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YIELDS $\text{HCl} + \text{HCO}$: DECREASED SENSITIVITY OF
STRATOSPHERIC OZONE TO CHLORINE
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The Reaction $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$: Decreased Sensitivity of Stratospheric Ozone to Chlorine Perturbations

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SENSITIVITY OF STRATOSPHERIC OZONE TO
CHLORINE PERTURBATIONS

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ABSTRACT

The absolute rate constant for the reaction $\text{Cl} + \text{H}_2\text{CO} \rightarrow \text{HCl} + \text{HCO}$ has been determined by the flash-photolysis-resonance fluorescence method to be $7.5 \pm 0.9 (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 298K and to have a negligible temperature dependence. This rate which is more than 2000 times faster than the rate of $\text{Cl} + \text{CH}_4$ indicates that formaldehyde (H_2CO) will compete significantly with methane (CH_4) for the conversion of active chlorine in the stratosphere to the inactive reservoir HCl. Chlorine will thus be a less efficient destroyer of stratospheric ozone than previously believed. Ambient stratospheric ozone will depend less on the ambient chlorine amount and the predicted response to chlorine perturbations will be lessened. One-dimensional eddy-diffusion photochemical model calculations indicate a factor of 1.1 less sensitivity to chlorine than recently reported. For a steady-state CFM release at 1975 rates (750,000 tons/year) the eventual ozone depletion is now calculated to be 14%.

H. Niki (personal communication) has recently measured the rate constant of Cl atoms with formaldehyde (H_2CO) relative to that of Cl atoms with ethane (C_2H_6). Since the rate constant for the ethane reaction is well characterized by direct methods (Manning and Kurylo, 1977), Niki's inferred room temperature value for the reaction



is $k_1 = 7.8 \pm 0.6 (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at $T=298\text{K}$. Furthermore, by comparison with $\text{Cl} + \text{C}_2\text{H}_6$, reaction (1) should have a negligible temperature dependence.

The specific purpose of this letter is to: (a) report on a direct measurement of the rate of reaction (1); (b) confirm, also through direct measurement, that (1) has negligible temperature dependence; and (c) show that stratospheric model calculations including (1) yield significantly lower sensitivity to chlorine perturbations.

The kinetic experiments were performed as described previously (Whytock et al., 1977 and Lee et al., 1977) by the flash-photolysis-resonance-fluorescence method. The results of 42 experiments at $T=298\text{K}$ give $k_1 = 7.5 \pm 0.9 (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. To date a partial study at $T = 200\text{K}$ of 15 experiments gives a preliminary value of $k_1 = 7.8 \pm 1.2 (2\sigma) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. To within the experimental uncertainty these results indicate no evidence for a temperature dependence. Thus, for stratospheric model calculations these results plus those of Niki indicate that a value of $7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ independent of temperature is appropriate.

Implications for Stratospheric Chemistry

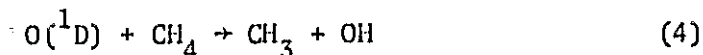
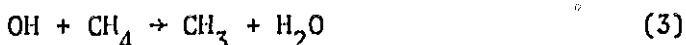
The role of (1) is to remove catalytically active chlorine (Cl + ClO) to the temporary inactive reservoir HCl. The primary reactions by which this transformation is accomplished in present stratospheric models are



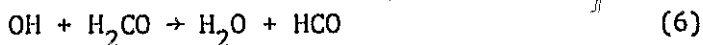
which have recommended rate constants of $7.3 \times 10^{-12} e^{-1260/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ respectively (see Hudson, 1977). At $T = 250\text{K}$, appropriate to ~ 40 km in the stratosphere where ozone is most sensitive to chlorine, k_{2a} is $4.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ or almost 2000 times slower than k_1 while k_{2b} is about a factor of 2 slower. Thus H_2CO concentrations of the order of 10^{-3} of the CH_4 concentration will have a significant effect on the chlorine chemistry of the stratosphere. Since CH_4 concentrations in the 40 km region are a few tenths of a part per million by volume (ppmv) (Ehhalt et al., 1972, Ackerman, et al., 1977), H_2CO concentrations of only a few tenths of a part per billion by volume (ppbv) would be significant. At 40 km this corresponds to about $2 \times 10^7 \text{ molecules cm}^{-3}$. The H_2CO concentration has never been measured in the stratosphere but several model calculations have yielded concentrations well within the above significant range.

Using values of some key parameters from the Goddard Space Flight Center one-dimensional-steady-state photochemical model the effect of reaction (1) on the chlorine cycle can be demonstrated by some simple algebraic manipulations. These estimates will then be compared with a complete numerical model calculation.

Formaldehyde is likely to be formed in a one-to-one correspondence with every molecule of methane that is oxidized (see e.g. Levy, 1972; Crutzen, 1973; Wofsy et al., 1973). Thus, its production rate can be estimated by knowing the methane destruction rate. The dominant methane destruction reactions in the stratosphere are



where $k_3 = 2.3 \times 10^{-12} e^{-1710/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_4 = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. At 40 km the volume methane destruction rate and hence the formaldehyde production rate is $k_{2a}[\text{Cl}][\text{CH}_4] + k_3[\text{OH}][\text{CH}_4] + k_4[\text{O}({}^1\text{D})][\text{CH}_4]$ which is approximately $(3 \times 10^5 \cdot 4.7 \times 10^{-14} + 1.7 \times 10^7 \cdot 2.5 \times 10^{-15} + 2 \times 10^2 \cdot 1.3 \times 10^{-10}) \cdot 2 \times 10^{10}$ or 1600 molecules $\text{cm}^{-3} \text{ sec}^{-1}$ at 40 km. Formaldehyde is destroyed in the stratosphere by 4 major processes; reaction (1) plus



At 40 km, $J_5 \sim 10^{-5} \text{ sec}^{-1}$, $k_6 \sim 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, $k_7 \sim 6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $k_1 = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Approximate diurnal average concentrations in molecules cm^{-3} at 40 km are $[\text{OH}] = 1.7 \times 10^7$, $[\text{O}] = 7.5 \times 10^8$ and $[\text{Cl}] = 3 \times 10^5$. Thus the loss frequencies for these reactions are:

$$(1) 3 \times 10^5 \times 7.5 \times 10^{-11} \sim 2.3 \times 10^{-5}$$

$$(5) 1 \times 10^{-5}$$

$$(6) 1.7 \times 10^7 \times 1 \times 10^{-11} \sim 17 \times 10^{-5}$$

$$(7) 7.5 \times 10^8 \times 6 \times 10^{-14} \sim 4.5 \times 10^{-5}$$

The total loss frequency is about 25×10^{-5} yielding a formaldehyde concentration of about $1600 / (25 \times 10^{-5}) = 6.4 \times 10^6$ molecules cm^{-3} .

This is somewhat smaller than would have been obtained ignoring reaction (1) and represents a smaller feedback on the direct effect on chlorine chemistry. This concentration is about 1/2000 of CH_4 and reaction (1) can thus be expected to compete effectively with reactions (2).

The effect on the ratio of active chlorine to HCl can now be examined. The loss frequency of Cl atoms for reaction (2a) is $2 \times 10^{10} \cdot 4.7 \times 10^{-14} = 9.4 \times 10^{-4} \text{ sec}^{-1}$ while that for (2b) is $3.2 \times 10^7 \cdot 3 \times 10^{-11} = 9.6 \times 10^{-4} \text{ sec}^{-1}$. For reaction (1) the loss frequency is $6.4 \times 10^6 \times 7.5 \times 10^{-11} = 4.8 \times 10^{-4} \text{ sec}^{-1}$. Thus ignoring reaction (1), $[\text{Cl} + \text{ClO}] / [\text{HCl}]$ is proportional to $1 / (19 \times 10^{-4})$ while inclusion of (1) gives $[\text{Cl} + \text{ClO}] / [\text{HCl}]$ proportional to $1 / (23.8 \times 10^{-4})$ a decrease of a factor of 1.25. The corresponding decrease in $[\text{ClO}] / [\text{ClX}]$ is a factor of 1.13. This approximate analysis is borne out by the complete model calculations which include methane oxidation chemistry using the Goddard Space Flight Center 1D - Steady-state model. The calculations show a decrease in the predicted steady-state CFM effect on the ozone column by a factor of 1.12, i.e. from 15.9% to 14.0%.

Figure 1 shows results from the model for column ozone changes (above ground level) due to injections of chlorine by CFM's as a function of the asymptotic value of the added ClX. The model behaves in essentially the same fashion with or without the inclusion of reaction (1) except that the sensitivity to added ClX is reduced by an amount depending on the value of the reaction rate. All of these deductions depend on

the accuracy with which formaldehyde concentrations can be calculated. Sensitivity studies (Butler, 1978) can be used to calculate the uncertainty bounds due to the imprecision in the measurement of the known atmospheric processes upon which formaldehyde concentrations depend. Figure 2 shows resultant 2σ bounds on H_2CO concentration where most of the uncertainty comes from the production and destruction processes for H_2CO and the reactions which determine OH concentrations. Because of the dependence on the very uncertain HO_x chemistry, significant uncertainties are found to exist in H_2CO , about a factor of 3 on either side. Thus the impact of reaction (1) on the sensitivity of a stratospheric model to ClX perturbations may be either greater or lesser than shown above.

Discussion and Conclusion

The most important implication of the fast rate for (1) is the reduction in model predictions of chlorine perturbations of stratospheric ozone. Since Molina and Rowland (1974) first pointed out the potential effect of continued chlorofluoromethane (CFM) release, numerous studies have been made including a National Research Council Panel (NRC, 1976) and a NASA workshop (Hudson, 1977). The standard measure of the magnitude of the effect that has developed is the model-predicted global average column ozone change when the 1973 release rates (or 1975 which are about the same) are continued indefinitely. This number has fluctuated with new cross section measurements, reaction rate measurements and model improvements but has generally remained within the bounds of 7% to 16%. Before the NAS report the steady-state ozone change was

generally agreed to be around 13%. The inclusion of chlorine nitrate (see Rowland et al., 1976) in the NAS report reduced the number to around 7%. Just before the NASA report, Howard and Evenson (1977) reported a much faster rate for $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ which along with many other minor changes raised the predicted ozone depletion to as high as 16% in many models. The inclusion of reaction (1) in our model is now found to reduce this number from 16% down to about 14%. If uncertainties are resolved such that H_2CO concentrations are significantly larger than presently calculated, then a larger reduction in the CFM perturbation will be deduced. Measurement of the stratospheric concentration of H_2CO would contribute significantly to the resolution of this uncertainty.

Other relatively stable members of the hydrocarbon oxidation chains should also be examined for their reaction with Cl atoms and their possible reduction in the sensitivity of column ozone to ClX injections.

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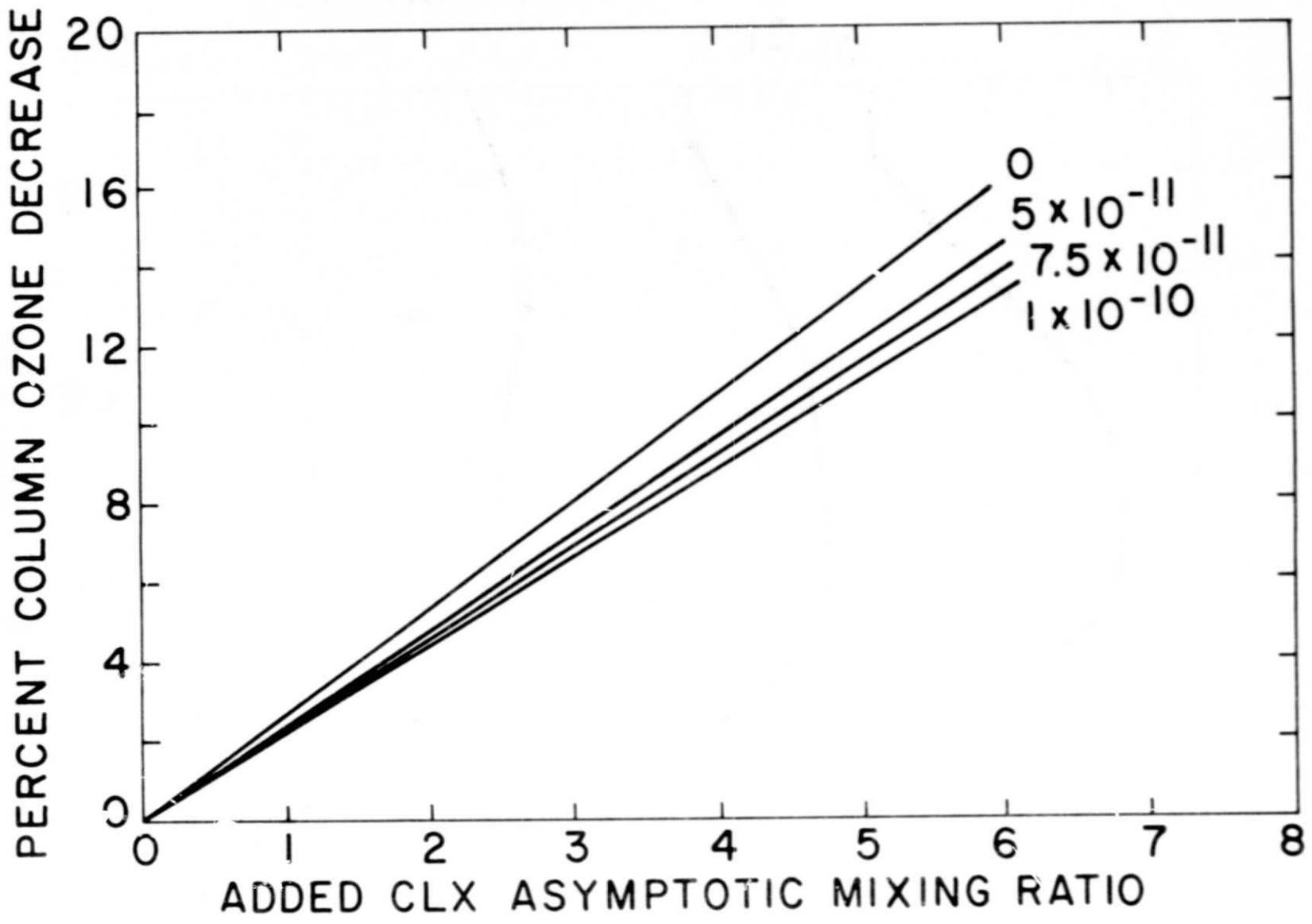
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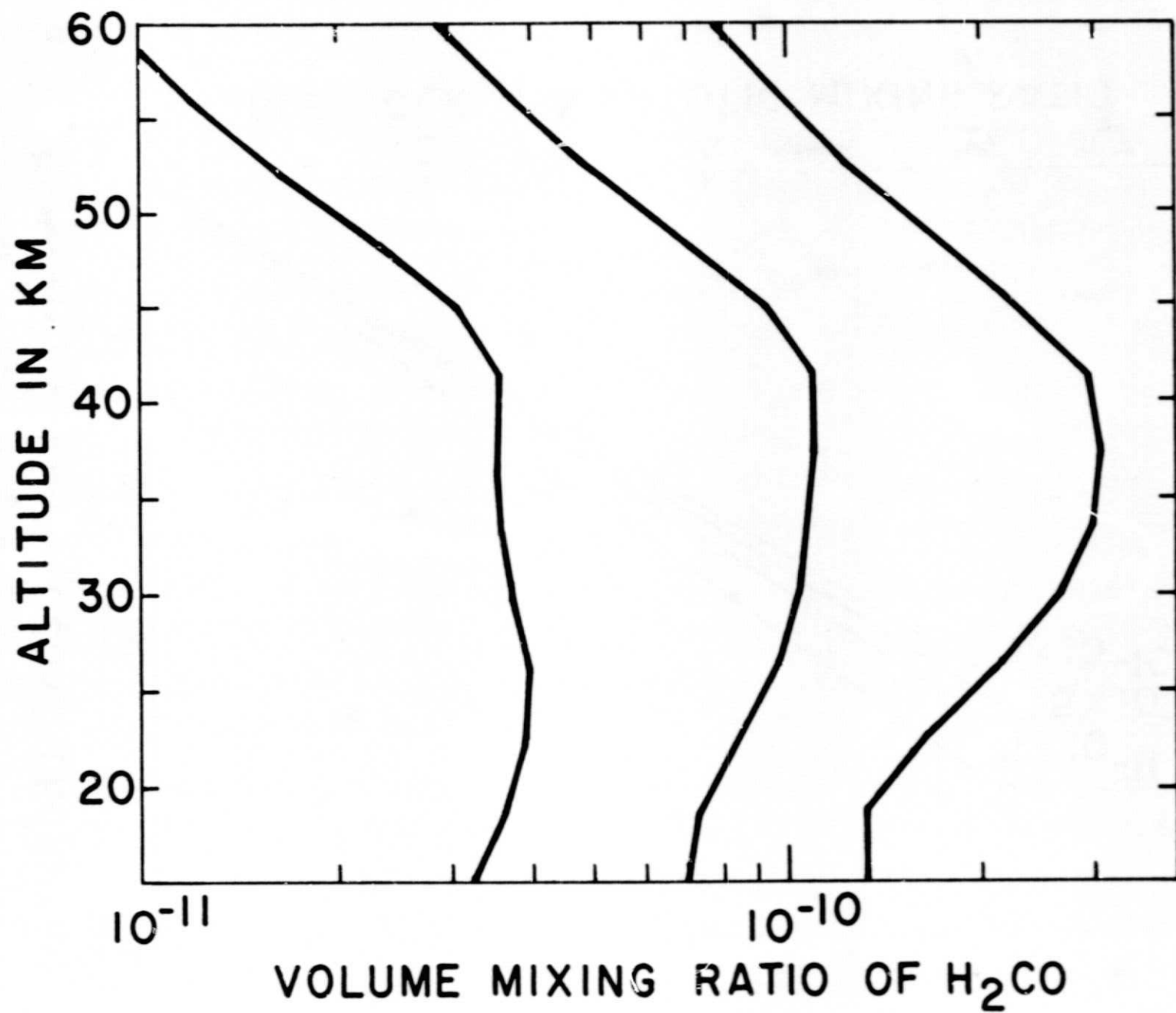
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Figure Captions

1. Column ozone change due to steady-state injection of stratospheric ClX as a function of the asymptotic value of ClX added. Curves shown include results neglecting reaction (1) as well as inclusion of reaction (1) at its measured value and at a larger and a smaller value.
2. Calculated formaldehyde concentration versus altitude indicating 2 σ uncertainties derived from sensitivity studies.





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