Photochemistry of the Stratosphere of Venus: Implications for Atmospheric Evolution

YUK L. YUNG

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

AND

W. B. DEMORE

Molecular Physics and Chemistry Section, Jet Propulsion Laboratory, Pasadena, California 91109

Received November 13, 1981; revised March 1, 1982

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 \( \text{H}_2 \) mixing ratio equal to \( 2 \times 10^{-5}, 5 \times 10^{-5}, \) and \( 1 \times 10^{-5} \), respectively. All models satisfactorily account for the observations of \( \text{CO}, \text{O}_2, \text{O}_2(\Delta), \) and \( \text{SO}_2 \) in the stratosphere, but only the last one may be able to account for the diurnal behavior of mesospheric \( \text{CO} \) and the \( \text{uv} \) albedo. Oxygen, derived from \( \text{CO}_2 \) photolysis, is primarily consumed by \( \text{CO}_2 \) recombination and oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \). Photolysis of \( \text{HCl} \) in the upper stratosphere provides a major source of odd hydrogen and free chlorine radicals, essential for the catalytic oxidation of \( \text{CO} \). Oxidation of \( \text{SO}_2 \) by \( \text{O} \) occurs in the lower stratosphere. In the high-\( \text{H}_2 \) model (model A) the \( \text{O}-\text{O} \) bond is broken mainly by \( \text{S}^+ + \text{O}_2 \) and \( \text{SO} + \text{HO}_2 \). In the low-\( \text{H}_2 \) models additional reactions for breaking the \( \text{O}-\text{O} \) bond must be invoked: \( \text{NO} + \text{HO}_2 \) in model B and \( \text{CICO} + \text{O}_2 \) in model C. It is shown that lightning in the lower atmosphere could provide as much as 30 ppb of \( \text{NO}_x \) 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, bleeding
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 \( \text{CO}_2 \). Small concentrations of chemically reactive species such as \( \text{CO}, \text{H}_2\text{O}, \text{HCl}, \text{O}_2(\Delta), \) and \( \text{SO}_2 \) have been detected in the stratosphere. The presence of \( \text{H}_2 \) 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 \( \text{O}_2 \) has not been reported to date. Pollack et al. (1980) tentatively identified \( \text{Cl}_2 \) as the long-wavelength ultraviolet absorber. Clancy et al. (1981) definitively established the diurnal asymmetry for mesospheric \( \text{CO} \).


2 Contribution No. 3692 of the Division of Geologival and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.
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 $f_x$)**

<table>
<thead>
<tr>
<th>Species</th>
<th>Abundance</th>
<th>Reference and remarks</th>
</tr>
</thead>
</table>
| CO      | $f_{CO} = 4.5 \times 10^{-3}$ at cloud top. | Connes et al. (1968)  
Effective region of line formation model dependent; should be around 200 mbar or 62 km. |
|         | $f_{CO} \sim 10^{-4}$ at 100 km, nightside abundance is lower. | Schloerb et al. (1980)  
Wilson et al. (1981)  
Clancy et al. (1981) |
| $O_2$   | $f_{O_2} < 1 \times 10^{-6}$ at cloud top. | Hoffman et al. (1980a)  
Traub and Carleton (1974)  
Region of line formation between 60 and 300 mbar. |
| $O_3^{(1\Delta)}$ Dayglow $= 1.5$ MR$^a$ Nightglow $= 1.2$ MR | Used terrestrial dayglow for calibration, error $\sim 70\%$. |
| $O_3$   | $f_{O_3} < 0.3$ MR. | Connes et al. (1979) |
| HCl     | $f_{HCl} = 4 \times 10^{-7}$ | Stewart et al. (1979) |
| $H_2O$  | $f_{H_2O} = 1 \times 10^{-6}$ | Fink et al. (1972)  
Barker (1975) |
| $SO_2$  | $f_{SO_2}$ at 40 mbar varies from $5$ to $100 \times 10^{-8}$, with weighted mean of $2 \times 10^{-8}$ 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). |
| $SO$    | $f_{SO} < 5 \times 10^{-8}$, $70$ km $< z < 90$ 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. |
| $S_x$   | $\sum_j S_{2j} \approx 8 \times 10^{-8}$ | San'ko (1980)  
Identification not unique |
| $Cl_2$  | $f_{Cl_2} < 10^{-6}$ 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 $= 1 \times 10^{12}$ photons cm$^{-2}$s$^{-1}$. 
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

stratospheric chemistry: breaking the O–O bond, oxidation of CO to CO₂ (essential for CO₂ stability), and oxidation of SO₂ to H₂SO₄. 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 CO₂ stability problem on Venus is reminiscent of a related problem on Mars. The classic work of McElroy and Donahue (1972) shows that CO₂ recombination is catalyzed by trace quantities of hydroxyl radicals derived from H₂O 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,

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H},$$
as it is on Mars? Or, is the catalytic cycle uniquely Venusian, driven by chlorine radicals,

$$\text{ClCO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{ClO}?$$

Our own recent experiments in laboratory kinetics suggest that both cycles are viable, and their relative importance depends on the abundance of H₂ 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

$$\text{Cl} + \text{CH}_4 \rightarrow \text{HCl} + \text{CH}_3$$
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 H₂ plays a similar role in controlling the abundance of active chlorine via the reaction

$$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}.$$ Since this reaction may initiate irreversible conversion of H₂ into H₂O, H₂ must be continually supplied by thermochemical reactions on the surface. Is the lower atmosphere capable of satisfying the stratospheric demand of H₂ 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 CO₂ occurs readily by absorption of photons shortward of 2040 Å (DeMore and Mosesman, 1971; Shemansky, 1972; DeMore and Papatoff, 1972),

$$\text{CO}_2 + \text{hv} \rightarrow \text{CO} + \text{O}. \quad (R1)$$
The recombination reaction

$$\text{CO} + \text{O} + \text{M} \rightarrow \text{CO}_2 + \text{M} \quad (R14)$$
is, however, spin-forbidden, and a major loss of atomic oxygen is the formation of O₂ via

$$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}, \quad (R17)$$
$$\text{O} + \text{ClO} \rightarrow \text{Cl} + \text{O}_2, \quad (R44)$$
$$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}. \quad (R28)$$

We can take the observations of O₉(Δ) → O₇(Σ) + hv airglow (Connes et al., 1979) as evidence that a substantial fraction of CO₂ photolysis leads to production of O₂. One would expect, on the basis of the photo-
chemistry of CO₂ alone, that CO and O₂ should be abundant, and that the ratio \( r = [\text{CO}]/[\text{O}_2] \) should be 2. The observed mixing ratio of CO at the cloud tops is \( 4.5 \times 10^{-5} \) (Connes et al., 1968; Young, 1972). The upper limit for O₂ is \( 1 \times 10^{-6} \) (Traub and Carleton, 1974). A successful chemical model must account for the deficiency of CO in the upper atmosphere, and the extreme scarcity of O₂ relative to CO \( (r > 45) \).

There are two obvious sinks for O₂:

1. Oxidation of CO to CO₂,
2. Oxidation of some sulfur compounds to \( \text{H}_2\text{SO}_4 \).

Early photochemical models have concentrated on the recombination of CO₂ catalyzed by cycles involving Cl₂, ClO, ClO₂, Cl₂ (Prinn, 1971) and HO₂ (H, OH, HO₂, H₂O₂) 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:

\[
\begin{align*}
\frac{1}{2}(\text{Cl} + \text{O}_2 + M &\rightarrow \text{ClOO} + M) \\
\frac{1}{2}(\text{ClOO} + \text{CO} &\rightarrow \text{CO}_2 + \text{ClO}) \\
\frac{1}{4}(\text{ClO} + \text{CO} &\rightarrow \text{Cl} + \text{CO}_2) \\
\text{net} &\quad \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\end{align*}
\]

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):

\[
\begin{align*}
\text{H} + \text{O}_2 + M &\rightarrow \text{HO}_2 + M \\
\text{O} + \text{HO}_2 &\rightarrow \text{OH} + \text{O}_2 \\
\text{CO} + \text{OH} &\rightarrow \text{CO}_2 + \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{net} &\quad \text{CO} + \text{O} \rightarrow \text{CO}_2 \\
\text{H} + \text{O}_2 + M &\rightarrow \text{HO}_2 + M \\
\frac{1}{2}(2 \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2) \\
\frac{1}{2}(\text{H}_2\text{O}_2 + \text{hv} &\rightarrow 2 \text{OH}) \\
\text{CO} + \text{OH} &\rightarrow \text{CO}_2 + \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{net} &\quad \text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2
\end{align*}
\]

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

\[
\begin{align*}
\text{Cl} + \text{CO} + M &\rightarrow \text{CICO} + M \\
\text{CICO} + \text{O} &\rightarrow \text{ClO} + \text{CO}_2 \\
\text{ClO} + \text{O} &\rightarrow \text{Cl} + \text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{net} &\quad \text{CO} + \text{O} \rightarrow \text{CO}_2
\end{align*}
\]

This scheme is actually more complicated than previously thought, as the reaction CICO with O₂ is mediated by an intermediate complex CICO₃. We consider three schemes:

\[
\begin{align*}
\text{Cl} + \text{CO} + M &\rightarrow \text{CICO} + M \\
\text{CICO} + \text{O}_2 + M &\rightarrow \text{CICO}_3 + M \\
\text{CICO}_3 + \text{O} &\rightarrow \text{Cl} + \text{CO}_2 + \text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{net} &\quad \text{CO} + \text{O} \rightarrow \text{CO}_2
\end{align*}
\]
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

\[
\begin{align*}
\text{Cl} + \text{CO} + M & \rightarrow \text{CICO} + M \quad (R99) \\
\text{CICO} + \text{O}_2 + M & \rightarrow \text{ClCO}_3 + M \quad (R101) \\
\text{ClCO}_3 + \text{Cl} & \rightarrow \text{Cl} + \text{CO}_2 + \text{ClO} \quad (R111) \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \quad (R44) \\
\text{net CO} + \text{O} & \rightarrow \text{CO}_2 \\
\end{align*}
\]

The third scheme associated with CICO \((4c)\) 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\(_2\)S 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 \textit{et al.}, 1973; Prinn, 1973, 1975; Sze and McElroy, 1975; Wofsy and Sze, 1975) that the availability of \text{O}_2 could limit the production rate of H\(_2\)SO\(_4\). Prinn (1973, 1975) proposed a scheme for oxidation of COS to H\(_2\)SO\(_4\) using the \text{O}_2 derived from CO\(_2\) photolysis:

\[
\begin{align*}
\text{COS} + \text{hv} & \rightarrow \text{CO} + \text{S(D)} \\
\text{S(D)} + \text{M} & \rightarrow \text{S} + \text{M} \\
\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O} \\
\text{SO} + \text{OH} & \rightarrow \text{SO}_2 + \text{H} \\
\text{SO}_2 + \text{HO}_2 & \rightarrow \text{SO}_3 + \text{OH} \\
\text{SO}_3 + \text{H}_2\text{O} + \text{M} & \rightarrow \text{H}_2\text{SO}_4 + \text{M} \\
\end{align*}
\]

This scheme can be roughly summarized as

\[
\text{COS} + 2\text{O}_2 + \text{H}_2\text{O} + (\text{HO}_x) \rightarrow \text{CO}_2 + \text{H}_2\text{SO}_4 + (\text{HO}_x),
\]

where the hydroxyl radicals \text{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 \text{O}_2 and producing \text{H}_2\text{SO}_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 \textit{et al.}, 1980a,b; Oyama \textit{et al.}, 1980). Prinn (1971, 1973, 1975, 1978, 1979) argued that COS could be readily destroyed by

\[
\text{COS} + \text{S} \rightarrow \text{CO} + \text{S}_2.
\]

Indeed, there is strong circumstantial evidence for the presence of polysulfur in the spectrum taken by Venera 11 and 12 below 38 km (Moroz \textit{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\(_2\)S 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 \textit{et al.}, 1980; Sze and Ko, 1980).

The discovery of the first gaseous sulfur species, \text{SO}_2, on Venus (Barker, 1979) and its confirmation by Conway \textit{et al.} (1979), Stewart \textit{et al.} (1979), and Esposito \textit{et al.} (1979) led Winick and Stewart (1980) to examine the photochemistry of \text{SO}_2 with a fairly comprehensive model involving the interaction of chlorine, hydrogen, oxygen, and sulfur compounds. The photochemistry of \text{SO}_2 is initiated by absorption of photons
shortward of 2190 Å (Okabe, 1978),

\[ \text{SO}_2 + h\nu \rightarrow \text{SO} + \text{O}. \]  

The recombination reaction

\[ \text{SO} + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{M}, \]  

with \( \text{M} = \text{CO}_2 \), is extremely fast (Leu, 1982) and hence photolysis of \( \text{SO}_2 \) does not always lead to net destruction. Oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \) is, of course, a net sink. In addition to oxidation schemes using \( \text{HO}_x \) radicals (Prinn, 1973, 1975), Winick and Stewart (1980) first recognized the importance of two new schemes,

\[
\begin{align*}
\frac{1}{2}(\text{SO} + h\nu & \rightarrow \text{S} + \text{O}) \quad \text{(R8)} \\
\frac{1}{2}(\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O}) \quad \text{(R46)} \quad \text{(6a)} \\
\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M} \quad \text{(R58)} \\
\text{SO}_3 + \text{H}_2\text{O} + \text{M} & \rightarrow \text{H}_2\text{SO}_4 + \text{M} \quad \text{(R65)}
\end{align*}
\]

\[
\begin{align*}
\text{net} & \quad \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \\
\frac{1}{2}(\text{SO}_2 + h\nu & \rightarrow \text{SO} + \text{O}) \quad \text{(R9)} \\
\frac{1}{2}(2\text{SO} & \rightarrow \text{SO}_2 + \text{S}) \quad \text{(R57)} \\
\frac{1}{2}(\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O}) \quad \text{(R46)} \quad \text{(6b)} \\
\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M} \quad \text{(R58)} \\
\text{SO}_3 + \text{H}_2\text{O} + \text{M} & \rightarrow \text{H}_2\text{SO}_4 + \text{M} \quad \text{(R65)}
\end{align*}
\]

\[
\begin{align*}
\text{net} & \quad \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \\
\frac{1}{2}(\text{SO}_2 + h\nu & \rightarrow \text{SO} + \text{O}) \quad \text{(R9)} \\
\frac{1}{2}(2\text{SO} & \rightarrow \text{SO}_2 + \text{S}) \quad \text{(R57)} \\
\frac{1}{2}(\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O}) \quad \text{(R46)} \quad \text{(6b)} \\
\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M} \quad \text{(R58)} \\
\text{SO}_3 + \text{H}_2\text{O} + \text{M} & \rightarrow \text{H}_2\text{SO}_4 + \text{M} \quad \text{(R65)}
\end{align*}
\]

The Winick–Stewart model successfully reproduces the observed \( \text{SO}_2 \) distribution, with an appropriate choice of the eddy diffusivity profile. But the model predictions for the concentrations of \( \text{CO} \) and \( \text{O}_2 \) at the cloud tops are about factors of 3 and 50, respectively, higher than those allowed by observations.

The large concentration of \( \text{O}_2 \) 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 \( \text{O}–\text{O} \) bond,

\[
\begin{align*}
\text{SO} + h\nu & \rightarrow \text{S} + \text{O} \quad \text{(R8)} \\
\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O} \quad \text{(R46)} \quad \text{(7a)} \\
\text{net} & \quad \text{O}_2 \rightarrow \text{2O} \\
\text{SO} + \text{SO} & \rightarrow \text{SO}_2 + \text{S} \quad \text{(R57)} \\
\text{SO}_2 + h\nu & \rightarrow \text{SO} + \text{O} \quad \text{(R9)} \quad \text{(7b)} \\
\text{S} + \text{O}_2 & \rightarrow \text{SO} + \text{O} \quad \text{(R46)} \\
\text{net} & \quad \text{O}_2 \rightarrow \text{2O}
\end{align*}
\]

These cycles constitute a crucial part of the \( \text{SO}_2 \) oxidation schemes (6a,b). Part of the reason for the high \( \text{O}_2 \) 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):

\[
\begin{align*}
\text{O} + \text{O}_3 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad \text{(R19)} \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \quad \text{(R39)} \quad \text{(8)} \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \quad \text{(R44)} \\
\text{net} & \quad \text{2O} \rightarrow \text{O}_2
\end{align*}
\]

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 \( \text{ClO} + \text{NO} \) competes with \( \text{ClO} + \text{O} \) (Logan et al., 1978) and can turn the chlorine cycle into a null cycle,
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:

\[
\begin{align*}
H + O_2 + M & \rightarrow HO_2 + M \\ (R22) \\
\frac{1}{2}(HO_2 + NO) & \rightarrow OH + NO_2 \\ (R81) \\
\frac{1}{2}(NO_2 + h\nu) & \rightarrow NO + O \\ (R67) \\
\frac{1}{2}(O + HO_2) & \rightarrow OH + O_2 \\ (R31) \\
CO + OH & \rightarrow CO_2 + H \\ (R25)
\end{align*}
\]

net CO + $\frac{1}{2}$O$_2$ → CO$_2$

\[
\begin{align*}
H + O_2 + M & \rightarrow HO_2 + M \\ (R22) \\
HO_2 + NO & \rightarrow OH + NO_2 \\ (R81) \\
NO_2 + h\nu & \rightarrow NO + O \\ (R67) \\
CO + OH & \rightarrow CO_2 + H \\ (R25) \\
SO_2 + O + M & \rightarrow SO_3 + M \\ (R58) \\
SO_3 + H_2O + M & \rightarrow H_2SO_4 + M \\ (R65)
\end{align*}
\]

net CO + SO$_2$ + O$_2$ + H$_2$O → CO$_2$ + H$_2$SO$_4$

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:

\[
\begin{align*}
NO + O + M & \rightarrow NO_2 + M \\ (R77) \\
NO_2 + O & \rightarrow NO + O_2 \\ (R83a)
\end{align*}
\]

net 2O → O$_2$ (11)

Recently Clyne and MacRobert (1981) showed that the reaction

\[
\begin{align*}
\text{ClO} + \text{SO} & \rightarrow \text{Cl} + \text{SO}_2 \\ (R56)
\end{align*}
\]

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

\[
\begin{align*}
O + O_2 + M & \rightarrow O_3 + M \\ (R19) \\
\text{Cl} + O_3 & \rightarrow \text{ClO} + O_2 \\ (R39)
\end{align*}
\]

\[
\begin{align*}
\text{ClO} + \text{SO} & \rightarrow \text{Cl} + \text{SO}_2 \\ (R56) \\
\text{SO}_2 + h\nu & \rightarrow \text{SO} + O \\ (R9)
\end{align*}
\]

net nothing

There is also an analog of cycle (10b), again with SO playing the role of NO:
Since ClO and HO$_2$ are chemically alike, we shall argue that the reaction

$$\text{HO}_2 + \text{SO} \rightarrow \text{OH} + \text{SO}_2 \quad (R55)$$

is also fast. We propose two new catalytic schemes for oxidizing CO and SO$_2$:

$$\text{CO} + \text{SO}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2\text{SO}_4$$

### The Hydrogen Budget

Winick and Stewart (1980) fixed the mixing ratio of H$_2$ to be $2 \times 10^{-7}$, 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,

$$\text{HCl} + \text{hv} \rightarrow \text{H} + \text{Cl} \quad (R2)$$
The reaction
\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} \] (R38)
turns an active chlorine radical into a relatively inert form of chlorine. However, there are important reactions that can reverse this process:
\[ \text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}, \] (R16)
\[ \text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}, \] (R21)
\[ \text{OH} + \text{HCl} \rightarrow \text{H}_2\text{O} + \text{Cl}. \] (R27)
An equilibrium distribution of HO, and ClO, can be readily established, determined by the rates of cycling by (R21), (R27), and (R38).

It is clear that a high level of H2 favors HO, radicals. ClO, radicals become more abundant at low levels of H2. The cycling between HO, and ClO, is not, however, a completely reversible process. Since photolysis of H2O in the stratosphere is nearly completely shielded by CO2, reaction (R27) OH + HCl is almost an irreversible sink for hydrogen. This hydrogen must be ultimately derived from H2 or HCl [the loss of oxygen in (R27) is trivial compared with the CO2 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 H2. The Soviet work (Krasnopolsky and Parshev, 1980a,b, 1981) first raised the possibility that this hydrogen might not be supplied by H2 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 H2, (3) the role of NO, in stratospheric chemistry, (4) the chemistry of CICO, 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 O2. The major uncertainty is the abundance of H2. We examine three models. In model A we adopt a high mixing ratio of H2, \(2 \times 10^{-5}\), 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 H2 must be postulated, because thermochemistry cannot produce the required amount. We propose, in Appendix B, a speculative mechanism for production of H2 via sulfur chemistry. In model B, we adopt a low mixing ratio for H2, \(5 \times 10^{-7}\), 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 O2, such as schemes (10a,b) with 30 ppb NO,. A lightning source of NO, comparable to that in the terrestrial troposphere (Chameides et al., 1979; Borucki et al., 1981), could adequately account for this amount of NO, if the only sink for NO, on Venus were in the upper atmosphere. In model C we assume that the stratosphere does not derive any H2 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 O2. 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

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Net chemical reaction</th>
<th>Current status</th>
<th>Reference and remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>CO + O₂ → CO₂</td>
<td>Not important</td>
<td>Prinn (1971, 1972)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O–O bond broken by CIOO + O₂</td>
</tr>
<tr>
<td>(2)</td>
<td>CO + O → CO₂</td>
<td>Important</td>
<td>McElroy et al. (1973)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in models A, B</td>
<td>Catalyzed by HO₆</td>
</tr>
<tr>
<td>(3)</td>
<td>CO + O₂ → CO₂</td>
<td>Not important</td>
<td>McElroy et al. (1973)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O–O bond broken by H₂O₂ + hv</td>
</tr>
<tr>
<td>(4a,b)</td>
<td>CO + O → CO₂</td>
<td>Important</td>
<td>Krasnopolsky and Parshev (1981)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in model C</td>
<td>and this work</td>
</tr>
<tr>
<td>(4c)</td>
<td>CO + SO₂ + O₂ + H₂O →</td>
<td>Important</td>
<td>This work O–O bond broken by CICO + O₂</td>
</tr>
<tr>
<td></td>
<td>CO₂ + H₂SO₄</td>
<td>in model C</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>COS + 2 O₂ + H₂O →</td>
<td>COS status</td>
<td>Winick and Stewart (1980)</td>
</tr>
<tr>
<td></td>
<td>CO₂ + H₂SO₄</td>
<td>uncertain</td>
<td>O–O bond broken by S + O₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Catalyzed by HO₂</td>
</tr>
<tr>
<td>(6a,b)</td>
<td>SO₂ + O₂ + H₂O → H₂SO₄</td>
<td>Important</td>
<td>Winick and Stewart (1980)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O–O bond broken by S + O₂</td>
</tr>
<tr>
<td>(7a,b)</td>
<td>O₂ → 2 O</td>
<td>Important</td>
<td>Sze and McElroy (1974)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Catalyzed by CIO₆</td>
</tr>
<tr>
<td>(8)</td>
<td>2 O → O₂</td>
<td>Important</td>
<td>Logan et al. (1978),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO suppresses cycle (8)</td>
</tr>
<tr>
<td>(9a)</td>
<td>O → O (net nothing)</td>
<td>Important</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in model B</td>
<td></td>
</tr>
<tr>
<td>(9b)</td>
<td>O → O (net nothing)</td>
<td>Important</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(10a)</td>
<td>CO + O₂ → CO₂</td>
<td>Important</td>
<td>Watson et al. (1979),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in model B</td>
<td>this work</td>
</tr>
<tr>
<td>(10b)</td>
<td>CO + SO₂ + O₂ + H₂O →</td>
<td>Important</td>
<td>Watson et al. (1979),</td>
</tr>
<tr>
<td></td>
<td>CO₂ + H₂SO₄</td>
<td>in model B</td>
<td>this work, O–O bond</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>broken by NO + HO₆</td>
</tr>
<tr>
<td>(11)</td>
<td>2O → O₂</td>
<td>Important</td>
<td>This work, catalyzed by NO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in model B</td>
<td></td>
</tr>
<tr>
<td>(12a)</td>
<td>CO + O₂ → CO₂</td>
<td>Important</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in model A</td>
<td></td>
</tr>
<tr>
<td>(12b)</td>
<td>CO + SO₂ + O₂ + H₂O →</td>
<td>Important</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>CO₂ + H₂SO₄</td>
<td>in model A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O–O bond broken by SO + HO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>O–O bond broken by SO + HO₂</td>
</tr>
</tbody>
</table>

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 NOₓ and CICO, to be used in models B and C. Miscellaneous reactions, of more speculative nature, related to the chemistry of HSO₃ and the dimer (SO₂)₂ are discussed in Appendices A and B, respectively. Our set of reactions encompasses most of those considered in previous
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R1) CO₂ + hν → CO + O</td>
<td>( J₁ = 1.5 \times 10^{-12} )</td>
<td>Shemansky (1972)</td>
</tr>
<tr>
<td>(R2) HCl + hν → H + Cl</td>
<td>( J₂ = 1.0 \times 10^{-7} )</td>
<td>Watson (1977)</td>
</tr>
<tr>
<td>(R3) H₂O + hν → H + OH</td>
<td>( J₃ = 2.2 \times 10^{-11} )</td>
<td>Watanabe (1958)</td>
</tr>
<tr>
<td>(R4a) O₂ + hν → O + O(D)</td>
<td>( J₄ₐ = 0 )</td>
<td>Ackerman (1971)</td>
</tr>
<tr>
<td>(R4b) O₂ + hν → 2O</td>
<td>( J₄ₜ = 7.4 \times 10^{-10} )</td>
<td>Watanabe (1958)</td>
</tr>
<tr>
<td>(R5a) O₃ + hν → O₂(D) + O(D)</td>
<td>( J₅ₐ = 8.6 \times 10^{-3} )</td>
<td>Ackerman (1971)</td>
</tr>
<tr>
<td>(R5b) O₃ + hν → O₂ + O</td>
<td>( J₅ₜ = 4.2 \times 10^{-4} )</td>
<td>Hudson and Reed (1979)</td>
</tr>
<tr>
<td>(R6) H₂O₂ + hν → 2OH</td>
<td>( J₆ = 9.9 \times 10^{-4} )</td>
<td>Schügerl and Welge (1968), Hudson and Reed (1979)</td>
</tr>
<tr>
<td>(R7) ClO + hν → Cl + O</td>
<td>( J₇ = 5.0 \times 10^{-3} )</td>
<td>Watson (1977)</td>
</tr>
<tr>
<td>(R8) SO + hν → S + O</td>
<td>( J₈ = 2.7 \times 10^{-4} )</td>
<td>Phillips (1981)</td>
</tr>
<tr>
<td>(R9) SO₂ + hν → SO + O</td>
<td>( J₉ = 1.5 \times 10^{-4} )</td>
<td>Warneck et al. (1964), Bhatki et al. (1982)</td>
</tr>
</tbody>
</table>

(continued)
### TABLE IIIa—Continued

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R31) HO₂ + O → OH + O₂</td>
<td>k₃₁ = 3.1 × 10⁻¹¹</td>
<td>c</td>
</tr>
<tr>
<td>(R32) HO₂ + O → OH + 2O₂</td>
<td>k₃₃₂ = 1.4 × 10⁻¹ⁱ e⁻⁴⁰⁰/T</td>
<td>c</td>
</tr>
<tr>
<td>(R33a) HO₂ + H → 2OH</td>
<td>k₃₀₆ = 3.2 × 10⁻¹¹</td>
<td>c</td>
</tr>
<tr>
<td>(R33b) HO₂ + H → H₂ + O₂</td>
<td>k₃₃₈ = 1.4 × 10⁻¹¹</td>
<td>c</td>
</tr>
<tr>
<td>(R33c) HO₂ + H → H₂O + O</td>
<td>k₃₃₆ = 9.4 × 10⁻¹₁</td>
<td>c</td>
</tr>
<tr>
<td>(R34) HO₂ + OH → H₂O₂ + O₂</td>
<td>k₃₄₆ = 8.0 × 10⁻¹²</td>
<td>d, updated</td>
</tr>
<tr>
<td>(R35) 2HO₂ → H₂O₂ + O₂</td>
<td>k₃₅₄ = 2.3 × 10⁻¹²</td>
<td>c</td>
</tr>
<tr>
<td>(R36) H₂O₂ + O → OH + H₂O₂</td>
<td>k₃₅₄ = 2.8 × 10⁻¹² e⁻⁴²³/T</td>
<td>d</td>
</tr>
<tr>
<td>(R37) H₂O₂ + OH → H₂O + HO₂</td>
<td>k₃₇₆ = 7.6 × 10⁻¹² e⁻⁶⁰⁰/T</td>
<td>c</td>
</tr>
<tr>
<td>(R38) Cl + H₂ → HCl + H</td>
<td>k₃₈₉ = 4.7 × 10⁻¹¹ e⁻²⁵⁴/T</td>
<td>c</td>
</tr>
<tr>
<td>(R39) Cl + O₁ → ClO + O₂</td>
<td>k₃₉₉ = 2.7 × 10⁻¹¹ e⁻⁵⁷⁰/T</td>
<td>c</td>
</tr>
<tr>
<td>(R40) Cl + OH → HCl + O</td>
<td>k₄₀₉ = 1.0 × 10⁻¹¹ e⁻³⁹⁰/T</td>
<td>n</td>
</tr>
<tr>
<td>(R41a) Cl + H₂O₂ → HCl + O₂</td>
<td>k₄₁₉₆ = 1.8 × 10⁻¹¹ e⁻¹⁰⁰/T</td>
<td></td>
</tr>
<tr>
<td>(R41b) Cl + HO₂ → ClO + OH</td>
<td>k₄₁₉₈ = 2.2 × 10⁻¹² e⁻¹⁰⁰/T</td>
<td></td>
</tr>
<tr>
<td>(R42) Cl + H₂O₂ → HCl + HO₂</td>
<td>k₄₂₉₆ = 1.1 × 10⁻¹¹ e⁻⁸⁰₀/T</td>
<td>c</td>
</tr>
<tr>
<td>(R43) ClO + CO → Cl + CO₂</td>
<td>k₄₃₉ = 1.0 × 10⁻¹² e⁻³⁵⁰/T</td>
<td>b</td>
</tr>
<tr>
<td>(R44) ClO + O → Cl + O₂</td>
<td>k₄₄₉ = 7.5 × 10⁻¹¹ e⁻¹²⁰/T</td>
<td>c</td>
</tr>
<tr>
<td>(R45) ClO + OH → Cl + HO₂</td>
<td>k₄₅₉ = 9.1 × 10⁻¹²</td>
<td>d</td>
</tr>
<tr>
<td>(R46) S + O₂ → SO + O</td>
<td>k₄₆₉ = 2.2 × 10⁻¹²</td>
<td>c</td>
</tr>
<tr>
<td>(R47) S + CO₂ → SO₂ + CO</td>
<td>k₄₇₉ = 1.0 × 10⁻¹⁰</td>
<td>u</td>
</tr>
<tr>
<td>(R48) S + O₂ → SO + O₂</td>
<td>k₄₈₉ = 1.2 × 10⁻¹¹</td>
<td>c</td>
</tr>
<tr>
<td>(R49) S + OH → SO + H</td>
<td>k₄₉₉ = k₃₈₉ = 3.8 × 10⁻¹¹</td>
<td>g</td>
</tr>
<tr>
<td>(R50) S + HO₂ → SO₂ + OH</td>
<td>k₅₀₉ = k₃₈₉ = 3.1 × 10⁻¹¹</td>
<td>g</td>
</tr>
<tr>
<td>(R51) SO + O + M → SO₂ + M</td>
<td>k₅₁₉ = 6.0 × 10⁻¹⁰</td>
<td>a,b,g</td>
</tr>
<tr>
<td>(R52) SO + O₂ → SO₂ + O</td>
<td>k₅₂₉ = 6.0 × 10⁻¹² e⁻³₃⁰₀/T</td>
<td>c</td>
</tr>
<tr>
<td>(R53) SO + O₁ → SO₂ + O₂</td>
<td>k₅₃₉ = 2.5 × 10⁻¹² e⁻¹₁₀⁰/T</td>
<td>c</td>
</tr>
<tr>
<td>(R54) SO + OH → SO₂ + H</td>
<td>k₅₄₉ = 1.2 × 10⁻¹⁰</td>
<td>c</td>
</tr>
<tr>
<td>(R55) SO + HO₂ → SO₂ + OH</td>
<td>k₅₅₉ = k₃₈₉ = 2.3 × 10⁻¹¹</td>
<td>g</td>
</tr>
<tr>
<td>(R56) SO + ClO + SO₂ + Cl</td>
<td>k₅₆₉ = 2.3 × 10⁻¹¹</td>
<td>c</td>
</tr>
<tr>
<td>(R57) 2SO → SO₂ + S</td>
<td>k₅₇₉ = 8.3 × 10⁻¹⁵</td>
<td>Herron and Huie (1980)</td>
</tr>
<tr>
<td>(R58) SO₂ + O + M → SO₃ + M</td>
<td>k₅₈₉ = 8.0 × 10⁻³² e⁻¹₀⁰₀/T</td>
<td>c,e</td>
</tr>
<tr>
<td>(R59) SO₂ + OH + M → HSO₃ + M</td>
<td>k₅₉₉ = k₃₈₉ = 4.2 × 10⁻³⁻² e⁻¹₀⁰₀/T</td>
<td>Harris et al. (1980)</td>
</tr>
<tr>
<td>(R60) SO₂ + HO₂ → SO₃ + OH</td>
<td>k₆₀₉ = 1.0 × 10⁻¹⁸</td>
<td>Sander and Watson (1981)</td>
</tr>
<tr>
<td>(R61) SO₂ + H₂O₂ + aerosol → J₆₁ = 4.3 × 10⁻⁵</td>
<td>See text</td>
<td></td>
</tr>
<tr>
<td>(R62) SO₂ + Cl + M → ClSO₂ + M</td>
<td>k₆₂₉ = 4.6 × 10⁻³⁻³</td>
<td>Strattan et al. (1979)</td>
</tr>
<tr>
<td>(R63) SO₂ + ClO → SO₃ + Cl</td>
<td>k₆₃₉ = k₆₄₉ = 1.0 × 10⁻¹⁸</td>
<td>n</td>
</tr>
<tr>
<td>(R64) SO₃ + SO₂ → 2SO₂</td>
<td>k₆₄₉ = 2.0 × 10⁻¹⁵</td>
<td>b</td>
</tr>
<tr>
<td>(R65) SO₃ + H₂O → H₂SO₄</td>
<td>k₆₅₉ = 9 × 10⁻¹³</td>
<td>c</td>
</tr>
</tbody>
</table>

**Note.** The units for mean photolysis rates (J), and two-body and three-body reactions (k) are sec⁻¹, cm⁶ sec⁻¹, and cm⁶ 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, A1, and B1.

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 = N₂, multiplied by 2.
f Calculated as the backward reaction of (R38); should be more accurate than that quoted in n.
g Estimated by present authors.
h⁻¹ = k₉⁻¹ + (k₉/M)⁻¹.
TABLE IIIb
LIST OF REACTIONS RELATED TO MISCELLANEOUS COMPOUNDS OF ODD NITROGEN (FOOTNOTES REFER TO TABLE IIIa)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R66) NO + hν → N + O</td>
<td>$J_{66}^*$</td>
<td>Yung and McElroy (1979)</td>
</tr>
<tr>
<td>(R67) NO$_2$ + hν → NO + O</td>
<td>$J_{67} = 1 \times 10^{-2}$</td>
<td>Yung et al. (1980)</td>
</tr>
<tr>
<td>(R68a) NO$_3$ + hν → NO$_2$ + O</td>
<td>$J_{68a} = 2 \times 10^{-2}$</td>
<td>Yung et al. (1980)</td>
</tr>
<tr>
<td>(R68b) NO$_3$ + hν → NO + O$_2$</td>
<td>$J_{68b} = 1 \times 10^{-2}$</td>
<td>Yung et al. (1980)</td>
</tr>
<tr>
<td>(R69) HNO + hν → H + NO</td>
<td>$J_{69} = 1 \times 10^{-3}$</td>
<td>Yung et al. (1980)</td>
</tr>
<tr>
<td>(R70) HNO$_2$ + hν → OH + NO</td>
<td>$J_{70} = 2 \times 10^{-3}$</td>
<td>Yung and McElroy (1979)</td>
</tr>
<tr>
<td>(R71) HNO$_3$ + hν → OH + NO$_2$</td>
<td>$J_{71} = 5.4 \times 10^{-5}$</td>
<td>Yung et al. (1980)</td>
</tr>
<tr>
<td>(R72a) N + O → NO + hν</td>
<td>$k_{72a} = 2.5 \times 10^{17}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R72b) N + O + M → NO + M</td>
<td>$k_{72b} = 1.9 \times 10^{-31}T^{-1/2}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R73) N + O$_2$ → NO + O</td>
<td>$k_{73} = 4.4 \times 10^{-12}e^{-3270/T}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R74) N + O$_2$ → NO + O$_2$</td>
<td>$k_{74} = 1 \times 10^{-15}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R75) N + OH → NO + H</td>
<td>$k_{75} = 5.3 \times 10^{-11}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R76) N + NO → N$_2$ + O</td>
<td>$k_{76} = 2.1 \times 10^{-11}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R77) NO + O + M → NO$_2$ + M</td>
<td>$k_{77} = 2.4 \times 10^{-31}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R78) NO + O$_2$ → NO$_2$ + O$_2$</td>
<td>$k_{78} = 2.3 \times 10^{-12}e^{-1450/T}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R79) NO + H + M → HNO + M</td>
<td>$k_{79} = 1.5 \times 10^{-25}e^{-300/T}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R80) NO + OH + M → HNO$_2$ + M</td>
<td>$k_{80} = 1.3 \times 10^{-26}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R81) NO + HO$_2$ → NO$_2$ + OH</td>
<td>$k_{81} = 3.5 \times 10^{-12}e^{-250/T}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R82) NO + ClO → NO$_2$ + Cl</td>
<td>$k_{82} = 6.5 \times 10^{-12}e^{-350/T}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R83a) NO$_2$ + O → NO + O$_2$</td>
<td>$k_{83a} = 9.3 \times 10^{-12}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R83b) NO$_2$ + O + M → NO$_2$ + M</td>
<td>$k_{83b} = 1.8 \times 10^{-31}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R84) NO$_2$ + OH + M → HNO$_2$ + M</td>
<td>$k_{84} = 5.2 \times 10^{-30}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R85) NO$_2$ + SO → NO + SO$_2$</td>
<td>$k_{85} = 1.4 \times 10^{-11}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R86) HNO + O → OH + NO</td>
<td>$k_{86} = k_{87} = 1 \times 10^{-13}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R87) HNO + H → H$_2$ + NO</td>
<td>$k_{87} = 1 \times 10^{-13}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R88) HNO + Cl → HCl + NO</td>
<td>$k_{88} = k_{87} = 1 \times 10^{-13}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R89) 2HNO → N$_2$O + H$_2$O</td>
<td>$k_{89} = 4 \times 10^{-13}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R90) HNO$_2$ + OH → H$_2$O + NO$_2$</td>
<td>$k_{90} = 6.6 \times 10^{-12}$</td>
<td>Stewart et al. (1980)</td>
</tr>
<tr>
<td>(R91) HNO$_3$ + OH → H$_2$O + NO$_3$</td>
<td>$k_{91} = 1.5 \times 10^{-14}$</td>
<td>Stewart et al. (1980)</td>
</tr>
</tbody>
</table>

* The mean dissociation rate for NO due to δ band absorption is given by $J_{66}(z) = 1.7 \times 10^{-6} \exp(-1.5\sigma_1N) + 1.2 \times 10^{-6} \exp(-1.5\sigma_2N)$, where $\sigma_1 = 2.8 \times 10^{-23}$ cm$^2$, $\sigma_2 = 5.6 \times 10^{-22}$ cm$^2$, and $N = \int dz \{CO_2\}$. 

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,

\[ 2O + M \rightarrow O_2 + M, \quad (R17) \]
\[ H + O_2 + M \rightarrow HO_2 + M, \quad (R22) \]
\[ H + H + M \rightarrow H_2 + M, \quad (R24) \]
\[ SO_2 + O + M \rightarrow SO_3 + M \quad (R58) \]

...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).
have for the most part not been measured for \( M = \text{CO}_2 \). We have taken the rate coefficients to be twice the corresponding values for \( M = \text{N}_2 \), to account for the greater efficiency of \( \text{CO}_2 \) as a third body.

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

\[
\text{SO} + h\nu \rightarrow \text{S} + \text{O}, \quad (R8)
\]

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 \( \text{O}_2 \) and \( \text{SO} \) 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

\[
2 \text{SO} \rightarrow \text{SO}_2 + \text{S} \quad (R57)
\]

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), \( \text{S} + \text{O}_2 \), which is the major sink for \( \text{S} \).
in our models (Table III). The reaction
\[ S + CO_2 \rightarrow CO + SO \] (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 \( 1 \times 10^{-20} \, \text{cm}^3 \, \text{sec}^{-1} \) is not ruled out, and (R47) could be marginally important.

Clyne and MacRobert (1981) reported a fast rate coefficient for
\[ SO + \text{ClO} \rightarrow SO_2 + \text{Cl}, \] (R56)
\[ k_{56} = 2.3 \times 10^{-11} \, \text{cm}^3 \, \text{sec}^{-1} \]. Since the bond strengths for Cl–O and HO–O are both equal to 64 kcal/mole, reactions of HO₂ frequently are similar in rate to analogous reactions involving ClO, as illustrated by the pair of reactions
\[ \text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl}, \]
\[ k_{82} = 1.8 \times 10^{-11} \, \text{cm}^3 \, \text{sec}^{-1} \],
\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}, \]
\[ k_{81} = 8.4 \times 10^{-12} \, \text{cm}^3 \, \text{sec}^{-1} \],
and the pair
\[ \text{O} + \text{ClO} \rightarrow \text{O}_2 + \text{Cl}, \]
\[ k_{44} = 5.0 \times 10^{-11} \, \text{cm}^3 \, \text{sec}^{-1} \],
\[ \text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH}, \]
\[ k_{31} = 3.1 \times 10^{-11} \, \text{cm}^3 \, \text{sec}^{-1} \]
(the rate coefficients have been evaluated at room temperature). We argue that the reaction
\[ SO + \text{HO}_2 \rightarrow SO_2 + \text{OH} \] (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
\[ SO + \text{HO}_2 \rightarrow \text{HSO} + \text{O}_2 \]
is probably slow, and is most probably followed by
\[ \text{O} + \text{HSO} \rightarrow \text{OH} + \text{SO}. \]
This would result in recycling HOₓ 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, \( k_{55} = 1 \times 10^{-14} \, \text{cm}^3 \, \text{sec}^{-1} \).

The efficiency of the catalytic scheme for oxidation of SO₂,
\[ SO_2 + \text{HO}_2 \rightarrow \text{SO}_3 + \text{OH}, \] (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 \( k_{60} < 10^{-18} \, \text{cm}^3 \, \text{sec}^{-1} \), which is orders of magnitude slower than that preferred by the previous authors.

SO₂ may provide a loss of HOₓ, as is assumed in the Winick–Stewart model
\[ SO_2 + \text{OH} + M \rightarrow \text{HSO}_3 + M, \] (R59)
but not in Prinn (1973, 1975). There can be additional sinks for HOₓ and ClOₓ radicals in the lower stratosphere. McElroy (1973) private communication and Sze and Smyth (1979) suggested that
\[ \text{SO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \, \text{(heterogeneous)} \] (R61)
could oxidize SO₂ and destroy HOₓ. Stratton et al. (1979) suggested that
\[ \text{Cl} + \text{SO}_2 + M \rightarrow \text{ClSO}_2 + M \] (R62)
could be a sink for ClOₓ. 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 HOₓ 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 $J = \frac{4}{3} \gamma v A N_a$, where $N_a$ = number density of aerosols (cm$^{-3}$), $A$ = mean surface area of aerosol (cm$^2$), $v$ = thermal velocity of gas molecules, and $\gamma$ = 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): $\gamma_{H_2O_2} = 1.6 \times 10^{-3}$, $\gamma_{\text{radicals}} \sim \gamma_{OH} = 1 \times 10^{-4}$. 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$_2$ or ClO$_2$. 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$_2$ radical tied by HSO$_3$ are

$$\text{HSO}_3 + \text{O} \rightarrow \text{OH} + \text{SO}_3, \quad (R116)$$
$$\text{HSO}_3 \cdot \text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{H}_2\text{SO}_4. \quad (R122)$$

The rate coefficient for this type of hydrogen abstraction reaction correlates with exothermicity, and on this basis we estimate a value of $1 \times 10^{-11}$ 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 $K_{eq} = k_{99}/k_{97}$ 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 CICO. Krasnopolsky and Parshev (1980a, b, 1981) and the present authors have considered the possible role of CICO in cycles (4). We will briefly discuss the chemistry of CICO, which is formed by the reaction

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

The rate constant has been measured by Clark et al. (1966), who obtained $k_{99} = 8.7 \times 10^{-34}$ for $M = \text{Ar}$ at 300 K, with an apparent activation energy of $-2$ kcal. Our value for $k_{99}$ with $M = \text{CO}_2$ is based on their data, with a factor of 4 increase in rate constant to allow for the higher third-body efficiency of CO$_2$. CICO is readily destroyed by thermal decomposition,

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

The equilibrium constant $k_{99}/k_{100}$ has been measured by Burns and Dainton (1952) by a somewhat indirect method. Reaction of CICO with O$_2$ was considered in early work (for review, see Heicklen, 1969) to be a direct four-center reaction

$$\text{CICO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{ClO}. \quad (R101)$$

Krasnopolsky and Parshev (1980a) accepted this mechanism and assumed $k_{99} = 3 \times 10^{-52}$ cm$^6$ sec$^{-1}$, $k_{100} = 1 \times 10^{-12} e^{-3200/\ell}$ cm$^6$ 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 CICO 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 CICO by O$_2$ occurs as a three-body process, involving an intermediate complex, the peroxychloroformyl radical,

$$\text{CICO} + \text{O}_2 + M \rightarrow \text{CICO}_3 + M. \quad (R101)$$

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

$$k_{101} = \frac{5.7 \times 10^{-15} e^{500/\ell}}{1 \times 10^{37} + 0.05 M} \text{ cm}^3 \text{ sec}^{-1},$$

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 $3.0 \times 10^{-31}$ cm$^6$ sec$^{-1}$, and should be compared with the rate coefficients for the following reactions of similar complexity under similar conditions:

\[ \text{CH}_3 + \text{O}_2 + M \rightarrow \text{CH}_3\text{O}_2 + M, \quad k = 2.2 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}, \]

\[ \text{C}_2\text{H}_5 + \text{O}_2 + M \rightarrow \text{C}_2\text{H}_5\text{O}_2 + M, \quad k = 7.5 \times 10^{-29} \text{ cm}^6 \text{ sec}^{-1} \]

(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):

\[
\text{Cl}-\text{C}=\overset{0}{}\text{O}
\]

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

\[ \text{ClC(O)O}_2 + \text{O} \rightarrow \text{ClC(O)O} + \text{O}_2. \]

The oxychloroformyl radical is unstable and decays by

\[ \text{ClC(O)O} \rightarrow \text{Cl} + \text{CO}_2. \]

The net result of these two reactions can be summarized by

\[ \text{ClC}_3 + \text{O} \rightarrow \text{Cl} + \text{CO}_2 + \text{O}_2. \] (R110)

There are obviously similar reactions with Cl and H,

\[ \text{ClC}_3 + \text{Cl} \rightarrow \text{Cl} + \text{CO}_2 + \text{ClO}, \] (R111)

\[ \text{ClC}_3 + \text{H} \rightarrow \text{Cl} + \text{CO}_2 + \text{OH}. \] (R112)

No experimental data are available for these reactions, and we estimate a rate coefficient for $1 \times 10^{-11}$ 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:

\[ \text{ClC}_3 + \text{NO} \rightarrow \text{Cl} + \text{CO}_2 + \text{NO}_2, \]

\[ 2\text{ClC}_3 \rightarrow 2\text{Cl} + 2\text{CO}_2 + \text{O}_2. \]

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

\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}, \] (R76)

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

\[ \text{NO} + \text{hv} \rightarrow \text{N} + \text{O}. \] (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,

\[ \text{H} + \text{NO} + M \rightarrow \text{HNO} + M, \] (R79)

\[ 2\text{HNO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}, \] (R89)

\[ \text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O}(^1\text{D}), \]

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$_2$O 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,

\[ \text{HNO} + \text{hv} \rightarrow \text{H} + \text{NO}, \] (R69)

since the appropriate cross sections have not been measured. The H–NO bond en-
ergy is 49 kcal/mole. For comparison the bond energies for HCO–H and H–CO are 88 and 18 kcal/mole, respectively. On the basis of this tenuous comparison we guess a photolysis rate of $1 \times 10^{-3}$ sec$^{-1}$, a value bracketed by $J_{HCO} = 10^{-4}$ sec$^{-1}$ and $J_{HCO} = 10^{-2}$ sec$^{-1}$ (Pinto et al., 1980).

3. MODEL ASSUMPTIONS AND APPROACH

The model atmosphere is taken from Winick and Stewart (1980). Our model extends from 58 to 110 km. The concentration of H$_2$O is fixed at a constant mixing ratio of $1 \times 10^{-6}$ (see Table I). The mixing ratio of H$_2$ equals $2 \times 10^{-5}$ and $5 \times 10^{-7}$ in models A and B, respectively. Only photochemically produced H$_2$ is considered in model C. The one-dimensional continuity equations are rigorously solved for all major species, with appropriate boundary conditions listed in Table VI. It is not necessary to group the species into families. We use a finite difference iterative algorithm with 2-km resolution (Logan et al., 1978; Allen et al., 1981), except at the boundaries, where the resolution is 0.4 km. The convergence criterion is the requirement that successive iterations yield solutions differing by less than one part in $10^4$.

The solar flux between Lyman-$\alpha$ and 4000 Å is taken from Ackerman (1971) and Mount et al. (1980) and averaged over appropriate 50-Å intervals. In the spectral region where the two sets of data overlap, the Mount et al. (1980) data are preferred. The dissociation cross sections for CO$_2$ are taken from Shemansky (1972), with temperature dependence correction based on DeMore and Patapoff (1972),

$$\frac{\sigma(\lambda, T)}{\sigma(\lambda, 298)} = \left\{1 - \frac{P(\lambda)}{100}\right\}^{298-T},$$

where

$P(\lambda) = 0.5 + 5 \times 10^{-3}(\lambda - 1740 \text{ Å}),$

1640 Å < $\lambda$ < 1900 Å,

$P(\lambda) = P(1900 \text{ Å}),$

1900 Å < $\lambda$ < 2040 Å.

The expression is taken from Allen et al. (1981). We choose to apply a uniform temperature correction at 250°K. Beyond 1900 Å, there are actually no laboratory data. Rather than extrapolating $P(\lambda)$ to alarming values, we set all the correction factors beyond 1900 Å to equal that at 1900 Å. The additional dissociation of O$_3$ at Chappuis bands is taken into account by adding a mean dissociation rate $3.3 \times 10^{-4}$ sec$^{-1}$ to $J_{3b}$ at all altitudes. The absorption cross sections of SO$_2$ have not been measured at temperatures appropriate to the stratosphere of Venus. We recently undertook these measurements at JPL (Bhatki et al., 1982). At 250°K, the cross sections in the spectral region of interest are about 15% lower than those at room temperature. In this work we adopt the JPL cross sections measured at 250°K. For dissociation cross sections we use quantum yields estimated from the fluorescence spectrum given by Okabe (1971). Since the cross sections for SO$_2$ and SO near 2000 Å are highly structured, we subdivide the region 1800–2320 Å into 10-Å intervals. The average solar flux and cross sections for CO$_2$, SO$_2$, HCI, and SO over this fine grid are given in Table IV. The mean dissociation rates $J_i$(sec$^{-1}$) for these species are calculated by the formula

$$J_i(z) = \frac{1}{2} \sum_{\lambda} \pi F_{\lambda} \sigma_{i\lambda} e^{-\tau_{\lambda}(z)\mu},$$

where

$\pi F = \text{incident normal solar flux at Venus},$

$\tau_{\lambda}(z) = \text{optical depth} = \sum_{\lambda} \sigma_{i\lambda} \int_{z}^{\infty} dz N_{\lambda}(z),$

$\mu = \text{average cosine of solar zenith angle},$

and the other symbols have their usual meanings. To simulate midlatitude insolation, we set $\mu = \frac{2}{3}$. In the lower stratosphere between 58 and 70 km, the solar radiation field is further attenuated by absorption by aerosols. This is roughly taken into account by reducing the incident solar flux by a transmission factor,
\[ T(z) = e^{-(70-z)/H}, \quad 58 \text{ km} \leq z \leq 70 \text{ km}, \]
\[ T(z) = 1, \quad z \geq 70 \text{ km}, \]

where \( H = 8 \text{ km} \). 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 \( 1 \times 10^{-6} \). 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 \( K = 4 \times 10^4 \text{ cm}^2 \text{ sec}^{-1} \) at the tropopause from Pioneer Venus radio scintillation measurements.

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 \( 2 \times 10^{-5} \), 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 \( 5 \times 10^{-7} \). 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**

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>$\pi F$</th>
<th>$\sigma$(CO$_2$)</th>
<th>$\sigma_d$(SO$_2$)</th>
<th>$\sigma$(SO$_2$)</th>
<th>$\sigma$(HCl)</th>
<th>$\sigma$(SO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1216</td>
<td>5.01(11)</td>
<td>7.3(-20)</td>
<td>3.7(-17)</td>
<td>2.0(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1250</td>
<td>1.72(10)</td>
<td>2.5(-19)</td>
<td>7.4(-17)</td>
<td>1.9(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1300</td>
<td>2.57(10)</td>
<td>6.7(-19)</td>
<td>1.9(-17)</td>
<td>1.7(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1350</td>
<td>4.04(10)</td>
<td>7.8(-19)</td>
<td>3.7(-18)</td>
<td>1.5(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>3.88(10)</td>
<td>6.1(-19)</td>
<td>3.7(-18)</td>
<td>1.4(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1450</td>
<td>4.29(10)</td>
<td>5.9(-19)</td>
<td>4.5(-18)</td>
<td>2.5(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>6.76(10)</td>
<td>5.4(-19)</td>
<td>5.2(-18)</td>
<td>3.4(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1550</td>
<td>1.33(11)</td>
<td>3.6(-19)</td>
<td>3.2(-18)</td>
<td>3.4(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>1.26(11)</td>
<td>1.8(-19)</td>
<td>1.3(-18)</td>
<td>2.7(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1650</td>
<td>2.37(11)</td>
<td>7.3(-20)</td>
<td>4.3(-19)</td>
<td>2.1(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>3.92(11)</td>
<td>1.8(-20)</td>
<td>4.5(-19)</td>
<td>1.4(-18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1750</td>
<td>5.89(11)</td>
<td>4.8(-21)</td>
<td>1.1(-18)</td>
<td>8.1(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1800</td>
<td>1.62(11)</td>
<td>1.0(-21)</td>
<td>2.6(-18)</td>
<td>5.9(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1850</td>
<td>1.93(11)</td>
<td>1.7(-22)</td>
<td>3.6(-18)</td>
<td>3.1(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1900</td>
<td>2.21(11)</td>
<td>1.3(-22)</td>
<td>3.9(-18)</td>
<td>2.8(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1950</td>
<td>2.57(11)</td>
<td>1.0(-22)</td>
<td>3.9(-18)</td>
<td>2.4(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>2.84(11)</td>
<td>7.4(-23)</td>
<td>3.8(-18)</td>
<td>2.0(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2050</td>
<td>3.11(11)</td>
<td>5.6(-23)</td>
<td>4.5(-18)</td>
<td>1.7(-19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2100</td>
<td>3.36(11)</td>
<td>4.3(-23)</td>
<td>5.0(-18)</td>
<td>1.5(-19)</td>
<td>9.9(-18)</td>
<td></td>
</tr>
<tr>
<td>2150</td>
<td>3.64(11)</td>
<td>2.8(-23)</td>
<td>5.5(-18)</td>
<td>1.2(-19)</td>
<td>1.2(-17)</td>
<td></td>
</tr>
<tr>
<td>2200</td>
<td>4.01(11)</td>
<td>1.8(-23)</td>
<td>5.1(-18)</td>
<td>1.1(-19)</td>
<td>1.1(-17)</td>
<td></td>
</tr>
<tr>
<td>2250</td>
<td>3.73(11)</td>
<td>1.4(-23)</td>
<td>6.0(-18)</td>
<td>7.8(-20)</td>
<td>1.1(-17)</td>
<td></td>
</tr>
<tr>
<td>2300</td>
<td>4.08(11)</td>
<td>1.2(-23)</td>
<td>6.0(-18)</td>
<td>6.5(-20)</td>
<td>1.2(-17)</td>
<td></td>
</tr>
<tr>
<td>2350</td>
<td>5.05(11)</td>
<td>1.0(-23)</td>
<td>5.3(-18)</td>
<td>6.2(-20)</td>
<td>1.3(-17)</td>
<td></td>
</tr>
<tr>
<td>2400</td>
<td>5.44(11)</td>
<td>5.4(-24)</td>
<td>6.5(-18)</td>
<td>5.4(-20)</td>
<td>1.4(-17)</td>
<td></td>
</tr>
<tr>
<td>2450</td>
<td>5.88(11)</td>
<td>3.3(-24)</td>
<td>6.3(-18)</td>
<td>4.5(-20)</td>
<td>1.5(-17)</td>
<td></td>
</tr>
<tr>
<td>2500</td>
<td>6.10(11)</td>
<td>2.3(-24)</td>
<td>5.1(-18)</td>
<td>3.8(-20)</td>
<td>1.5(-17)</td>
<td></td>
</tr>
<tr>
<td>2550</td>
<td>6.31(11)</td>
<td>1.7(-24)</td>
<td>6.7(-18)</td>
<td>3.2(-20)</td>
<td>1.4(-17)</td>
<td></td>
</tr>
<tr>
<td>2600</td>
<td>6.89(11)</td>
<td>1.3(-24)</td>
<td>6.1(-18)</td>
<td>2.6(-20)</td>
<td>1.6(-17)</td>
<td></td>
</tr>
<tr>
<td>2650</td>
<td>7.58(11)</td>
<td>9.0(-25)</td>
<td>4.9(-18)</td>
<td>2.2(-20)</td>
<td>9.6(-18)</td>
<td></td>
</tr>
<tr>
<td>2700</td>
<td>8.10(11)</td>
<td>6.0(-25)</td>
<td>6.8(-18)</td>
<td>1.8(-20)</td>
<td>1.6(-17)</td>
<td></td>
</tr>
<tr>
<td>2750</td>
<td>8.85(11)</td>
<td>4.8(-25)</td>
<td>5.7(-18)</td>
<td>1.5(-20)</td>
<td>8.6(-18)</td>
<td></td>
</tr>
<tr>
<td>2800</td>
<td>9.97(11)</td>
<td>4.3(-25)</td>
<td>4.6(-18)</td>
<td>1.3(-20)</td>
<td>1.7(-17)</td>
<td></td>
</tr>
<tr>
<td>2850</td>
<td>1.09(12)</td>
<td>—</td>
<td>5.9(-18)</td>
<td>9.8(-21)</td>
<td>8.1(-18)</td>
<td></td>
</tr>
<tr>
<td>2900</td>
<td>1.14(12)</td>
<td>—</td>
<td>4.3(-18)</td>
<td>8.6(-21)</td>
<td>1.4(-17)</td>
<td></td>
</tr>
<tr>
<td>2950</td>
<td>1.25(12)</td>
<td>—</td>
<td>5.9(-18)</td>
<td>7.2(-21)</td>
<td>4.6(-18)</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>1.43(12)</td>
<td>—</td>
<td>4.3(-18)</td>
<td>6.0(-21)</td>
<td>1.4(-17)</td>
<td></td>
</tr>
<tr>
<td>3050</td>
<td>1.82(12)</td>
<td>—</td>
<td>3.2(-18)</td>
<td>5.0(-21)</td>
<td>4.3(-18)</td>
<td></td>
</tr>
<tr>
<td>3100</td>
<td>2.52(12)</td>
<td>—</td>
<td>4.3(-18)</td>
<td>4.0(-21)</td>
<td>1.4(-17)</td>
<td></td>
</tr>
<tr>
<td>3150</td>
<td>3.12(12)</td>
<td>—</td>
<td>2.7(-18)</td>
<td>2.6(-18)</td>
<td>3.3(-21)</td>
<td>4.3(-18)</td>
</tr>
<tr>
<td>3200</td>
<td>3.45(12)</td>
<td>—</td>
<td>3.7(-18)</td>
<td>3.5(-18)</td>
<td>2.7(-21)</td>
<td>9.5(-18)</td>
</tr>
<tr>
<td>3250</td>
<td>3.51(12)</td>
<td>—</td>
<td>2.4(-18)</td>
<td>2.2(-18)</td>
<td>2.1(-21)</td>
<td>5.5(-18)</td>
</tr>
<tr>
<td>3300</td>
<td>3.90(12)</td>
<td>—</td>
<td>2.4(-18)</td>
<td>2.0(-18)</td>
<td>1.8(-21)</td>
<td>3.0(-18)</td>
</tr>
<tr>
<td>3350</td>
<td>4.28(12)</td>
<td>—</td>
<td>2.4(-18)</td>
<td>1.9(-18)</td>
<td>1.4(-21)</td>
<td>9.5(-18)</td>
</tr>
<tr>
<td>3400</td>
<td>3.92(12)</td>
<td>—</td>
<td>1.2(-18)</td>
<td>9.4(-19)</td>
<td>1.1(-21)</td>
<td>2.4(-18)</td>
</tr>
<tr>
<td>3450</td>
<td>3.64(12)</td>
<td>—</td>
<td>1.9(-18)</td>
<td>1.4(-18)</td>
<td>9.0(-22)</td>
<td>5.6(-18)</td>
</tr>
<tr>
<td>3500</td>
<td>4.42(12)</td>
<td>—</td>
<td>8.7(-19)</td>
<td>6.4(-19)</td>
<td>7.0(-22)</td>
<td>4.0(-18)</td>
</tr>
<tr>
<td>3550</td>
<td>5.31(12)</td>
<td>—</td>
<td>1.3(-18)</td>
<td>8.8(-19)</td>
<td>6.0(-22)</td>
<td>1.5(-18)</td>
</tr>
<tr>
<td>3600</td>
<td>5.63(12)</td>
<td>—</td>
<td>8.3(-19)</td>
<td>—</td>
<td>4.8(-22)</td>
<td>4.4(-18)</td>
</tr>
</tbody>
</table>
TABLE IV—Continued

<table>
<thead>
<tr>
<th>λ</th>
<th>$\pi F$</th>
<th>$\sigma(\text{CO}_2)$</th>
<th>$\sigma(\text{SO}_2)\sigma(\text{SO}_2)$</th>
<th>$\sigma(\text{HCl})$</th>
<th>$\sigma(\text{SO})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2210</td>
<td>5.05(12)</td>
<td>—</td>
<td>9.1(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2220</td>
<td>5.14(12)</td>
<td>—</td>
<td>5.3(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2230</td>
<td>6.89(12)</td>
<td>—</td>
<td>3.6(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2240</td>
<td>7.43(12)</td>
<td>—</td>
<td>3.4(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2250</td>
<td>6.68(12)</td>
<td>—</td>
<td>2.7(−20)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2260</td>
<td>5.40(12)</td>
<td>—</td>
<td>2.9(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2270</td>
<td>4.71(12)</td>
<td>—</td>
<td>1.6(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2280</td>
<td>5.72(12)</td>
<td>—</td>
<td>2.0(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2290</td>
<td>6.14(12)</td>
<td>—</td>
<td>6.8(−20)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2300</td>
<td>6.32(12)</td>
<td>—</td>
<td>1.4(−19)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2310</td>
<td>6.41(12)</td>
<td>—</td>
<td>6.8(−20)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2320</td>
<td>2.24(12)</td>
<td>—</td>
<td>4.5(−20)</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Note. The solar flux at 1 AU, $\pi F$, 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. $\sigma_n$ is absorption cross section. $a(-b)$ reads as $a \times 10^{b}$.

Between 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**

<table>
<thead>
<tr>
<th></th>
<th>Model A</th>
<th>Model B</th>
<th>Model C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{\text{H}_2}$</td>
<td>$2 \times 10^{-6}$</td>
<td>$5 \times 10^{-7}$</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>$f_{\text{HCl}}$</td>
<td>$4 \times 10^{-7}$</td>
<td>$4 \times 10^{-7}$</td>
<td>$8 \times 10^{-7}$</td>
</tr>
<tr>
<td>$f_{\text{SO}_2}$</td>
<td>0</td>
<td>$3 \times 10^{-8}$</td>
<td>0</td>
</tr>
<tr>
<td>Eddy diffusivity profile (Fig. 1b)</td>
<td>A</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>Reaction set</td>
<td>Table IIIa</td>
<td>Tables IIIa + b + c + Al</td>
<td>Tables IIIa + c + Al</td>
</tr>
<tr>
<td>Heterogeneous sinks*</td>
<td>Included</td>
<td>Excluded</td>
<td>Excluded</td>
</tr>
</tbody>
</table>

* Value refers to lower boundary, determined by photochemical equilibrium.

### TABLE VI

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

<table>
<thead>
<tr>
<th>Model</th>
<th>Species</th>
<th>Lower boundary (58 km)</th>
<th>Upper boundary (110 km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>CO</td>
<td>$f = 4.5 \times 10^{-5}$</td>
<td>$\phi = -1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>$v = -6.2 \times 10^{-2}$</td>
<td>$\phi = -1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>$v = -6.2 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>$f = 1.5 \times 10^{-4}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td>B</td>
<td>CO</td>
<td>$f = 4.5 \times 10^{-5}$</td>
<td>$\phi = -1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>$v = -3.1 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>$v = -3.1 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>$f = 1.7 \times 10^{-4}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>NO</td>
<td>$f = 3.0 \times 10^{-4}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>$\phi = 0$</td>
<td>$\phi = -1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>C</td>
<td>CO</td>
<td>$f = 4.5 \times 10^{-5}$</td>
<td>$\phi = -1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>$v = -2.0 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>O$_2$</td>
<td>$v = -2.0 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>SO$_2$</td>
<td>$f = 4.0 \times 10^{-4}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>Cl$_2$</td>
<td>$v = -2.0 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
<tr>
<td></td>
<td>H$_2$</td>
<td>$v = -2.0 \times 10^{-2}$</td>
<td>$\phi = 0$</td>
</tr>
</tbody>
</table>

* The mixing ratio for H$_2$O is held fixed at 1 ppm in all models. The mixing ratios for H$_2$ in models A and B are $2 \times 10^{-5}$ and $5 \times 10^{-5}$, respectively. For short-lived species not explicitly listed here photochemical equilibrium is assumed (flux = 0) at both boundaries. The symbols $f$, $\phi$, and $v$, respectively, denote mixing ratio, flux (cm$^{-2}$ sec$^{-1}$), and velocity (cm sec$^{-1}$). The sign convention for $v$ and $\phi$ 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

<table>
<thead>
<tr>
<th>Model parameter or rate coefficient</th>
<th>Value adopted in model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P71</td>
</tr>
<tr>
<td>( f_{H_2} )</td>
<td>1.0(-5)</td>
</tr>
<tr>
<td>( K(60,\text{km}) )</td>
<td>1.0(6)</td>
</tr>
<tr>
<td>( K(70,\text{km}) )</td>
<td>1.0(6)</td>
</tr>
<tr>
<td>( k_{16} ) O + HCl</td>
<td>—</td>
</tr>
<tr>
<td>( k_{21} ) H + HCl</td>
<td>7.0(-15)</td>
</tr>
<tr>
<td>( k_{27} ) OH + HCl</td>
<td>2.5(-14)</td>
</tr>
<tr>
<td>( k_{38} ) Cl + H_2</td>
<td>4.4(-15)</td>
</tr>
<tr>
<td>( k_{41a} ) Cl + HO_2</td>
<td>—</td>
</tr>
<tr>
<td>( k_{51} ) SO + O + M</td>
<td>—</td>
</tr>
<tr>
<td>( k_{56} ) SO + HO_2</td>
<td>—</td>
</tr>
<tr>
<td>( k_{37} ) SO + SO</td>
<td>—</td>
</tr>
<tr>
<td>( k_{58} ) SO_2 + O + M</td>
<td>—</td>
</tr>
<tr>
<td>( k_{59} ) SO_2 + OH + M</td>
<td>—</td>
</tr>
<tr>
<td>( k_{60} ) SO_2 + HO_2</td>
<td>—</td>
</tr>
<tr>
<td>( k_{61} ) NO + HO_2</td>
<td>—</td>
</tr>
<tr>
<td>( k_{101} ) CICO + O_2</td>
<td>—</td>
</tr>
</tbody>
</table>

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 Parshuram (1980a). \( f_{H_2} \) is mixing ratio of \( H_2 \). \( H(z) \) is eddy diffusion coefficient (cm² 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. |

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 \( 1 \times 10^{18} \) 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 photolysis, and the lower atmosphere, dominated by thermochemical equilibrium. The net result of stratospheric chemistry is the production of disequilibrium products, \( CO_2 + SO_2 + H_2O + h\nu \rightarrow CO + H_2SO_4 \). 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 \( 1 \times 10^{18} \) 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 photolysis, and the lower atmosphere, dominated by thermochemical equilibrium. The net result of stratospheric chemistry is the production of disequilibrium products, \( CO_2 + SO_2 + H_2O + h\nu \rightarrow CO + H_2SO_4 \).
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 $1.1 \times 10^8$, $6 \times 10^6$, and $1 \times 10^6$ sec, respectively. The column density of H$_2$SO$_4$ above 58 km, as implied by the data of Knollenberg and Hunten (1980), is $7 \times 10^{18}$ cm$^{-2}$. The Stokes falling velocity for particles of radius equal to 1 μm is $2.7 \times 10^{-2}$ cm sec$^{-1}$ and must be added to the eddy velocity. The estimated downward flux of H$_2$SO$_4$ is $1 \times 10^{12}$ cm$^{-2}$ sec$^{-1}$. Our column production rate for H$_2$SO$_4$ 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$_2$O. For production rates on the

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.

Fig. 3. The major reactions producing and consuming oxygen in model A: (R1) CO$_2$ + hv → CO + O$_2$, (R25) CO + OH → CO$_2$ + H, and (R58) SO$_2$ + O + M → 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 $1 \times 10^{12}$ molecules cm$^{-2}$. The flux units are $10^{12}$ molecules cm$^{-2}$ sec$^{-1}$.
order of this magnitude or higher, the availability of H$_2$O 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$_2$O$_2$) 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 + hv 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$_2$O at the

---

**Fig. 5.** Number densities of H, OH, HO$_2$, H$_2$O$_2$, Cl, and ClO computed in model A.

**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. 7.** Sources and sinks of HO$_x$ and ClO$_x$ in model A. The sources are (R2) HCl + hv and (R16) O + HCl. The major sinks are (R41) Cl + HO$_2$, (R59) OH + SO$_2$ + M, and (R62) Cl + SO$_2$ + M.

**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$_2$. 

---

YUNG AND DEMORE
rate of $1.5 \times 10^{11}$ cm$^{-2}$ sec$^{-1}$. The stratosphere is a net chemical source of H$_2$O. The overall equation can be written as

$$\text{H}_2 + \text{CO}_2 + h\nu \rightarrow \text{H}_2\text{O} + \text{CO}.$$ 

Since the production of H$_2$O 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

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad \text{(R25)}$$

for CO$_2$ recombination. Let $S$ and $P$ be the integrated rate of CO$_2$ photolysis and H$_2$O production, respectively:

$$S = \int dz \ J_1 (\text{CO}_2),$$
$$P = \int dz \ k_{26} \ [\text{CO}] [\text{OH}],$$

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

$$P \sim \frac{k_{27}[\text{HCl}]}{k_{26}[\text{CO}]} \sim 0.01.$$ 

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, $3 \times 10^9$ cm$^{-2}$ sec$^{-1}$.

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 + H$_2$O, 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$_2(\Delta)$ 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 recombinaiton of O atoms on Pyrex glass. In our computation we assume a somewhat higher average quantum yield of 67% for producing O$_2(\Delta)$ by (R17), (R31), (R39), and (R44). If the quenching rate coefficient is $3 \times 10^{-20}$ (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

**Fig. 9.** Altitude profiles for oxygen species O, O$_2$, and O$_3$ in model A. The concentrations of O (\textsuperscript{1}D) (<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 + H$_2$O.
rates of $O_3(\Delta) \rightarrow O_2(\Sigma)$ at 1.27 $\mu$m for (R17), (R31), (R39), and (R44) are $3.9 \times 10^{11}$, $3.5 \times 10^{11}$, $3.0 \times 10^{10}$, and $3.0 \times 10^{10}$ cm$^{-2}$ sec$^{-1}$, respectively, giving a total emission rate of $0.8 \times 10^{12}$ 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 $O_2(\Delta)$ is about 30 MR, and is dominated by contributions from

\[ O_3 + h\nu \rightarrow O_2(\Delta) + O(\text{D}). \] (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 $7 \times 10^{14}$ 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 VIIa). If the quantum yield for producing $O_2(\Delta)$ by (R17), (R31), (R39), and (R44) were only $\sim 30\%$, we must adopt a lower quenching coefficient. Alternatively, we may argue that the uncertainties in the $O_2(\Delta)$ 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>
<thead>
<tr>
<th>Model</th>
<th>Reaction</th>
<th>$k_{18\nu} = 1 \times 10^{-20}$</th>
<th>$k_{18\nu} = 3 \times 10^{-20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(R5a) $O_3 + h\nu$</td>
<td>0.89</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>(R17) O + O</td>
<td>0.93</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>(R31) O + HO$_2$</td>
<td>0.80</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>(R39) Cl + O$_3$</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>(R44) ClO + O</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E = 1.2$</td>
<td>$E = 0.79$</td>
</tr>
<tr>
<td>B</td>
<td>(R5a)</td>
<td>1.80</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>(R17)</td>
<td>0.82</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>(R31)</td>
<td>0.36</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>(R39)</td>
<td>0.31</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(R44)</td>
<td>0.34</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E = 2$</td>
<td>$E = 0.8$</td>
</tr>
<tr>
<td>C</td>
<td>(R5a)</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(R17)</td>
<td>0.72</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>(R31)</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>(R39)</td>
<td>0.37</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>(R44)</td>
<td>0.72</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E = 1.3$</td>
<td>$E = 0.76$</td>
</tr>
</tbody>
</table>

*Note: E, the nightglow, is computed by $E = q \times ([\text{R17} + (\text{R31}) + (\text{R39}) + (\text{R44})]$, where $q = \frac{8}{9}$. The dayglow equals the sum of $E$ and (R5a). All units are in $10^{12}$ cm$^{-2}$ sec$^{-1}$ or MR.*
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

FIG. 11. Number densities for the major sulfur species, S, SO, SO₂, and SO₃ computed by model A. and Stewart (1980), in conflict with the O₂ observations.

Model B

Altitude profiles for the mixing ratios of CO, O₂, and SO₂ 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) SO₂ + O are the most important sinks for oxygen.

The altitude profiles for HOₓ and ClOₓ 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 H₂ concentration and the assumption that there is no heterogeneous sink for HOₓ or ClOₓ via reactions with SO₂. The major reactions producing and destroying HOₓ−ClOₓ are presented in Fig. 18. The production rate of H₂O by (R27) OH + HCl is 1.5 x 10¹¹ cm⁻² sec⁻¹, as expected on the basis of the discussion in section Model A. The concentrations of S, SO, SO₂, and SO₃ are given in Fig. 19. NO is important for catalytically recombining SO and O via the cycle

\[
\text{NO + O + M} \rightarrow \text{NO₂ + M} \quad \text{(R77)}
\]

\[
\text{NO₂ + SO} \rightarrow \text{NO + SO₂} \quad \text{(R85)}
\]

The model predicts a column-integrated production rate for H₂SO₄ equal to 9 x 10¹¹ cm⁻² sec⁻¹.
cm$^{-2}$ sec$^{-1}$, in good agreement with $1 \times 10^{22}$ 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 $3 \times 10^{-8}$ 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 $2.2 \times 10^8$ and $1 \times 10^9$ molecules of NO$_x$ cm$^{-2}$ sec$^{-1}$, respectively. This should be compared with the estimate by Cha-
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

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, O₂, and SO₂ 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) CICO + O₂ is now the major sink for CO and O₂. 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 CICO 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 HO₂ are given in Fig. 27. As expected, the low level of H₂ in the ambient atmosphere favors low concentrations of HO₂. The number densities of ClO₂ are shown in Fig. 28. The total free chlorine mixing ratio (mostly in the form of Cl₂) 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. 18. Same as Fig. 7, for model B. The reactions (R59) OH + SO₂ + M and (R62) Cl + SO₂ + M are not sinks for HO₂ and ClO₂ in model B.

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

Fig. 20. Number densities of NO₂ (N, NO, NO₂, NO₃, HNO, HNO₂, HNO₃) computed in model B.

Fig. 21. Major reaction destroying NO₂ 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) NO₂ + O.

Fig. 24. Reactions leading to the breaking of the O–O bond in model B: (R46) S + O₂, (R55) SO + HO₂, (R101) CICO + O₂, and (R81) NO + HO₂.

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

Fig. 26. Same as Fig. 3, for model C. (R101) CICO + O₂ + M has been added.

Fig. 27. Number densities of HO₂ (H, OH, HO₂) computed 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$_2$ is 0.1 ppm at 100 km even though H$_2$ = 1 x 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 is now an important sink, as first pointed out by Krasnopolsky and Parshev (1980a,b, 1981). The principal reactions producing H$_2$ and H$_2$O 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$_2$O (and subsequent scavenging by SO$_x$ to form H$_2$SO$_4$) is a permanent hydrogen sink in the stratosphere. The net reaction can be schematically summarized as

\[ 2\text{HCl} + \text{CO}_2 + h\nu \rightarrow \text{H}_2\text{O} + \text{CO} + \text{Cl}_2. \]

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 x 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$_3$ at airglow, along with comparisons between models, are given in Table VIIIa.
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,

$$\text{CO}_2 + h\nu \rightarrow \text{CO} + O. \quad (R1)$$

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

$$O + O \xrightarrow{\text{ClO}_x} O_2. \quad (8)$$

The chlorine-catalyzed recombination reactions are sufficiently exothermic to produce oxygen molecules in the \( '\Delta \) state. [The quantum yields for producing O$_2('\Delta)$ 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 peroxycchloroformyl radical:

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

$$\text{CICO} + \text{O}_2 + M \rightarrow \text{CICO}_3 + M \quad (R101)$$

$$\text{CICO}_3 + \text{Cl} \rightarrow \text{Cl} + \text{CO}_2 + \text{ClO} \quad (R110)$$

net CO + O$_2$ + Cl → CO$_2$ + ClO

Whether this scheme results in a net consumption of O$_2$ depends on the fate of ClO. If ClO reacts with O,

$$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2. \quad (R44)$$

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

$$\text{CO} + \text{O} \rightarrow \text{CO}_2.$$  

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,

$$\text{ClO} + h\nu \rightarrow \text{Cl} + O. \quad (R7)$$

or reacts with SO, followed by photolysis,

$$\text{ClO} + \text{SO} \rightarrow \text{Cl} + \text{SO}_2 \quad (R56)$$

$$\text{SO}_2 + h\nu \rightarrow \text{SO} + O \quad (R9)$$

net ClO → Cl + O

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

$$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + O.$$  

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$_2$O in model C.](image1)

![Fig. 30. Same as Fig. 11, for model C.](image2)
(R56) is more important than (R44). We can now clearly see the close coupling between the ClO and SO 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$_2$. Herein lies its simplicity, and hence its strength.

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 $1.5 \times 10^{11}$ cm$^{-2}$ sec$^{-1}$ from the troposphere. Model C uses the new scheme (R101) CICO + 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. 31. Same as Fig. 9, for model C.

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

FIG. 33. Reactions showing the fate of O$_2$ in CICO$_3$ 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).

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$_3$(λΔ) 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.

In the extensive study on the distribution and source of ultraviolet absorption in the Venusian atmosphere, Pollack et al. (1980) and Wilson et al. (1981) indicated 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$_2$SO$_4$ droplets can explain the UV and visible albedo. But the requirement of NO$_2$ 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$_2$O, (SO)$_2$, H$_2$S$_2$O$_5$, and H$_2$S$_2$O$_3$. 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$_2$S$_2$O$_5$, and H$_2$S$_2$O$_3$ 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,

---

**TABLE VIIIb**

<table>
<thead>
<tr>
<th>Comparison of Major Predictions of Models A, B, and C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical quantity</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>$f_{CO}$ (62 km)</td>
</tr>
<tr>
<td>$f_{CO}$ (100 km)</td>
</tr>
<tr>
<td>$f_{CO}$ (150 km)</td>
</tr>
<tr>
<td>CO column abundance</td>
</tr>
<tr>
<td>O$_3$ column abundance</td>
</tr>
<tr>
<td>Ratio of CO to O$_3$ column abundances</td>
</tr>
<tr>
<td>$f_{SO_2}$ (70 km)</td>
</tr>
<tr>
<td>Scale height of SO$_2$ at 70 km (km)</td>
</tr>
<tr>
<td>(R1) CO$_2$ + hv</td>
</tr>
<tr>
<td>(R25) CO + OH</td>
</tr>
<tr>
<td>(R101) CICO + O$_3$</td>
</tr>
<tr>
<td>(R102) CICO + O</td>
</tr>
<tr>
<td>(R27) OH + HCl</td>
</tr>
<tr>
<td>$\phi_{OH}$</td>
</tr>
<tr>
<td>$\phi_{O_2}$</td>
</tr>
<tr>
<td>O$_3$(λΔ) dayglow</td>
</tr>
<tr>
<td>O$_3$(λΔ) nightglow</td>
</tr>
</tbody>
</table>

**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 $4.5 \times 10^{-5}$. The column abundance of CO$_2$ is $5 \times 10^{24}$ cm$^{-2}$. 
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

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 \( \text{N}_2\text{O} \) 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

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

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

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

could play a similar role if \( \text{H}_2 \) 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

\[
\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2 \quad (R82)
\]

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

\[
\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2. \quad (R44)
\]

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

\[
\text{ClO} + \text{SO} \rightarrow \text{Cl} + \text{SO}_2 \quad (R56)
\]

which plays a similar role as (R82).

Removal of active radicals, such as OH, Cl, and \( \text{H}_2\text{O}_2 \), 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

<table>
<thead>
<tr>
<th>TABLE IX</th>
<th>COMPARISON OF THE ESSENTIAL ASPECTS OF THE CHEMISTRY OF THE STRATOSPHERE OF EARTH AND VENUS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Earth</td>
</tr>
<tr>
<td>Altitude</td>
<td>20–40 km</td>
</tr>
<tr>
<td>Pressure</td>
<td>100–5 mbar</td>
</tr>
<tr>
<td>Temperature</td>
<td>200–250 K</td>
</tr>
<tr>
<td>Total chlorine mixing ratio</td>
<td>( 2.3 \times 10^{-9} )</td>
</tr>
<tr>
<td>Total sulfur mixing ratio</td>
<td>( \sim 1 \times 10^{-9} )</td>
</tr>
<tr>
<td>Total NO(_2) mixing ratio</td>
<td>( 2 \times 10^{-8} )</td>
</tr>
<tr>
<td>Molina–Rowland chlorine cycle inhibitor of</td>
<td>Important</td>
</tr>
<tr>
<td>chlorine cycle (1)</td>
<td>Cl + CH(_4)</td>
</tr>
<tr>
<td>Molina–Rowland chlorine cycle inhibitor of</td>
<td>ClO + NO</td>
</tr>
<tr>
<td>chlorine cycle (2)</td>
<td>Important</td>
</tr>
<tr>
<td>Heterogeneous loss</td>
<td>Not important in quiescent atmosphere</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction breaking O–O bond</td>
<td>NO + HO(_2)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\text{Note.} \text{ Data for the Earth’s stratosphere was taken from Logan et al. (1978), Turco et al. (1979), and Yung et al. (1980).}
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),

$$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH},$$

which produces odd oxygen. On Venus, results of model B indicate that NO$_2$ can produce and destroy odd oxygen. Reaction (R55),

$$\text{SO} + \text{HO}_2 \rightarrow \text{SO}_2 + \text{OH},$$
is analogous to (R81), and together with (R46) and (R101),

$$\text{S} + \text{O}_2 \rightarrow \text{SO} + \text{O},$$
$$\text{CICO} + \text{O}_2 \rightarrow \text{CICO}_3,$$

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$_2$O. Photochemical destruction of H$_2$O 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 $1.5 \times 10^{11}$ cm$^{-2}$ sec$^{-1}$. Thermochemical equilibrium in the lower atmosphere yields the following relations between H$_2$, H$_2$O, H$_2$S, CO, CO$_2$, and COS:

$$\frac{[\text{H}_2][\text{CO}_2]}{[\text{CO}][\text{H}_2\text{O}]} = K_1 = \begin{cases} 8.8 \times 10^4 & T = 300^\circ \text{K} \\ 1.3 \times 10^2 & T = 500^\circ \text{K} \\ 6.1 & T = 750^\circ \text{K}, \end{cases}$$

$$\frac{[\text{H}_2][\text{COS}]}{[\text{H}_2\text{S}][\text{CO}]} = K_2 = \begin{cases} 1.5 \times 10^{-1} & T = 300^\circ \text{K} \\ 4.9 \times 10^{-2} & T = 500^\circ \text{K} \\ 3.5 \times 10^{-2} & T = 750^\circ \text{K}, \end{cases}$$
The equilibrium constants $K_1$, $K_2$, and $K_3$ have been evaluated using data presented in the JANAF Thermochemical Tables (1971). Note that $K_1 = K_2 K_3$. 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 $1.2 \times 10^{-8}$, 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

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

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:

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

$$3 \text{FeMgSiO}_4 + CO_2 = 3 \text{MgSiO}_3 + \text{Fe}_3\text{O}_4 + CO,$$

$$3 \text{FeSiO}_3 + CO_2 = 3 \text{SiO}_2 + \text{Fe}_3\text{O}_4 + CO,$$
2 Fe$_3$O$_4$ + CO$_2$ = 3 Fe$_2$O$_3$ + CO,
Fe + CO$_2$ = FeO + CO,
3 FeO + CO$_2$ = Fe$_3$O$_4$ + 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 $\sim$ 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 x 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

$$2\text{NO} \rightarrow \text{N}_2\text{O} + \text{O}$$

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 x 10$^8$ years. The fate of NO$_x$ in the Venustian 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$^5$ 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$_2$O, with mixing ratio equal to 1 x 10^{-4} [Moroz *et al.* (1979), with correction by A. T. Young (1981, private communication)]. This is equivalent to a column abundance of 2 x 10$^{23}$ molecules cm$^{-2}$ or 6 g cm$^{-2}$. In contrast, the water abundance on Earth is 3 x 10$^4$ 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

$$\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}^\circ,$$
$$\text{OH}^\circ + e \rightarrow \text{O} + \text{H}^\circ,$$
$$\text{CO}_2^+ + \text{H}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{H}^\circ,$$
$$\text{CO}_2\text{H}^+ + e \rightarrow \text{CO}_2 + \text{H}^\circ,$$

where H$^\circ$ denotes a hot hydrogen atom that may escape from Venus (Kumar and Hun-
The escape flux of hydrogen has been estimated by Kumar et al. (1981) to be $3 \times 10^3$ atoms cm$^{-2}$ sec$^{-1}$. At this rate the half-life for the present amount of water on Venus is only $2 \times 10^7$ years, a geologically insignificant time. The high abundance of H$_2$ (20 ppm) is about 10$^4$ times higher than that expected on the basis of the equilibrium reaction

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$

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

$$4\text{SO}_2 + 4\text{H}_2\text{O} + \text{hv} \rightarrow 3\text{H}_2\text{SO}_4 + \text{S} + \text{H}_2.$$  

This scheme must extract H$_2$ from H$_2$O at a rate exceeding $1.4 \times 10^{-1}$ 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$_2$O 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

$$2\text{HCl} + \text{CO}_2 + \text{hv} \rightarrow \text{H}_2\text{O} + \text{CO} + \text{Cl}_2.$$  

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$_2$O in the lower atmosphere were, respectively, $2 \times 10^6$ 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-

PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS 237
YUNG AND DEMORE

assumed a drastically different character, as described by model C. This, we believe, is the current state of the atmosphere, the end point of a long sustained period of evolution. Hydrogen is still escaping at a significant rate, supplied by the HCl-H\(_2\)O cycle. With further loss of hydrogen in the next few billion years even model C will break down, leaving the atmosphere with an enriched mixture of CO, Cl\(_2\), and COCl\(_2\). The above description of the evolution of Venus' atmosphere is consistent with and complements recent studies by McElroy et al. (1982a), which emphasized the escape mechanics in the exosphere, and Donahue et al. (1982) on the interpretation of the HDO/H\(_2\)O ratio in the lower atmosphere. We have also implicitly assumed that the flux of H\(_2\) from the interior of Venus has been negligible in the recent past, due to the presence of an overthickened basaltic crust which inhibits terrestrial-style tectonics (Anderson, 1981).

7. CONCLUSIONS

The difficulties of current photochemical models of Venus with regard to O\(_2\) have been demonstrated by Winick and Stewart (1980). To overcome these difficulties we must explore new assumptions and new chemical schemes. We investigated three models. Model A is motivated by Kumar et al. (1981) report of 20 ppm H\(_2\) in the bulk atmosphere. It is shown in model A that high H\(_2\) abundance (~10 ppm) favors a high concentration of HO\(_2\). In this case the reaction (R25) CO + OH can readily consume most of the oxygen derived from CO\(_2\) photolysis. The O–O bond is broken by (R46) S + O\(_2\) and (R55) SO + HO\(_2\). Model B is in response to McElroy et al.'s (1982a) challenge to Kumar et al.'s (1981) inference of H\(_2\). We assume in this model an abundance of H\(_2\) equal to 0.5 ppm. It is shown that in this case we must invoke the presence of about 30 ppb NO\(_2\), most probably derived from a lightning source (Watson et al., 1979; Chameides et al., 1979), to drive the O\(_2\) bond-breaking reaction (R81) NO + HO\(_2\). Model C is partly motivated by Pollack et al.'s (1980) tentative identification of Cl\(_2\) in the uv reflection spectrum of Venus. In this model there is no tropospheric input of H\(_2\). It is shown that the new scheme (R101) CICO + O\(_2\) (Krasnopolsky and Parshev, 1980a,b, 1981; this work) is important for the oxidation of CO. The most serious weakness of model A is the need to invoke a large photochemical source for H\(_2\). This difficulty is not insurmountable, as discussed in Appendix B, but uncomfortable. The main difficulty of model B is the requirement of an exceedingly long lifetime, >4000 years, for NO\(_2\) in the lower atmosphere. But this is consistent with our current knowledge of NO\(_2\) chemistry in the gas phase. Model C is the only model capable of describing all observations to date, including the diurnal behavior of mesospheric CO. This suggests that the current atmospheric composition may be the direct result of extensive loss of hydrogen in the past, driven by the combination of photochemistry and thermoequilibrium chemistry.

The uncertainties in the models can be removed by suitable observations and laboratory experiments. A recommended list is summarized in Table X. The species O\(_2\), SO, ClO, NO\(_2\), and H\(_2\) occupy a central position in our chemical schemes. They have not been detected in the stratosphere by direct spectroscopic observations. The quantum yields for producing O\(_2\)(\(^1\)\(\Delta\)) in reactions (R31), (R39), and (R44) have not been measured. The rate coefficient for the O–O bond-breaking reaction (R55) has not been measured. In addition, the chemistry of (SO)\(_2\) dimer, which could lead to the formation of interesting compounds such as S\(_2\), H\(_2\)S\(_2\)O\(_2\), and H\(_2\)S\(_2\)O\(_3\), is almost totally unknown.

The distribution of major chemical species in the stratosphere has been observed to be inhomogeneous horizontally. The one-dimensional photochemical model is a crude approximation and can only reproduce the observations to within factors of
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

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

<table>
<thead>
<tr>
<th>Observations</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic confirmation of $H_2$</td>
<td>Can use the Lyman bands around 1606 Å (Feldman and Fastie, 1973; Moos, 1974).</td>
</tr>
<tr>
<td>Spectroscopic detection of $O_2$</td>
<td>Traub and Carleton (1974) upper limit could be improved.</td>
</tr>
<tr>
<td>Spectroscopic detection of ClO and $NO_2$ in stratosphere</td>
<td>This is important for pinning down the source, transport, and sink of CO and O.</td>
</tr>
<tr>
<td>Global and diurnal variation of CO and O in the mesosphere and upper stratosphere</td>
<td>Wilson et al.'s (1981) upper limit could be improved.</td>
</tr>
<tr>
<td>Spectroscopic detection of SO</td>
<td></td>
</tr>
<tr>
<td>Laboratory kinetics</td>
<td></td>
</tr>
<tr>
<td>$k_{55} \text{SO} + \text{HO}_3$</td>
<td>The reaction breaks an O–O bond</td>
</tr>
<tr>
<td>$k_{198} \text{O}_2(\Delta) + M$</td>
<td>Major sources of $O_2(\Delta)$</td>
</tr>
<tr>
<td>Quantum yield for producing $O_2(\Delta)$ by (R31) $\text{O} + \text{HO}_3$</td>
<td></td>
</tr>
<tr>
<td>(R39) $\text{Cl} + \text{O}_3$</td>
<td></td>
</tr>
<tr>
<td>(R44) $\text{O} + \text{ClO}$</td>
<td></td>
</tr>
<tr>
<td>Chemistry of HSO$_3$, CISO$_2$</td>
<td></td>
</tr>
<tr>
<td>Chemistry of (SO)$_2$</td>
<td></td>
</tr>
<tr>
<td>(R100) $\text{HNO} + h\nu$</td>
<td></td>
</tr>
<tr>
<td>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$_2$SO$_4$ aerosols are needed.</td>
<td></td>
</tr>
<tr>
<td>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) CICO + 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.</td>
<td></td>
</tr>
<tr>
<td>APPENDIX A: CHEMISTRY OF HSO$_3$ AND CISO$_2$</td>
<td></td>
</tr>
<tr>
<td>The reaction $\text{SO}_2 + \text{OH} + M \rightarrow \text{HSO}_3 + M$ (R59)</td>
<td></td>
</tr>
<tr>
<td>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$_2$SO$_4$ 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 $\text{SO}_2 + \text{OH} \rightarrow \text{SO}_3 + \text{H}$.</td>
<td></td>
</tr>
</tbody>
</table>
Reaction (R59) is probably not as important as schemes (6a,b) and (12a,b) for oxidation of \( \text{SO}_2 \) on Venus, but could be important as a sink for \( \text{HO}_x \). In addition, there are similar reactions possibly leading to the loss of \( \text{HO}_x \) and \( \text{ClO}_x \):

\[
\begin{align*}
\text{SO}_2 + \text{H}_2\text{O}_2 & \rightarrow \\
\text{H}_2\text{SO}_4 \text{ (heterogeneous)}, & \quad (R61) \\
\text{SO}_2 + \text{Cl} + M & \rightarrow \\
\text{ClSO}_2 + M. & \quad (R62)
\end{align*}
\]

Table AI summarizes a set of reactions related to the chemistry of \( \text{HSO}_3 \). This chemistry is adopted in models B and C, with the consequence that the reaction

\[
(\text{R59}) \quad \text{SO}_2 + \text{OH} + M \rightarrow \text{HSO}_3 + M
\]

is now no longer a permanent sink for \( \text{HO}_x \) in the lower stratosphere. The details of this chemical model are somewhat speculative. The maximum concentrations of \( \text{HSO}_3 \) and \( \text{HSO}_3 \cdot \text{H}_2\text{O} \) in the model are \( 4 \times 10^6 \) and \( 2 \times 10^9 \text{ cm}^{-3} \), respectively. The column-integrated production rate for \( \text{H}_2\text{S}_2\text{O}_6 \) is on the order of \( 1 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1} \).

**APPENDIX B: CHEMISTRY OF THE DIMER \((\text{SO}_2)_2\)**

The photochemistry of \( \text{SO}_2 \) is further complicated (and enriched) by the chemistry of \( (\text{SO}_2)_2 \) dimer, formed by

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

(Herron and Huie, 1980). The structure of the dimer is known (Lovas et al., 1974). The \( \text{OS} \)-\( \text{SO} \) 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,

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

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

\[
(\text{SO}_2)_2 + \text{SO} \rightarrow \text{S}_2\text{O} + \text{SO}_2. \quad (R134)
\]

\( \text{S}_2\text{O} \) is readily removed by reaction with \( \text{O} \) and \( \text{S} \),

\[
\begin{align*}
\text{S}_2\text{O} + \text{O} & \rightarrow 2\text{SO}, \quad (R129) \\
\text{S}_2\text{O} + \text{S} & \rightarrow \text{S}_2 + \text{SO}, \quad (R130)
\end{align*}
\]

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

\[
\text{S}_2\text{O} + h\nu \rightarrow \text{S} + \text{SO} \quad (R127)
\]

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

\[
(\text{SO}_2)_2 + \text{O} \rightarrow \text{S}_2\text{O} + \text{O}_2 \quad (R133)
\]

is as fast as (R134).

The homogeneous chemistry of \( (\text{SO}_2)_2 \) can be summarized by two catalytic cycles:

\[
\begin{align*}
\text{SO} + \text{SO} + M & \rightarrow (\text{SO}_2)_2 + M \quad (R128) \\
(\text{SO}_2)_2 + \text{SO} & \rightarrow \text{SO}_2 + \text{S}_2\text{O} \quad (R134) \\
\text{S}_2\text{O} + \text{O} & \rightarrow 2\text{SO} \quad (R129)
\end{align*}
\]

(B1)

\[
\begin{align*}
\text{SO} + \text{SO} + M & \rightarrow (\text{SO}_2)_2 + M \quad (R128) \\
(\text{SO}_2)_2 + \text{O} & \rightarrow \text{S}_2\text{O} + \text{O}_2 \quad (R133) \\
\text{S}_2\text{O} + \text{O} & \rightarrow 2\text{SO} \quad (R129)
\end{align*}
\]

(B2)

\[
\begin{align*}
\text{net} & \quad \text{SO} + \text{O} \rightarrow \text{SO}_2 \\
\text{SO} + \text{SO} + M & \rightarrow (\text{SO}_2)_2 + M \quad (R128) \\
(\text{SO}_2)_2 + \text{O} & \rightarrow \text{S}_2\text{O} + \text{O}_2 \quad (R133) \\
\text{S}_2\text{O} + \text{O} & \rightarrow 2\text{SO} \quad (R129)
\end{align*}
\]

(B2)

\[
\begin{align*}
\text{net} & \quad \text{O} + \text{O} \rightarrow \text{O}_2
\end{align*}
\]
Cycle (B1) catalytically recombines SO and O and can be interpreted as an increase in the rate coefficient for
\[ \text{SO} + \text{O} + \text{M} \rightarrow \text{SO}_2 + \text{M} \quad \text{(R51)} \]
or decrease in the photolysis rate of \( \text{SO}_2 \).
\[ \text{SO}_2 + \text{hv} \rightarrow \text{SO} + \text{O}. \quad \text{(R9)} \]
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 \( \text{S}_2\text{O} \) is the anhydride of thiosulfurous acid (\( \text{H}_2\text{S}_2\text{O}_2 \)). Friend (1981, private communication) suggested that \( (\text{SO})_2 \) could be the anhydride of thiosulfuric acid (\( \text{H}_2\text{S}_2\text{O}_3 \)). We propose three speculative schemes for the production of miscellaneous sulfur compounds:

\[
\begin{align*}
3(\text{SO}_2 + \text{hv} & \rightarrow \text{SO} + \text{O}) \quad \text{(R9)} \\
2\text{SO} + \text{M} & \rightarrow (\text{SO})_2 + \text{M} \quad \text{(R128)} \\
(\text{SO})_2 + \text{SO} & \rightarrow \text{S}_2\text{O} + \text{SO}_2 \quad \text{(R134)} \quad \text{(B3)} \\
\text{S}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{S}_2\text{O}_2 \quad \text{(R131)} \\
3(\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M}) \quad \text{(R58)} \\
3(\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4) \quad \text{(R65)} \\
\text{net} \quad 5\text{SO}_2 + 4\text{H}_2\text{O} & \rightarrow \text{H}_2\text{S}_2\text{O}_2 + 3\text{H}_2\text{SO}_4
\end{align*}
\]

\[
\begin{align*}
2(\text{SO}_2 + \text{hv} & \rightarrow \text{SO} + \text{O}) \quad \text{(R9)} \\
2\text{SO} + \text{M} & \rightarrow (\text{SO})_2 + \text{M} \quad \text{(R128)} \\
(\text{SO})_2 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{S}_2\text{O}_3 \quad \text{(R135)} \quad \text{(B4)} \\
2(\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M}) \quad \text{(R58)} \\
2(\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4) \quad \text{(R65)} \\
\text{net} \quad 4\text{SO}_2 + 3\text{H}_2\text{O} & \rightarrow \text{H}_2\text{S}_2\text{O}_2 + 2\text{H}_2\text{SO}_4
\end{align*}
\]

\[
\begin{align*}
4(\text{SO}_2 + \text{hv} & \rightarrow \text{SO} + \text{O}) \quad \text{(R9)} \\
2(2\text{SO} + \text{M} & \rightarrow (\text{SO})_2 + \text{M}) \quad \text{(R128)} \\
2(\text{SO}_2 + \text{SO} & \rightarrow \text{S}_2\text{O} + \text{SO}_2) \quad \text{(R134)} \\
\text{S}_2\text{O} + \text{hv} & \rightarrow \text{S} + \text{SO} \quad \text{(R127)} \quad \text{(B5)} \\
\text{S} + \text{S}_2\text{O} & \rightarrow \text{S}_2 + \text{SO} \quad \text{(R130)} \\
4(\text{SO}_2 + \text{O} + \text{M} & \rightarrow \text{SO}_3 + \text{M}) \quad \text{(R58)} \\
4(\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4) \quad \text{(R65)} \\
\text{net} \quad 6\text{SO}_2 + 4\text{H}_2\text{O} & \rightarrow 4\text{H}_2\text{SO}_4 + \text{S}_2
\end{align*}
\]

The significance of schemes (B3)–(B5) is twofold. First, these are the first known schemes for producing \( \text{H}_2\text{SO}_4 \) from \( \text{SO}_2 \) without using \( \text{CO}_2 \)-derived oxygen. Second, atmospheric photochemistry can start with \( \text{SO}_2 \) (oxidation state = +4) and segregate it into a more oxidized sulfur compound, \( \text{H}_2\text{SO}_4 \) (oxidation state = +6), and reduced sulfur compounds, \( \text{H}_2\text{S}_2\text{O}_2 \) (oxida-

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

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

LIST OF SPECULATIVE REACTIONS RELATED TO HSO₃⁻ AND THEIR RATE COEFFICIENTS, BASED ON DAVIS et al. (1979) AND FRIEND et al. (1980), AND OUR OWN ESTIMATES (FOOTNOTES REFER TO TABLE IIIa)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R115) HSO₃⁻ + H₂O + M → HSO₃⁻ · H₂O</td>
<td>( k_{115} = 3.9 \times 10^{-10} )</td>
<td>Friend et al. (1980)</td>
</tr>
<tr>
<td>(R116) HSO₃⁻ + O → OH + SO₃⁻</td>
<td>( k_{116} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R117) HSO₃⁻ + H₂ + SO₃⁻</td>
<td>( k_{117} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R118) HSO₃⁻ + OH → H₂O + SO₃⁻</td>
<td>( k_{118} = 3.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R119) HSO₃⁻ + Cl → HCl + SO₃⁻</td>
<td>( k_{119} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R120) 2HSO₃⁻ → H₂S₂O₆⁻</td>
<td>( k_{120} = 6.0 \times 10^{-14} )</td>
<td>Friend et al. (1980)</td>
</tr>
<tr>
<td>(R121) HSO₃⁻ + H₂O + M → HSO₃⁻ + H₂O + M</td>
<td>( k_{121} = 1.0 \times 10^{-19} )</td>
<td>Hamilton and Lii (1977)</td>
</tr>
<tr>
<td>(R122) HSO₃⁻ + H₂O + O → OH + H₂SO₄⁻</td>
<td>( k_{122} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R123) HSO₃⁻ + H₂O + H → H₂ + H₂SO₄⁻</td>
<td>( k_{123} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R124) HSO₃⁻ + H₂O + OH → H₂O + H₂SO₄⁻</td>
<td>( k_{124} = 3.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R125) HSO₃⁻ + H₂O + Cl → HCl + H₂SO₄⁻</td>
<td>( k_{125} = 1.0 \times 10^{-11} )</td>
<td></td>
</tr>
<tr>
<td>(R126) HSO₃⁻ + H₂O + HSO₃⁻ → H₂S₂O₆⁻ · H₂O</td>
<td>( k_{126} = 3.0 \times 10^{-12} )</td>
<td>Friend et al. (1980)</td>
</tr>
</tbody>
</table>

The table summarizes a speculative scheme involving reactions with (SO₂)₂. A model incorporating the chemistry of model A and Table AI has been studied. The details of the model need not be discussed here. The choice of rate constants presented in Table AI does allow for modest production rates for H₂S₂O₆⁻, H₂S₂O₅⁻, and S₂ (oxidation state = 0). Since these schemes are not limited by oxygen supplied by CO₂ photolysis, the production rates are limited only by an SO₂ 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 H₂S by an exchange reaction in the liquid phase,

\[
H₂S₂O₅⁻ + H₂O \rightarrow H₂SO₄ + H₂S
\]

(Bassett and Durrant, 1927). The production of H₂S by this mechanism can have
PHOTOCHEMISTRY OF THE STRATOSPHERE OF VENUS

243

profound implications for the budget of H₂ in the lower atmosphere of Venus.

ACKNOWLEDGMENTS

We thank J. J. Margitan, S. H. Jaffe, L. Phillips, K. S. Bhatki, M. Patapoff, M. T. Leu, C. J. Howard, L. W. Esposito, D. O. Muhleman, and R. T. Clancy for communication of experimental data prior to publication. We benefited from helpful discussions with M. B. McElroy, R. G. Prinn, D. M. Hunten, S. Kumar, T. M. Donahue, J. Blamont, O. B. Toon, W. T. Huntress, Jr., M. Allen, and J. P. Pinto, and critical comments given by the referees Drs. S. C. Wofsy and V. A. Krasnopolsky. This research was supported by NASA Ames Research Center Grant NCC 2-61 to California Institute of Technology. This also represented one phase of NASA-sponsored research carried out at the Jet Propulsion Laboratory under Contract NAS7-100.

REFERENCES


NAS (1976). Halocarbons: Effects on Stratospheric


Stewart, A. I., and C. A. Barth (1979). Ultraviolet


STRAITAN, L. W., R. E. EIBLING, AND M. KAUFMAN (1979). Rate constant of the reaction between chlorine atoms and sulfur dioxide and its significance for stratospheric chlorine chemistry. Atmos. Environ. 13, 175.


