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Photochemistry of the Stratosphere of Venus: Implications for Atmospheric Evolution[1,2]

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The photochemistry of the stratosphere of Venus was modeled using an updated and expanded chemical scheme, combined with the results of recent observations and laboratory studies. We examined three models, with H_2 mixing ratio equal to 2×10^{-5}, 5×10^{-7}, and 1×10^{-13}, respectively. All models satisfactorily account for the observations of CO, O_2, $O_2(^1\Delta)$, and SO_2 in the stratosphere, but only the last one may be able to account for the diurnal behavior of mesospheric CO and the uv albedo. Oxygen, derived from CO_2 photolysis, is primarily consumed by CO_2 recombination and oxidation of SO_2 to H_2SO_4. Photolysis of HCl in the upper stratosphere provides a major source of odd hydrogen and free chlorine radicals, essential for the catalytic oxidation of CO. Oxidation of SO_2 by O occurs in the lower stratosphere. In the high-H_2 model (model A) the O–O bond is broken mainly by $S + O_2$ and $SO + HO_2$. In the low-H_2 models additional reactions for breaking the O–O bond must be invoked: $NO + HO_2$ in model B and $ClCO + O_2$ in model C. It is shown that lightning in the lower atmosphere could provide as much as 30 ppb of NO_x in the stratosphere. Our modeling reveals a number of intriguing similarities, previously unsuspected, between the chemistry of the stratosphere of Venus and that of the Earth. Photochemistry may have played a major role in the evolution of the atmosphere. The current atmosphere, as described by our preferred model, is characterized by an extreme deficiency of hydrogen species, having probably lost the equivalent of 10^2–10^3 times the present hydrogen content.

> April is the cruelest month, breeding
> Lilacs out of the dead land, mixing
> Memory and desire, stirring
> Dull roots with spring rain.
>
> *The Waste Land*, T. S. Eliot

1. INTRODUCTION

Overview

The atmosphere of Venus is composed primarily of CO_2. Small concentrations of chemically reactive species such as CO, H_2O, HCl, $O_2(^1\Delta)$, and SO_2 have been detected in the stratosphere. The presence of H_2 in the bulk atmosphere has been inferred from ionospheric measurements (Kumar *et al.*, 1981), but this interpretation was questioned by McElroy *et al.* (1982a). Detection of O_2 has not been reported to date. Pollack *et al.* (1980) tentatively identified Cl_2 as the long-wavelength ultraviolet absorber. Clancy *et al.* (1981) definitively established the diurnal asymmetry for mesospheric CO.

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The current status regarding the abundance and distribution of the important chemical species in the stratosphere is summarized in Table I. The purpose of this paper is to propose and examine photochemical models that can best satisfy the observational constraints, and at the same time are consistent with current experiments in chemical kinetics, some of which have recently been performed at the authors' institution. Unfortunately, neither the observations nor the kinetics can be considered complete and definitive, and this paper can only aspire to provide a tentative theory and some motivation and useful guidelines for further work in both areas.

The two most outstanding problems in the chemistry of the atmosphere of Venus today are:

(a) What controls the abundance of O_2 in the stratosphere?

(b) What is the abundance of H_2 in the bulk atmosphere?

The first problem brings us to the heart of

TABLE I

SUMMARY OF OBSERVATIONS AND UPPER LIMITS OF SELECTED CHEMICAL SPECIES RELEVANT TO THE STRATOSPHERE OF VENUS (VOLUME MIXING RATIO FOR SPECIES x IS DENOTED BY f_x)

Species	Abundance	Reference and remarks
CO	$f_{CO} = 4.5 \times 10^{-5}$ at cloud top.	Connes *et al.* (1968) Young (1972) Effective region of line formation model dependent; should be around 200 mbar or 62 km.
	$f_{CO} \sim 10^{-3}$ at 100 km, nightside abundance is lower.	Schloerb *et al.* (1980) Wilson *et al.* (1981) Clancy *et al.* (1981)
	$f_{CO} = 20 \pm 0.4 \times 10^{-6}$ at 20 km	Hoffman *et al.* (1980a)
O_2	$f_{O_2} < 1 \times 10^{-6}$ at cloud top.	Traub and Carleton (1974) Region of line formation between 60 and 300 mbar.
$O_2(^1\Delta)$	Dayglow = 1.5 MR[a] Nightglow = 1.2 MR	Connes *et al.* (1979) Used terrestrial dayglow for calibration, error ~ 70%.
O_3	$O_2(^1\Delta)$ dayglow due to $O_3 < 0.3$ MR.	Connes *et al.* (1979)
	$\tau_{O_3} < 0.1$ at $\lambda = 2550$ Å	Stewart *et al.* (1979)
HCl	$f_{HCl} = 4 \times 10^{-7}$	Connes *et al.* (1967) Young (1972)
H_2O	$f_{H_2O} = 1 \times 10^{-6}$	Fink *et al.* (1972) Barker (1975)
SO_2	f_{SO_2} at 40 mbar varies from 5 to 100×10^{-9}, with weighted mean of 2×10^{-8} and scale height 1 to 3 km.	Barker (1979) Esposito *et al.* (1979) Esposito and Gates (1981) The Pioneer Venus OUVS results quoted here are from Esposito and Gates (1981).
SO	$f_{SO} < 5 \times 10^{-8}$, $70\text{ km} < z < 90\text{ km}$ $f_{SO} < 2 \times 10^{-8}$, $z > 95$ km	Wilson *et al.* (1981)
H_2	$f_{H_2} = 2 \times 10^{-5}$ in the stratosphere.	Kumar *et al.* (1981) Based on H_2^+ measurement in the thermosphere. The alternative interpretation by McElroy *et al.* (1982a) is that D^+, instead of H_2^+, was observed.
S_x	$\sum_j j\, S_{2j} \approx 8 \times 10^{-8}$	San'ko (1980) Identification not unique
Cl_2	$f_{Cl_2} \sim 10^{-6}$ at 70 km	Pollack *et al.* (1980), tentative identification. Cl_2 provides the best match to albedo longward of 0.32 μm.
HDO	$HDO/H_2O = 1.6 \times 10^{-2}$	Donahue *et al.* (1982)

[a] 1 MR = 1×10^{12} photons $cm^{-2}s^{-1}$.

stratospheric chemistry: breaking the O–O bond, oxidation of CO to CO_2 (essential for CO_2 stability), and oxidation of SO_2 to H_2SO_4. The second problem is related to the state of oxidation of the atmosphere and the escape and evolution of hydrogen (and water) on Venus. As we shall show, these two problems are intimately related. Indeed, stratospheric photochemistry may be inexorably driving the evolution of the atmosphere, bleeding hydrogen out of a desiccated dead land.

Our conceptual understanding of the atmosphere of Venus is closely linked to that of the sister planets Mars and Earth. The CO_2 stability problem on Venus is reminiscent of a related problem on Mars. The classic work of McElroy and Donahue (1972) shows that CO_2 recombination is catalyzed by trace quantities of hydroxyl radicals derived from H_2O photolysis. On Venus it is generally accepted that odd hydrogen and free chlorine radicals derived from HCl photolysis should play a similar role (McElroy, 1970). But is the catalytic cycle driven primarily by hydroxyl radicals,

$$CO + OH \rightarrow CO_2 + H,$$

as it is on Mars? Or, is the catalytic cycle uniquely Venusian, driven by chlorine radicals,

$$ClCO + O_2 \rightarrow CO_2 + ClO?$$

Our own recent experiments in laboratory kinetics suggest that both cycles are viable, and their relative importance depends on the abundance of H_2 in the ambient atmosphere.

The efficiency of chlorine catalytic cycles in the terrestrial stratosphere has been extensively studied in recent years (see, for example, Logan *et al.*, 1978). It is now known that the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3$$

controls the abundance of active chlorine (such as Cl and ClO) relative to HCl, a more inert form of chlorine. Stratospheric methane is irreversibly destroyed by the above reaction and must be continually supplied by biological processes on the surface. On Venus H_2 plays a similar role in controlling the abundance of active chlorine via the reaction

$$Cl + H_2 \rightarrow HCl + H.$$

Since this reaction may initiate irreversible conversion of H_2 into H_2O, H_2 must be continually supplied by thermochemical reactions on the surface. Is the lower atmosphere capable of satisfying the stratospheric demand of H_2 at present? What are the consequences of meeting or not meeting this requirement for photochemistry today and evolution in the past? These and related questions will be posed and explored in this paper. It is hoped that we are at least asking the right questions à la Socrates. However, Venus, the Goddess of Love, may be considerably more subtle and artful than our crude attempts to unveil her secrets.

The Oxygen Budget

The stratosphere of Venus above the cloud tops (~60 km) is the region where the bulk of solar ultraviolet radiation is absorbed. Photolysis of CO_2 occurs readily by absorption of photons shortward of 2040 Å (DeMore and Mosesman, 1971; Shemansky, 1972; DeMore and Patapoff, 1972),

$$CO_2 + h\nu \rightarrow CO + O. \quad (R1)$$

The recombination reaction

$$CO + O + M \rightarrow CO_2 + M \quad (R14)$$

is, however, spin-forbidden, and a major loss of atomic oxygen is the formation of O_2 via

$$O + O + M \rightarrow O_2 + M, \quad (R17)$$
$$O + ClO \rightarrow Cl + O_2, \quad (R44)$$
$$O + OH \rightarrow O_2 + H. \quad (R28)$$

We can take the observations of $O_2(^1\Delta) \rightarrow O_2(^3\Sigma) + h\nu$ airglow (Connes *et al.*, 1979) as evidence that a substantial fraction of CO_2 photolysis leads to production of O_2. One would expect, on the basis of the photochemistry of CO_2 alone, that CO and O_2 should be abundant, and that the ratio $r = [CO]/[O_2]$ should be 2. The observed mixing ratio of CO at the cloud tops is 4.5×10^{-5} (Connes *et al.*, 1968; Young, 1972). The upper limit for O_2 is 1×10^{-6} (Traub and Carleton, 1974). A successful chemical model must account for the deficiency of CO in the upper atmosphere, and the extreme scarcity of O_2 relative to CO ($r > 45$). There are two obvious sinks for O_2: oxidation of CO to CO_2, and oxidation of some sulfur compounds to H_2SO_4.

Early photochemical models have concentrated on the recombination of CO_2 catalyzed by cycles involving ClO_x (Cl, ClO, ClOO, Cl_2) (Prinn, 1971) and HO_x (H, OH, HO_2, H_2O_2) radicals (McElroy *et al.*, 1973; Sze and McElroy, 1975), derived from photolysis of HCl (Connes *et al.*, 1967; McElroy, 1970). Prinn (1971) proposed the scheme

$$\begin{array}{rll}
 & \tfrac{1}{2}(\mathrm{Cl} + \mathrm{O_2} + M \rightarrow \mathrm{ClOO} + M) & (\mathrm{R96}) \\
 & \tfrac{1}{2}(\mathrm{ClOO} + \mathrm{CO} \rightarrow \mathrm{CO_2} + \mathrm{ClO}) & \qquad (1) \\
 & \tfrac{1}{2}(\mathrm{ClO} + \mathrm{CO} \rightarrow \mathrm{Cl} + \mathrm{CO_2}) & (\mathrm{R43}) \\ \hline
\text{net} & \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} &
\end{array}$$

Recognizing the possible importance of hydroxyl radicals, McElroy *et al.* (1973) considered two schemes, first proposed for the Martian atmosphere (McElroy and Donahue, 1972; Parkinson and Hunten, 1972):

$$\begin{array}{rlll}
 & \mathrm{H} + \mathrm{O_2} + M \rightarrow \mathrm{HO_2} + M & (\mathrm{R22}) & \\
 & \mathrm{O} + \mathrm{HO_2} \rightarrow \mathrm{OH} + \mathrm{O_2} & (\mathrm{R31}) & (2) \\
 & \mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{CO_2} + \mathrm{H} & (\mathrm{R25}) & \\ \hline
\text{net} & \mathrm{CO} + \mathrm{O} \rightarrow \mathrm{CO_2} & &
\end{array}$$

$$\begin{array}{rlll}
 & \mathrm{H} + \mathrm{O_2} + M \rightarrow \mathrm{HO_2} + M & (\mathrm{R22}) & \\
 & \tfrac{1}{2}(2\ \mathrm{HO_2} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2}) & (\mathrm{R35}) & (3) \\
 & \tfrac{1}{2}(\mathrm{H_2O_2} + h\nu \rightarrow 2\ \mathrm{OH}) & (\mathrm{R6}) & \\
 & \mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{CO_2} + \mathrm{H} & (\mathrm{R25}) & \\ \hline
\text{net} & \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} & &
\end{array}$$

More recently Krasnopolsky and Parshev (1980a,b, 1981) and the present authors (Yung and DeMore, 1981) independently considered the scheme

$$\begin{array}{rll}
 & \mathrm{Cl} + \mathrm{CO} + M \rightarrow \mathrm{ClCO} + M & (\mathrm{R99}) \\
 & \mathrm{ClCO} + \mathrm{O_2} \rightarrow \mathrm{ClO} + \mathrm{CO_2} & \\
 & \mathrm{ClO} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{O_2} & (\mathrm{R44}) \\ \hline
\text{net} & \mathrm{CO} + \mathrm{O} \rightarrow \mathrm{CO_2} &
\end{array}$$

This scheme is actually more complicated than previously thought, as the reaction ClCO with O_2 is mediated by an intermediate complex $ClCO_3$. We consider three schemes:

$$\begin{array}{rlll}
 & \mathrm{Cl} + \mathrm{CO} + M \rightarrow \mathrm{ClCO} + M & (\mathrm{R99}) & \\
 & \mathrm{ClCO} + \mathrm{O_2} + M \rightarrow \mathrm{ClCO_3} + M & (\mathrm{R101}) & (4a) \\
 & \mathrm{ClCO_3} + \mathrm{O} \rightarrow \mathrm{Cl} + \mathrm{CO_2} + \mathrm{O_2} & (\mathrm{R110}) & \\ \hline
\text{net} & \mathrm{CO} + \mathrm{O} \rightarrow \mathrm{CO_2} & &
\end{array}$$

$$\begin{array}{rcll}
\mathrm{Cl} + \mathrm{CO} + M & \rightarrow & \mathrm{ClCO} + M & \text{(R99)} \\
\mathrm{ClCO} + \mathrm{O_2} + M & \rightarrow & \mathrm{ClCO_3} + M & \text{(R101)} \quad \text{(4b)} \\
\mathrm{ClCO_3} + \mathrm{Cl} & \rightarrow & \mathrm{Cl} + \mathrm{CO_2} + \mathrm{ClO} & \text{(R111)} \\
\mathrm{ClO} + \mathrm{O} & \rightarrow & \mathrm{Cl} + \mathrm{O_2} & \text{(R44)} \\
\hline
\text{net} \quad \mathrm{CO} + \mathrm{O} & \rightarrow & \mathrm{CO_2} &
\end{array}$$

The third scheme associated with ClCO (4c) will be discussed in a later part of this section. We may note that the effectiveness of the catalytic cycles (1)–(4) depends critically on the abundance of trace amounts of radical species.

The presence of COS and H_2S in the lower atmosphere of Venus was predicted by Lewis (1970) on geochemical grounds. The possibility of oxidation of reduced sulfur to oxidized sulfur compounds was discussed by Prinn (1971). Following the suggestion that the clouds of Venus are composed of sulfuric acid (Sill, 1972; Young and Young, 1973), it was recognized (McElroy *et al.*, 1973; Prinn, 1973, 1975; Sze and McElroy, 1975; Wofsy and Sze, 1975) that the availability of O_2 could limit the production rate of H_2SO_4. Prinn (1973, 1975) proposed a scheme for oxidation of COS to H_2SO_4 using the O_2 derived from CO_2 photolysis:

$$\begin{array}{rcll}
\mathrm{COS} + h\nu & \rightarrow & \mathrm{CO} + \mathrm{S(^1D)} & \\
\mathrm{S(^1D)} + M & \rightarrow & \mathrm{S} + M & \\
\mathrm{S} + \mathrm{O_2} & \rightarrow & \mathrm{SO} + \mathrm{O} & \text{(R46)} \quad \text{(5)} \\
\mathrm{SO} + \mathrm{OH} & \rightarrow & \mathrm{SO_2} + \mathrm{H} & \text{(R54)} \\
\mathrm{SO_2} + \mathrm{HO_2} & \rightarrow & \mathrm{SO_3} + \mathrm{OH} & \text{(R60)} \\
\mathrm{SO_3} + \mathrm{H_2O} + M & \rightarrow & \mathrm{H_2SO_4} + M & \text{(R65)}
\end{array}$$

This scheme can be roughly summarized as

$$\mathrm{COS} + 2\mathrm{O_2} + \mathrm{H_2O} + (\mathrm{HO}_x) \rightarrow \mathrm{CO_2} + \mathrm{H_2SO_4} + (\mathrm{HO}_x),$$

where the hydroxyl radicals HO_x play a crucial role as catalyst. Qualitative calculations performed by Prinn (1973, 1975) demonstrated that scheme (5) could indeed be a major pathway for destroying O_2 and producing H_2SO_4. However, (R60) is not currently believed to be important because of its slow rate. Further, COS has not been positively identified in the lower atmosphere (Hoffman *et al.*, 1980a,b; Oyama *et al.*, 1980). Prinn (1971, 1973, 1975, 1978, 1979) argued that COS could be readily destroyed by

$$\mathrm{COS} + \mathrm{S} \rightarrow \mathrm{CO} + \mathrm{S_2}.$$

Indeed, there is strong circumstantial evidence for the presence of polysulfur in the spectrum taken by Venera 11 and 12 below 38 km (Moroz *et al.*, 1979; San'ko, 1980). This lends support to Prinn's argument. In this work we will not discuss the chemistry of COS. The chemistry of COS and H_2S involves too intimately the chemistry of the lower atmosphere and can only be treated adequately in another paper. We refer the reader to previous work on the subject on Venus (Prinn, 1973, 1975; Sze and Smyth, 1979) and recent work on Earth's atmosphere (McElroy *et al.*, 1980; Sze and Ko, 1980).

The discovery of the first gaseous sulfur species, SO_2, on Venus (Barker, 1979) and its confirmation by Conway *et al.* (1979), Stewart *et al.* (1979), and Esposito *et al.* (1979) led Winick and Stewart (1980) to examine the photochemistry of SO_2 with a fairly comprehensive model involving the interaction of chlorine, hydrogen, oxygen, and sulfur compounds. The photochemistry of SO_2 is initiated by absorption of photons shortward of 2190 Å (Okabe, 1978),

$$SO_2 + h\nu \rightarrow SO + O. \quad (R9)$$

The recombination reaction

$$SO + O + M \rightarrow SO_2 + M, \quad (R51)$$

with $M = CO_2$, is extremely fast (Leu, 1982) and hence photolysis of SO_2 does not always lead to net destruction. Oxidation of SO_2 to H_2SO_4 is, of course, a net sink. In addition to oxidation schemes using HO_x radicals (Prinn, 1973, 1975), Winick and Stewart (1980) first recognized the importance of two new schemes,

$$\begin{array}{lrll}
 & \tfrac{1}{2}(SO + h\nu \rightarrow S + O) & (R8) & \\
 & \tfrac{1}{2}(S + O_2 \rightarrow SO + O) & (R46) & (6a) \\
 & SO_2 + O + M \rightarrow SO_3 + M & (R58) & \\
 & SO_3 + H_2O + M \rightarrow H_2SO_4 + M & (R65) & \\
\hline
\text{net} & SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow H_2SO_4 & &
\end{array}$$

$$\begin{array}{lrll}
 & \tfrac{1}{2}(SO_2 + h\nu \rightarrow SO + O) & (R9) & \\
 & \tfrac{1}{2}(2SO \rightarrow SO_2 + S) & (R57) & \\
 & \tfrac{1}{2}(S + O_2 \rightarrow SO + O) & (R46) & (6b) \\
 & SO_2 + O + M \rightarrow SO_3 + M & (R58) & \\
 & SO_3 + H_2O + M \rightarrow H_2SO_4 + M & (R65) & \\
\hline
\text{net} & SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow H_2SO_4 & &
\end{array}$$

The Winick–Stewart model successfully reproduces the observed SO_2 distribution, with an appropriate choice of the eddy diffusivity profile. But the model predictions for the concentrations of CO and O_2 at the cloud tops are about factors of 3 and 50, respectively, higher than those allowed by observations.

The large concentration of O_2 predicted by the Winick–Stewart model is remarkable in view of the fact that the authors have introduced two new powerful catalytic cycles for breaking the O–O bond,

$$\begin{array}{lrll}
 & SO + h\nu \rightarrow S + O & (R8) & \\
 & S + O_2 \rightarrow SO + O & (R46) & (7a) \\
\hline
\text{net} & O_2 \rightarrow 2O & &
\end{array}$$

$$\begin{array}{lrll}
 & SO + SO \rightarrow SO_2 + S & (R57) & \\
 & SO_2 + h\nu \rightarrow SO + O & (R9) & (7b) \\
 & S + O_2 \rightarrow SO + O & (R46) & \\
\hline
\text{net} & O_2 \rightarrow 2O & &
\end{array}$$

These cycles constitute a crucial part of the SO_2 oxidation schemes (6a,b). Part of the reason for the high O_2 predicted by the model lies in the efficiency of the classic chlorine cycle for converting odd oxygen into molecular oxygen, first proposed for the Earth's stratosphere (Wofsy and McElroy, 1974; Stolarski and Cicerone, 1974; Molina and Rowland, 1974):

$$\begin{array}{lrll}
 & O + O_2 + M \rightarrow O_3 + M & (R19) & \\
 & Cl + O_3 \rightarrow ClO + O_2 & (R39) & (8) \\
 & ClO + O \rightarrow Cl + O_2 & (R44) & \\
\hline
\text{net} & 2O \rightarrow O_2 & &
\end{array}$$

An inspection of Figs. 4b and c in Winick and Stewart (1980) reveals that, indeed, the effects of cycles (7a) and (7b) are nearly neutralized by cycle (8).

Is the efficiency of cycle (8), as described in Winick and Stewart (1980), unrealistic? Again, analogy with the chlorine chemistry in the Earth's stratosphere will illuminate the discussion. In the Earth's stratosphere the reaction ClO + NO competes with ClO + O (Logan *et al.*, 1978) and can turn the chlorine cycle into a null cycle,

$$\begin{array}{rcll}
O + O_2 + M & \rightarrow & O_3 + M & \text{(R19)} \\
Cl + O_3 & \rightarrow & ClO + O_2 & \text{(R39)} \quad \text{(9a)} \\
ClO + NO & \rightarrow & Cl + NO_2 & \text{(R82)} \\
NO_2 + h\nu & \rightarrow & NO + O & \text{(R67)} \\
\hline
\text{net} & & \text{nothing} &
\end{array}$$

N_2 and NO have been detected on Venus (Oyama *et al.*, 1980; Stewart *et al.*, 1979; Feldman *et al.*, 1979; Stewart and Barth, 1979). The chemistry of odd nitrogen NO_x (N, NO, NO_2, NO_3, HNO, HNO_2, HNO_3) on Venus should be similar to that on Mars (Yung *et al.*, 1977) and in the primitive atmosphere of the Earth (Yung and McElroy, 1979). Following reports of detection of lightning on Venus (Ksanfomaliti, 1979), Watson *et al.* (1979) and Chameides *et al.* (1979) investigated the potential role of NO_x in the lower atmosphere and the stratosphere. The possible importance of the reaction NO + HO_2 for breaking the O–O bond was suggested. This can lead to two oxidation schemes:

$$\begin{array}{rcll}
H + O_2 + M & \rightarrow & HO_2 + M & \text{(R22)} \\
\tfrac{1}{2}(HO_2 + NO & \rightarrow & OH + NO_2) & \text{(R81)} \\
\tfrac{1}{2}(NO_2 + h\nu & \rightarrow & NO + O) & \text{(R67)} \quad \text{(10a)} \\
\tfrac{1}{2}(O + HO_2 & \rightarrow & OH + O_2) & \text{(R31)} \\
CO + OH & \rightarrow & CO_2 + H & \text{(R25)} \\
\hline
\text{net} \quad CO + \tfrac{1}{2}O_2 & \rightarrow & CO_2 &
\end{array}$$

$$\begin{array}{rcll}
H + O_2 + M & \rightarrow & HO_2 + M & \text{(R22)} \\
HO_2 + NO & \rightarrow & OH + NO_2 & \text{(R81)} \\
NO_2 + h\nu & \rightarrow & NO + O & \text{(R67)} \\
CO + OH & \rightarrow & CO_2 + H & \text{(R25)} \quad \text{(10b)} \\
SO_2 + O + M & \rightarrow & SO_3 + M & \text{(R58)} \\
SO_3 + H_2O + M & \rightarrow & H_2SO_4 + M & \text{(R65)} \\
\hline
\text{net} \quad CO + SO_2 + O_2 + H_2O & \rightarrow & CO_2 + H_2SO_4 &
\end{array}$$

However, no quantitative computations have been carried out. Of course, breaking the O–O bond by NO_x represents only one possibility. Due to the presence of large concentrations of atomic oxygen in the stratosphere, NO_x can also catalyze the recombination of odd oxygen:

$$\begin{array}{rcll}
NO + O + M & \rightarrow & NO_2 + M & \text{(R77)} \\
NO_2 + O & \rightarrow & NO + O_2 & \text{(R83a)} \quad \text{(11)} \\
\hline
\text{net} \quad 2O & \rightarrow & O_2 &
\end{array}$$

Recently Clyne and MacRobert (1981) showed that the reaction

$$ClO + SO \rightarrow Cl + SO_2 \quad \text{(R56)}$$

is fast. Hence, we have a null chlorine cycle, in which SO plays the role equivalent to NO in cycle (9a),

$$\begin{array}{rcll}
O + O_2 + M & \rightarrow & O_3 + M & \text{(R19)} \\
Cl + O_3 & \rightarrow & ClO + O_2 & \text{(R39)} \\
 & & & \quad \text{(9b)} \\
ClO + SO & \rightarrow & Cl + SO_2 & \text{(R56)} \\
SO_2 + h\nu & \rightarrow & SO + O & \text{(R9)} \\
\hline
\text{net} & & \text{nothing} &
\end{array}$$

There is also an analog of cycle (10b), again with SO playing the role of NO:

$$\begin{array}{llll}
 & \mathrm{Cl + CO} + M \rightarrow \mathrm{ClCO} + M & \mathrm{(R99)} & \\
 & \mathrm{ClCO + O_2} + M \rightarrow \mathrm{ClCO_3} + M & \mathrm{(R101)} & \\
 & \mathrm{ClCO_3 + Cl \rightarrow Cl + CO_2 + ClO} & \mathrm{(R111)} & \\
 & \mathrm{ClO + SO \rightarrow Cl + SO_2} & \mathrm{(R56)} & \mathrm{(4c)} \\
 & \mathrm{SO_2} + h\nu \rightarrow \mathrm{SO + O} & \mathrm{(R9)} & \\
 & \mathrm{SO_2 + O} + M \rightarrow \mathrm{SO_3} + M & \mathrm{(R58)} & \\
 & \mathrm{SO_3 + H_2O} + M \rightarrow \mathrm{H_2SO_4} + M & \mathrm{(R65)} & \\
\hline
\text{net} & \mathrm{CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4} & &
\end{array}$$

Since ClO and HO_2 are chemically alike, we shall argue that the reaction

$$\mathrm{HO_2 + SO \rightarrow OH + SO_2} \quad \mathrm{(R55)}$$

is also fast. We propose two new catalytic schemes for oxidizing CO and SO_2:

$$\begin{array}{llll}
 & \mathrm{H + O_2} + M \rightarrow \mathrm{HO_2} + M & \mathrm{(R22)} & \\
 & \tfrac{1}{2}\mathrm{(SO + HO_2 \rightarrow SO_2 + OH)} & \mathrm{(R55)} & \\
 & \tfrac{1}{2}(\mathrm{SO_2} + h\nu \rightarrow \mathrm{SO + O}) & \mathrm{(R9)} & \mathrm{(12a)} \\
 & \tfrac{1}{2}\mathrm{(O + HO_2 \rightarrow OH + O_2)} & \mathrm{(R31)} & \\
 & \mathrm{CO + OH \rightarrow CO_2 + H} & \mathrm{(R25)} & \\
\hline
\text{net} & \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2 \rightarrow CO_2} & &
\end{array}$$

$$\begin{array}{llll}
 & \mathrm{H + O_2} + M \rightarrow \mathrm{HO_2} + M & \mathrm{(R22)} & \\
 & \mathrm{SO + HO_2 \rightarrow SO_2 + OH} & \mathrm{(R55)} & \\
 & \mathrm{SO_2} + h\nu \rightarrow \mathrm{SO + O} & \mathrm{(R9)} & \mathrm{(12b)} \\
 & \mathrm{CO + OH \rightarrow CO_2 + H} & \mathrm{(R25)} & \\
 & \mathrm{SO_2 + O} + M \rightarrow \mathrm{SO_3} + M & \mathrm{(R58)} & \\
 & \mathrm{SO_3 + H_2O} + M \rightarrow \mathrm{H_2SO_4} + M & \mathrm{(R65)} & \\
\hline
\text{net} & \mathrm{CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4} & &
\end{array}$$

The Hydrogen Budget

Winick and Stewart (1980) fixed the mixing ratio of H_2 to be 2×10^{-7}, a value first suggested by McElroy *et al.* (1973) and Sze and McElroy (1975) on the basis of thermodynamic considerations. Recent work, based on the Pioneer Venus mission (Hoffman *et al.*, 1980a; Kumar *et al.*, 1981), preferred a much higher concentration of H_2 in the upper and lower atmosphere of Venus. But such claims are controversial. The Hoffman *et al.* (1980a) experiment used CH_4 as a calibration gas and it has not been proven beyond doubt that the observed H_2 peak was of atmospheric origin. The mass 2 ion detected by the Pioneer Venus ion mass spectrometer could be either H_2^+ (Kumar *et al.*, 1981) or D^+ (McElroy *et al.*, 1982a). In this work we consider the abundance of H_2 in the atmosphere as an ill-defined parameter. We examine models encompassing a wide range of values for H_2, and use the comparison between model predictions and observations to make an independent judgement. The role of H_2 in the photochemistry of chlorine compounds is somewhat similar to that of CH_4 in the stratosphere of the Earth (Logan *et al.*, 1978). The primary source of HO_x and ClO_x radicals is photolysis of HCl,

$$\mathrm{HCl} + h\nu \rightarrow \mathrm{H + Cl}. \quad \mathrm{(R2)}$$

The reaction

$$Cl + H_2 \rightarrow HCl + H \quad (R38)$$

turns an active chlorine radical into a relatively inert form of chlorine. However, there are important reactions that can reverse this process:

$$O + HCl \rightarrow OH + Cl, \quad (R16)$$
$$H + HCl \rightarrow H_2 + Cl, \quad (R21)$$
$$OH + HCl \rightarrow H_2O + Cl. \quad (R27)$$

An equilibrium distribution of HO_x and ClO_x can be readily established, determined by the rates of cycling by (R21), (R27), and (R38).

It is clear that a high level of H_2 favors HO_x radicals. ClO_x radicals become more abundant at low levels of H_2. The cycling between HO_x and ClO_x is not, however, a completely reversible process. Since photolysis of H_2O in the stratosphere is nearly completely shielded by CO_2, reaction (R27) OH + HCl is almost an irreversible sink for hydrogen. This hydrogen must be ultimately derived from H_2 or HCl [the loss of oxygen in (R27) is trivial compared with the CO_2 photolysis source]. In all previous work performed in the United States (Prinn, 1971; McElroy *et al.*, 1973; Sze and McElroy, 1975; Winick and Stewart, 1980) it was implicitly assumed that the hydrogen consumed by (R27) comes from H_2. The Soviet work (Krasnopolsky and Parshev, 1980a,b, 1981) first raised the possibility that this hydrogen might not be supplied by H_2 and must, therefore, be extracted from HCl, with the consequence of building up enormous concentrations of free chlorine in the stratosphere. Unfortunately the Soviet work was based on outdated chemical kinetics and it is clearly important to assess this work in light of an updated chemical model.

Outline of Approach

We have briefly discussed the photochemistry of the atmosphere of Venus in terms of 12 major chemical schemes and cycles summarized in Table II. The discussion reveals at least five aspects of Venus photochemistry where previous treatments are inadequate: (1) the photochemistry of SO, (2) the sensitivity of photochemical models to the abundance of H_2, (3) the role of NO_x in stratospheric chemistry, (4) the chemistry of ClCO, and (5) the interaction between the upper and lower atmosphere. The central problem in the photochemistry of the stratosphere is to devise a chemical scheme for the rapid removal of O_2. The major uncertainty is the abundance of H_2. We examine three models. In model A we adopt a high mixing ratio of H_2, 2×10^{-5}, as suggested by Kumar *et al.* (1981). It will be shown that in this case schemes (2) and (12a,b) are sufficient to account for the observations. But then a *photochemical* source for H_2 must be postulated, because thermochemistry cannot produce the required amount. We propose, in Appendix B, a speculative mechanism for production of H_2 via sulfur chemistry. In model B, we adopt a low mixing ratio for H_2, 5×10^{-7}, a value higher than that predicted by the water gas equilibrium in the lower atmosphere (Donahue, 1968; McElroy *et al.*, 1973) but still consistent with the analysis of McElroy *et al.* (1982a). In this case, as we shall show, we must invoke additional mechanisms for destroying O_2, such as schemes (10a,b) with 30 ppb NO_x. A lightning source of NO_x, comparable to that in the terrestrial troposphere (Chameides *et al.*, 1979; Borucki *et al.*, 1981), could adequately account for this amount of NO_x if the *only* sink for NO_x on Venus were in the upper atmosphere. In model C we assume that the stratosphere does not derive any H_2 from the lower atmosphere. It will be shown, in this case, that the buildup of large concentrations of free chlorine is inevitable and that cycles (4a,b,c) become the dominant processes for removing CO and O_2. This paper will concentrate on these models. A critical discussion on chemical kinetics will be given, followed by modeling results and comparisons between the model predictions

TABLE II

SUMMARY OF IMPORTANT CHEMICAL SCHEMES DISCUSSED IN THE TEXT AND THEIR CURRENT STATUS ON VENUS

Scheme	Net chemical reaction	Current status	Reference and remarks
(1)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	Not important	Prinn (1971, 1972) O–O bond broken by $ClOO + O_2$
(2)	$CO + O \rightarrow CO_2$	Important in models A, B	McElroy *et al.* (1973) Catalyzed by HO_x
(3)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	Not important	McElroy *et al.* (1973) O–O bond broken by $H_2O_2 + h\nu$
(4a,b)	$CO + O \rightarrow CO_2$	Important in model C	Krasnopolsky and Parshev (1981) and this work O–O bond broken by $ClCO + O_2$
(4c)	$CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4$	Important in model C	This work O–O bond broken by $ClCO + O_2$
(5)	$COS + 2\,O_2 + H_2O \rightarrow CO_2 + H_2SO_4$	COS status uncertain	Prinn (1973, 1975) O–O bond broken by $S + O_2$ Catalyzed by HO_x
(6a,b)	$SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4$	Important	Winick and Stewart (1980) O–O bond broken by $S + O_2$
(7a,b)	$O_2 \rightarrow 2\,O$	Important	Winick and Stewart (1980) O–O bond broken by $S + O_2$
(8)	$2\,O \rightarrow O_2$	Important	Sze and McElroy (1974) Catalyzed by ClO_x
(9a)	$O \rightarrow O$ (net nothing)	Important in model B	Logan *et al.* (1978), this work NO suppresses cycle (8)
(9b)	$O \rightarrow O$ (net nothing)	Important	This work SO suppresses cycle (8)
(10a)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	Important in model B	Watson *et al.* (1979), this work O–O bond broken by $NO + HO_2$
(10b)	$CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4$	Important in model B	Watson *et al.* (1979), this work, O–O bond broken by $NO + HO_2$
(11)	$2O \rightarrow O_2$	Important in model B	This work, catalyzed by NO_x
(12a)	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	Important in model A	This work O–O bond broken by $SO + HO_2$
(12b)	$CO + SO_2 + O_2 + H_2O \rightarrow CO_2 + H_2SO_4$	Important in model A	This work O–O bond broken by $SO + HO_2$

and observations and between stratospheric chemistry of Venus and Earth. The implications of our chemical models for atmospheric evolution will be discussed.

2. PHOTOCHEMISTRY AND CHEMICAL KINETICS

Table IIIa lists the most important reactions for the major compounds of carbon, oxygen, hydrogen, chlorine, and sulfur, along with preferred values of their rate coefficients, to be used in model A. Tables IIIb and IIIc include additional important reactions involving NO_x and ClCO, to be used in models B and C. Miscellaneous reactions, of more speculative nature, related to the chemistry of HSO_3 and the dimer $(SO)_2$ are discussed in Appendices A and B, respectively. Our set of reactions encompasses most of those considered in previous

TABLE IIIa

LIST OF ESSENTIAL REACTIONS FOR THE STRATOSPHERE OF VENUS WITH THEIR PREFERRED RATE COEFFICIENTS

	Reaction	Rate coefficient	Reference
(R1)	$CO_2 + h\nu \rightarrow CO + O$	$J_1 = 1.5 \times 10^{-12}$	Shemansky (1972) DeMore and Patapoff (1972)
(R2)	$HCl + h\nu \rightarrow H + Cl$	$J_2 = 1.0 \times 10^{-7}$	Watson (1977)
(R3)	$H_2O + h\nu \rightarrow H + OH$	$J_3 = 2.2 \times 10^{-11}$	Watanabe (1958) Hudson (1971) Prather (1981)
(R4a)	$O_2 + h\nu \rightarrow O + O(^1D)$	$J_{4a} = 0$	Watanabe (1958) Ackerman (1971) Carver *et al.* (1977)
(R4b)	$O_2 + h\nu \rightarrow 2O$	$J_{4b} = 7.4 \times 10^{-10}$	Watanabe (1958) Hudson (1974) Hudson and Reed (1979)
(R5a)	$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	$J_{5a} = 8.6 \times 10^{-3}$	Ackerman (1971) Hudson and Reed (1979)
(R5b)	$O_3 + h\nu \rightarrow O_2 + O$	$J_{5b} = 4.2 \times 10^{-4}$	Ackerman (1971) Hudson and Reed (1979)
(R6)	$H_2O_2 + h\nu \rightarrow 2OH$	$J_6 = 9.9 \times 10^{-5}$	Schügers and Welge (1968), Hudson and Reed (1979)
(R7)	$ClO + h\nu \rightarrow Cl + O$	$J_7 = 5.0 \times 10^{-3}$	Watson (1977)
(R8)	$SO + h\nu \rightarrow S + O$	$J_8 = 2.7 \times 10^{-4}$	Phillips (1981)
(R9)	$SO_2 + h\nu \rightarrow SO + O$	$J_9 = 1.5 \times 10^{-4}$	Warneck *et al.* (1964) Bhatki *et al.* (1982) Okabe (1971)
(R10)	$O(^1D) + M \rightarrow O + M$	$k_{10} = 6.8 \times 10^{-11}e^{117/T}$	[a]
(R11)	$O(^1D) + H_2 \rightarrow OH + H$	$k_{11} = 2.0 \times 10^{-10}$	[c]
(R12)	$O(^1D) + HCl \rightarrow OH + Cl$	$k_{12} = 1.4 \times 10^{-10}$	[d]
(R13)	$O(^1D) + H_2O \rightarrow 2OH$	$k_{13} = 2.8 \times 10^{-10}$	[c]
(R14)	$O + CO + M \rightarrow CO_2 + M$	$k_{14} = 6.5 \times 10^{-33}e^{-2180/T}$	[c]
(R15)	$O + H_2 \rightarrow OH + H$	$k_{15} = 1.6 \times 10^{-11}e^{-4570/T}$	[b]
(R16)	$O + HCl \rightarrow OH + Cl$	$k_{16} = 1.1 \times 10^{-11}e^{-3370/T}$	[c]
(R17)	$2O + M \rightarrow O_2 + M$	$k_{17} = 8.6 \times 10^{-28}T^{-2}$	[b,e]
(R18a)	$O_2(^1\Delta) + M \rightarrow O_2 + M$	$k_{18a} = 3.0 \times 10^{-20}$	Noxon *et al.* (1976) Traub *et al.* (1979) Connes *et al.* (1979)
(R18b)	$O_2(^1\Delta) \rightarrow O_2 + h\nu$	$k_{18b} = 2.6 \times 10^{-4}$	Okabe (1978)
(R19)	$O_2 + O + M \rightarrow O_3 + M$	$k_{19} = 1.35 \times 10^{-33}$	[b]
(R20)	$O_3 + O \rightarrow 2O_2$	$k_{20} = 1.5 \times 10^{-11}e^{-2218/T}$	[d]
(R21)	$H + HCl \rightarrow H_2 + Cl$	$k_{21} = 2.4 \times 10^{-11}e^{-1740/T}$	[f]
(R22)	$H + O_2 + M \rightarrow HO_2 + M$	$k_{22} = 3.6 \times 10^{-29}T^{-1}$	[c,e]
(R23)	$H + O_3 \rightarrow OH + O_2$	$k_{23} = 1.4 \times 10^{-10}e^{-480/T}$	[c]
(R24)	$2H + M \rightarrow H_2 + M$	$k_{24} = 6.6 \times 10^{-31}T^{-0.65}$	Trainor *et al.* (1973) Prather *et al.* (1978) [e]
(R25)	$OH + CO \rightarrow H + CO_2$	$k_{25} = 1.4 \times 10^{-13}(1 + P\ \mathrm{atm})$	[d]
(R26)	$OH + H_2 \rightarrow H + H_2O$	$k_{26} = 1.8 \times 10^{-11}e^{-2330/T}$	[c]
(R27)	$OH + HCl \rightarrow H_2O + Cl$	$k_{27} = 3.0 \times 10^{-12}e^{-425/T}$	[c]
(R28)	$OH + O \rightarrow H + O_2$	$k_{28} = 3.8 \times 10^{-11}$	[c]
(R29)	$OH + O_3 \rightarrow HO_2 + O_2$	$k_{29} = 1.9 \times 10^{-12}e^{-1000/T}$	[c]
(R30)	$2OH \rightarrow H_2O + O$	$k_{30} = 1.8 \times 10^{-12}$	[c]

TABLE IIIa—*Continued*

	Reaction	Rate coefficient	Reference
(R31)	$HO_2 + O \rightarrow OH + O_2$	$k_{31} = 3.1 \times 10^{-11}$	^{c}
(R32)	$HO_2 + O_3 \rightarrow OH + 2O_2$	$k_{32} = 1.4 \times 10^{-14}e^{-600/T}$	^{c}
(R33a)	$HO_2 + H \rightarrow 2OH$	$k_{33a} = 3.2 \times 10^{-11}$	^{c}
(R33b)	$HO_2 + H \rightarrow H_2 + O_2$	$k_{33b} = 1.4 \times 10^{-11}$	^{c}
(R33c)	$HO_2 + H \rightarrow H_2O + O$	$k_{33c} = 9.4 \times 10\ ^{13}$	^{c}
(R34)	$HO_2 + OH \rightarrow H_2O + O_2$	$k_{34} = 8.0 \times 10^{-11}$	^{d}, updated
(R35)	$2HO_2 \rightarrow H_2O_2 + O_2$	$k_{35} = 2.3 \times 10^{-12}$	^{c}
(R36)	$H_2O_2 + O \rightarrow OH + HO_2$	$k_{36} = 2.8 \times 10^{-12}e^{-2125/T}$	^{d}
(R37)	$H_2O_2 + OH \rightarrow H_2O + HO_2$	$k_{37} = 7.6 \times 10^{-12}e^{-670/T}$	^{c}
(R38)	$Cl + H_2 \rightarrow HCl + H$	$k_{38} = 4.7 \times 10^{-11}e^{-2340/T}$	^{c}
(R39)	$Cl + O_3 \rightarrow ClO + O_2$	$k_{39} = 2.7 \times 10^{-11}e^{-257/T}$	^{c}
(R40)	$Cl + OH \rightarrow HCl + O$	$k_{40} = 1.0 \times 10^{-11}e^{-2970/T}$	^{a}
(R41a)	$Cl + HO_2 \rightarrow HCl + O_2$	$k_{41a} = 1.8 \times 10^{-11}e^{180/T}$	Lee and Howard (1982)
(R41b)	$Cl + HO_2 \rightarrow ClO + OH$	$k_{41b} = 2.2 \times 10^{-10}e^{-1000/T}$	
(R42)	$Cl + H_2O_2 \rightarrow HCl + HO_2$	$k_{42} = 1.1 \times 10^{-11}e^{-980/T}$	^{c}
(R43)	$ClO + CO \rightarrow Cl + CO_2$	$k_{43} = 1 \times 10^{-12}e^{-3700/T}$	^{b}
(R44)	$ClO + O \rightarrow Cl + O_2$	$k_{44} = 7.5 \times 10^{-11}e^{-120/T}$	^{c}
(R45)	$ClO + OH \rightarrow Cl + HO_2$	$k_{45} = 9.1 \times 10\ ^{12}$	^{d}
(R46)	$S + O_2 \rightarrow SO + O$	$k_{46} = 2.2 \times 10^{-12}$	^{c}
(R47)	$S + CO_2 \rightarrow SO + CO$	$k_{47} = 1.0 \times 10^{-20}$	^{g}
(R48)	$S + O_3 \rightarrow SO + O_2$	$k_{48} = 1.2 \times 10^{-11}$	^{c}
(R49)	$S + OH \rightarrow SO + H$	$k_{49} = k_{28} = 3.8 \times 10^{-11}$	^{g}
(R50)	$S + HO_2 \rightarrow SO + OH$	$k_{50} = k_{31} = 3.1 \times 10^{-11}$	^{g}
(R51)	$SO + O + M \rightarrow SO_2 + M$	$k_{51} = 6.0 \times 10^{-31}$	^{b,g}
(R52)	$SO + O_2 \rightarrow SO_2 + O$	$k_{52} = 6.0 \times 10^{-13}e^{-3300/T}$	^{c}
(R53)	$SO + O_3 \rightarrow SO_2 + O_2$	$k_{53} = 2.5 \times 10^{-12}e^{-1100/T}$	^{c}
(R54)	$SO + OH \rightarrow SO_2 + H$	$k_{54} = 1.2 \times 10^{-10}$	Fair and Thrush (1969)
(R55)	$SO + HO_2 \rightarrow SO_2 + OH$	$k_{55} = k_{56} = 2.3 \times 10^{-11}$	^{g}
(R56)	$SO + ClO + SO_2 + Cl$	$k_{56} = 2.3 \times 10^{-11}$	Clyne and MacRobert (1981)
(R57)	$2SO \rightarrow SO_2 + S$	$k_{57} = 8.3 \times 10^{-15}$	Herron and Huie (1980)
(R58)	$SO_2 + O + M \rightarrow SO_3 + M$	$k_{58} = 8.0 \times 10^{-32}e^{-1000/T}$	^{c,e}
(R59)	$SO_2 + OH + M \rightarrow HSO_3 + M$	$k_{59} = \begin{cases} k_0 = 4.2 \times 10^{-32}e^{1000/T} \\ k_\infty = 2.0 \times 10^{-12} \end{cases}$	Harris *et al.* (1980) Leu (1982)
(R60)	$SO_2 + HO_2 \rightarrow SO_3 + OH$	$k_{60} = 1.0 \times 10^{-18}$	Sander and Watson (1981) ^{c,g}
(R61)	$SO_2 + H_2O_2 + \text{aerosol} \rightarrow H_2SO_4$	$J_{61} = 4.3 \times 10^{-5}$	See text
(R62)	$SO_2 + Cl + M \rightarrow ClSO_2 + M$	$k_{62} = 4.6 \times 10^{-33}$	Strattan *et al.* (1979) ^{c}
(R63)	$SO_2 + ClO \rightarrow SO_3 + Cl$	$k_{63} = k_{60} = 1.0 \times 10^{-18}$	^{g}
(R64)	$SO_3 + SO \rightarrow 2SO_2$	$k_{64} = 2.0 \times 10^{-15}$	^{b}
(R65)	$SO_3 + H_2O \rightarrow H_2SO_4$	$k_{65} = 9 \times 10^{-13}$	^{c}

Note. The units for mean photolysis rates (J), and two-body and three-body reactions (k) are sec^{-1}, $cm^3\ sec^{-1}$, and $cm^6\ sec^{-1}$, respectively. For removal by aerosol, the collision rate ($J\ sec^{-1}$) of the minor constituent with aerosol is considered as the rate-limiting step. The numerical values for photolysis refer to 70 km, mid-latitude. Extended sets of reactions are included in Tables IIIb,c, AI, and BI.

[a] Data drawn from Hampson and Garvin (1978).

[b] Data drawn from Hampson (1980).

[c] Data drawn from Baulch *et al.* (1980), CODATA review.

[d] Data drawn from DeMore *et al.* (1981), JPL 4.

[e] Value based on $M = N_2$, multiplied by 2.

[f] Calculated as the backward reaction of (R38); should be more accurate than that quoted in [a].

[g] Estimated by present authors.

[h] $k^{-1} = k_0^{-1} + (k_\infty/M)^{-1}$.

TABLE IIIb

List of Reactions Related to Miscellaneous Compounds of Odd Nitrogen (Footnotes Refer to TABLE IIIa)

	Reaction	Rate coefficient	Reference
(R66)	$NO + h\nu \rightarrow N + O$	J_{66}*	Yung and McElroy (1979)
(R67)	$NO_2 + h\nu \rightarrow NO + O$	$J_{67} = 1 \times 10^{-2}$	Yung *et al.* (1980)
(R68a)	$NO_3 + h\nu \rightarrow NO_2 + O$	$J_{68a} = 2 \times 10^{-2}$	Yung *et al.* (1980)
(R68b)	$NO_3 + h\nu \rightarrow NO + O_2$	$J_{68b} = 1 \times 10^{-2}$	Yung *et al.* (1980)
(R69)	$HNO + h\nu \rightarrow H + NO$	$J_{69} = 1 \times 10^{-3}$	g
(R70)	$HNO_2 + h\nu \rightarrow OH + NO$	$J_{70} = 2 \times 10^{-3}$	Yung and McElroy (1979)
(R71)	$HNO_3 + h\nu \rightarrow OH + NO_2$	$J_{71} = 5.4 \times 10^{-5}$	Yung *et al.* (1980)
(R72a)	$N + O \rightarrow NO + h\nu$	$k_{72a} = 2.5 \times 10^{-17}$	Stewart *et al.* (1980)
(R72b)	$N + O + M \rightarrow NO + M$	$k_{72b} = 1.9 \times 10^{-31} T^{-1/2}$	Stewart *et al.* (1980
(R73)	$N + O_2 \rightarrow NO + O$	$k_{73} = 4.4 \times 10^{-12} e^{-3270/T}$	d
(R74)	$N + O_3 \rightarrow NO + O_2$	$k_{74} = 1 \times 10^{-15}$	d
(R75)	$N + OH \rightarrow NO + H$	$k_{75} = 5.3 \times 10^{-11}$	d
(R76)	$N + NO \rightarrow N_2 + O$	$k_{76} = 2.1 \times 10^{-11}$	Stewart *et al.* (1980)
(R77)	$NO + O + M \rightarrow NO_2 + M$	$k_{77} = 2.4 \times 10^{-31}$	c,e
(R78)	$NO + O_3 \rightarrow NO_2 + O_2$	$k_{78} = 2.3 \times 10^{-12} e^{-1450/T}$	d
(R79)	$NO + H + M \rightarrow HNO + M$	$k_{79} = 1.5 \times 10^{-32} e^{300/T}$	a
(R80)	$NO + OH + M \rightarrow HNO_2 + M$	$k_{80} = 1.3 \times 10^{-30}$	c,e
(R81)	$NO + HO_2 \rightarrow NO_2 + OH$	$k_{81} = 3.5 \times 10^{-12} e^{250/T}$	d
(R82)	$NO + ClO \rightarrow NO_2 + Cl$	$k_{82} = 6.5 \times 10^{-12} e^{280/T}$	d
(R83a)	$NO_2 + O \rightarrow NO + O_2$	$k_{83a} = 9.3 \times 10^{-12}$	c
(R83b)	$NO_2 + O + M \rightarrow NO_3 + M$	$k_{83b} = 1.8 \times 10^{-31}$	c,e
(R84)	$NO_2 + OH + M \rightarrow HNO_3 + M$	$k_{84} = 5.2 \times 10^{-30}$	c,e
(R85)	$NO_2 + SO \rightarrow NO + SO_2$	$k_{85} = 1.4 \times 10^{-11}$	c
(R86)	$HNO + O \rightarrow OH + NO$	$k_{86} = k_{87} = 1 \times 10^{-13}$	g
(R87)	$HNO + H \rightarrow H_2 + NO$	$k_{87} = 1 \times 10^{-13}$	b
(R88)	$HNO + Cl \rightarrow HCl + NO$	$k_{88} = k_{87} = 1 \times 10^{-13}$	g
(R89)	$2HNO \rightarrow N_2O + H_2O$	$k_{89} = 4 \times 10^{-15}$	a
(R90)	$HNO_2 + OH \rightarrow H_2O + NO_2$	$k_{90} = 6.6 \times 10^{-12}$	a
(R91)	$HNO_3 + OH \rightarrow H_2O + NO_3$	$k_{91} = 1.5 \times 10^{-14}$	d

* The mean dissociation rate for NO due to δ band absorption is given by $J_{66}(z) = 1.7 \times 10^{-6} \exp(-1.5\sigma_1 N) + 1.2 \times 10^{-6} \exp(-1.5\sigma_2 N)$, where $\sigma_1 = 2.8 \times 10^{-23}$ cm², $\sigma_2 = 5.6 \times 10^{-22}$ cm², and $N = \int_z^\infty dz[CO_2]$.

works, but has been critically assessed and updated. In general, the chemistry of carbon, oxygen, hydrogen, nitrogen, and chlorine species is well defined, due, in part, to recent progress in the chemistry of the Martian atmosphere (McElroy and Donahue, 1972) and the Earth's stratosphere (NAS, 1976; Logan *et al.*, 1978; NASA, 1977, 1979). Our understanding of the chemistry of sulfur is still at a rather primitive stage, even for the Earth's atmosphere (Crutzen, 1976; Turco *et al.*, 1979; Sze and Ko, 1980).

Most reactions in Tables IIIa,b, and c have recently been evaluated by Hampson and Garvin (1978), Hampson (1980), Baulch *et al.* (1980), and DeMore *et al.* (1981), and the reader is referred to these publications for a critical discussion. The rate constants for the following three-body reactions,

$$2\,O + M \rightarrow O_2 + M, \quad (R17)$$

$$H + O_2 + M \rightarrow HO_2 + M, \quad (R22)$$

$$H + H + M \rightarrow H_2 + M, \quad (R24)$$

$$SO_2 + O + M \rightarrow SO_3 + M \quad (R58)$$

$$SO_2 + Cl + M \rightarrow ClSO_2 + M, \quad (R62)$$
$$NO + O + M \rightarrow NO_2 + M, \quad (R77)$$
$$Cl + Cl + M \rightarrow Cl_2 + M, \quad (R107)$$

have for the most part not been measured for $M = CO_2$. We have taken the rate coefficients to be twice the corresponding values for $M = N_2$, to account for the greater efficiency of CO_2 as a third body.

The photochemistry of SO plays a key role in breaking the O–O bond in schemes (6a,b) (see Table II). The cross sections for SO photolysis,

$$SO + h\nu \rightarrow S + O, \quad (R8)$$

have recently been measured at JPL by Phillips (1981). The results are close to those estimated by Winick and Stewart (1980) on the basis of analogy between the O_2 and SO Schumann–Runge bands (Okabe, 1978; McGarvey and McGrath, 1964; Colin, 1969; Krupenie, 1972; Smith and Liszt, 1971), and thus confirm the importance of scheme (5a). The rate coefficient for

$$2\ SO \rightarrow SO_2 + S \quad (R57)$$

is probably an order of magnitude faster than that adopted by Winick and Stewart (1980), as suggested by Herron and Huie's (1980) experiment, and thus scheme (6b) could be even more important than was thought.

The success of schemes (6a,b) critically depends on the bond-breaking reaction (R46), $S + O_2$, which is the major sink for S

TABLE IIIc

LIST OF REACTIONS RELATED TO MISCELLANEOUS COMPOUNDS OF CHLORINE (FOOTNOTES REFER TO TABLE IIIa).

	Reaction	Rate coefficient	Reference
(R92)	$Cl_2 + h\nu \rightarrow 2Cl$	$J_{92} = 2.4 \times 10^{-3}$	Yung *et al.* (1980)
(R93)	$COCl_2 + h\nu \rightarrow COCl + Cl$	$J_{93} = 5 \times 10^{-5}$	[c]
(R94)	$HOCl + h\nu \rightarrow OH + Cl$	$J_{94} = 4 \times 10^{-4}$	Yung *et al.* (1980)
(R95)	$NOCl + h\nu \rightarrow NO + Cl$	$J_{95} = 1.4 \times 10^{-3}$	Okabe (1978)
(R96)	$Cl + O_2 + M \rightarrow ClOO + M$	$k_{96} = 3.3 \times 10^{-30} T^{-1.3}$	[d]
(R97)	$ClOO + M \rightarrow Cl + O_2 + M$	$k_{97} = 2.7 \times 10^{-9} e^{-2650/T}$	[d]
(R98)	$Cl + H + M \rightarrow HCl + M$	$k_{98} = 1 \times 10^{-32}$	[g]
(R99)	$Cl + CO + M \rightarrow ClCO + M$	$k_{99} = 1.3 \times 10^{-34} e^{1000/T}$	Clark *et al.* (1966)
(R100)	$ClCO + M \rightarrow Cl + CO + M$	$k_{100} = 6 \times 10^{-11} e^{-2250/T}$	See text
(R101)	$ClCO + O_2 + M \rightarrow ClCO_3 + M$	$k_{101} = \dfrac{5.7 \times 10^{-15} e^{500/T}}{1 \times 10^{17} + 0.05M}$	See text
(R102a)	$ClCO + O \rightarrow CO_2 + Cl$	$k_{102a} = 3 \times 10^{-11}$	[g]
(R102b)	$ClCO + O \rightarrow CO + ClO$	$k_{102b} = 3 \times 10^{-12}$	[g]
(R103)	$ClCO + H \rightarrow HCl + CO$	$k_{103} = 1 \times 10^{-11}$	[g,*]
(R104)	$ClCO + Cl \rightarrow CO + Cl_2$	$k_{104} = 1 \times 10^{-11}$	[g,*]
(R105)	$ClCO + Cl_2 \rightarrow COCl_2 + Cl$	$k_{105} = 6 \times 10^{-13} e^{-1400/T}$	Kranopolsky and Parshev (1980a)
(R106)	$2ClCO \rightarrow COCl_2 + CO$	$k_{106} = 1 \times 10^{-11}$	[g,*]
(R107)	$2Cl + M \rightarrow Cl_2 + M$	$k_{107} = 1.2 \times 10^{-33} e^{900/T}$	[b,e]
(R108)	$Cl_2 + O \rightarrow ClO + Cl$	$k_{108} = 4.2 \times 10^{-12} e^{-1370/T}$	[a]
(R109)	$Cl_2 + H \rightarrow HCl + Cl$	$k_{109} = 1.5 \times 10^{-10} e^{-593/T}$	[a]
(R110)	$ClCO_3 + O \rightarrow CO_2 + Cl + O_2$	$k_{110} = 1 \times 10^{-11}$	See text
(R111)	$ClCO_3 + Cl \rightarrow CO_2 + Cl + ClO$	$k_{111} = 1 \times 10^{-11}$	See text
(R112)	$ClCO_3 + H \rightarrow CO_2 + Cl + OH$	$k_{112} = 1 \times 10^{-11}$	See text
(R113)	$Cl + O + M \rightarrow ClO + M$	$k_{113} = 5 \times 10^{-32}$	[g]
(R114)	$ClO + HO_2 \rightarrow HOCl + O_2$	$k_{114} = 4.6 \times 10^{-13} e^{710/T}$	[d]

[*] Reactions with ClCO based on analogy with HCO (Pinto *et al.*, 1980).

in our models (Table III). The reaction

$$S + CO_2 \rightarrow CO + SO \quad (R47)$$

is only slightly endothermic, with $\Delta H = 2.6$ kcal/mole, and can compete with (R46). The activation energy is probably very high, but a rate coefficient as low as 1×10^{-20} cm^3 sec^{-1} is not ruled out, and (R47) could be marginally important.

Clyne and MacRobert (1981) reported a fast rate coefficient for

$$SO + ClO \rightarrow SO_2 + Cl, \quad (R56)$$

$k_{56} = 2.3 \times 10^{-11}$ cm^3 sec^{-1}. Since the bond strengths for Cl–O and HO–O are both equal to 64 kcal/mole, reactions of HO_2 frequently are similar in rate to analogous reactions involving ClO, as illustrated by the pair of reactions

$$NO + ClO \rightarrow NO_2 + Cl, \quad k_{82} = 1.8 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1},$$

$$NO + HO_2 \rightarrow NO_2 + OH, \quad k_{81} = 8.4 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1},$$

and the pair

$$O + ClO \rightarrow O_2 + Cl, \quad k_{44} = 5.0 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1},$$

$$O + HO_2 \rightarrow O_2 + OH, \quad k_{31} = 3.1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$$

(the rate coefficients have been evaluated at room temperature). We argue that the reaction

$$SO + HO_2 \rightarrow SO_2 + OH \quad (R55)$$

should be similar in rate to (R56), and could provide a major pathway for breaking the O–O bond [schemes (11) and (12)]. The alternative branch

$$SO + HO_2 \rightarrow HSO + O_2$$

is probably slow, and is most probably followed by

$$O + HSO \rightarrow OH + SO.$$

This would result in recycling HO_x radicals, and would be of secondary importance even if the branching ratio were to equal unity. Reaction (R55) seems to have been first noted by Sze and Smyth (1979) in an unpublished NASA report. However, prior to the result of Clyne and MacRobert (1981), the authors made a much lower estimate for the rate coefficient, $k_{55} = 1 \times 10^{-14}$ cm^3 sec^{-1}.

The efficiency of the catalytic scheme for oxidation of SO_2,

$$SO_2 + HO_2 \rightarrow SO_3 + OH, \quad (R60)$$

as considered by Prinn (1973, 1975) and Winick and Stewart (1980), is probably overestimated. The recent work of Graham *et al.* (1979) and Sander and Watson (1981) strongly suggests that $k_{60} < 10^{-18}$ cm^3 sec^{-1}, which is orders of magnitude slower than that preferred by the previous authors.

SO_2 may provide a loss of HO_x, as is assumed in the Winick–Stewart model

$$SO_2 + OH + M \rightarrow HSO_3 + M, \quad (R59)$$

but *not* in Prinn (1973, 1975). There can be additional sinks for HO_x and ClO_x radicals in the lower stratosphere. McElroy (1973) private communication and Sze and Smyth (1979) suggested that

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \text{ (heterogeneous)} \quad (R61)$$

could oxidize SO_2 and destroy HO_x. Strattan *et al.* (1979) suggested that

$$Cl + SO_2 + M \rightarrow ClSO_2 + M \quad (R62)$$

could be a sink for ClO_x. The detailed mechanisms for radical losses implied by (R59), (R61), and (R62) have never been elucidated. The work of Davis *et al.* (1979) and Friend *et al.* (1980) offers plausible arguments that (R59) results in the loss of a HO_x in *terrestrial* environments. We shall examine the validity of these arguments for conditions appropriate to Venus in Appendix A.

An investigation of heterogeneous reactions is not the main thrust of this work. Removal of gas molecules by aerosols is simply modeled as a net loss rate given by $J = \frac{1}{4} \gamma v A N_a$, where N_a = number density of aerosols (cm^{-3}), A = mean surface area of aerosol (cm^2), v = thermal velocity of gas molecules, and γ = sticking coefficient. The profiles for N_a and A are taken from Knollenberg and Hunten (1980). The sticking coefficients are based on Baldwin and Golden (1979) and Golden (1981, private communication): $\gamma_{H_2O_2} = 1.6 \times 10^{-3}$, $\gamma_{radicals} \sim \gamma_{OH} = 1 \times 10^{-4}$. It can be shown that heterogeneous losses are not important for most species considered in our model, with the possible exception of those initiated by (R59), (R61), and (R62). In Table IIIa (model A) we assumed, for simplicity, that these three reactions result in net destruction of HO_x or ClO_x. In models B and C we adopt an alternative set of reactions involving HSO_3 as given in Table A1 (Appendix A). The crucial reactions that can retrieve the HO_x radical tied by HSO_3 are

$$HSO_3 + O \rightarrow OH + SO_3, \quad \text{(R116)}$$
$$HSO_3 \cdot H_2O + O \rightarrow OH + H_2SO_4. \quad \text{(R122)}$$

The rate coefficient for this type of hydrogen abstraction reaction correlates with exothermicity, and on this basis we estimate a value of 1×10^{-11} cm^3 sec^{-1} for k_{105} and k_{111}. We have little information on the thermodynamics and chemical kinetics of $ClSO_2$. We assume that its properties are similar to HSO_3.

Prinn (1971) suggested that ClOO could be important as a key species for breaking the O–O band via cycle (1). Subsequent laboratory results (Cox *et al.*, 1979) indicate, however, that the equilibrium constant $K_{eq} = k_{96}/k_{97}$ is smaller than Prinn's estimate (Prinn, 1972). Further, there is no evidence that ClOO reacts rapidly with CO. Thus cycle (1) does not play a significant role in the Venus atmosphere. There is, however, a close analog to the ClOO cycle, which involves the well-known radical ClCO. Krasnopolsky and Parshev (1980a,b, 1981) and the present authors have considered the possible role of ClCO in cycles (4). We will briefly discuss the chemistry of ClCO, which is formed by the reaction

$$Cl + CO + M \rightarrow ClCO + M. \quad \text{(R99)}$$

The rate constant has been measured by Clark *et al.* (1966), who obtained $k_{99} = 8.7 \times 10^{-34}$ for M = Ar at 300°K, with an apparent activation energy of −2 kcal. Our value for k_{99} with $M = CO_2$ is based on their data, with a factor of 4 increase in rate constant to allow for the higher third-body efficiency of CO_2. ClCO is readily destroyed by thermal decomposition,

$$ClCO + M \rightarrow CO + Cl + M. \quad \text{(R100)}$$

The equilibrium constant k_{99}/k_{100} has been measured by Burns and Dainton (1952) by a somewhat indirect method. Reaction of ClCO with O_2 was considered in early work (for review, see Heicklen, 1969) to be a direct four-center reaction

$$ClCO + O_2 \rightarrow CO_2 + ClO.$$

Krasnopolsky and Parshev (1980a) accepted this mechanism and assumed $k_{99} = 3 \times 10^{-33}$ cm^6 sec^{-1}, $k_{100} = 1 \times 10^{-12}\ e^{-3200/T}$ cm^3 sec^{-1}, and $k = 2 \times 10^{-14}$ cm^3 sec^{-1} for the four-center reaction. However, these values give an equilibrium constant k_{99}/k_{100} which is about three orders of magnitude higher than that measured by Burns and Dainton (1952). Thus the high efficiency for the ClCO scheme claimed by Krasnopolsky and Parshev (1981) is unrealistic. Recent work by Spence *et al.* (1978), Ohta and Mizoguchi (1982), and in our own laboratory (DeMore *et al.*, 1982) has shown that the oxidation of ClCO by O_2 occurs as a three-body process, involving an intermediate complex, the peroxychloroformyl radical,

$$ClCO + O_2 + M \rightarrow ClCO_3 + M. \quad \text{(R101)}$$

The rate coefficient, based on our own laboratory studies, can be approximated as

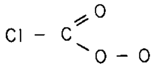
$$k_{101} = \frac{5.7 \times 10^{-15} e^{500/T}}{1 \times 10^{17} + 0.05\ M}\ cm^6\ sec^{-1},$$

where M is the number density of CO_2 in molecules per cubic centimeter. The value of k_{101} in the low-pressure limit at room temperature is 3.0×10^{-31} cm^6 sec^{-1}, and should be compared with the rate coefficients for the following reactions of similar complexity under similar conditions:

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M, \quad k = 2.2 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1},$$

$$C_2H_5 + O_2 + M \rightarrow C_2H_5O_2 + M, \quad k = 7.5 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1}$$

(DeMore *et al.*, 1981; Plumb and Ryan, 1981). The comparison shows that the rate coefficient k_{101} we obtained is reasonable. The structure of the peroxychloroformyl radical is known (Spence *et al.*, 1978):



Reaction with the radical should proceed most readily via the unbonded oxygen, as, for instance, in

$$ClC(O)O_2 + O \rightarrow ClC(O)O + O_2.$$

The oxychloroformyl radical is unstable and decays by

$$ClC(O)O \rightarrow Cl + CO_2.$$

The net result of these two reactions can be summarized by

$$ClCO_3 + O \rightarrow Cl + CO_2 + O_2. \quad \text{(R110)}$$

There are obviously similar reactions with Cl and H,

$$ClCO_3 + Cl \rightarrow Cl + CO_2 + ClO, \quad \text{(R111)}$$
$$ClCO_3 + H \rightarrow Cl + CO_2 + OH. \quad \text{(R112)}$$

No experimental data are available for these reactions, and we estimate a rate coefficient for 1×10^{-11} cm^3 sec^{-1} for all three. Fortunately, the exact rate coefficients are not critical because O and Cl are the dominant radicals and other competing pathways are not important. We have not included in our model two reactions of interest to laboratory studies, but probably of limited application to the atmosphere of Venus:

$$ClCO_3 + NO \rightarrow Cl + CO_2 + NO_2,$$
$$2ClCO_3 \rightarrow 2Cl + 2CO_2 + O_2.$$

The chemistry of nitrogen compounds shown in Table IIIb is straightforward, and is based on McConnell and McElroy (1973), Yung *et al.* (1977), and Yung and McElroy (1979). In the mesosphere the major loss of NO_x is by the reaction

$$N + NO \rightarrow N_2 + O, \quad \text{(R76)}$$

where the N atoms are derived either from ionospheric reactions (Rusch and Cravens, 1979) or from photolysis of NO,

$$NO + h\nu \rightarrow N + O. \quad \text{(R66)}$$

The procedure for calculating loss of NO_x by (R76) is a well-defined one, the only uncertainty being the eddy diffusion coefficient in the mesosphere.

There could be another major chemical sink for NO_x in an atmosphere with an abundant supply of atomic hydrogen. Kasting (1979) first suggested that the following sequence of reactions,

$$H + NO + M \rightarrow HNO + M, \quad \text{(R79)}$$
$$2HNO \rightarrow N_2O + H_2O, \quad \text{(R89)}$$
$$N_2O + h\nu \rightarrow N_2 + O(^1D),$$

could be an important sink for NO_x in the primitive atmosphere of the Earth. This scheme is adopted in Table IIIb. Although the detailed mechanism for the disproportionation reaction (R89) is not well understood, the reaction has been studied by Kohout and Lampe (1967), and recently by Cheskis *et al.* (1981). The product N_2O was positively identified by Kohout and Lampe. The latter group reported a rate constant that is about five times slower than that obtained by the former group. However, there is a major uncertainty in computing the photolysis rate for HNO,

$$HNO + h\nu \rightarrow H + NO, \quad \text{(R69)}$$

since the appropriate cross sections have not been measured. The H–NO bond en-

$$T(z) = e^{-(70-z)/H}, \qquad 58 \text{ km} \leq z \leq 70 \text{ km},$$
$$T(z) = 1, \qquad z \geq 70 \text{ km},$$

where $H = 8$ km. This choice of $T(z)$ has been guided by the ultraviolet photometric observations of Ragent and Blamont (1980) over this altitude range.

The eddy diffusivity profile in the upper atmosphere near the homopause (~140 km) has been determined by von Zahn *et al.* (1979), who proposed the expression

$$K(z) = 2 \times 10^{13}/M^{1/2} \text{ cm}^2 \text{ sec}^{-1},$$

where M = number density of ambient atmosphere in molecules per cubic centimeter. Between 58 and 110 km $K(z)$ has not been determined, and we are guided only by the theoretical work of Prinn (1975) and the measurements of thermal structure by Seiff *et al.* (1980). Figure 1a gives the temperature lapse rate derived from the day probe data of Seiff *et al.* (1980) by Pechmann (1981, private communication). As pointed out by Seiff *et al.* (1980), the region of the atmosphere above the cloud tops exhibits a stable lapse rate and should be appropriately designated the principal Venus stratosphere. Hence the trend of von Zahn *et al.*'s (1979) $K(z)$ extrapolated to the lower stratosphere must be correct. By trial and error, we arrive at profile A for model A and profile B for models B and C as shown in Fig. 1b. The high value around 70 km is essential for ensuring rapid downward transport of O_2 to be used by SO_2 and thus keeping its mixing ratio at about or below 1×10^{-6}. The decrease between 70 and 58 km is needed for reproducing the correct scale height of SO_2 around 70 km. Our choices of $K(z)$ are consistent with the recent work by Woo and Ishimaru (1981), who deduced $K = 4 \times 10^4$ cm² sec⁻¹ at the tropopause from Pioneer Venus radio scintillation measurements.

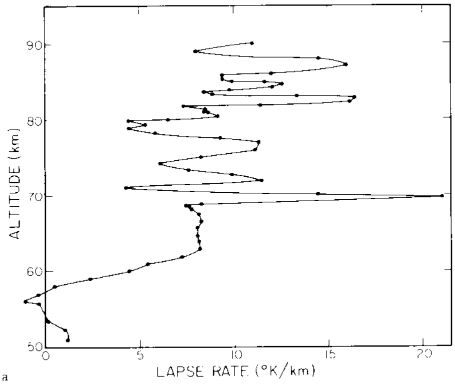


FIG. 1a. Temperature lapse rate for the stratosphere of Venus, based on the data of Seiff *et al.* (1980). The lapse rate is evaluated using the expression $\Gamma = g/cp - (\sigma g/RT)(dT/d\sigma)$, where $\sigma = \ln p/p_0$ (Pechmann, 1981, private communication).

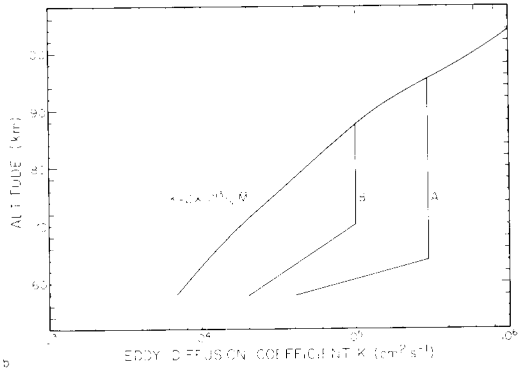


FIG. 1b. The eddy diffusivity profile $K(z)$. von Zahn *et al.*'s (1979) suggestion is $K(z) = 2 \times 10^{13}/M^{1/2}$. Profile A is used in model A, profile B is used in models B and C.

We consider three models. The key assumptions and boundary conditions for the models are summarized in Tables V and VI. Model A adopts the set of reactions given in Table IIIa. The mixing ratio of H_2 equals 2×10^{-5}, as suggested by Kumar *et al.* (1981). Models B and C adopt additional sets of reactions listed in Tables IIIb,c and A1. The mixing ratio of H_2 in model B is 5×10^{-7}. In model C, H_2 is calculated by the photochemical model with no tropospheric input. The adjustment of certain parameters, all within current uncertainties, is intended to optimize the agreement between model predictions and observations.

4. RESULTS AND DISCUSSION

The results for models A, B, and C will be discussed separately. A comparison be-

TABLE IV

SOLAR FLUX AND CROSS SECTIONS

λ	πF	σ(CO_2)	σ_a(SO_2)	σ(SO_2)	σ(HCl)	σ(SO)
1216	5.01(11)	7.3(−20)	3.7(−17)		2.0(−18)	↑
1250	1.72(10)	2.5(−19)	7.4(−17)		1.9(−18)	
1300	2.57(10)	6.7(−19)	1.9(−17)		1.7(−18)	
1350	4.04(10)	7.8(−19)	3.7(−18)		1.5(−18)	
1400	3.88(10)	6.1(−19)	3.7(−18)		1.4(−18)	
1450	4.29(10)	5.9(−19)	4.5(−18)		2.5(−18)	
1500	6.76(10)	5.4(−19)	5.2(−18)		3.4(−18)	
1550	1.33(11)	3.6(−19)	3.2(−18)		3.4(−18)	
1600	1.26(11)	1.8(−19)	1.1(−18)		2.7(−18)	
1650	2.37(11)	7.3(−20)	4.1(−19)		2.1(−18)	
1700	3.92(11)	1.8(−20)	4.5(−19)		1.4(−18)	1.0(−18)
1750	5.89(11)	4.8(−21)	1.1(−18)		8.1(−19)	
1800	1.62(11)	1.0(−21)	2.6(−18)		5.9(−19)	
1810	1.82(11)	7.5(−22)	2.6(−18)		5.4(−19)	
1820	1.98(11)	5.6(−22)	2.7(−19)		4.8(−19)	
1830	2.00(11)	3.6(−22)	3.1(−18)		4.2(−19)	
1840	1.93(11)	2.6(−22)	3.3(−18)		3.5(−19)	
1850	1.93(11)	1.7(−22)	3.6(−18)		3.1(−19)	
1860	2.21(11)	1.3(−22)	3.9(−18)		2.8(−19)	
1870	2.57(11)	1.0(−22)	3.9(−18)		2.4(−19)	
1880	2.84(11)	7.4(−23)	3.8(−18)		2.0(−19)	
1890	3.11(11)	5.6(−23)	4.5(−18)		1.7(−19)	↓
1900	3.36(11)	4.3(−23)	5.0(−18)		1.5(−19)	9.9(−18)
1910	3.64(11)	2.8(−23)	5.5(−18)		1.2(−19)	1.2(−17)
1920	4.01(11)	1.8(−23)	5.1(−18)		1.1(−19)	1.1(−17)
1930	3.73(11)	1.4(−23)	6.0(−18)		7.8(−20)	1.1(−17)
1940	4.08(11)	1.2(−23)	6.0(−18)		6.5(−20)	1.2(−17)
1950	5.05(11)	1.0(−23)	5.3(−18)		6.2(−20)	1.3(−17)
1960	5.44(11)	5.4(−24)	6.5(−18)		5.4(−20)	1.4(−17)
1970	5.88(11)	3.3(−24)	6.3(−18)		4.5(−20)	1.5(−17)
1980	6.10(11)	2.3(−24)	5.1(−18)		3.8(−20)	1.5(−17)
1990	6.31(11)	1.7(−24)	6.7(−18)		3.2(−20)	1.4(−17)
2000	6.89(11)	1.3(−24)	6.1(−18)		2.6(−20)	1.6(−17)
2010	7.58(11)	9.0(−25)	4.9(−18)		2.2(−20)	9.6(−18)
2020	8.10(11)	6.0(−25)	6.8(−18)		1.8(−20)	1.6(−17)
2030	8.85(11)	4.8(−25)	5.7(−18)		1.5(−20)	8.6(−18)
2040	9.97(11)	4.3(−25)	4.6(−18)		1.3(−20)	1.7(−17)
2050	1.09(12)	—	5.9(−18)		9.8(−21)	8.1(−18)
2060	1.14(12)	—	4.3(−18)		8.6(−21)	1.4(−17)
2070	1.25(12)	—	5.9(−18)		7.2(−21)	4.6(−18)
2080	1.43(12)	—	4.3(−18)		6.0(−21)	1.4(−17)
2090	1.82(12)	—	3.2(−18)		5.0(−21)	4.3(−18)
2100	2.52(12)	—	4.3(−18)		4.0(−21)	1.4(−17)
2110	3.12(12)	—	2.7(−18)	2.6(−18)	3.3(−21)	4.3(−18)
2120	3.45(12)	—	3.7(−18)	3.5(−18)	2.7(−21)	9.5(−18)
2130	3.51(12)	—	2.4(−18)	2.2(−18)	2.1(−18)	5.5(−18)
2140	3.90(12)	—	2.4(−18)	2.0(−18)	1.8(−21)	3.0(−18)
2150	4.28(12)	—	2.4(−18)	1.9(−18)	1.4(−21)	9.5(−18)
2160	3.92(12)	—	1.2(−18)	9.4(−19)	1.1(−21)	2.4(−18)
2170	3.64(12)	—	1.9(−18)	1.4(−18)	9.0(−22)	5.6(−18)
2180	4.42(12)	—	8.7(−19)	6.4(−19)	7.0(−22)	4.0(−18)
2190	5.31(12)	—	1.3(−18)	8.8(−19)	6.0(−22)	1.5(−18)
2200	5.63(12)	—	8.3(−19)	—	4.8(−22)	4.4(−18)

TABLE IV—*Continued*

λ	πF	$\sigma(CO_2)$	$\sigma_a(SO_2)$	$\sigma(SO_2)$	$\sigma(HCl)$	$\sigma(SO)$
2210	5.05(12)	—	9.1(−19)	—	—	9.0(−19)
2220	5.14(12)	—	5.3(−19)	—	—	2.8(−19)
2230	6.89(12)	—	3.6(−19)	—	—	2.7(−18)
2240	7.43(12)	—	3.4(−19)	—	—	1.2(−19)
2250	6.68(12)	—	2.7(−20)	—	—	9.0(−19)
2260	5.40(12)	—	2.9(−19)	—	—	1.1(−18)
2270	4.71(12)	—	1.6(−19)	—	—	4.9(−20)
2280	5.72(12)	—	2.0(−19)	—	—	2.5(−19)
2290	6.14(12)	—	6.8(−20)	—	—	7.2(−19)
2300	6.32(12)	—	1.4(−19)	—	—	4.6(−21)
2310	6.41(12)	—	6.8(−20)	—	—	1.2(−19)
2320	2.24(12)	—	4.5(−20)	—	—	5.3(−19)

Note. The solar flux at 1 AU, πF, is given for Ly α, 1250–1800 Å, and 1800–2320 Å in units of photons cm^{-2} sec^{-1}, cm^{-2} sec^{-1} $(50\ Å)^{-1}$, cm^{-2} sec^{-1} $(10\ Å)^{-1}$, respectively. The appropriately averaged cross sections (cm^2) are based on references cited in Table IIIa. The cross sections of CO_2 and SO_2 were evaluated at 250°K. σ_a is absorption cross section. $a\ (-b)$ reads as $a \times 10^{-b}$.

tween model predictions and observations will follow. To facilitate comparisons with previous work, we cross-reference a selected set of the crucial parameters and rate coefficients in Table VII. All rate coefficients have been evaluated at 250°K. The large differences between the various models reflect the progress that has been made in the past decade, and the uncertainties that remain. The essential element in model A is the high H_2 abundance, which sustains the HO_x schemes for the oxidation of CO and SO_2, and suppresses the ClO_x scheme for the production of O_2. In model B, the amount of H_2 is much less, and NO_x chemistry plays a major role in breaking the O–O bond. In model C, the major catalytic

TABLE V

MODELS AND ASSUMPTIONS

	Model A	Model B	Model C
f_{H_2}	2×10^{-5}	5×10^{-7}	1×10^{-13}[a]
f_{HCl}	4×10^{-7}	4×10^{-7}	8×10^{-7}
f_{NO_x}	0	3×10^{-8}	0
Eddy diffusivity profile (Fig. 1b)	A	B	B
Reaction set	Table IIIa	Tables IIIa + b + c + AI	Tables IIIa + c + AI
Heterogeneous sinks[b]	Included	Excluded	Excluded

[a] Value refers to lower boundary, determined by photochemical equilibrium.

[b] (R59) SO_2 + OH, (R62) SO_2 + Cl.

TABLE VI

BOUNDARY CONDITIONS FOR CHEMICAL SPECIES SOLVED IN THE ONE-DIMENSIONAL PHOTOCHEMICAL MODELS (TABLE V)

Model	Species	Lower boundary (58 km)	Upper boundary (110 km)
A	CO	$f = 4.5 \times 10^{-5}$	$\phi = -1.0 \times 10^{12}$
	O	$v = -6.2 \times 10^{-2}$	$\phi = -1.0 \times 10^{12}$
	O_2	$v = -6.2 \times 10^{-2}$	$\phi = 0$
	SO_2	$f = 1.5 \times 10^{-6}$	$\phi = 0$
B	CO	$f = 4.5 \times 10^{-5}$	$\phi = -1.0 \times 10^{12}$
	O	$v = -3.1 \times 10^{-2}$	$\phi = -1.0 \times 10^{12}$
	O_2	$v = -3.1 \times 10^{-2}$	$\phi = 0$
	SO_2	$f = 1.7 \times 10^{-6}$	$\phi = 0$
	NO	$f = 3.0 \times 10^{-8}$	$\phi = 0$
	N	$\phi = 0$	$\phi = -1.0 \times 10^{10}$
C	CO	$f = 4.5 \times 10^{-5}$	$\phi = -1.0 \times 10^{12}$
	O	$v = -2.0 \times 10^{-2}$	$\phi = -1.0 \times 10^{12}$
	O_2	$v = -2.0 \times 10^{-2}$	$\phi = 0$
	SO_2	$f = 4.0 \times 10^{-6}$	$\phi = 0$
	Cl_2	$v = -2.0 \times 10^{-2}$	$\phi = 0$
	H_2	$v = -2.0 \times 10^{-2}$	$\phi = 0$

Note. The mixing ratio for H_2O is held fixed at 1 ppm in all models. The mixing ratios for H_2 in models A and B are 2×10^{-5} and 5×10^{-7}, respectively. For short-lived species not explicitly listed here photochemical equilibrium is assumed (flux = 0) at both boundaries. The symbols f, φ, and v, respectively, denote mixing ratio, flux (cm^{-2} sec^{-1}), and velocity (cm sec^{-1}). The sign convention for φ and v is positive for upward flow. The maximum deposition velocity at the lower boundary is given by $v = -K/H$, where K = eddy diffusion coefficient and H = scale height.

TABLE VII

COMPARISON OF ESSENTIAL MODEL PARAMETERS AND RATE COEFFICIENTS FOR IMPORTANT REACTIONS IN OUR MODELS AND THOSE IN PREVIOUS WORKS

Model parameter or rate coefficient		Value adopted in model						
		P71	MSY73	SM74	P73,75	WS80	KP80	This work
	f_{H_2}	1.0(−5)	7.0(−8)	2.0(−7)	—	2.0(−7)	≈3.0(−10)	2(−5)^a 5(−7) 1(−13)
	K(60 km)	1.0(6)	1.0(6)	2.6(5)	5.0(4)	8.1(3)	2.1(4)	4.0(4)^a 2.0(4) 2.0(4)
	K(70 km)	1.0(6)	1.0(6)	6.3(5)	1.0(4)	1.9(4)	4.8(4)	3.0(5)^a 1.0(5) 1.0(5)
k_{16}	$O + HCl$	—	—	2.1(−16)	—	1.4(−17)	2.1(−16)	1.5(−17)
k_{21}	$H + HCl$	7.0(−15)	—	1.6(−14)	—	1.3(−14)	1.6(−14)	2.3(−14)
k_{27}	$OH + HCl$	2.5(−14)	—	5.8(−14)	—	5.5(−13)	5.8(−14)	5.5(−14)
k_{38}	$Cl + H_2$	4.4(−15)	3.9(−15)	3.9(−15)	—	1.1(−15)	3.9(−15)	4.0(−15)
k_{41a}	$Cl + HO_2$	—	—	1.0(−13)	—	3.0(−11)	1.0(−13)	4.1(−11)
k_{51}	$SO + O + M$	—	—	—	—	1.9(−31)	5.0(−31)	6.0(−31)
k_{55}	$SO + HO_2$	—	—	—	—	—	—	2.3(−11)
k_{57}	$SO + SO$	—	—	—	—	8.3(−16)	3.0(−15)	8.3(−15)
k_{58}	$SO_2 + O + M$	—	—	—	2.6(−32)	3.7(−34)	1.0(−32)	1.5(−33)
k_{59}	$SO_2 + OH + M$	—	—	—	5.4(−32)	1.6(−31)	—	2.3(−30)
k_{60}	$SO_2 + HO_2$	—	—	—	3.0(−16)	9.0(−16)	3.0(−16)	1.0(−18)
k_{81}	$NO + HO_2$	—	—	—	—	—	—	9.5(−12)
k_{101}	$ClCO + O_2$	—	—	—	—	—	2.0(−14)	4.2(−31)^b

Note. P71 = Prinn (1971); MSY = McElroy, Sze, and Yung (1973); SM = Sze and McElroy (1974); P73,75 = Prinn (1973, 1975); WS80 = Winick and Stewart (1980); KP80 = Krasnopolsky and Parshev (1980a). f_{H_2} is mixing ratio of H_2. $K(z)$ is eddy diffusion coefficient (cm^2 sec^{-1}). All rate coefficients are evaluated at 250°K. a $(-b)$ reads as $a \times 10^{-b}$.

[a] Values refer to models A, B, and C, respectively.

[b] Three-body limit, see text.

cycles are driven primarily by chlorine chemistry, without invoking the assistance of large amounts of H_2 or NO_x. In short, models A, B, and C test, respectively, the H_2 hypothesis, the NO_x hypothesis, and the new chlorine chemistry.

Model A

Altitude profiles for the concentrations of CO, O_2, and SO_2, as predicted by model A, and their comparisons with observations are presented in Fig. 2. Reaction rates for the major reactions involved in the production and consumption of oxygen, (R1) $CO_2 + h\nu$, (R25) $CO + OH$, and (R58) $SO_2 + O$, are given in Fig. 3. Detailed inventories, tracing through the budgets and flows of the major species, are shown in Figs. 4a and b. In Fig. 4b, the column abundances above the cloud tops are given in units of 1×10^{18} molecules cm^{-2}. The flux units are 10^{12} molecules cm^{-2} sec^{-1}. Figures 4a,b reveal the intimate relations between the chemistry of the upper atmosphere, driven by photochemistry, and the lower atmosphere, dominated by thermochemical equilibrium. The net result of stratospheric chemistry is the production of disequilibrium products,

$$CO_2 + SO_2 + H_2O + h\nu \rightarrow CO + H_2SO_4.$$

TABLE VII

COMPARISON OF ESSENTIAL MODEL PARAMETERS AND RATE COEFFICIENTS FOR IMPORTANT REACTIONS IN OUR MODELS AND THOSE IN PREVIOUS WORKS

Model parameter or rate coefficient		Value adopted in model						
		P71	MSY73	SM74	P73,75	WS80	KP80	This work
	f_{H_2}	1.0(−5)	7.0(−8)	2.0(−7)	—	2.0(−7)	≈3.0(−10)	2(−5)[a] 5(−7) 1(−13)
	K(60 km)	1.0(6)	1.0(6)	2.6(5)	5.0(4)	8.1(3)	2.1(4)	4.0(4)[a] 2.0(4) 2.0(4)
	K(70 km)	1.0(6)	1.0(6)	6.3(5)	1.0(4)	1.9(4)	4.8(4)	3.0(5)[a] 1.0(5) 1.0(5)
k_{16}	O + HCl	—	—	2.1(−16)	—	1.4(−17)	2.1(−16)	1.5(−17)
k_{21}	H + HCl	7.0(−15)	—	1.6(−14)	—	1.3(−14)	1.6(−14)	2.3(−14)
k_{27}	OH + HCl	2.5(−14)	—	5.8(−14)	—	5.5(−13)	5.8(−14)	5.5(−14)
k_{38}	$Cl + H_2$	4.4(−15)	3.9(−15)	3.9(−15)	—	1.1(−15)	3.9(−15)	4.0(−15)
k_{41a}	$Cl + HO_2$	—	—	1.0(−13)	—	3.0(−11)	1.0(−13)	4.1(−11)
k_{51}	SO + O + M	—	—	—	—	1.9(−31)	5.0(−31)	6.0(−31)
k_{55}	$SO + HO_2$	—	—	—	—	—	—	2.3(−11)
k_{57}	SO + SO	—	—	—	—	8.3(−16)	3.0(−15)	8.3(−15)
k_{58}	SO_2 + O + M	—	—	—	2.6(−32)	3.7(−34)	1.0(−32)	1.5(−33)
k_{59}	SO_2 + OH + M	—	—	—	5.4(−32)	1.6(−31)	—	2.3(−30)
k_{60}	$SO_2 + HO_2$	—	—	—	3.0(−16)	9.0(−16)	3.0(−16)	1.0(−18)
k_{81}	$NO + HO_2$	—	—	—	—	—	—	9.5(−12)
k_{101}	$ClCO + O_2$	—	—	—	—	—	2.0(−14)	4.2(−31)[b]

Note. P71 = Prinn (1971); MSY = McElroy, Sze, and Yung (1973); SM = Sze and McElroy (1974); P73,75 = Prinn (1973, 1975); WS80 = Winick and Stewart (1980); KP80 = Krasnopolsky and Parshev (1980a). f_{H_2} is mixing ratio of H_2. $K(z)$ is eddy diffusion coefficient ($cm^2\ sec^{-1}$). All rate coefficients are evaluated at 250°K. $a\ (-b)$ reads as $a \times 10^{-b}$.

[a] Values refer to models A, B, and C, respectively.

[b] Three-body limit, see text.

cycles are driven primarily by chlorine chemistry, without invoking the assistance of large amounts of H_2 or NO_x. In short, models A, B, and C test, respectively, the H_2 hypothesis, the NO_x hypothesis, and the new chlorine chemistry.

Model A

Altitude profiles for the concentrations of CO, O_2, and SO_2, as predicted by model A, and their comparisons with observations are presented in Fig. 2. Reaction rates for the major reactions involved in the production and consumption of oxygen, (R1) $CO_2 + h\nu$, (R25) CO + OH, and (R58) SO_2 + O, are given in Fig. 3. Detailed inventories, tracing through the budgets and flows of the major species, are shown in Figs. 4a and b. In Fig. 4b, the column abundances above the cloud tops are given in units of 1×10^{18} molecules cm^{-2}. The flux units are 10^{12} molecules $cm^{-2}\ sec^{-1}$. Figures 4a,b reveal the intimate relations between the chemistry of the upper atmosphere, driven by photochemistry, and the lower atmosphere, dominated by thermochemical equilibrium. The net result of stratospheric chemistry is the production of disequilibrium products,

$$CO_2 + SO_2 + H_2O + h\nu \rightarrow CO + H_2SO_4.$$

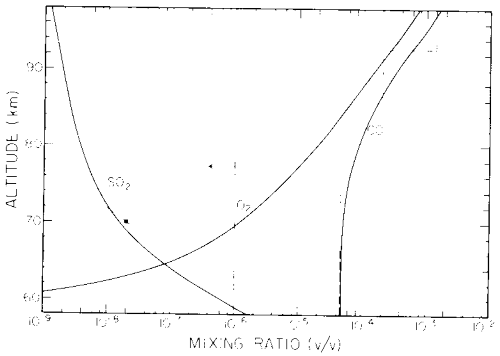


FIG. 2. Comparison of the abundances of CO, O_2 and SO_2 predicted by model A and observations. The SO_2 observations are from Esposito and Gates (1981). The upper limit for O_2 is based on Traub and Carleton (1974). The CO data for the upper atmosphere is Schloerb *et al.*'s (1980) microwave measurement. The CO data for the lower stratosphere is from Connes *et al.* (1968). See Table I for details.

These compounds are transported to the lower atmosphere, where the reverse of the above reaction takes place. To conserve the state of oxidation of the atmosphere the downward flux of CO must equal the upward flux of SO_2. The mean lifetimes of the gases CO, O_2, and SO_2 in the upper atmosphere are 1.1×10^8, 6×10^6, and 1×10^6 sec, respectively. The column density of H_2SO_4 above 58 km, as implied by the data of Knollenberg and Hunten (1980), is 7×10^{18} cm^{-2}. The Stokes falling velocity for particles of radius equal to 1 μm is 2.7×10^{-2} cm sec^{-1} and must be added to the eddy velocity. The estimated downward flux of H_2SO_4 is 1×10^{12} cm^{-2} sec^{-1}. Our column production rate for H_2SO_4 is a factor of 2 larger, but probably within the limits of the uncertainties of the measurements. We have assumed a constant mixing ratio for H_2O. For production rates on the

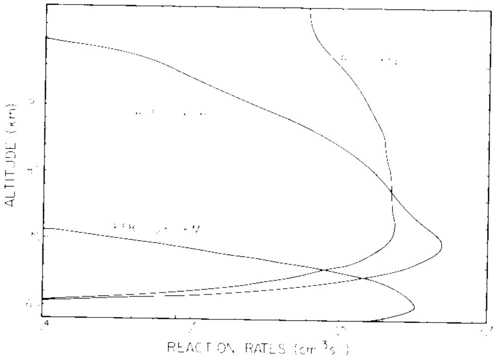


FIG. 3. The major reactions producing and consuming oxygen in model A: (R1) $CO_2 + h\nu \rightarrow CO + O$, (R25) $CO + OH \rightarrow CO_2 + H$, and (R58) $SO_2 + O + M \rightarrow SO_3 + M$.

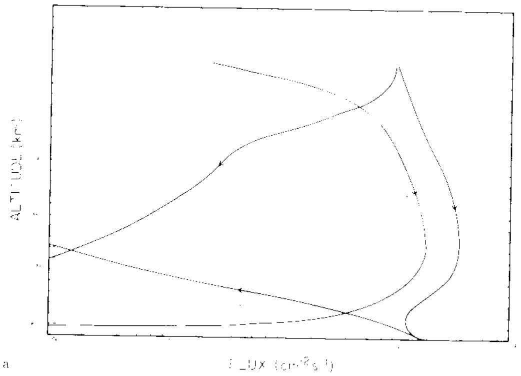


FIG. 4a. Fluxes of O, O_2, CO, and SO_2 computed in model A. The units are molecules cm^{-2} sec^{-1}.

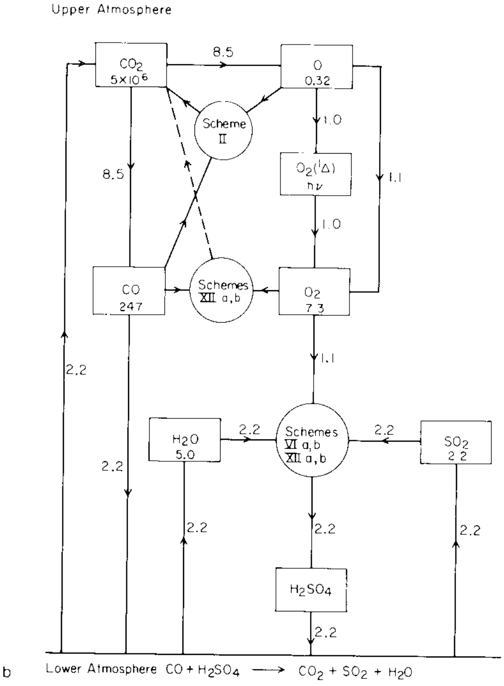


FIG. 4b. Schematic diagram summarizing the budgets and flows of the major oxygen-bearing species. The column abundances above the cloud tops are in units of 1×10^{18} molecules cm^{-2}. The flux units are 10^{12} molecules cm^{-2} sec^{-1}.

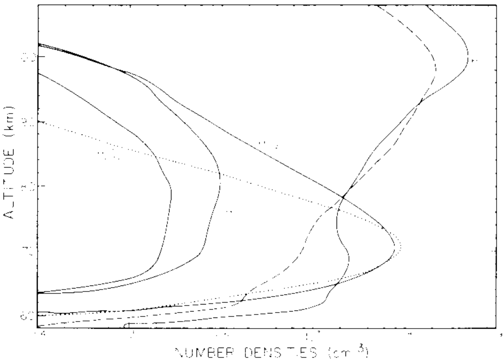


FIG. 5. Number densities of H, OH, HO_2, H_2O_2, Cl, and ClO computed in model A.

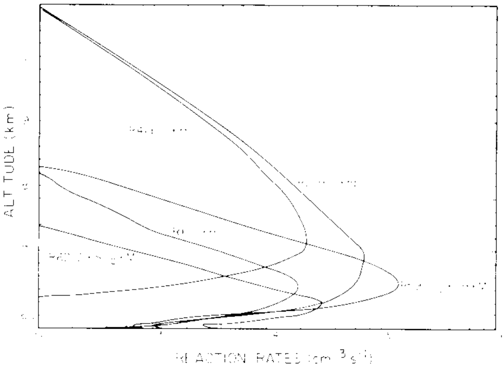


FIG. 7. Sources and sinks of HO_x and ClO_x in model A. The sources are (R2) HCl + $h\nu$ and (R16) O + HCl. The major sinks are (R41) Cl + HO_2, (R59) OH + SO_2 + M, and (R62) Cl + SO_2 + M.

order of this magnitude or higher, the availability of H_2O may be a limiting factor, and may account for the lack of horizontal homogeneity in the SO_2 abundances (Esposito and Gates, 1981). The predicted concentration of O_2 is in good agreement with the observed upper limit quoted by Traub and Carleton (1974). The predicted ratio between the column abundances of CO and O_2 is 35, only slightly lower than the lower limit of 45 implied by the combination of the data by Connes *et al.* (1968) and Traub and Carleton (1974).

Altitude profiles for the major HO_x (H, OH, HO_2, H_2O_2) and ClO_x (Cl, ClO) species are presented in Fig. 5. A schematic diagram showing the sources, sinks, and partitioning between the HO_x and ClO_x species is given in Fig. 6. Reaction rates for the major reactions that produce HO_x and ClO_x, (R2) HCl + $h\nu$ and (R16) O + HCl, and major reactions that destroy HO_x and ClO_x, (R41a) Cl + HO_2, (R59) SO_2 + OH, and (R62) SO_2 + Cl, are given in Fig. 7. Reaction rates for (R38) Cl + H_2, (R21) H + HCl, and (R27) OH + HCl, which determine the partitioning between HO_x and ClO_x, are given in Fig. 8. The concentration of ClO_x in our model is much lower than those in Sze and McElroy (1975), mainly due to the larger rate coefficient for (R41a) (see Table VII). The HO_x concentrations are much higher than those given by Winick and Stewart (1980). The main reason is the higher abundance of H_2 in our model. Reaction (R27) OH + HCl produces H_2O at the

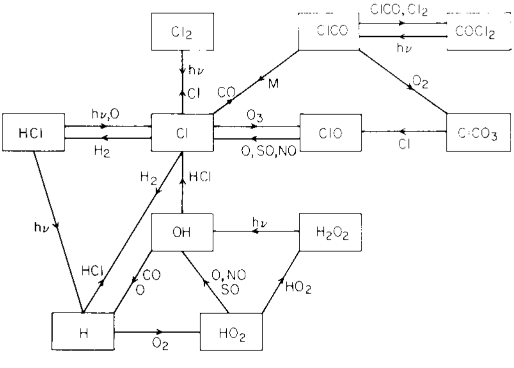


FIG. 6. Schematic diagram showing the major sources, sinks, and recycling paths for HO_x and ClO_x. Not all reactions are included in model A.

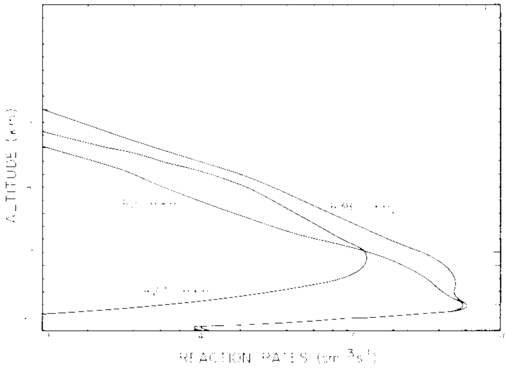


FIG. 8. Reaction rates for reactions controlling the partitioning between HO_x and ClO_x in model A: (R21) H + HCl, (R27) OH + HCl, and (R38) Cl + H_2.

rate of 1.5×10^{11} cm^{-2} sec^{-1}. The stratosphere is a net chemical source of H_2O. The overall equation can be written as

$$H_2 + CO_2 + h\nu \rightarrow H_2O + CO.$$

Since the production of H_2O by (R27) is an inevitable photochemical consequence, model A is valid only when the supply of H_2 by the lower atmosphere is adequate. We can prove that this demand on the order of 10^{11} cm^{-2} sec^{-1} must be a general result for *all* photochemical models which utilize, as the principal scheme, the Martian reaction

$$CO + OH \rightarrow CO_2 + H \qquad \text{(R25)}$$

for CO_2 recombination. Let S and P be the integrated rate of CO_2 photolysis and H_2O production, respectively:

$$\begin{aligned} S &= \int dz\, J_1\, [CO_2] \\ &= \int dz\, k_{25}\, [CO]\, [OH], \\ P &= \int dz\, k_{27}\, [HCl]\, [OH]. \end{aligned}$$

To first order, both CO and HCl are well-mixed. Taking the ratio of the above expressions, we have

$$\frac{P}{S} \sim \frac{k_{27}[HCl]}{k_{25}[CO]} \sim 0.01.$$

Since $S \sim 10^{13}$ cm^{-2} sec^{-1}, we have $P \sim 1 \times 10^{11}$ cm^{-2} sec^{-1}. Whether the lower atmosphere can deliver H_2 at this rate will be discussed in Section 5, entitled Lower Atmospheres. The enormous magnitude of the required flux of H_2 can be best appreciated by comparing it with the flux of methane produced by the entire terrestrial biosphere, 3×10^{10} cm^{-2} sec^{-1}.

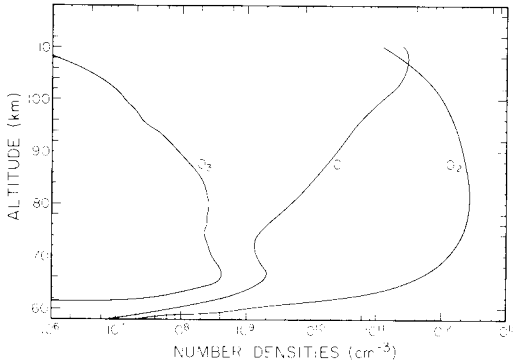


FIG. 9. Altitude profiles for oxygen species O, O_2, and O_3 in model A. The concentrations of O (^1D) (<1 cm^{-3}) are not shown.

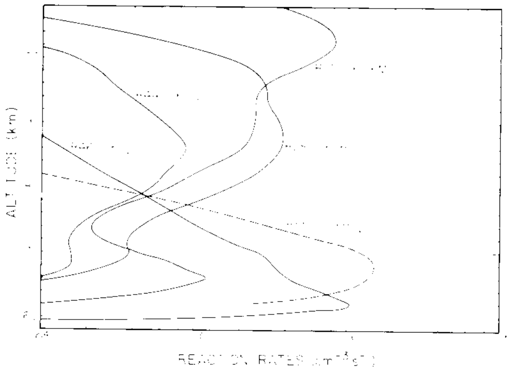


FIG. 10. Reactions leading to the formation of the O–O bond in model A: (R17) O + O + M. (R28) O + OH, and (R44) O + ClO; and reactions breaking the O–O bond: (R46) S + O_2 and (R55) SO + HO_2.

The concentrations of oxygen species O, O_2, and O_3 are given in Fig. 9. Reaction rates for reactions leading to the formation of the O–O bond, (R17) O + O + M, (R28) O + OH, and (R44) O + ClO, and those leading to the breaking of the O–O bond, (R46) S + O_2 and (R55) SO + HO_2, are given in Fig. 10. It can be seen that (R55), first postulated in this paper, is extremely important. The reactions (R17) O + O + M, (R31) O + HO_2, (R39) Cl + O_3, and (R44) O + ClO are exothermic enough to produce an O_2 molecule in the excited $^1\Delta$ state. The quantum yield for producing an $O_2(^1\Delta)$ in (R17) has been estimated to be about 30% by Ogryzlo (1981, private communication), in agreement with the yield obtained by Black and Slanger (1982) for recombination of O atoms on Pyrex glass. In our computation we assume a somewhat higher average quantum yield of 67% for producing $O_2(^1\Delta)$ by (R17), (R31), (R39), and (R44). If the quenching rate coefficient is 3×10^{-20} (Noxon *et al.*, 1976; Traub *et al.*, 1979; Connes *et al.*, 1979; McLaren *et al.*, 1981) only production above 92 km will contribute significantly to the airglow observed by Connes *et al.* (1979). The column emission rates of $O_2(^1\Delta) \rightarrow O_2(^3\Sigma)$ at 1.27 μm for (R17), (R31), (R39), and (R44) are 3.9×10^{11}, 3.5×10^{11}, 3.0×10^{10}, and 3.0×10^{10} cm^{-2} sec^{-1}, respectively, giving a total emission rate of 0.8×10^{12} cm^{-2} sec^{-1} or 0.8 MR. This value should be compared with the observed brightness 1.2 MR on the nightside (Connes *et al.*, 1979). In the Earth's atmosphere, the dayglow $O_2(^1\Delta)$ is about 30 MR, and is dominated by contributions from

$$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D). \quad \text{(R5a)}$$

The nightglow is about 100 kR, arising most probably from the same reactions (R17), (R31) in the mesosphere (Thomas and Young, 1981). Connes *et al.* (1979) recognized that the lack of a large contrast in the Venusian dayglow and nightglow can be used to set an upper limit to the abundance of O_3. In our model, the column abundance of O_3 is 7×10^{14} cm^{-2}, and the additional contribution to the dayglow by (R5a) is 0.4 MR, in good agreement with the observed difference between dayglow and nightglow (see Table VIIIa). If the quantum yield for producing $O_2(^1\Delta)$ by (R17), (R31), (R39), and (R44) were only ~30%, we must adopt a lower quenching coefficient. Alternatively, we may argue that the uncertainties in the $O_2(^1\Delta)$ airglow measurements are large, and there is no serious discrepancy between model predictions and observations.

Altitude profiles of the major sulfur species S, SO, SO_2, and SO_3 are shown in Fig. 11. The speculative chemistry involving the dimer $(SO)_2$ is not considered in this model. The major reactions that control the cycling between SO_2 and SO are given in Fig. 12: (R9) $SO_2 + h\nu$, (R51) $SO + O + M$, (R55) $SO + HO_2$, (R56) $SO + ClO$, and (R57) $SO + SO$. Figure 13 gives the major reactions that control the cycling between SO and S: (R8) $SO + h\nu$, (R46) $S + O_2$, and (R57) $SO + SO$.

A number of runs have been made to test the sensitivity of model A to H_2. The results indicate that the essential features of the solution discussed in the previous sections are not changed for 10 ppm $< H_2 <$ 50 ppm. However, as H_2 is decreased toward 1 ppm, we approach the solution of Winick

TABLE VIIIa

$O_2(^1\Delta)$ EMISSIONS PREDICTED BY MODELS A, B, AND C FOR QUENCHING COEFFICIENT $k_{18a} = 1 \times 10^{-20}$ AND 3×10^{-20} cm^3 sec^{-1}

Model		Reaction	$k_{18a} = 1 \times 10^{-20}$		$k_{18b} = 3 \times 10^{-20}$	
A	(R5a)	$O_3 + h\nu$	0.89		0.39	
	(R17)	$O + O$	0.93	$E = 1.2$	0.39	$E = 0.79$
	(R31)	$O + HO_2$	0.80		0.35	
	(R39)	$Cl + O_3$	0.06		0.03	
	(R44)	$ClO + O$	0.06		0.03	
B	(R5a)		1.80		0.73	
	(R17)		0.82	2	0.70	0.8
	(R31)		0.36		0.21	
	(R39)		0.31		0.13	
	(R44)		0.34		0.16	
C	(R5a)		0.18		0.13	
	(R17)		0.72	1.3	0.65	0.76
	(R31)		0.06		0.05	
	(R39)		0.37		0.15	
	(R44)		0.72		0.29	

Note. E, the nightglow, is computed by $E = q \times [(R17) + (R31) + (R39) + (R44)]$, where $q = \frac{2}{3}$. The dayglow equals the sum of E and (R5a). All units are in 10^{12} cm^{-2} sec^{-1} or MR.

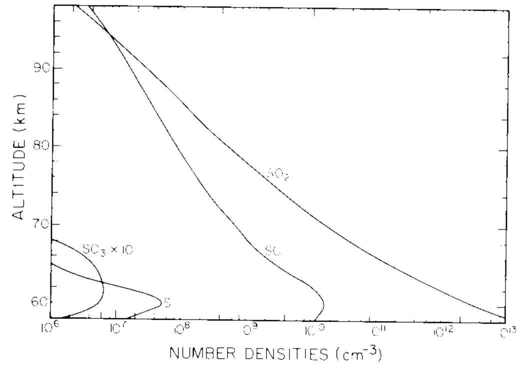


FIG. 11. Number densities for the major sulfur species, S, SO, SO_2, and SO_3 computed by model A.

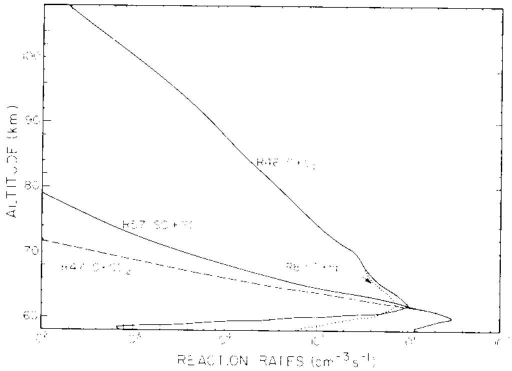


FIG. 13. Major reactions that control the cycling between SO and S in model A: (R8) SO + $h\nu$, (R46) S + O_2, (R47) S + CO_2, and (R57) SO + SO.

and Stewart (1980), in conflict with the O_2 observations.

Model B

Altitude profiles for the mixing ratios of CO, O_2, and SO_2 are presented in Fig. 14. The agreement between theory and experiment is not as good as in model A, but is probably within the limits of uncertainty of the observations. Reaction rates for the major reactions producing and destroying oxygen are given in Fig. 15. It can be seen that (R25) CO + OH and (R58) SO_2 + O are the most important sinks for oxygen.

The altitude profiles for HO_x and ClO_x are given in Figs. 16 and 17, respectively. These profiles are significantly different from those given for model A in Fig. 5. The main reasons for the differences are the assumption of a lower H_2 concentration and the assumption that there is no heterogeneous sink for HO_x or ClO_x via reactions with SO_2. The major reactions producing and destroying HO_x–ClO_x are presented in Fig. 18. The production rate of H_2O by (R27) OH + HCl is 1.5×10^{11} cm^{-2} sec^{-1}, as expected on the basis of the discussion in section Model A. The concentrations of S, SO, SO_2, and SO_3 are given in Fig. 19. NO is important for catalytically recombining SO and O via the cycle

$$
\begin{array}{lll}
 & NO + O + M \rightarrow NO_2 + M & (R77) \\
 & \underline{NO_2 + SO \rightarrow NO + SO_2} & \underline{(R85)} \\
\text{net} & SO + O \rightarrow SO_2 &
\end{array}
$$

The model predicts a column-integrated production rate for H_2SO_4 equal to 9×10^{11}

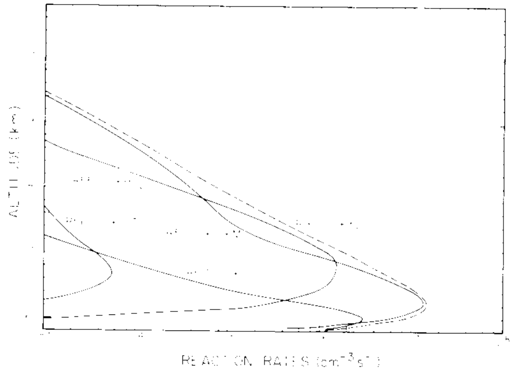


FIG. 12. Major reactions that control the cycling between SO_2 and SO in model A: (R9) SO_2 + $h\nu$, (R51) SO + O + M, (R55) SO + HO_2, (R56) SO + ClO, and (R57) SO + SO.

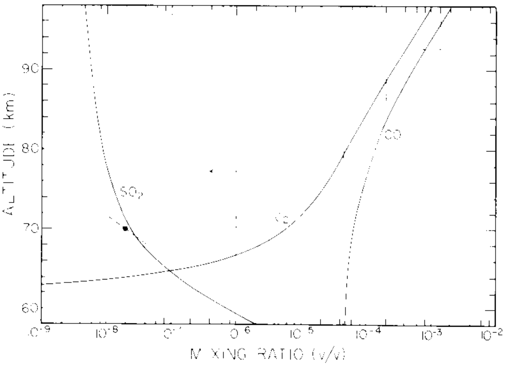


FIG. 14. Same as Fig. 2, for model B.

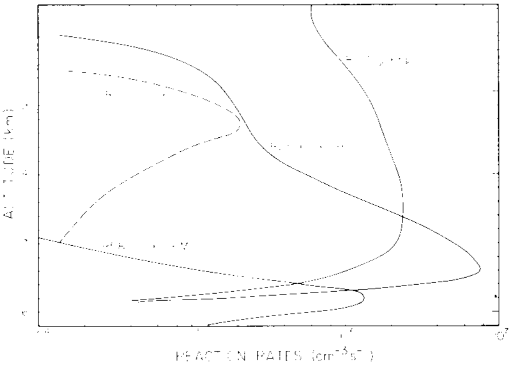


FIG. 15. Same as Fig. 3, for model B. (R101) ClCO + O_2 has been added.

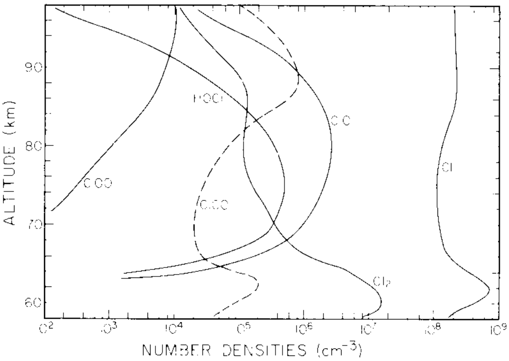


FIG. 17. Number densities of ClO_x (Cl, ClO, ClOO, Cl_2, HOCl) computed in model B.

cm^{-2} sec^{-1}, in good agreement with 1×10^{12} cm^{-2} sec^{-1} deduced from the observations of Knollenberg and Hunten (1980). The concentrations of NO_x (N, NO, NO_2, NO_3, HNO, HNO_2, HNO_3) are given in Fig. 20. In modeling the distribution of NO_x in the stratosphere we adopted a mixing ratio of 3×10^{-8} at the lower boundary. Figure 21 shows the major reactions for destroying NO_x. Due to the uncertainties in the photochemistry of HNO we must regard the computed loss rate of NO_x by (R89) HNO + HNO as an order of magnitude estimate. The column-integrated destruction rates due to (R76) N + NO and (R89) HNO + HNO are 2.2×10^8 and 1×10^9 molecules of NO_x cm^{-2} sec^{-1}, respectively. This should be compared with the estimate by Chameides *et al.* (1979), 5×10^8 molecules of NO_x cm^{-2} sec^{-1}, for generation of NO_x on Venus by lightning similar to that on Earth (Scarf *et al.*, 1980; Borucki *et al.*, 1981).[3] Hence the amount of NO_x assumed in model B must be close to the maximum possible. It should be noted that, in the absence of a lightning source, downward flux of NO_x from the mesosphere predicts a mixing ratio of NO_x equal to 3×10^{-12} in the stratosphere.

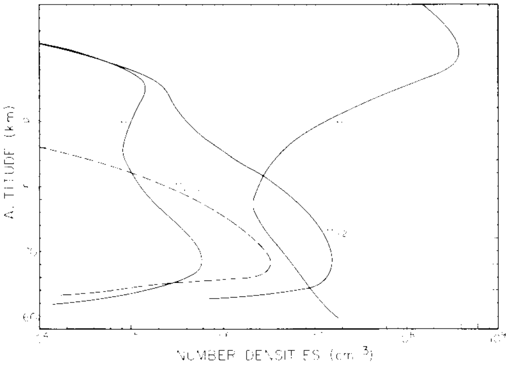


FIG. 16. Number of densities of HO_x (H, OH, HO_2, H_2O_2) computed in model B.

Figure 22 gives the density profiles for the major oxygen species: O, O_2, and O_3. The main reactions that lead to the formation of the O–O bond, (R17) O + O, (R28) O + OH, (R44) ClO + O, and (R83a) NO_2 + O, are shown in Fig. 23. The predicted airglow for $O_2(^1\Delta)$ is similar to that in model A and is summarized and compared in Table VIII. The reactions that break the O–O bond, (R46) S + O_2, (R55) SO + HO_2, (R81) NO + HO_2, and (R101) ClCO + O_2, are presented in Fig. 24. Comparison of Figs. 23 and 24 illustrates the interesting dual roles of ClO_x and NO_x toward oxygen. (R44) ClO + O destroys odd oxygen, whereas (R101) ClCO + O_2 destroys O_2, (R83a) NO_2 + O destroys odd oxygen, whereas (R81) NO + HO_2 produces odd oxygen. The dual role of NO_x toward ozone in

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[3] The lightning observations are actually upper limits.

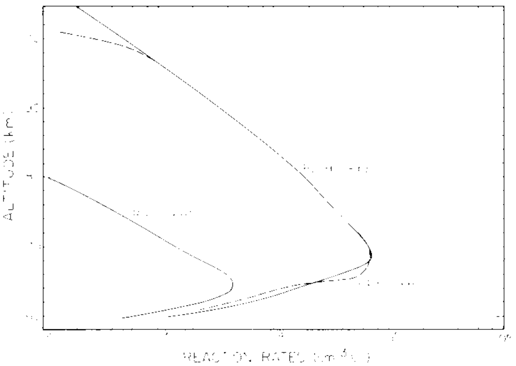

FIG. 18. Same as Fig. 7, for model B. The reactions (R59) OH + SO_2 + M and (R62) Cl + SO_2 + M are not sinks for HO_x and ClO_x in model B.

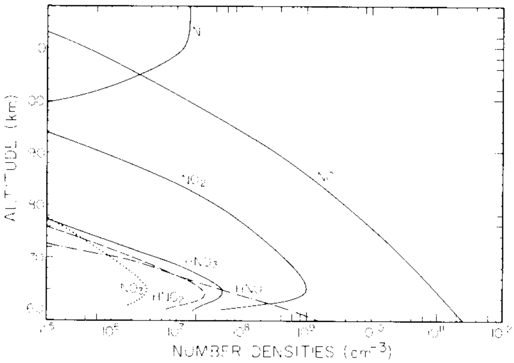

FIG. 20. Number densities of NO_x (N, NO, NO_2, NO_3, HNO, HNO_2, HNO_3) computed in model B.

the terrestrial stratosphere has been well established (see, for example, NASA, 1979). The possible dual role for chlorine on Venus is first pointed out here and apparently has no terrestrial analog.

Model C

Altitude profiles for the mixing ratios of CO, O_2, and SO_2 are presented in Fig. 25. The agreement with observations is of the same quality as in model B. The major reactions producing and consuming oxygen are shown in Fig. 26. Reaction (R101) ClCO + O_2 is now the major sink for CO and O_2. The fact that CO is in approximate photochemical equilibrium (production rate ~ loss rate) around 80 km is significant and may provide a clue for understanding the otherwise puzzling observations of the depletion of mesospheric CO on the nightside (Schloerb *et al.*, 1980; Wilson *et al.*, 1981; Clancy *et al.*, 1981). The main reason for the bulge in (R101) at high altitudes is the greater stability of the ClCO radical at lower temperatures in this region. Thus the character of CO destruction in model C is very different from that in models A and B.

The altitude profiles for HO_x are given in Fig. 27. As expected, the low level of H_2 in the ambient atmosphere favors low concentrations of HO_x. The number densitites of ClO_x are shown in Fig. 28. The total free chlorine mixing ratio (mostly in the form of Cl_2) exceeds 0.1 ppm, about 2–3 orders of magnitude higher than those in models A and B. The reason will become clear in the following paragraph.

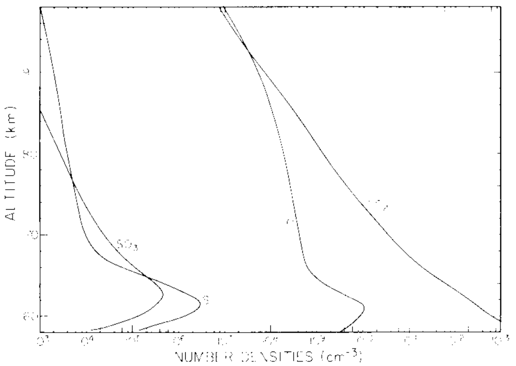

FIG. 19. Same as Fig. 11, for model B.

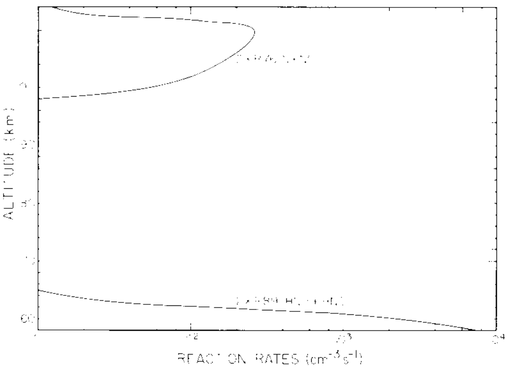

FIG. 21. Major reaction destroying NO_x in model B: (R76) N + NO, (R89) HNO + HNO.

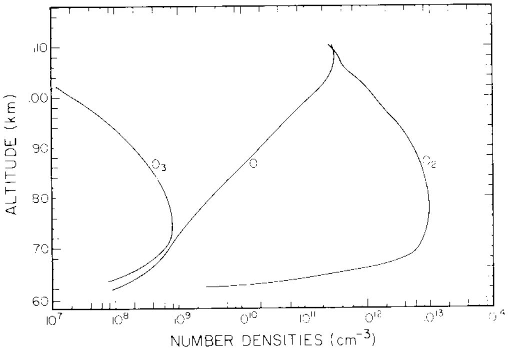

FIG. 22. Same as Fig. 9, for model B.

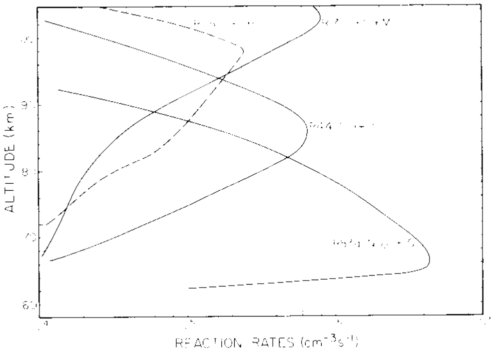

FIG. 23. Reactions leading to the formation of the O–O bond in model B: (R17) O + O + *M*, (R28) O + OH, (R44) ClO + O, and (R83a) NO_2 + O.

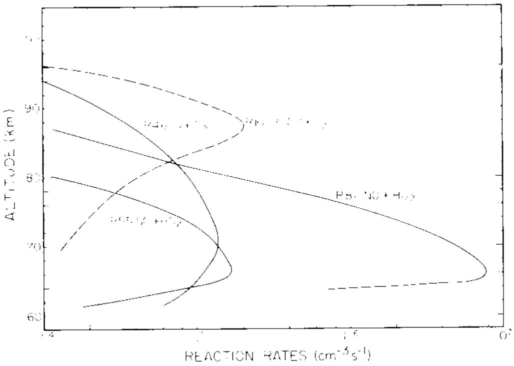

FIG. 24. Reactions leading to the breaking of the O–O bond in model B: (R46) S + O_2, (R55) SO + HO_2, (R101) ClCO + O_2, and (R81) NO + HO_2.

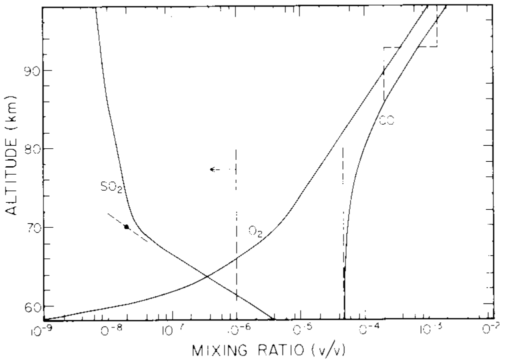

FIG. 25. Same as Fig. 2, for model C.

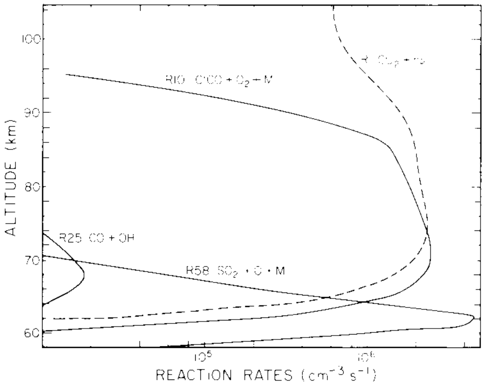

FIG. 26. Same as Fig. 3, for model C. (R101) ClCO + O_2 + *M* has been added.

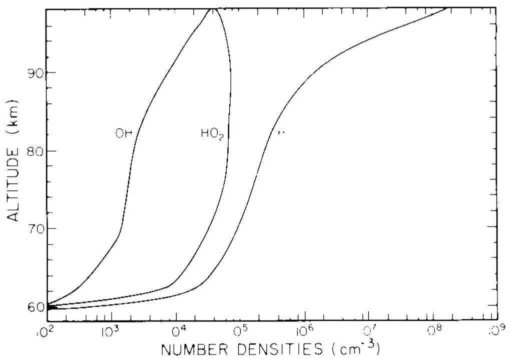

FIG. 27. Number densities of HO_x (H, OH, HO_2) computed in model C.

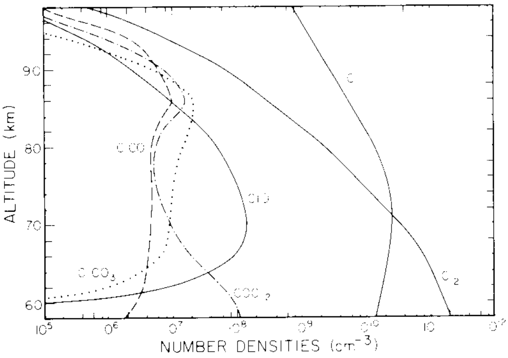

FIG. 28. Number densities of ClO_x(Cl, ClO, Cl_2, ClCO, $COCl_2$, $ClCO_3$) computed in model C.

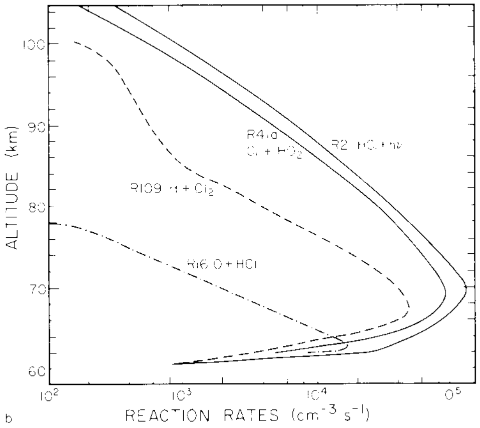

FIG. 29b. Sources and sinks of HO_x and ClO_x in model C.

The altitude profiles for H_2 and HCl are shown in Fig. 29a. This abundance of H_2 is predicted by the photochemical model under the assumption of no tropospheric input. It is of interest to note that $H_2 \sim 0.1$ ppm at 100 km even though $H_2 = 1 \times 10^{-13}$ at the lower boundary. Hence at the low levels of H_2, the exospheric hydrogen budget is largely controlled by HCl photochemistry. The sources and sinks for HO_x and ClO_x are shown in Fig. 29b. Reaction (R109) H + Cl_2 is now an important sink, as first pointed out by Krasnopolsky and Parshev (1980a,b, 1981). The principal reactions producing H_2 and H_2O are shown in Fig. 29c. The ultimate source of hydrogen in either compound is HCl in this model. Whereas the production of H_2 represents only a temporary sink for hydrogen, because of (R38) Cl + H_2, the production of H_2O (and subsequent scavenging by SO_3 to form H_2SO_4) is a permanent hydrogen sink in the stratosphere. The net reaction can be schematically summarized as

$$2HCl + CO_2 + h\nu \rightarrow H_2O + CO + Cl_2.$$

The buildup and downward flux of free chlorine is the only way to conserve the state of oxidation of the atmosphere in this model. The predicted flux of Cl_2 is 3.0×10^{9} cm^{-2} sec^{-1}. Since the residence time for total chlorine in the stratosphere is about 2 years, this implies a column abundance of Cl_2 on the order of 10^{17} cm^{-2}, sufficient to cause appreciable ultraviolet extinction (Pollack *et al.*, 1980).

Figure 30 shows the number densities of the major sulfur species. The SO_2 abundance at 70 km is somewhat larger than that in the previous models. A recent interpretation of the observations (Belton, 1982) suggests that there should be more SO_2 than previously thought. Figure 31 summarizes the altitude profiles for O, O_2, and O_3. The reactions leading to the formation and breaking of the O–O bond are shown in Figs. 32 and 33, respectively. The major reactions for recycling between SO_2 and SO are shown in Fig. 34. The rates for production of $O_2(^1\Delta)$ airglow, along with comparisons between models, are given in Table VIIIa.

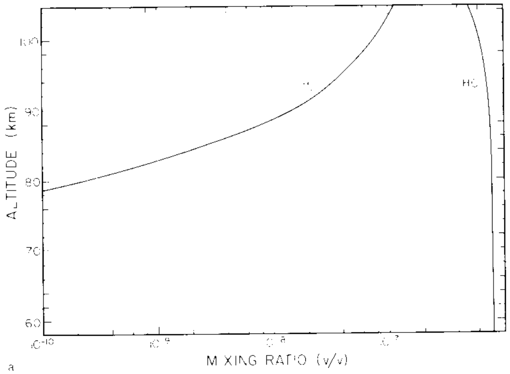

FIG. 29a. Altitude profiles of H_2 and HCl in model C.

It is clear from the above discussion that ClO_x plays a crucial role in this model. We will briefly describe the essential aspects. Photolysis of CO_2 leads to the production of oxygen atoms,

$$CO_2 + h\nu \rightarrow CO + O. \quad (R1)$$

Most of the oxygen atoms are recombined via the Molina–Rowland cycle

$$O + O \xrightarrow{ClO_x} O_2. \qquad (8)$$

The chlorine-catalyzed recombination reactions are sufficiently exothermic to produce oxygen molecules in the ${}^1\Delta$ state. [The quantum yields for producing $O_2({}^1\Delta)$ by (R39) and (R44) are not known. A laboratory measurement can provide a critical test for the model.] Oxidation of CO proceeds via the formation of the peroxychloroformyl radical:

$$\begin{array}{lll}
 & Cl + CO + M \rightarrow ClCO + M & (R100) \\
 & ClCO + O_2 + M \rightarrow ClCO_3 + M & (R101) \\
 & ClCO_3 + Cl \rightarrow Cl + CO_2 + ClO & (R110) \\
\hline
\text{net} & CO + O_2 + Cl \rightarrow CO_2 + ClO &
\end{array}$$

Whether this scheme results in a net consumption of O_2 depends on the fate of ClO. If ClO reacts with O,

$$ClO + O \rightarrow Cl + O_2. \quad (R44)$$

The combined scheme (R100) + (R101) + (R110) + (R44) becomes

$$CO + O \rightarrow CO_2.$$

Note that there is no net destruction of O_2 in this case. O_2 still plays an important role, albeit only as a catalyst for combining CO and O. If ClO dissociates,

$$ClO + h\nu \rightarrow Cl + O, \quad (R7)$$

or reacts with SO, followed by photolysis,

$$\begin{array}{lll}
 & ClO + SO \rightarrow Cl + SO_2 & (R56) \\
 & SO_2 + h\nu \rightarrow SO + O & (R9) \\
\hline
\text{net} & ClO \rightarrow Cl + O &
\end{array}$$

the net result is the production of an oxygen atom. The combined scheme (R100) and (R101) + (R110) and (R7) or (R56) + (R9) becomes

$$CO + O_2 \rightarrow CO_2 + O.$$

In this case there is a net destruction of O_2. The success of our model in removing O_2 obviously depends on the fact that (R7) +

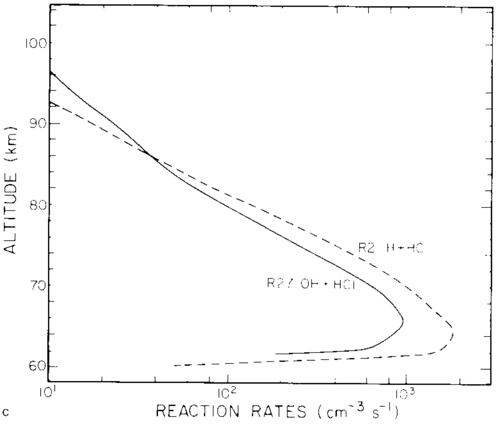

FIG. 29c. (R21) H + HCl, major reaction producing H_2, and (R27) OH + HCl, major reaction producing H_2O in model C.

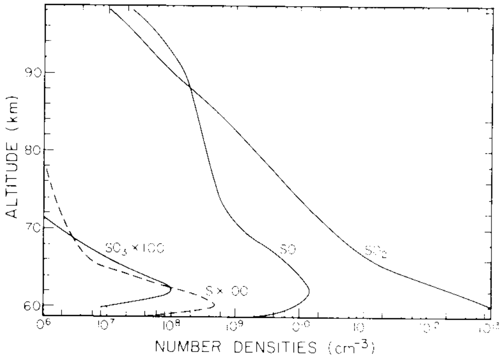

FIG. 30. Same as Fig. 11, for model C.

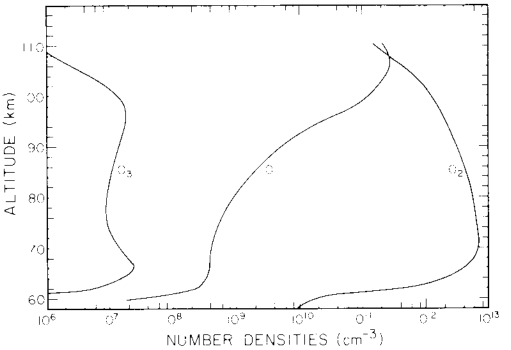

FIG. 31. Same as Fig. 9, for model C.

(R56) is more important than (R44). We can now clearly see the close coupling between the ClO_x and SO_x chemistry. In (R56) SO acts like NO in removing the oxygen atom from ClO. This oxygen atom is finally released by photolysis of SO_2 (as in the analogous case of NO_2). We note that at 70 km the photolysis rate of SO_2 is on the order of 10^{-5} sec^{-1}, compared with 10^{-10} sec^{-1} for O_2. Thus SO_2 acts to photosensitize the dissociation of ClO.

The closely knitted chemistry between carbon dioxide, oxygen, chlorine, and sulfur has hitherto been unsuspected, but is consistent with all existing knowledge of chemical kinetics and the atmosphere of Venus. Furthermore, this model dispenses with the need for larger amounts of H_2 and NO_x. Herein lies its simplicity, and hence its strength.

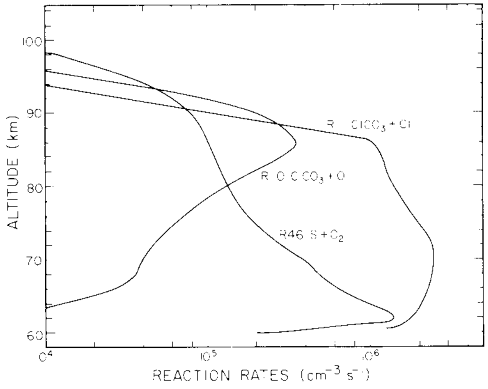

FIG. 33. Reactions showing the fate of O_2 in $ClCO_3$ and the breaking of the O–O bond by (R46). Note that in (R110) a new O–O bond is actually formed. (R111) does not always lead to the breaking of the O–O bond, depending on the fate of the product ClO (see text).

Comparisons between Models and Observations

The models we have described are conceptually simple. The results are also intuitively obvious. In all models the major sink for oxygen is CO oxidation. SO_2 oxidation is a minor but significant sink, mostly in the lower stratosphere. Models A and B use the Martian scheme (R25) CO + OH and require an upward flux of H_2 equal to 1.5×10^{11} cm^{-2} sec^{-1} from the troposphere. Model C uses the new scheme (R101) ClCO + O_2 and predicts about 0.1 ppm Cl_2 in the stratosphere. Reaction (R58) SO_2 + O is primarily responsible for oxidizing SO_2.

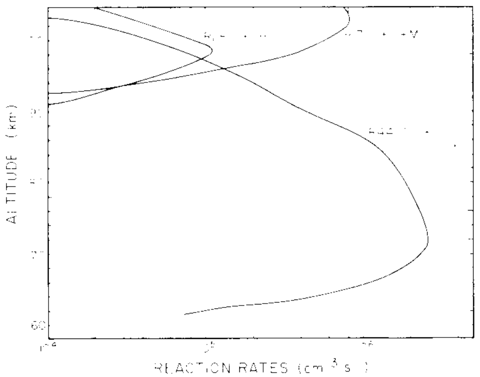

FIG. 32. Same as Fig. 23, for model C.

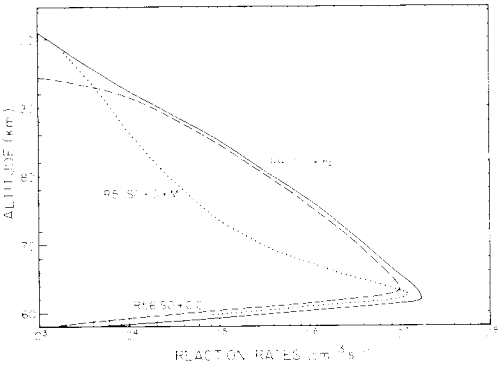

FIG. 34. Same as Fig. 12, for model C.

The major predictions of the models are summarized in Table VIIIb.

The relative merits of the models, and hence their claims to legitimacy, must be judged by how well the predictions match the observations as summarized in Table I. Within limits of the uncertainties of the measurements all three models perform fairly well with regard to O_2, SO_2 scale height, and $O_2(^1\Delta)$ airglow. However, there are two observations that clearly suggest that model C may be preferred. The early microwave observations of mesospheric CO by Schloerb *et al.* (1980) and Wilson *et al.* (1981) indicated a curious nightside depletion relative to the dayside around 80–90 km. Recent work by Clancy *et al.* (1981) provides definitive confirmation of this phenomenon. In models A and B the bulk of CO is destroyed around 70 km. There is no significant chemical sink in the mesosphere between 80 and 90 km, and there should be no diurnal variation in CO concentration. In model C, however, major destruction of CO takes place at high altitudes, between 80 and 90 km (see Figs. 3, 15, and 26). Hence CO is in approximate photochemical equilibrium, and we expect a nightside depletion. A detailed comparison between model predictions for the diurnal behavior of CO and the microwave data will be reported elsewhere.

TABLE VIIIb

COMPARISON OF MAJOR PREDICTIONS OF MODELS A, B, AND C

Physical quantity	Model A	Model B	Model C
f_{CO} (62 km)	4.6×10^{-5}	4.7×10^{-5}	4.8×10^{-5}
f_{CO} (100 km)	2.1×10^{-3}	2.8×10^{-3}	2.5×10^{-3}
f_{O_2} (62 km)	6.4×10^{-9}	1.6×10^{-10}	1.5×10^{-7}
CO column abundance	2.5×10^{20}	2.8×10^{20}	2.8×10^{20}
O_2 column abundance	7.3×10^{18}	2.3×10^{19}	1.8×10^{19}
Ratio of CO to O_2 column abundances	35	12	16
f_{SO_2} (70 km)	1.7×10^{-8}	2.7×10^{-8}	3.2×10^{-8}
Scale height of SO_2 at 70 km (km)	2.3	2.4	2.5
(R1) $CO_2 + h\nu$	8.5×10^{12}	7.7×10^{12}	7.6×10^{12}
(R25) CO + OH	6.3×10^{12}	6.8×10^{12}	4.9×10^{10}
(R101) ClCO + O_2	0	2.0×10^{11}	5.0×10^{12}
(R102) ClCO + O	0	0	1.2×10^{12}
$\phi_{SO_2} = -\phi_{CO}$	2.2×10^{12}	7×10^{11}	1.4×10^{12}
(R27) OH + HCl	1.4×10^{11}	1.5×10^{11}	3.0×10^{9}
ϕ_{H_2}	1.4×10^{11}	1.5×10^{11}	0
ϕ_{Cl_2}	0	0	-3.0×10^{9}
$O_2(^1\Delta)$ dayglow	1.2×10^{12}	1.5×10^{12}	0.90×10^{12}
$O_2(^1\Delta)$ nightglow	0.79×10^{12}	0.8×10^{12}	0.76×10^{12}

Note. The column abundances and column production rates are integrals from 58 to 110 km in units of cm^{-2} and cm^{-2} sec^{-1}, respectively. f_{CO} has been fixed at 58 km to equal 4.5×10^{-5}. The column abundance of CO_2 is 5×10^{24} cm^{-2}.

In the extensive study on the distribution and source of ultraviolet absorption in the Venusian atmosphere, Pollack *et al.* (1980) concluded that the absorption from 0.2 to 0.32 μm could be adequately accounted for by SO_2, but the identity of the absorber for the region 0.32 to 0.40 μm is uncertain. Sill (1982) suggests that nitrosylsulfuric acid ($NOHSO_4$) dissolved in H_2SO_4 droplets can explain the uv and visible albedo. But the requirement of NO_x in excess of parts per million may pose a serious difficulty. In our photochemical model (Appendix B), we explore the chemistry of a number of interesting sulfur compounds: S_2, S_2O, $(SO)_2$, $H_2S_2O_2$, and $H_2S_2O_3$. It is conceivable that some of these compounds may explain the observed uv absorption longward of 0.32 μm. However, until experiments on the optical properties of S_2, $(SO)_2$, $H_2S_2O_2$, and $H_2S_2O_3$ are done to assess this possibility, Pollack *et al.*'s idea that the long-wavelength absorber is gaseous Cl_2 is the simplest and the most appealing. We show, in model C but not in models A and B, that the required abundance of Cl_2 in the stratosphere can be generated from HCl photolysis.

Comparison with Earth's Stratosphere

In recent years, considerable effort has been directed toward understanding the processes that control the abundance of ozone in the Earth's stratosphere, and to assessing the impact of perturbations by supersonic transport (SST) aviation (Crutzen, 1970; Johnston, 1971; McElroy *et al.*, 1974), the release of chlorofluoromethanes (Molina and Rowland, 1974; Cicerone *et al.*, 1974; Wofsy *et al.*, 1975; NAS, 1976; NASA, 1977, 1979; Crutzen *et al.*, 1978), and the release of N_2O associated with the use of fertilizers in agriculture (McElroy *et al.*, 1977; Logan *et al.*, 1978). The chemistry of the stratosphere of Venus offers a valuable system for testing and extending our knowledge of the chemistry of the Earth's stratosphere. In fact, historically, the chlorine chemistry of Venus was developed before the importance of chlorine chemistry in the Earth's atmosphere was recognized (Prinn, 1971; McElroy *et al.*, 1973).

Table IX summarizes a comparison of some essential aspects of stratospheric chemistry on the two planets. The ambient pressures and temperatures are comparable. The abundances of chlorine and sulfur species on Venus are about 200 and 500 times, respectively, larger than those on Earth. The Molina–Rowland chlorine cycle for catalytic conversion of odd oxygen into molecular oxygen is eminently important for both planets. In the Earth's stratosphere, the effectiveness of the chlorine cycle is suppressed by the reaction

$$Cl + CH_4 \rightarrow HCl + CH_3$$

which turns an active chlorine radical into a relatively inert form as HCl. On Venus, reaction (R38),

$$Cl + H_2 \rightarrow HCl + H,$$

could play a similar role if H_2 were abundant.

Logan *et al.* (1978) pointed out that there is an interactive effect between ozone perturbations by chlorine and odd nitrogen, such that the impact of the Molina–Rowland cycle is mitigated. The crucial reaction is

$$ClO + NO \rightarrow Cl + NO_2 \quad (R82)$$

which leads to a net nothing cycle and competes with the reaction that destroys odd oxygen,

$$ClO + O \rightarrow Cl + O_2. \quad (R44)$$

On Venus, in addition to (R82), we also have the reaction

$$ClO + SO \rightarrow Cl + SO_2 \quad (R56)$$

which plays a similar role as (R82).

TABLE IX

COMPARISON OF THE ESSENTIAL ASPECTS OF THE CHEMISTRY OF THE STRATOSPHERE OF EARTH AND VENUS

	Earth	Venus
Altitude	20–40 km	60–80 km
Pressure	100–5 mbar	300–5 mbar
Temperature	200–250°K	270–200°K
Total chlorine mixing ratio	2.3×10^{-9}	4×10^{-7}
Total sulfur mixing ratio	$\sim 1 \times 10^{-9}$	$\sim 2 \times 10^{-6}$
Total NO_x mixing ratio	2×10^{-8}	$\leq 3 \times 10^{-8}$
Molina–Rowland chlorine cycle	Important	Important
Inhibitor of chlorine cycle (1)	$Cl + CH_4$	$Cl + H_2$
Inhibitor of chlorine cycle (2)	$ClO + NO$	$ClO + SO$
Heterogeneous loss	Not important in quiescent atmosphere	$SO_2 + OH$ $SO_2 + Cl$ could be important
Reaction breaking O–O bond	$NO + HO_2$	$SO + HO_2$ $S + O_2$ $NO + HO_2$ $ClCO + O_2$

Note. Data for the Earth's stratosphere was taken from Logan *et al.* (1978), Turco *et al.* (1979), and Yung *et al.* (1980).

Removal of active radicals, such as OH, Cl, and H_2O_2, by heterogeneous processes in the Earth's stratosphere is a subject of great interest, since such losses could reduce the impact of chlorofluorocarbons on ozone. The current understanding is that heterogeneous processes are not important (Baldwin and Golden, 1979; NASA, 1979), except perhaps during periods of enhanced volcanic activity (Strattan *et al.*, 1979). However, in the stratosphere of Venus, SO_2 is much more abundant and provides an important heterogeneous sink for OH and Cl in model A. Unfortunately, the kinetics of heterogeneous chemistry of sulfur compounds is not sufficiently well understood to firmly establish the importance of this possibility.

In the assessment of the impact of SST aviation on the ozone layer (McElroy *et al.*, 1974), a major revision of the conclusions had to be made on account of reaction (R81) (Howard and Evenson, 1977),

$$NO + HO_2 \rightarrow NO_2 + OH,$$

which produces odd oxygen. On Venus, results of model B indicate that NO_x can produce and destroy odd oxygen. Reaction (R55),

$$SO + HO_2 \rightarrow SO_2 + OH,$$

is analogous to (R81), and together with (R46) and (R101),

$$S + O_2 \rightarrow SO + O,$$
$$ClCO + O_2 \rightarrow ClCO_3,$$

are extremely important for breaking up and using molecular oxygen. Although the rate coefficient k_{55} has not been measured, we believe that our estimate, as given in Table IIIa must be good to within a factor of 2.

5. LOWER ATMOSPHERES

In the theory of the Martian atmosphere, photochemical processes alone can account for the present composition and past evolution of the atmosphere (McElroy and Donahue, 1972; McElroy, 1972). The atmosphere of Venus is slightly more complicated, and is driven above the cloud tops by photochemistry and below the clouds by thermochemical equilibrium chemistry. It is this interaction that makes the chemistry of the atmosphere of Venus rich and interesting. Our three models are based on three diversely different assumptions with regard to the state of oxidation of the lower atmosphere. Unfortunately, the current data basis for the lower atmosphere is plagued with uncertainties and ambiguities. We adopted an unbiased approach and used stratospheric photochemistry as a tool, via the boundary conditions and continuity equations, to investigate the lower atmosphere.

Molecular Hydrogen and Carbon Monoxide

In model A we adopt the high concentration of H_2 recently inferred by Kumar *et al.* (1981). The presence of about 10 ppm is needed to drive the OH-mediated CO_2 recombination catalytic cycles and for suppressing the chlorine cycle that leads to production of O_2. It remains a challenging problem to understand why the Venusian atmosphere has so much H_2, if it is indeed there. The only known reservoirs of hydrogen species in the stratosphere are HCl and H_2O. Photochemical destruction of H_2O is exceedingly slow due to nearly complete shielding of ultraviolet radiation by CO_2. Conversion of HCl into H_2 by (R21) H + HCl is possible, but cannot compete with the destruction of H_2 by (R26) OH + H_2 and (R38) Cl + H_2. The net destruction rate of H_2 in the stratosphere is 1.5×10^{11} cm^{-2} sec^{-1}. Thermochemical equilibrium in the lower atmosphere yields the following relations between H_2, H_2O, H_2S, CO, CO_2, and COS:

$$\frac{[H_2][CO_2]}{[CO][H_2O]} = K_1 = \begin{cases} 8.8 \times 10^4 & T = 300^\circ K \\ 1.3 \times 10^2 & T = 500^\circ K \\ 6.1 & T = 750^\circ K, \end{cases}$$

$$\frac{[H_2][COS]}{[H_2S][CO]} = K_2 = \begin{cases} 1.5 \times 10^{-1} & T = 300^\circ K \\ 4.9 \times 10^{-2} & T = 500^\circ K \\ 3.5 \times 10^{-2} & T = 750^\circ K, \end{cases}$$

$$\frac{[H_2S][CO_2]}{[H_2O][COS]} = K_3 = \begin{cases} 6.1 = 10^5 & T = 300°K \\ 2.7 = 10^3 & T = 500°K \\ 1.7 \times 10^2 & T = 750°K. \end{cases}$$

The equilibrium constants K_1, K_2, and K_3 have been evaluated using data presented in the JANAF Thermochemical Tables (1971). Note that $K_1 = K_2K_3$. These equilibrium relations reveal that H_2O and H_2S could provide a source of H_2, at least in principle. However, in the regions of the atmosphere where equilibrium can be rapidly established, the predicted f_{H_2} is 1.2×10^{-8}, assuming $f_{CO} = 2 \times 10^{-5}$ and $f_{H_2O} = 1 \times 10^{-4}$ (Hoffman *et al.*, 1980a; Moroz *et al.*, 1979). Hence it is unlikely that thermochemical equilibrium chemistry can maintain a concentration of H_2 on the order of 10 ppm in the lower atmosphere. On the contrary, the lower atmosphere near the surface may be an important sink for H_2, converting H_2 into H_2O, which is more stable thermodynamically.

As pointed out by Kumar *et al.* (1981), the production of H_2 in the lower atmosphere probably involves disequilibrium chemistry, driven perhaps by absorption of near ultraviolet or visible radiation by sulfur polymers (Prinn, 1978, 1979). There has been no theoretical or experimental study on the production of polysulfur from SO_2. On the basis of the reaction

$$S + O_2 \rightarrow SO + O \quad \text{(R46)}$$

Winick and Stewart (1980) argued that generation of polysulfur is photochemically not possible. We have extended the work of Winick and Stewart (1980), and presented in Appendix B the possibility of making a variety of disequilibrium sulfur compounds: S_2, S_2O, $(SO)_2$, $H_2S_2O_2$, and $H_2S_2O_3$. In all previous photochemical studies of Venus the direction of oxidation was assumed to be in the direction of oxidized sulfur compounds, such as from COS to H_2SO_4 (Prinn, 1973, 1975) and SO_2 to H_2SO_4 (Winick and Stewart, 1980). In this work (Appendix B) we first raise the possibility of the simultaneous segregation of this chemical system into a more reduced and a more oxidized set of compounds by the schemes (B3)–(B5). The photochemical production and downward transport of this set of highly reduced disequilibrium products may have profound implications for the chemistry of the lower atmosphere, such as production of H_2S. Once H_2S is produced, either by the scheme described in Appendix B or by direct thermoequilibrium chemistry (Lewis, 1970), it is relatively easy to derive H_2 from it. Photolysis of H_2S can occur even below the cloud tops by absorption of diffusively transmitted photons shortward of 3170 Å,

$$H_2S + h\nu \rightarrow H + HS.$$

The reaction

$$H + H_2S \rightarrow H_2 + HS$$

is extremely fast, with rate constant $k = 1.29 \times 10^{-11}\ e^{860/T}$ (Kurylo *et al.*, 1971). However, the lack of sufficient laboratory data does not permit us presently to evaluate these possibilities quantitatively.

The mixing ratio of CO in the lower atmosphere was measured by Hoffman *et al.* (1980a) to be 20 ppm. What controls the abundance of CO? McElroy *et al.* (1982b) suggested that the state of oxidation of the atmosphere of Venus may be regulated by the escape of hydrogen and oxygen. Lewis (1970) proposed six buffering mechanisms for CO to be in equilibrium with the surface of Venus:

$$\text{C (graphite)} + CO_2 = 2CO,$$

$$3\ FeMgSiO_4 + CO_2 = 3\ MgSiO_3 + Fe_3O_4 + CO,$$

$$3\ FeSiO_3 + CO_2 = 3\ SiO_2 + Fe_3O_4 + CO,$$

$$2\,Fe_3O_4 + CO_2 = 3\,Fe_2O_3 + CO,$$
$$Fe + CO_2 = FeO + CO,$$
$$3\,FeO + CO_2 = Fe_3O_4 + CO.$$

We assumed in our models, for simplicity, that the ratio CO/CO_2 is controlled by the surface. Of course, evolution of the atmosphere could have disturbed the oxidation state of the surface, but as long as we are dealing with models that produce at most amounts of oxygen ~ 1 kg cm^{-2} over the age of the planet, the constancy of the CO/CO_2 ratio seems to be a reasonable assumption (Lewis and Kreimendahl, 1980).

Stability of NO_x below the Cloud Tops

In model B we adopt a mixing ratio of NO_x in the bulk atmosphere equal to 3×10^{-8}. Lightning in the lower atmosphere, comparable to that in the terrestrial atmosphere, has been reported by Borucki *et al.* (1981), and could provide a sufficient source of NO_x if the only sink for NO_x were in the upper atmosphere. This suggests that the lifetime of NO_x in the lower atmosphere must exceed 4000 years. Prinn (1981, private communication) argued that the deposition of nitrate on the surface is probably not a major sink for NO_x due to the instability of simple nitrates at high temperature. The reaction

$$2NO \rightarrow N_2O + O$$

could, in principle, be important, but the rate constant recommended by Baulch *et al.* (1973), $k = 8.3 \times 10^{-10} e^{-29000/T}$, implies a lifetime in excess of 8×10^4 years. The fate of NO_x in the Venusian troposphere may be compared to that of nitrate in the terrestrial oceans. In the deep oceans odd nitrogen has no significant chemical sink. The lifetime for nitrate, associated with denitrification in upwelling regions, is about 10^4 years (McElroy, 1976). However, on Venus we cannot rule out efficient NO_x destruction, such as the above disproportionation reaction, catalyzed by the surface. So, until direct detection, we must regard the presence of 30 ppb of NO_x in the bulk atmosphere as only hypothetical.

6. EVOLUTION OF THE ATMOSPHERE

The major form of hydrogen in the bulk atmosphere of Venus is H_2O, with mixing ratio equal to 1×10^{-4} [Moroz *et al.* (1979), with correction by A. T. Young (1981, private communication)]. This is equivalent to a column abundance of 2×10^{23} molecules cm^{-2} or 6 g cm^{-2}. In contrast, the water abundance on Earth is 3×10^5 g cm^{-2}. According to Lewis (1970, 1972, 1974a,b), Venus formed with less water than Earth. But it is hard to understand this enormous depletion factor of $\sim 10^5$. Pollack and Yung (1980) argued that even the capture of carbonaceous meteorites could be a significant source of water on Venus. They estimated an initial endowment of water on Venus no less than 1% the terrestrial value. Extensive evolution of the atmosphere must have occurred.

Early works on the evolution of the atmosphere of Venus by Walker *et al.* (1970) and Walker (1975) investigated the escape of an amount of water equivalent to the terrestrial value. The atmospheric chemical environment that prevailed during this period of massive loss of water must be totally different from what it is today. Hence, all such theories must necessarily be somewhat speculative. In this work we shall address a more restricted problem: what photochemical mechanisms control the escape of hydrogen at present and in the recent past under conditions similar to those at present?

The high abundance of H_2 in model A implies a high escape rate for hydrogen, driven by exothermic ionic reactions such as

$$O^+ + H_2 \rightarrow OH^+ + H^*,$$
$$OH^+ + e \rightarrow O + H^*,$$
$$CO_2{}^+ + H_2 \rightarrow CO_2H^+ + H^*,$$
$$CO_2H^+ + e \rightarrow CO_2 + H^*,$$

where H^* denotes a hot hydrogen atom that may escape from Venus (Kumar and Hunten, 1974; Sze and McElroy, 1975). The escape flux of hydrogen has been estimated by Kumar *et al.* (1981) to be 3×10^8 atoms cm^{-2} sec^{-1}. At this rate the half-life for the present amount of water on Venus is only 2×10^7 years, a geologically insignificant time. The high abundance of H_2 (20 ppm) is about 10^3 times higher than that expected on the basis of the equilibrium reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

and must be maintained ultimately by photochemical processes. Our conjecture, based on Appendix B and the previous section entitled Molecular Hydrogen, can be summarized roughly as

$$4\ SO_2 + 4\ H_2O + h\nu \rightarrow 3\ H_2SO_4 + S + H_2.$$

This scheme must extract H_2 from H_2O at a rate exceeding 1.4×10^{11} cm^{-2} sec^{-1} in order for Model A to be valid. The escape of hydrogen is thus intimately tied to the photochemistry of sulfur compounds in the stratosphere, and not to the water gas equilibrium. Since photolysis of SO_2 is the only ultimate limit for such schemes, sulfur photochemistry can, in principle, generate H_2 from H_2O at the rate of 10^{13} cm^{-2} sec^{-1}. This possibility may have interesting implications for the problem investigated by Walker *et al.* (1970) and Walker (1975). However, model A is not our preferred model for Venus at the present epoch, and further discussion of the sulfur-driven hydrogen escape is not justified. In model B the abundance of H_2 is 0.5 ppm, 50 times above the equilibrium value given by the water gas reaction. Even this lower amount of H_2 must be maintained by photochemical processes, as in model A. Hydrogen escape in low H_2 models has been studied by Kumar and Hunten (1974), Sze and McElroy (1975), and recently by McElroy *et al.* (1982a). The escape rate is estimated to be on the order of 10^7 cm^{-2} sec^{-1}.

In model C we postulate that the lower atmosphere is not capable of supplying any H_2 to the upper atmosphere. The major consequence of the model for the hydrogenous compounds in the stratosphere is expressed by

$$2\ HCl + CO_2 + h\nu \rightarrow H_2O + CO + Cl_2.$$

The cycle must be completed in the lower atmosphere by reversing the above process with thermochemical equilibrium chemistry. However, the cycle is not perfect and there is a permanent and irreversible leakage of hydrogen due to escape. The abundances of H and H_2 at 100 km in model C are on the order of 0.1 ppm and can readily supply an escape flux on the order of 10^7 cm^{-2} sec^{-1}. Thus chlorine chemistry alone is capable of extracting hydrogen from water and feeding the escape of hydrogen at this rate in the total absence of any contribution of H_2 by the water gas equilibrium reaction. This must be the asymptotic state for the evolution of Venus. We believe that the Venus atmosphere has reached this stage at present.

Since model C is our preferred model for the present atmosphere, we can regard models A and B as representative of the early history of the Venusian atmosphere. The abundances of H_2 in models A and B could be maintained by the water gas equilibrium if the concentration of H_2O in the lower atmosphere were, respectively, 2×10^3 and 50 times higher. A reconstruction of the evolution of Venus is roughly as follows. Venus' atmosphere started with an initial amount of water equal to about 1% of the terrestrial value, as proposed by Pollack and Yung (1980). The water gas equilibrium supplied large quantities of H_2 in the upper atmosphere, where hydrogen readily escaped, as in model A. As Venus lost water, the abundance of H_2 must decrease and we passed an intermediate stage as described by model B. Finally, with the further loss of water, the water gas equilibrium failed to deliver any appreciable quantity of H_2 to the upper atmosphere. The photochemistry of the stratosphere as-

TABLE X

RECOMMENDED LIST OF FUTURE OBSERVATIONS AND CHEMICAL KINETICS EXPERIMENTS FOR THE STRATOSPHERE OF VENUS

Observations	Remarks
Spectroscopic confirmation of H_2	Can use the Lyman bands around 1606 Å (Feldman and Fastie, 1973; Moos, 1974).
Spectroscopic detection of O_2	Traub and Carleton (1974) upper limit could be improved.
Spectroscopic detection of ClO and NO_2 in stratosphere	
Global and diurnal variation of CO and O in the mesosphere and upper stratosphere	This is important for pinning down the source, transport, and sink of CO and O.
Spectroscopic detection of SO	Wilson *et al.*'s (1981) upper limit could be improved.
Laboratory kinetics	
k_{55} SO + HO_2	The reaction breaks an O–O bond
k_{18a} $O_2(^1\Delta) + M$	$M = CO_2$
Quantum yield for producing $O_2(^1\Delta)$ by	Major sources of $O_2(^1\Delta)$
(R31) O + HO_2	
(R39) Cl + O_3	
(R44) O + ClO	
Chemistry of HSO_3, $ClSO_2$	Determines whether HSO_3 and $ClSO_2$ are sinks for HO_x and ClO_x
Chemistry of $(SO)_2$	Determines production and fate of $(SO)_2$ compounds as possible source of H_2.
(R100) HNO + $h\nu$	Major sink for HNO in model B

2–3. To realistically model the stratosphere, and to study the latitudinal and longitudinal variation, we must resort to at least a two-dimensional model. Observations of the global distributions of CO, SO_2, O, O_2, and H_2SO_4 aerosols are needed.

The chemistry of the stratosphere of Venus bears interesting similarities to that of the Earth. On both planets, the classic Molina–Rowland cycle for catalytic conversion of odd oxygen into molecular oxygen [cycle (8)] is important. In the terrestrial stratosphere, the efficiency of cycle (8) is inhibited by Cl + CH_4 and ClO + NO. Similar inhibiting reactions are also present in the Venusian stratosphere as (R38) Cl + H_2 and (R56) ClO + SO. The reaction NO + HO_2, which is critical for the assessment of the impact of SST and fertilizer on the ozone layer in the terrestrial stratosphere, could also be important on Venus. Reactions (R55) SO + HO_2 and (R101) ClCO + O_2 play a similar role. In view of such obvious similarities between the chemistry of the stratospheres of Venus and the Earth, comparative studies of both planets will continue to be fruitful.

APPENDIX A: CHEMISTRY OF HSO_3 AND $ClSO_2$

The reaction

$$SO_2 + OH + M \rightarrow HSO_3 + M \quad (R59)$$

has been extensively studied (see Baulch *et al.*, 1980) in connection with homogeneous gas-phase oxidation of SO_2 to sulfate. Davis *et al.* (1979) and Friend *et al.* (1980) have suggested that the ultimate fate of HSO_3 in the atmosphere is formation of H_2SO_4 or related compounds. It is assumed that the hydroxyl radical in reaction (R58) is consumed and not recycled. The possibility of recycling HO_x was noted by Turco *et al.* (1979), who, without discussing a detailed mechanism, proposed a net reaction equivalent to

$$SO_2 + OH \rightarrow SO_3 + H.$$

Reaction (R59) is probably not as important as schemes (6a,b) and (12a,b) for oxidation of SO_2 on Venus, but could be important as a sink for HO_x. In addition, there are similar reactions possibly leading to the loss of HO_x and ClO_x:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \text{ (heterogeneous)}, \quad \text{(R61)}$$

$$SO_2 + Cl + M \rightarrow ClSO_2 + M. \quad \text{(R62)}$$

Table AI summarizes a set of reactions related to the chemistry of HSO_3. This chemistry is adopted in models B and C, with the consequence that the reaction (R59) $SO_2 + OH + M \rightarrow HSO_3 + M$ is now no longer a permanent sink for HO_x in the lower stratosphere. The details of this chemical model are somewhat speculative. The maximum concentrations of HSO_3 and $HSO_3 \cdot H_2O$ in the model are 4×10^6 and 2×10^9 cm^{-3}, respectively. The column-integrated production rate for $H_2S_2O_6$ is on the order of 1×10^{10} cm^{-2} sec^{-1}.

APPENDIX B: CHEMISTRY OF THE DIMER $(SO)_2$

The photochemistry of SO_2 is further complicated (and enriched) by the chemistry of $(SO)_2$ dimer, formed by

$$SO + SO + M \rightarrow (SO)_2 + M \quad \text{(R128)}$$

(Herron and Huie, 1980). The structure of the dimer is known (Lovas *et al.*, 1974). The OS–SO bond strength has been estimated to be 30–70 kcal/mole (Benson, 1978; Herron and Huie, 1980). An analysis of Herron and Huie's experiment suggests that the rate coefficient for decomposition by collision,

$$(SO)_2 + M \rightarrow 2\,SO + M, \quad \text{(R132)}$$

must be less than 1×10^{-20} cm^{-3} sec^{-1}. The fate of the dimer is of great importance to the atmosphere of Venus. Herron and Huie (1980) suggested

$$(SO)_2 + SO \rightarrow S_2O + SO_2. \quad \text{(R134)}$$

S_2O is readily removed by reaction with O and S,

$$S_2O + O \rightarrow 2SO, \quad \text{(R129)}$$

$$S_2O + S \rightarrow S_2 + SO, \quad \text{(R130)}$$

(Stedman *et al.*, 1974) or by photolysis,

$$S_2O + h\nu \rightarrow S + SO \quad \text{(R127)}$$

(Okabe, 1978). Since the bond strengths for OS–O (131 kcal/mole) and O–O (119 kcal/mole) are similar, we postulate that the reaction

$$(SO)_2 + O \rightarrow S_2O + O_2 \quad \text{(R133)}$$

is as fast as (R134).

The homogeneous chemistry of $(SO)_2$ can be summarized by two catalytic cycles:

$$\begin{array}{lll} SO + SO + M \rightarrow (SO)_2 + M & \text{(R128)} & \\ (SO)_2 + SO \rightarrow SO_2 + S_2O & \text{(R134)} & \text{(B1)} \\ \underline{S_2O + O \rightarrow 2SO} & \underline{\text{(R129)}} & \\ \text{net} \quad SO + O \rightarrow SO_2 & & \end{array}$$

$$\begin{array}{lll} SO + SO + M \rightarrow (SO)_2 + M & \text{(R128)} & \\ (SO)_2 + O \rightarrow S_2O + O_2 & \text{(R133)} & \text{(B2)} \\ \underline{S_2O + O \rightarrow 2SO} & \underline{\text{(R129)}} & \\ \text{net} \quad O + O \rightarrow O_2 & & \end{array}$$

Cycle (B1) catalytically recombines SO and O and can be interpreted as an increase in the rate coefficient for

$$SO + O + M \rightarrow SO_2 + M \quad (R51)$$

or decrease in the photolysis rate of SO_2,

$$SO_2 + h\nu \rightarrow SO + O. \quad (R9)$$

The net result is the suppression of cycles (6a,b) and (12a,b). Cycle (B2) is based on analogy with cycle (B1) and results in catalytically recombining oxygen atoms.

Nair *et al.* (1963) suggested that S_2O is the anhydride of thiosulfurous acid ($H_2S_2O_2$. Friend (1981, private communication)[4] suggested that $(SO)_2$ could be the anhydride of thiosulfuric acid ($H_2S_2O_3$). We propose three speculative schemes for the production of miscellaneous sulfur compounds:

$$\begin{array}{rrcll}
 & 3(SO_2 + h\nu & \rightarrow & SO + O) & (R9) \\
 & 2SO + M & \rightarrow & (SO)_2 + M & (R128) \\
 & (SO)_2 + SO & \rightarrow & S_2O + SO_2 & (R134) \quad (B3) \\
 & S_2O + H_2O & \rightarrow & H_2S_2O_2 & (R131) \\
 & 3(SO_2 + O + M & \rightarrow & SO_3 + M) & (R58) \\
 & 3(SO_3 + H_2O & \rightarrow & H_2SO_4) & (R65) \\
\hline
\text{net} & 5SO_2 + 4H_2O & \rightarrow & H_2S_2O_2 + 3H_2SO_4 &
\end{array}$$

$$\begin{array}{rrcll}
 & 2(SO_2 + h\nu & \rightarrow & SO + O) & (R9) \\
 & 2SO + M & \rightarrow & (SO)_2 + M & (R128) \\
 & (SO)_2 + H_2O & \rightarrow & H_2S_2O_3 & (R135) \quad (B4) \\
 & 2(SO_2 + O + M & \rightarrow & SO_3 + M) & (R58) \\
 & 2(SO_3 + H_2O & \rightarrow & H_2SO_4) & (R65) \\
\hline
\text{net} & 4SO_2 + 3H_2O & \rightarrow & H_2S_2O_3 + 2H_2SO_4 &
\end{array}$$

$$\begin{array}{rrcll}
 & 4(SO_2 + h\nu & \rightarrow & SO + O) & (R9) \\
 & 2(2SO + M & \rightarrow & (SO)_2 + M) & (R128) \\
 & 2(S_2O_2 + SO & \rightarrow & S_2O + SO_2) & (R134) \\
 & S_2O + h\nu & \rightarrow & S + SO & (R127) \quad (B5) \\
 & S + S_2O & \rightarrow & S_2 + SO & (R130) \\
 & 4(SO_2 + O + M & \rightarrow & SO_3 + M) & (R58) \\
 & 4(SO_3 + H_2O & \rightarrow & H_2SO_4) & (R65) \\
\hline
\text{net} & 6SO_2 + 4H_2O & \rightarrow & 4H_2SO_4 + S_2 &
\end{array}$$

The significance of schemes (B3)–(B5) is twofold. First, these are the first known schemes for producing H_2SO_4 from SO_2 without using CO_2-derived oxygen.[5] Second, atmospheric photochemistry can start with SO_2 (oxidation state = +4) and segregate it into a more oxidized sulfur compound, H_2SO_4 (oxidation state = +6), and reduced sulfur compounds, $H_2S_2O_2$ (oxida-

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[5] This possibility seems to have been recognized by Krasnopolsky and Parshev (1980b). However, these authors did not provide detailed chemical schemes.

[4] We are also indebted to J. P. Pinto for drawing our attention to thiosulfuric acid. It should be noted that going from $(SO)_2$ to $H_2S_2O_3$ involves a major rearrangement of the sulfur and oxygen atoms.

TABLE AI

LIST OF SPECULATIVE REACTIONS RELATED TO HSO_3, AND THEIR RATE COEFFICIENTS, BASED ON DAVIS *et al.* (1979) AND FRIEND *et al.* (1980), AND OUR OWN ESTIMATES (FOOTNOTES REFER TO TABLE IIIa)

	Reaction	Rate coefficient	Reference
(R115)	$HSO_3 + H_2O + M \rightarrow HSO_3 \cdot H_2O$	$k_{115} = 3.9 \times 10^{-30}$	Friend *et al.* (1980)
(R116)	$HSO_3 + O \rightarrow OH + SO_3$	$k_{116} = 1.0 \times 10^{-11}$	″
(R117)	$HSO_3 + H \rightarrow H_2 + SO_3$	$k_{117} = 1.0 \times 10^{-11}$	″
(R118)	$HSO_3 + OH \rightarrow H_2O + SO_3$	$k_{118} = 3.0 \times 10^{-11}$	″
(R119)	$HSO_3 + Cl \rightarrow HCl + SO_3$	$k_{119} = 1.0 \times 10^{-11}$	″
(R120)	$2HSO_3 \rightarrow H_2S_2O_6$	$k_{120} = 6.0 \times 10^{-14}$	Friend *et al.* (1980)
(R121)	$HSO_3 \cdot H_2O + M \rightarrow HSO_3 + H_2O + M$	$k_{121} = 1.0 \times 10^{-19}$	Hamilton and Lii (1977)
(R122)	$HSO_3 \cdot H_2O + O \rightarrow OH + H_2SO_4$	$k_{122} = 1.0 \times 10^{-11}$	″
(R123)	$HSO_3 \cdot H_2O + H \rightarrow H_2 + H_2SO_4$	$k_{123} = 1.0 \times 10^{-11}$	″
(R124)	$HSO_3 \cdot H_2O + OH \rightarrow H_2O + H_2SO_4$	$k_{124} = 3.0 \times 10^{-11}$	″
(R125)	$HSO_3 \cdot H_2O + Cl \rightarrow HCl + H_2SO_4$	$k_{125} = 1.0 \times 10^{-11}$	″
(R126)	$HSO_3 \cdot H_2O + HSO_3 \rightarrow H_2S_2O_2 \cdot H_2O$	$k_{126} = 3.0 \times 10^{-12}$	Friend *et al.* (1980)

tion state = +1), $H_2S_2O_3$ (oxidation state = +2), and S_2 (oxidation state = 0).

Table BI summarizes a speculative scheme involving reactions with $(SO)_2$. A model incorporating the chemistry of model A and Table BI has been studied. The details of the model need not be discussed here. The choice of rate constants presented in Table BI does allow for modest production rates for $H_2S_2O_2$, $H_2S_2O_3$, and S_2 equal to 1×10^{10}, 3×10^9, and 1×10^9 cm^{-2} sec^{-1}, respectively. It is clear that if we were to adjust the rate coefficients of the reactions (R131), (R135), and (R130) we could enormously increase the efficiencies of the schemes (B3), (B4), and (B5) for production of $H_2S_2O_2$, $H_2S_2O_3$, and S_2. Since these schemes are not limited by oxygen supplied by CO_2 photolysis, the production rates are limited only by an SO_2 photolysis rate of $\sim 1 \times 10^{13}$ cm^{-2} sec^{-1}. Such a scenario is unlikely above the cloud tops, though.

Perhaps a most interesting consequence of the production of this set of reduced sulfur compounds is the possibility of generating H_2S by an exchange reaction in the liquid phase,

$$H_2S_2O_3 + H_2O \rightarrow H_2SO_4 + H_2S$$

(Bassett and Durrant, 1927). The production of H_2S by this mechanism can have

TABLE BI

LIST OF SPECULATIVE REACTIONS RELATED TO $(SO)_2$, AND THEIR RATE COEFFICIENTS, BASED ON HERRON AND HUIE (1980) AND OUR OWN ESTIMATES (FOOTNOTES REFER TO TABLE IIIa)

	Reaction	Rate coefficient	Reference
(R127)	$S_2O + h\nu \rightarrow S + SO$	$k_{127} = 3.0 \times 10^{-7}$	″
(R128)	$2SO + M \rightarrow (SO)_2 + M$	$k_{128} = 4.4 \times 10^{-31}$	Herron and Huie (1980)
(R129)	$S_2O + O \rightarrow 2SO$	$k_{129} = 1.5 \times 10^{-12}$	Stedman *et al.* (1974)
(R130)	$S_2O + S \rightarrow S_2 + SO$	$k_{130} = 1 \times 10^{-13}$	″
(R131)	$S_2O + H_2O \rightarrow H_2S_2O_2$	$k_{131} = 1 \times 10^{-20}$	″
(R132)	$(SO)_2 + M \rightarrow 2SO + M$	$k_{132} = 9.0 \times 10^{-23}$	″
(R133)	$(SO)_2 + O \rightarrow S_2O + O_2$	$k_{133} = k_{134} = 3.3 \times 10^{-14}$	″
(R134)	$(SO)_2 + SO \rightarrow S_2O + SO_2$	$k_{134} = 3.3 \times 10^{-14}$	Herron and Huie (1980)
(R135)	$(SO)_2 + H_2O \rightarrow H_2S_2O_3$	$k_{135} = 1 \times 10^{-20}$	″

profound implications for the budget of H_2 in the lower atmosphere of Venus.

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