIX levels are due to stated future emission rates of CCl₂F₂, CCl₃F, and CH₃CCl₃. We show two model calculations of ΔO₃, models M and N, that result from the CIX versus time curve. As shown in Table 4, a fast k₁₂ (rate of formation of ClONO₂) is adopted in model M and a slow rate, about one-fourth as fast is adopted for k₁₂ in model N. The NASA/JPL [1982] critical review of chemical rate constants states that both of these choices for k₁₂ are presently acceptable, although in reality the true rate is either the fast rate or the slow rate, and not their average. If the fast rate applies, our model finds that ozone increases slowly until about A.D. 2010 and then ozone decreases rapidly with further increases of CIX. Table 5 shows that the total ozone decrease attained at CIX = 9.38 ppb (or ΔCIX = 8.23 ppb) is 6.78% in model M. In model N, total ozone decreased by 8.95% in going to CIX = 9.12 ppb (ΔCIX = 7.96 ppb).

The small, but potentially important, O₃ increases shown for model M in Table 5 and Figure 4 and for model L in Table 5 are not due to numerical inaccuracy in our model as three facts indicate. First, our numerical convergence criterion, that each variable must converge to better than 10⁻³ at each spatial grid point before terminating the iteration (see appendix), forces the
converged solution for the O₃ vertical profile to be at least this accurate. Even if the O₃ density at each altitude were systematically in error in the same direction (highly unlikely), the O₃ column would be in error by less than 1/1000. Table 5 shows that ozone increases of 2.5 parts in 1000 are calculated in model M, larger increases than our maximum possible numerical error. In practice, errors at one altitude should partially cancel those at another altitude, and the column integral would be more accurate. Second, we repeated certain calculations for model M but with a convergence criterion 10 times stricter (i.e., 10⁻⁴), and we found an ozone column (above 10 km) identical through four decimal places to that found earlier. Both in total O₃ column and O₃ densities at individual altitudes the stricter convergence criterion led to nearly identical results through four decimal places. At only three altitudes out of 36 did the calculated O₃ density differ by as much as one unit in the fourth decimal place. Finally, as was mentioned earlier, we found similar nonlinearities in the O₃ response to ClX with the chemical family approach model of Liu et al. [1976].

Vertical profiles of several key gas concentrations are shown in Figures 5 and 6. These profiles were calculated through the fully time-dependent model described in section 2 and the appendix. Figure 5a shows noontime concentrations of OH, HO₂, ClO, HOCl, and HCl versus altitude calculated with the standard photochemical data specified in Tables 2 and 3 (i.e., model E of Table 4) with ClX = 2.44 ppb at 50 km. Figure 5b shows noontime concentrations of these species calculated with the photochemical data specified by model M of Table 4 and 2.56 ppb ClX. Compare the values for the Cl-containing species: relative to Figure 3a, the ClO concentrations in Figure 3b are 0.73, 0.82, 1.10, and 1.15 at 26, 30, 40, and 44 km, respectively, when ClX values are normalized to 2.56 ppb. Corresponding relative concentrations for HOCl are 0.77, 0.87, 1.09, and 1.14. For HCl they are 0.67, 0.68, 0.91, and 0.95. The high-altitude increases in ClO are clearly due to the higher value of k₆₇ used in model M. An interesting feature of Figure 5b is the local minimum in HCl near 30 km. It results from use of the NASA/JPL fast rate for k₇₂ and the new, faster value for k₆₇ in model M. Such a minimum has been observed in total acidic chlorine measurements of Lazrus et al. [1977]. When one adds calculated HCl and HOCl values one finds a much less pronounced, gentle local minimum just below 30 km. Although contributions to stratospheric ClX from CH₃CCl₃, C₂F₃Cl₃, and several other minor species are neglected in these diurnal calculations, the ClX value (2.56 ppb) for which these calculations apply is close to what is calculated for 1982 when all known sources are included [see e.g., Wuebbles et al., 1983]. In the present calculation this was accomplished by adjusting the lower boundary fluxes of CF₂Cl₂ and CFCl₃.
Figures 6a and 6b show calculated vertical profiles of HOCI, ClONO$_2$, and HNO$_x$ for time of ground sunset, Figure 6a for model E and Figure 6b for model M. In the calculation, ClONO$_2$ increases further to 0.86 ppb at 30 km by time 1830. These profiles are displayed because as is apparent in Table 5, the stratospheric ozone response is sensitive to the differences in chemical rate constants between model E and M as are the profiles of these species, and none of the species HOCI, ClONO$_2$, and HNO$_x$ has been measured or positively detected in the stratosphere at this writing.

Calculations have also been performed to simulate the effects of increasing atmospheric N$_2$O concentrations. In these calculations the input flux of N$_2$O was increased above the value needed to sustain a 300 ppb mixing ratio at 10 km. With all standard rate constants except for the new, faster $k_{57}$ (i.e., model K) increasing the N$_2$O input flux by 50% led to a 5.27% total ozone decrease. With $k_{72}$ twice as fast (i.e., model M) total ozone decreased 5.56% and with the slow rate of ClONO$_2$ formation (i.e., model N) total ozone decreased 5.04%. These calculations with 150% normal N$_2$O flux inputs lead to N$_2$O mixing ratios of 440 ± 3 ppb at 10 km. The calculations took fixed fluxes of CH$_3$Cl, CCl$_4$, CF$_2$Cl$_2$, and CFCl$_3$; ClX began at about 2.52 ppb and dropped to about 2.42 ppb as N$_2$O increased. When the ClX background was raised to 5.3 ppb and the N$_2$O flux subsequently increased by 50%, the added N$_2$O led to total ozone decreases of 3.05, 3.38, and 2.85% for models K, M, and N rate constants, respectively. Further calculations were performed to examine the linearity of the O$_3$ response to added N$_2$O. The input flux of N$_2$O was varied between the value needed to produce 300 ppb N$_2$O at 10 km in an unperturbed atmosphere to flux values 1.2, 1.5, and 2.2 times larger. With near-present ClX background, i.e., 2.52 ppb, a slight nonlinearity appeared in the sense that the percentage ozone loss per ppb of added N$_2$O decreased as N$_2$O increased. At higher, presumably future levels of stratospheric ClX (5.3 ppb), the nonlinearity switched sense (i.e., the O$_3$ loss per unit of added N$_2$O increased).

The corresponding increased production of stratospheric NO and downward flux of odd nitrogen into the troposphere would tend to increase the tropospheric odd nitrogen. This may in turn increase tropospheric ozone.

4. Discussion and Conclusion

In this report we have shown that a distinctly nonlinear response of the stratospheric ozone column to chlorine injections is likely, or at least, this is the response predicted by our updated 1-D photochemical models. Specifically, Table 5 and Figure 2 showed that the sensitivity of total stratospheric ozone to added ClX, $\Delta O_3/\Delta ClX$, is a strong function of ClX, especially in the range of $1 < ClX < 4$ ppb, or $0 < ClX < 3$ ppb, where $\Delta ClX$ is the ClX not attributable to CH$_3$Cl and CCl$_4$. The only model calculations that showed weak or moderate nonlinearities were those that employed out-of-date rate constants for OH + HNO$_3$, CH$_3$OH + HNO$_3$, and CH$_3$OH + HO$_2$ or which assumed that ClONO$_2$ + h$\nu$ → ClO + NO$_2$, products not deduced in the NASA/JPL [1982] critical review. Given that the present ClX mixing ratio (at 50 km) is now approximately 2.5 ppb (i.e., $\Delta ClX = 1.4$ or 1.5 ppb) and that ClX = 4 ppb (or $\Delta ClX$ about = 3 ppb) is not predicted to be attained until A.D. 1995 or 2000 [Logan et al., 1978; Cicerone, 1981], the problem of ozone trend assessment takes on a new complexity. If our calculations are accurate (see caveats below), then CFM-induced stratospheric ozone depletions of order 1% will not materialize until after A.D. 2000 when ClX reaches 5 ppb or more. This latter figure comes from Table 5, models K, L, M, N, the models with presently most credible rate constants for chemical reactions. Further, as is shown in Figure 2 and Table 5, $\Delta O_3/\Delta ClX$ becomes very strongly negative for ClX > 5 ppb so that the rate of ozone decrease in the early 21st century could accelerate greatly. Eventual ozone column reductions due to continued release of CCl$_3$F and CCl$_2$F are estimated to lie between 6.8 and 9.0% assuming a new, faster rate for OH + HCl → H$_2$O + Cl from M. J. Molina (private communication, 1982).

The nonlinearities evident in our results arose from an essentially controlled numerical experiment in which (1) a fixed CH$_4$ mixing ratio was assumed at 10 km, (2) fixed fluxes of N$_2$O, CH$_3$Cl, and CCl$_4$ were input at 10 km, and (3) stratospheric CO$_2$ and temperature were held constant. In reality, all of these factors appear to be varying; see discussion and references in section 1. Further, and very important for ground-based total ozone-column trend assessment, secular trends in tropospheric ozone are possible [see, e.g., Liu et al., 1980]. A 10% change in tropospheric O$_3$ is about a 1% change in total ozone. The present calculations do predict large future decreases in O$_3$ concentrations near 40 km altitude, however, as did previous calculations.

The possibility of small stratospheric ozone-column increases cannot be eliminated. Indeed our calculations (models L and M) found this kind of result for ClX < 3 or 4 ppb when the rate of formation, $k_{57}$, of ClONO$_2$ (chlorine nitrate) was set equal to the faster of the two rates in NASA/JPL [1982]. With the slower rate for $k_{57}$, i.e., one-fourth the fast rate, no ozone increases were calculated nor were they when an intermediate rate (standard rate in Table 3) was assumed. Accordingly, it appears very important to (1) settle the issue of possible isomer formation in ClO + NO$_2$ + M → products and to determine the rate of formation of ClONO$_2$ at stratospheric pressures and temperatures, and (2) obtain quantitative measurements of stratospheric ClONO$_2$. Many other photochemical processes, e.g., the products of HNO$_4$ photodissociation need further investigations.

Our results do not depend on model assumptions such as chemical family groupings or on the exact choice of $K(z)$, the eddy-diffusion coefficient. More rigorous calculations with models that embody stratospheric dynamical meteorology are clearly needed, however. Also, while it is well known that the efficiency of ozone destruction by chlorine atoms is an increasing function of altitude [Cicerone et al., 1974; Wuebbles, 1983] and that the stratosphere of the future will receive Cl atoms from an increasingly wide spectrum of chlorocarbons and chlorofluorocarbons, our present results will not be very sensitive to changes in this input-species spectrum. Further, our small adjustment to O$_3$ cross sections in the Herzberg continuum (see section 2) did not affect the nonlinear character of the O$_3$ response to ClX. If present-day stratospheric ClX concentrations greatly exceed the commonly believed 2.5 ppb the total ozone response to added ClX could differ greatly from that shown in Figure 4 because of the strong dependence of $\Delta O_3/\Delta ClX$ on ClX shown in Figure 2 and Table 5.

Finally, our calculated loss of total stratospheric O$_3$ due to 50% increases in upward N$_2$O fluxes from the troposphere are about 5% when background ClX is near presently assumed values (2.5 ppb) and near 3% if ClX grows to 5.3 ppb. Small nonlinearities were observed in the ozone response to increases in N$_2$O levels.
APPENDIX. NUMERICAL METHODS

The analytic, one-dimensional, steady state system of continuity equations for gas-phase atmospheric trace constituents is

\[ \frac{d\Phi}{dz} = Q(z, f) \quad (1a) \]

\[ \Phi = -KN \frac{df}{dz} \quad (1b) \]

\[ \hat{Q}(z, \hat{f}) = \hat{P}(z, \hat{f}) - \hat{L}(z, \hat{f}) \quad (1c) \]

where

\[ \hat{f} = (f_1, \ldots, f_k)^T; \]

\[ f(z) \text{ trace species mixing ratio vector (length } k \text{ for } k \text{ species);} \]

\[ \hat{Q}(z) \text{ flux vector;} \]

\[ K(z) \text{ eddy diffusion scalar;} \]

\[ N(z) \text{ total atmospheric density scalar;} \]

\[ \hat{Q}(z, \hat{f}) \text{ vector of photochemical forcing;} \]

\[ \hat{P}(z, \hat{f}) \text{ vector of photochemical production;} \]

\[ \hat{L}(z, \hat{f}) \text{ vector of photochemical loss;} \]

\[ z \text{ vertical spatial coordinate (} z_t < z < z_u) \]

with attendant boundary conditions for each species in one of the following forms:

\[ -KN \frac{df}{dz} \bigg|_{z_u} = g_i(z_u, f(z_u)) \quad (1d) \]

\[ g_i(z_u, f(z_u)) = 0 \quad (1e) \]

where

\[ z_u = z_i \quad z_u \]

Condition (1e) for species \( i \) must explicitly include \( f_i \). We solve system (1) in a two-phase process. First, the self-adjoint flux-divergence term is replaced with a standard, centered finite difference approximation:

\[ \frac{d}{dz} \left( KN \frac{df}{dz} \right)_{z_j} = \frac{(KN)_{j+1/2}}{\Delta z_j + \Delta z_{j+1}} \times \hat{f}_{j+1} - \frac{(KN)_{j-1/2}}{\Delta z_j + \Delta z_{j+1}} \times \hat{f}_{j-1} \quad (2) \]

for \( j = 0, 1, \ldots, J \) where \( \hat{f}_{j} \) is a discrete solution vector at \( z_j \) \((j = 0, J), \Delta z_j = z_j - z_{j-1} (j = 1, J), (KN)_{j+1/2} = KN|z_j + \frac{1}{2} \Delta z_{j+1}, (KN)_{j-1/2} = KN|z_j - \frac{1}{2} \Delta z_j \).

Approximation (2) is second order (first order) accurate on a uniform, (nonuniform) spatial grid, respectively. Flux boundary conditions, type (1d), are transformed via

\[ KN \frac{df}{dz} \bigg|_{z_0} = \frac{1}{2} \left\{ KN \frac{df}{dz} \bigg|_{z_0} + KN \frac{df}{dz} \bigg|_{z_{-1/2}} \right\} \]

\[ = \frac{1}{2} \left[ KN \times \hat{f}_{j,0} - \hat{f}_{j,-1/2} + KN \right] \Delta z_0 \]

\[ \times \hat{f}_{j,-1/2} - \hat{f}_{j,0} \Delta z_0 \quad (3) \]

where \( j_0 = 0; J \) and \( \Delta z_0 = \Delta z_1; \Delta z_{J-1} \).

Analogous (2) and (3) are combined to yield a nonlinear system of algebraic equations for the solution vector \( \hat{f} \). This system can be written as

\[ F(\hat{f}) = T \times \hat{f} + G(\hat{f}) = 0 \quad (4) \]

where \( \hat{f} \) is a discrete solution vector, \( F = \text{vector of nonlinear equations, } G = \text{vector of discrete photochemistry forcing, } T = \text{matrix containing discrete representation of the flux divergence operator with boundary conditions.} \)

All vectors in (4) contain \( k \times (J + 1) \) components and are organized in the following manner:

\[ \hat{f} = (f_1, \ldots, f_k) \quad \hat{f}_0^T \]

\[ \hat{f}_0 = (f_1, \ldots, f_k) \quad \hat{f}_0^T \]

In this representation each subvector \( \hat{f} \) represents a discrete approximation to the \( k \) analytic-solution variables at altitude \( z_j \). For convenience, in photodissociation calculations the spatial grid is mapped from top down (i.e., \( z_0 = z_u; z_j = z_t \)). The flux boundary-condition approximation, although non-standard, is designed to force numerical conservation of the discrete equations. When the continuity equation for a compound with flux boundary conditions is numerically integrated via the trapezoidal rule, the discrete solution will give exact numerical conservation.

Completing the solution process, system (4) is iterated via a modified Newton-Raphson scheme until acceptable convergence. A relative error criterion is applied, in a max-norm sense, to the solution vector \( \hat{f} \) in that the Newton-Raphson stepsize is constrained to be less than a given epsilon of the current discrete approximation. Additionally, \( F \) must be reduced over the entire iterative process. In our simulations we use an epsilon equal to \( 10^{-3} \). As one test of overall accuracy, we have repeated certain calculations with \( e = 10^{-4} \) as discussed in the text. To enhance efficiency, the Jacobian matrix in the Newton-Raphson scheme is updated only when internal checks signal convergence difficulty. Every effort has been taken to vectorize the main program for operation on the CRAY 1A. Furthermore, essential subroutines to decompose the banded Jacobian and solve for the iteration step are encoded in near optimal CRAY assembly code. This has resulted in worst-case chemical simulations requiring at most one CPU second on the CRAY 1A.

In our steady state simulations we solve for 32 discrete mixing ratios at 36 spatial grid points, thereby yielding a vector system (4) of length 1152.

The time-dependent simulation exactly parallels the development of the steady state case. All spatial operator approximations in the analytic equation and boundary conditions are identical. However, the analogous system to equation (4) now represents the following system of ordinary differential equations:

\[ \vec{N} \times \frac{df(t)}{dt} = T(t) \times \hat{f}(t) + G(t, \hat{f}) \quad (5) \]

All vectors and matrices are as defined in equation (4) with additional dependence on the temporal variable \( t \). Furthermore, \( \vec{N} \) is a block diagonal matrix of order \( J + 1 \) of total atmospheric density. Each diagonal block matrix is a diagonal matrix of order \( k \) wherein each entry is the total atmospheric density at altitude \( z_j \).

We solve system (5) by applying the second-order exponential fitting scheme of Liniger and Willoughby [1970] at a fixed partition of a diurnal cycle. In our adaption of the exponential fitting, we determine the basic coefficients by fitting.
TABLE 8. Boundary Conditions for Each of the 32 Species Calculated in the Steady State, 24-hour Averaged Model

| Species | Upper Boundary Conditions | Lower Boundary Conditions |
|---------|---------------------------|---------------------------|
| H2O     | \( \text{flux} = J_{14}[\text{H}_2\text{O}][\text{H}] \) | MR (3.0 ppm) |
| HCl     | \( \text{flux} = J_{14}[\text{HCl}][\text{H}] \) | [HCl] = 0.9925 x OCF/v |
| H2      | MR(0.76 ppm) | MR(1.60 ppm) |
| CO      | \( \text{flux} = J_{14}[\text{CH}_4][\text{H}] \) | MR(0.5 ppm) |
| N2O     | \( \text{flux} = J_{14}[\text{N}_2\text{O}][\text{H}] \) | flux \( \approx 1.4 \times 10^6 \) adjustable, see text |
| CH3Cl   | \( \text{flux} = J_{14}[\text{CH}_3\text{Cl}][\text{H}] \) | flux \( \approx 10^6 \) adjustable, see text |
| CCl4    | \( \text{flux} = J_{14}[\text{CCl}_4][\text{H}] \) | flux \( \approx 1.3 \times 10^6 \) adjustable, see text |
| CClF    | \( \text{flux} = J_{14}[\text{CCl}_3\text{F}][\text{H}] \) | 0 \( \leq \text{flux} \leq 10^7 \), see text |
| CCl3F2  | \( \text{flux} = J_{14}[\text{CCl}_3\text{F}_2][\text{H}] \) | 0 \( \leq \text{flux} \leq 1.5 \times 10^7 \), see text |
| CH3O    | PCE | PCE |
| O       | \( \text{flux} = 1.4 \times 10^{10} \) | \( \text{flux} = -[\text{O}_3]/v \) |
| O2      | \( \text{flux} = -9.1 \times 10^{10} \) | \( \text{flux} = -[\text{O}]/v \) |
| NO, NO2 | flux = 0 | \( \text{flux} = -[x]/v, x = \text{N, NO, NO}_2 \) |
| NO3, N2O | flux = 0 | \( \text{flux} = -[y]/v, y = \text{NO}_3, \text{N}_2\text{O} \) |
| HNO3, HNO4 | flux = 0 | \( \text{flux} = -[z]/v, z = \text{HNO}_3, \text{HNO}_4 \) |
| Cl      | PCE | PCE |
| CI      | \( \text{flux} = -J_{14}[\text{HCl}][\text{H}] \) | flux \( \approx 7.5 \times 10^{-3} \text{OCF}([\text{Cl}],[\text{ClO}]_3) \), iterative |
| CH3, CH2O, CH3O2 | PCE | PCE |
| CH3OOH, CH2O | PCE | PCE |

Fluxes are in units of molecules/cm²/s and are positive upward. v = 0.3 cm/s. MR means fixed mixing ratio. OCF, the organic chlorine flux, = \[2\phi_{\text{CCl}_4} + 3\phi_{\text{CCl}_3\text{F}} + 4\phi_{\text{CH}_3\text{Cl}} + \phi_{\text{CH}_3\text{O}} \] where \( \phi \) is the upward flux at the lower boundary. \( \text{ClO}_3 = \text{Cl} + \text{ClO} + \text{HOCI} + \text{ClONO}_2 \). It is the scale height for each individual species at the upper boundary, 80 km. PCE means photochemical equilibrium.

Convergence is determined in exactly the same manner as the steady state algorithm. Specifically, the convergence parameter epsilon is \( 10^{-3} \). In the diurnal simulations, we solve for 23 boundaries.

TABLE 9. Boundary Conditions for Each of the 23 Species Calculated in the Time-Dependent Diurnal Model.

| Species | Upper Boundary Conditions | Lower Boundary Conditions |
|---------|---------------------------|---------------------------|
| HCl     | \( \text{flux} = J_{14}[\text{HCl}][\text{H}] \) | \( \text{flux} = 0 \) |
| H2O     | \( \text{flux} = J_{14}[\text{HCl}][\text{H}] \) | \( \text{flux} = 0 \) |
| O3      | \( \text{flux} = -[\text{O}_3]/v \) | \( \text{flux} = -[\text{O}]/v \) |
| O       | \( \text{flux} = -[x]/v, x = \text{N, NO, NO}_2 \) | \( \text{flux} = -[y]/v, y = \text{NO}_3, \text{N}_2\text{O} \) |
| NO, NO2 | \( \text{flux} = -[z]/v, z = \text{HNO}_3, \text{HNO}_4 \) | \( \text{flux} = -[\text{Cl}][\text{ClO}_3] \), iterative |
| Cl      | \( \text{flux} = -J_{14}[\text{HCl}][\text{H}] \) | \( \text{flux} = -[\text{Cl}][\text{ClO}_3] \), iterative |
| CH3, CH2O, CH3O2 | PCE | PCE |
| CH3OOH, CH2O | PCE | PCE |

All symbols are the same as listed in Table 8.
discrete variables at 36 spatial grid points. The diurnal temporal cycle is partitioned into 35 nonuniform temporal steps ranging from 2 min to 2 hours. A typical 12 day simulation of this system takes roughly 70 CPU seconds on the CRAY 1A.

Boundary conditions for the 32 species calculated in the steady state, 24-hour averaged model are shown in Table 8, and for the 23 species calculated in the time-dependent diurnal model are shown in Table 9. In both programs the species HCO, O3(D), and CIO are calculated from photochemical equilibrium equations at all spatial grid points and times. In the time-dependent calculation, the total downward flux of O3, (O and O3) at the upper boundary (80 km) integrated over a 24-hour period equals 10.5 × 10^-11 cm^-2 s^-1 as in the 24-hour averaged model (see Table 8). In the time-dependent calculation, it is approximated as follows: the O3 flux is a sinusoidal function with period 24 hours. In the day, all the flux is in O atoms; the function g(t) peaks at noon. At sunset the O atom flux decreases with an e folding time of 4.5 hours; h(t) = [flux of O3] × exp [-(t - 1800 h)/4.5]. The O3 flux is zero at 1800 hours and rises with an e folding time of 4.5 hours. Its flux = f(t) = [O3 flux] × [1 - exp (-(t - 1800 h)/4.5)].

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