Photochemistry of the Venus Atmosphere

MICHAEL B. MCELROY, NIEN DAK SZE AND YUK LING YUNG

Center for Earth and Planetary Physics, Harvard University, Cambridge, Mass. 02138

(Manuscript received 14 May 1973, in revised form 27 June 1973)

ABSTRACT

Carbon monoxide, produced in the Venus atmosphere by photolysis of CO₂, is removed mainly by reaction with OH. The radical OH is formed in part by photolysis of H₂O, in part by reaction of O with HO₂. Photolysis of HCl provides a major source of H radicals near the visible clouds of Venus and plays a major role in the overall photochemistry. The mixing ratio of O₂ is estimated to be approximately 10⁻⁷, about a factor of 10 less than a recent observational upper limit reported by Traub and Carleton. A detailed model, which accounts for the photochemical stability of Venus CO₂, is presented and discussed.

1. Introduction

The atmosphere of Venus is composed primarily of CO₂, but contains detectable trace quantities of CO, H₂O, HCl and HF. Carbon dioxide is dissociated readily by sunlight at wavelengths <2000 Å, and the observed abundance of CO, approximately 5×10⁻⁸ that of CO₂, could be produced photochemically in as little as 200 years. Similar remarks apply to O₂. Spectroscopic observations by Traub and Carleton (1973) suggest an upper limit to the O₂ mixing ratio of about 10⁻⁶, and an abundance in excess of this limit could be formed photochemically in less than 10 years. Our present task is to account for the stability of CO₂ in the atmosphere of Venus and, in so doing, to provide an explanation for the remarkable deficiency of CO and O₂.

A similar problem has arisen for Mars and was treated recently by McElroy and Donahue (1972) and by Parkinson and Hunten (1972). It appears that recombination of CO₂ in the Martian atmosphere is catalyzed by trace quantities of H and OH, produced by photolysis of H₂O. Removal of CO proceeds by two main paths:

\[ \text{H} + \text{O} + \text{CO} \rightarrow \text{HCO} + \text{O}, \]  
\[ \text{O} + \text{HOO} \rightarrow \text{OH} + \text{O}_2, \]  
\[ \text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \]  

and

\[ 2\text{[H} + \text{O} + \text{CO} \rightarrow \text{HOO} + \text{CO}_2]\]  
\[ 2\text{HOO} \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  
\[ \text{hv} + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  
\[ 2\text{[CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}] \]  

The first corresponds to the net reaction

\[ \text{H} + \text{CO} + \text{O} \rightarrow \text{H} + \text{CO}_2, \]  

and the second is equivalent to

\[ 2\text{H} + 2\text{CO} + \text{O}_2 \rightarrow 2\text{H} + 2\text{CO}_2, \]  

with an additional contribution from the global reaction

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2. \]  

We shall argue here that recombination of CO₂ in the atmosphere of Venus proceeds by a combination of (1) and (2). The necessary source of H is provided by

\[ \text{hv} + \text{HCl} \rightarrow \text{H} + \text{Cl}, \]  

followed by

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

Reactions (3) and (4) lead to net dissociation of H₂, the rate of which can be estimated if the concentration of HCl is taken as given.

2. Assumptions and general approach

Using the observed mixing ratio of HCl, about 6×10⁻⁷ according to Connes et al. (1967), we estimate a global mean rate for production of H atoms by (3) and (4) equal to 4×10¹⁴ cm⁻² sec⁻¹. The corresponding rate for destruction of H₂ is 2×10¹⁰ cm⁻² sec⁻¹ and must be balanced by a source of comparable magnitude. As we shall see, the necessary H₂ source is provided in part by

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

with Reaction (5) occurring primarily above the visible cloud tops, where the atmospheric pressure is about 0.2 atm and the temperature about 250K. Reaction (6) occurs mainly in the deep atmosphere, near the surface, where the pressure is about 95 atm and the temperature about 750K.

We shall assume that CO in the atmosphere of Venus is produced primarily by photolysis of CO₂. We assume further that CO is mixed uniformly throughout the atmosphere. The total abundance of CO is then about 10²⁹ molecules cm⁻² and there must be a comparable
amount of free oxygen. Our model should account for this oxygen reservoir. The observations of Traub and Carleton (1973) seem to rule out O$_2$ as the major component of the reservoir. A more likely candidate is water, formed by the reaction sequence

\[
\begin{align*}
\text{hv} + \text{HCl} & \rightarrow \text{H} + \text{Cl} \\
\text{Cl} + \text{H}_2 & \rightarrow \text{HCl} + \text{H} \\
2[\text{H} + \text{O}_2 + \text{CO}_2 & \rightarrow \text{HO}_2 + \text{CO}_2] \\
2\text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{hv} + \text{H}_2\text{O}_2 & \rightarrow 2\text{OH} \\
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{CO}_2 & \rightarrow \text{HO}_2 + \text{CO}_2 \\
\text{OH} + \text{HO}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

for which the equivalent stoichiometric equation is

\[
\text{H}_2 + \text{O}_2 + \text{CO} \rightarrow \text{H}_2\text{O} + \text{CO}_2.
\] (7')

Our detailed models assume, therefore, that the total abundance of H$_2$O must be at least as large as that of CO, i.e., that the mixing ratio of H$_2$O in the lower atmosphere must be $5 \times 10^{-6}$ or larger. This assumption is consistent with, but not required by, the available observational data. Reported mixing ratios for H$_2$O range from low values of order $10^{-6}$ (Young, 1972; Fink et al., 1972) to high values of order $10^{-5}$ (Avduevsky et al., 1970; Vinogradov et al., 1971). The low values are associated with low wavelength studies which emphasize conditions near or above the visible cloud deck. The highest mixing ratios were detected by Venera probes and refer to conditions near the 1-atm pressure level. It is clear, however, from recent studies of the Venus emission spectrum at radio wavelengths (Janssen et al., 1973) that the Venera measurements cannot represent planetary mean conditions. The average mixing ratio of H$_2$O must be less than $2 \times 10^{-5}$ at pressure levels of about 2 atm (Janssen et al., 1973). Radio (Berger and Greisen, 1969; Sinclair et al., 1972) and radar (Rogers et al., 1972) data would permit, but do not require, larger mixing ratios, $\sim 5 \times 10^{-5}$, at lower atmospheric levels.

In view of the present uncertainties regarding the abundance and height distribution of Venus H$_2$O, we propose here to consider two distinct models, one dry, one wet. The dry model assumes that the mixing ratio of H$_2$O in the stratosphere may be significantly less than that in the lower atmosphere. This result could hold if H$_2$O were a major component of the Venus clouds. It would be appropriate, in particular, if the main clouds were composed of H$_2$SO$_4$ as suggested recently by Young (1973). The wet model assumes that the stratospheric mixing ratio is the same as the mixing ratio in the lower atmosphere. The wet model, as implied earlier, is constrained to give a H$_2$O mixing ratio greater than or equal to that of CO at all heights.

Water formed by reactions (7) must be removed elsewhere at an equivalent rate. In the models discussed here, removal of H$_2$O occurs in the upper atmosphere by photolysis followed by

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

with additional loss in the lower atmosphere associated with reaction (6).

The strategy adopted for this work is as follows. We assume that CO, O$_2$, HCl, H$_2$ and H$_2$O are mixed homogeneously with CO$_2$, at least above the visible cloud deck. We assume further that the abundances of odd hydrogen, odd oxygen and free chlorine are given by photochemical equilibrium. For present purposes, O, OH, HO$_2$ and H$_2$O$_2$ are considered as odd hydrogen; O$_2$, OH and O$_3$ as odd oxygen; and Cl and Cl$_2$ as free chlorine.

The assumption of photochemical equilibrium for odd H is equivalent (see Appendix A) to the statement

\[
\phi\left(\text{H}_2\right) + \phi\left(\text{H}_2\text{O}\right) = 0,
\] (9)

where $\phi\left(i\right)$ denotes the net rate for production of species $i$ at height $z$. Similarly, photochemical equilibrium for odd O and free chlorine requires

\[
\phi\left(\text{CO}_2\right) + \phi\left(\text{H}_2\text{O}\right) + 2\phi\left(\text{O}_2\right) = 0, \quad \phi\left(\text{HCl}\right) = 0.
\] (10)

Acceptable physical solutions must satisfy the additional constraints

\[
\int_0^\infty \phi\left(i\right)dz = 0,
\] (12)

where $i$ denotes CO$_2$, O$_2$, H$_2$O$_2$, H$_2$ and HCl. If we assume (9)–(11) as given, then (12) introduces an additional pair of independent constraints. If (12) is satisfied for any pair of linearly independent constituents, for example O$_2$ and H$_2$ or O$_2$ and CO$_2$, then Eqs. (9)–(11) ensure that (12) must be satisfied for all $i$.

In practice, we take the mixing ratios of HCl and H$_2$O as given. We then vary the mixing ratios of O$_2$ and CO in an attempt to satisfy the integral constraints (12) for all major species. There is, of course, no guarantee that any physically acceptable solution should exist to the problem as posed. Indeed, we find it necessary in the dry model to allow for removal of H$_2$O in the lower atmosphere by reaction (6). The magnitude of the downward flux of H$_2$O is a function of the value assumed for the rate constant for

\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2.
\] (13)

Somewhat arbitrarily, we adopted a value $10^{-10}$ cm$^3$ sec$^{-1}$ for this constant in the dry model, a factor of 2 less than that used in the wet model. It is possible in the wet model to find an acceptable solution in which height-integrated production and loss rates are in balance for all major constituents without the need to invoke lower atmospheric chemistry. Both wet and dry
models provide satisfactory solutions to the overall stability problem.

The present work does not explicitly allow for atmospheric dynamics. We assumed implicitly that dynamics plays a dominant role for CO₂, CO, O₂, H₂O, H₂ and HCl, but that chemistry dominates for odd H, odd O and free Cl. In order to assess the validity of these assumptions we compute chemical time constants for major photochemically active species. It seems probable that CO₂, O₂, H₂O, H₂ and HCl are indeed uniformly mixed with CO₂ over the major height range of interest here. On the other hand, the assumption of photochemical equilibrium may be suspect for H, O and Cl, particularly at higher altitudes. The neglect of dynamics is unlikely, however, to introduce any major error in the present discussion. We offer a qualitative discussion of the possible effects of dynamics.

3. Chemical model

The model atmosphere adopted for present purposes is summarized in Table 1. The height scale is referred to a zero reference level near the top of the visible cloud deck, at a planetocentric distance of 6112 km. A more detailed description of the model, which was constructed on the basis of the available spacecraft data, is given elsewhere (NASA, 1972).

Solar fluxes in the visual and near-ultraviolet were taken from the Handbook of Geophysics and Space Environments (1965). We used data by Detwiler et al. (1961), as tabulated by Brinkmann et al. (1966), for the wavelength interval 1750-3000 Å. Below 1750 Å we used more recent observations by Widing et al. (1970). Absorption cross sections for CO₂, HCl and H₂O were taken from Shemansky (1972), Romand and Vodar (1948) and Thompson et al. (1963), respectively.

The detailed chemical model is summarized in Table 2 and the relevant photochemical equations are presented and discussed in Appendix A. For both wet and dry models, loss of odd hydrogen proceeds primarily by (5). Below 6 km, the relative concentrations of H, OH and HO₂ are controlled by k₁, k₂, k₃ and J₆. Then

$$[\text{HO}_2] = \left[ \frac{k₃[\text{O}_2][\text{CO}_2][J₆[\text{H}_2\text{O}]+J₆[\text{HCl}]]}{2k₃k₁₀} \right]^\dagger, \quad (14)$$

$$[\text{H}] = \left[ \frac{2k₄}{[\text{O}_2][\text{CO}_2]}[k₅k₁₀]^{J₆[\text{H}_2\text{O}]+J₆[\text{HCl}]} \right]^\dagger, \quad (15)$$

$$[\text{OH}] = \left[ \frac{2k₅k₆[\text{CO}_2]}{[\text{O}_2][\text{CO}_2]}[J₆[\text{H}_2\text{O}]+J₆[\text{HCl}]] \right]^\dagger, \quad (16)$$

Between 6 km and 18 km, reactions k₄ and k₁₂ are more important than k₉ and J₆. In this case

$$[\text{HO}_2] = \left[ \frac{k₉[\text{O}_2][\text{CO}_2][J₆[\text{HCl}]+J₆[\text{H}_2\text{O}]]}{k₉J₆[\text{CO}_2]} \right]^{J₆[\text{CO}_2]}, \quad (17)$$

### Table 1. Height, z, above the visible cloud tops, taken at a planetocentric distance of 6112 km, number density n, and temperature T for the model atmosphere.

<table>
<thead>
<tr>
<th>Height (km)</th>
<th>Number density (cm⁻³)</th>
<th>Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6.8(18)</td>
<td>255</td>
</tr>
<tr>
<td>2</td>
<td>4.2(18)</td>
<td>376</td>
</tr>
<tr>
<td>4</td>
<td>2.1(18)</td>
<td>246</td>
</tr>
<tr>
<td>6</td>
<td>1.0(18)</td>
<td>232</td>
</tr>
<tr>
<td>8</td>
<td>0.9(18)</td>
<td>217</td>
</tr>
<tr>
<td>10</td>
<td>0.8(18)</td>
<td>200</td>
</tr>
<tr>
<td>12</td>
<td>0.7(18)</td>
<td>188</td>
</tr>
<tr>
<td>14</td>
<td>0.7(18)</td>
<td>175</td>
</tr>
<tr>
<td>16</td>
<td>0.6(18)</td>
<td>165</td>
</tr>
<tr>
<td>18</td>
<td>0.6(18)</td>
<td>153</td>
</tr>
<tr>
<td>20</td>
<td>0.5(18)</td>
<td>143</td>
</tr>
</tbody>
</table>

### Table 2. Reactions and rate constants for Venus. Rate constants for 2- and 3-body reactions have units cm³ sec⁻¹ and cm² sec⁻¹, respectively. Planetary mean rates for photolysis have units sec⁻¹, and numerical values are presented for an approximate elevation of 30 km above the visible cloud deck.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂+CO₂</td>
<td>CO + O₂</td>
<td>J₈ = 1 x 10⁻¹⁸ (see text)</td>
</tr>
<tr>
<td>H₂+O₂</td>
<td>O₂ + O₂</td>
<td>J₈ = 1 x 10⁻⁴ (see text)</td>
</tr>
<tr>
<td>H₂+H₂O</td>
<td>H₂O + H₂</td>
<td>J₈ = 1 x 10⁻⁹ (see text)</td>
</tr>
<tr>
<td>H₂+H₂</td>
<td>H₂ + O₂</td>
<td>J₈ = 1 x 10⁻⁷ (see text)</td>
</tr>
<tr>
<td>H₂+Cl₂</td>
<td>Cl₂ + Cl</td>
<td>J₈ = 1 x 10⁻⁸ (see text)</td>
</tr>
<tr>
<td>CO₂+CO₂</td>
<td>CO₂ + CO₂</td>
<td>k₈ = 2 x 10⁻¹⁷ (a)</td>
</tr>
<tr>
<td>O₂+O₂</td>
<td>O₂ + O₂</td>
<td>k₈ = 3 x 10⁻¹⁴ (T/300)⁻¹⁻¹ (b)</td>
</tr>
<tr>
<td>H₂+H₂O</td>
<td>H₂O + H₂</td>
<td>k₈ = 2 x 10⁻¹⁴ (T/273)⁻¹⁻¹ (c)</td>
</tr>
<tr>
<td>H₂+O₂</td>
<td>O₂ + H₂</td>
<td>k₈ = 7 x 10⁻¹⁵ (d)</td>
</tr>
<tr>
<td>CO₂+OH</td>
<td>CO₂ + H₂</td>
<td>k₈ = 9 x 10⁻¹⁵ exp(-500/T) (e)</td>
</tr>
<tr>
<td>H₂+OH</td>
<td>OH + H₂</td>
<td>k₈ = 2.6 x 10⁻¹⁵ (f)</td>
</tr>
<tr>
<td>O₂+O₂</td>
<td>O₂ + O₂</td>
<td>k₈ = 1.4 x 10⁻¹⁵ (T/300)⁻¹⁻¹ (g)</td>
</tr>
<tr>
<td>O₂+OH</td>
<td>O₂ + OH</td>
<td>k₈ = 5 x 10⁻¹¹ (h)</td>
</tr>
<tr>
<td>HO₂+H₂O</td>
<td>HO₂ + H₂O</td>
<td>k₈ = 9.5 x 10⁻¹¹ (i)</td>
</tr>
<tr>
<td>H₂+Cl₂</td>
<td>Cl₂ + H₂</td>
<td>k₈ = 1 x 10⁻¹¹ (j)</td>
</tr>
<tr>
<td>OH+H₂O</td>
<td>OH + H₂O</td>
<td>k₈ = 2 x 10⁻¹⁰ (k)</td>
</tr>
<tr>
<td>H₂+CO₂</td>
<td>H₂ + CO₂</td>
<td>k₈ = 2.6 x 10⁻¹⁰ (l)</td>
</tr>
<tr>
<td>Cl₂+H₂</td>
<td>Cl₂ + H₂</td>
<td>k₈ = 8 x 10⁻¹⁰ exp(-2480/T) (m)</td>
</tr>
<tr>
<td>Cl₂+Cl₂</td>
<td>Cl₂ + Cl₂</td>
<td>k₈ = 2.7 x 10⁻¹⁰ (n)</td>
</tr>
</tbody>
</table>

Above 20 km, OH and HOCI are controlled by $k_8$ and $k_{13}$, and

$$[\text{H}] = \frac{J_4[\text{CO}_2]}{k_8[\text{HOCI}][\text{CO}_2]},$$

$$[\text{OH}] = \frac{k_{13}[\text{CO}_2]}{k_8[\text{O}_2][\text{CO}_2][J_4[\text{HOCI}]+J_4[\text{H}_2\text{O}]]},$$

$$[\text{O}] = \frac{J_1}{2k_8}.$$

Relation (18) holds approximately for the height ranges as indicated and provide a valuable analytic framework for interpretation of the detailed numerical results. We note in particular that the rates given here imply that the rate $R$ for recombination of CO can be approximated by

$$R(\text{CO}) = \frac{k_9k_{11}[\text{O}_2][\text{CO}_2][J_4[\text{H}_2\text{O}]+J_4[\text{HCl}]]}{k_9k_{10}[\text{CO}]},$$

for the height ranges 0–6 km, 6–18 km, and above 20 km respectively. Recombination of CO takes place primarily below 20 km. Both (1) and (2) are important and the height-integrated rate for recombination of CO varies approximately as $f_{O_2}$ where $f_{O_2}$ is the mixing ratio of O$_2$. It is interesting to note that the height-integrated rate for recombination of CO is essentially independent of $f_{O_2}$ if loss of odd hydrogen proceeds mainly by (13) (see Appendix A), in which case H$_2$ cannot be conserved.

The relative rates for production of H$_2$O and H$_2$ depend on the abundances of OH and H. Most of the H$_2$O is formed below 5 km where the formation rate is given by

$$R(\text{H}_2\text{O}) = 2k_9k_{11}[\text{O}_2][\text{CO}_2][J_4[\text{H}_2\text{O}]+J_4[\text{HCl}]],$$

The height-integrated rate for production of H$_2$O is thus directly proportional to $k_{11}f_{O_2}$ and inversely proportional to $k_{18}f_{CO}$.

Dissociation of CO$_2$ above 20 km is followed by production of O$_2$, which is transported to lower altitudes and removed mainly by (2). Approximately half the oxygen formed by photolysis of CO$_2$ recombines by (1), the remainder by (2).

4. Results

Figure 1 shows planetary mean rates for photodissociation of CO$_2$, HCl and H$_2$O. These results were obtained with the dry atmospheric model in which the mixing ratios of HCl and H$_2$O are $7.5 \times 10^{-7}$ and $1.0 \times 10^{-6}$, respectively. The atmospheric capacity is due primarily to CO$_2$, and results for H$_2$O and HCl can be readily scaled to allow for different mixing ratios of these species. In particular, dissociation rates for H$_2$O in the wet model, for which the H$_2$O mixing ratio is $5 \times 10^{-6}$, are simply obtained by multiplying the relevant data in Fig. 1 by a factor of 50. Effects of cloud opacity were not explicitly considered in the present calculations but are not expected to seriously modify the conclusions.

The results shown here differ in at least one important respect from calculations presented earlier by Prinn (1971). We note that dissociation of CO$_2$ is significant at all altitudes in Fig. 1. In contrast, Prinn's analysis assumed that dissociation of CO$_2$ should be negligible below 20 km. The discrepancy is attributed to differences in the choice of absorption cross section for CO$_2$. Prinn (1971) used data summarized by Schultz and Holland (1963) and treated only absorption at wavelengths $< 1795 \ \text{Å}$. The present analysis uses Shemansky's more recent cross sections (1972). We assumed that the quantum yield from CO$_2$ photolysis was unity at wavelengths $> 1670 \ \text{Å}$, as suggested by Inn and Heimerl (1971). Dissociation in the height range 0–20 km is primarily due to absorption of radiation in the wavelength band 1975–2075 Å.
The height-integrated rate for photolysis of H2O in the dry model is small compared with the height-integrated rate for photolysis of HCl. It is consequently difficult to find a balance for H2O in the dry model. We must choose the parameters in such a way as to minimize production of H2O at low altitudes. In our judgment, the most uncertain parameters are $f_{O_2}$, $k_{10}$ and $k_{11}$, arranged in order of increasing uncertainty. But, the ratio $f_{O_2}/k_{10}$ is fixed by the need to find a balance for CO [see Eq. (25)]. Production of H2O, as given by (28), varies as $k_{11}/f_{O_2}/k_{10}$. It follows that only $k_{11}$ is at our disposal in order to optimize the photochemical solution. We chose $k_{11} = 10^{-10}$ cm$^3$ sec$^{-1}$ for the dry model, a factor of 2 less than the room temperature measurement reported by Hochanadel et al. (1972). The discrepancy could reflect an inaccuracy in the laboratory determination of the density of H02 and in order to cover this possibility we also adjusted the value of $k_3$. The value listed in Table 2 was taken from Hochanadel et al. In the dry model we took $k_3 = 3 \times 10^{-12}$ cm$^2$ sec$^{-1}$. Other parameters of the dry model are as listed in Table 2.

Densities for H, O, OH, H2O and H2O2 computed with the dry model are illustrated in Fig. 2. Densities of CO2 are also included for comparison. The mixing ratio of O2 is $9.4 \times 10^{-4}$, and the corresponding value for CO is $8.8 \times 10^{-5}$. The abundances of O2 and H2O2 are comparable at lower altitudes. The number density of H2O2 is $7.4 \times 10^{-6}$ cm$^{-3}$ at $z = 0$, which should be compared with number densities of $6.8 \times 10^{-3}$, $5.1 \times 10^{-4}$ and $6.4 \times 10^{-4}$ cm$^{-3}$ for H2O, HCl and O3, respectively.

Rates for some key reactions in the dry model are illustrated in Fig. 3. Molecular oxygen is formed mainly above 18 km, with the major contribution coming from $k_2$. Dissociation of CO2 below 18 km is balanced by recombination via the reaction sequence (1). The height-integrated rate for production of O2 is $3 \times 10^{-4}$ cm$^{-2}$ sec$^{-2}$, this production being balanced by removal through the reaction sequence (2). The height-integrated rate for production of H2 is $2.2 \times 10^{14}$ cm$^{-2}$ sec$^{-1}$, which should be compared with a computed loss rate of $2.3 \times 10^{14}$ cm$^{-2}$ sec$^{-1}$. Production of H2O exceeds removal of H2O by $1.3 \times 10^{20}$ cm$^{-2}$ sec$^{-1}$, and there is a similar small imbalance for CO.

Continuity of species requires upward fluxes of CO2 and H2 and corresponding downward fluxes of CO and H2O. The fluxes of individual species must be equal in magnitude and must have the common numerical value $1.3 \times 10^{20}$ cm$^{-2}$ sec$^{-1}$. The downward flux of CO is approximately equal to 0.1% of the total photolytic production of CO. Fluxes of this magnitude are readily transported vertically, provided that the vertical eddy coefficient$^1$ is greater than about $10^6$ cm$^2$ sec$^{-1}$. The chemical cycle should be completed in the hot lower atmosphere where there should be efficient conversion of CO and H2O to CO2 and H2 in the global reaction

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

The time constant associated with (29) can be readily estimated using data presented by Graven and Long (1954). The effective rate constant (cm$^3$ sec$^{-1}$) is given approximately by

$$k_{10} = 2 \times 10^9 \exp(-67.3/RT)[\text{CO}]^{-1},$$

and the time constant associated with (29) is approximately $2 \times 10^5$ sec at the surface of Venus if the mixing ratios of H2O and CO are taken equal to $8.8 \times 10^{-4}$. On the other hand, the time constant associated with the downward flux of CO and H2O from the upper atmosphere is much longer, approximately $10^{12}$ sec. It follows that the downward flux should introduce a trivial perturbation to conditions in the lower atmosphere, and the relative concentrations of CO, CO2, H2 and H2O should be consistent with thermodynamic equilibrium.

We can now estimate the mixing ratio of H2. If we assume that the relative concentrations of CO, CO2, H2

$^1$This value was derived under the assumption that the mixing ratio of H2 was approximately $10^5$. Note also, as discussed later, that a consideration of O3 chemistry reinforces the conclusion that the eddy coefficient must exceed $10^6$ cm$^2$ sec$^{-1}$. 

**Fig. 2.** Concentrations of H, OH, H02, H2O2, O and CO2 for the dry model.

**Fig. 3.** Production rates for key reactions leading to production of H2 (H+H+M and H+H02), O (O+OH and O+O+M), CO4 (CO+OH) and H2O (H02+OH), in the dry model.
and H₂O are controlled by (29) and its inverse, then

$$f_{\text{H}_2} = K f_{\text{H}_2O} / f_{\text{CO}}$$

(31)

where \( K \) is the appropriate equilibrium constant. Using data presented in the JANAF tables we find

$$f_{\text{H}_2} = 7 \times 10^{-6};$$

(32)

if

$$f_{\text{CO}} = f_{\text{H}_2O} = 8.8 \times 10^{-6}. $$

(33)

Chemical time constants for long-lived species (CO, O₂, CO₂, H₂, H₂O) are illustrated in Fig. 4; corresponding data for short-lived species (OH, H₂O₂, H, O, H₂O₂) are shown in Fig. 5. Fig. 5 also includes time constants for odd H, odd O and free Cl. The various time constants are defined in Appendix B. We note that the assumptions of the present model require that time constants in Fig. 4 must be long compared with time constants for vertical motion. In like manner, time constants in Fig. 5 must be short compared with dynamical times. For reference, we indicate in both Figs. 5 and 6 the dynamical time constants which would apply if vertical motion were characterized by an effective eddy coefficient \( K = 10^6 \text{ cm}^2 \text{ sec}^{-1} \). If the eddy coefficient had this value, then the present analysis would be valid over the height range 5–27 km. Odd hydrogen would be in dynamical equilibrium above 27 km. The distribution of O₂ below 5 km would be determined by a combination of chemistry and dynamics. Some small correction would be required for H, OH and HO₂ above 27 km but the correction would be generally trivial in the present context. The mixing ratio of O₂ would be an increasing function of height between 0 and 5 km, with a mean value of about \( 10^{-7} \). The mixing ratio of O₂ at higher altitudes could be somewhat higher than this value.

If the eddy coefficient were less than \( 10^6 \text{ cm}^2 \text{ sec}^{-1} \), a much larger correction would be required for lower altitude O₂. Indeed, as discussed in Appendix C, it would appear that physically acceptable solutions can be obtained only if the eddy coefficient exceeds \( 4 \times 10^4 \text{ cm}^2 \text{ sec}^{-1} \) over the height range 0–6 km. If the eddy coefficient were larger than \( 10^6 \text{ cm}^2 \text{ sec}^{-1} \) then the present analysis would be valid over the height range 5–27 km. Odd hydrogen would be in dynamical equilibrium above 27 km. The distribution of O₂ below 5 km would be determined by a combination of chemistry and dynamics. Some small correction would be required for H, OH and HO₂ above 27 km but the correction would be generally trivial in the present context. The mixing ratio of O₂ would be an increasing function of height between 0 and 5 km, with a mean value of about \( 10^{-7} \). The mixing ratio of O₂ at higher altitudes could be somewhat higher than this value.

Computed number densities for H, OH, H₂O₂, H₂O and O are shown in Fig. 6 for the wet model. The mixing ratios of H₂O₂, H₂O and HCl are \( 4.8 \times 10^{-5}, 4.8 \times 10^{-5}, 7 \times 10^{-8} \) and \( 8 \times 10^{-7} \), respectively. The height-integrated production rates for CO₂, O₂, H₂ and H₂O are, within tolerable limits, equal to the corresponding height integrated loss rates. The production rates are \( 1.1 \times 10^{13}, 3.2 \times 10^{12}, 2.5 \times 10^{11} \) and \( 3.7 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1} \) for CO₂, O₂, H₂ and H₂O, respectively. Volume rates for several important reactions are shown in Fig. 7. As in the dry model, O₂ is formed above 18 km by \( k_8 \) and \( k_8, \) and removed below 5 km by \( k_2, \) Water is formed at low altitudes by \( k_{11} \) and removed at the same rate at high altitudes by \( J_6, \) Molecular hydrogen is catalytically removed by Cl and reformed by \( k_{10} \) and \( k_{10} \)
Ozone is an exceedingly rare component in both wet and dry models. The column abundance is approximately $10^{-8}$ cm atm, with a peak concentration of about $3 \times 10^{13}$ cm$^{-3}$ at 10 km. The predicted concentration of O$_3$ depends critically on the concentration of O$_2$ above 10 km. The prediction is thus sensitive to the value of the eddy mixing coefficient at low altitudes. If the eddy coefficient is less than $3 \times 10^{4}$ cm$^2$ sec$^{-1}$, then the concentrations of O$_3$ and therefore O$_2$ will be larger than values derived here. The observational upper limit on the eddy mixing coefficient at low altitudes.

The recombination path is similar to that believed appropriate for Mars and is catalyzed by trace hydrogenous species such as H, OH, HO$_2$ and H$_2$O$_2$. Carbon monoxide is removed by

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}, \quad (34)$$

with OH formed either by

$$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2, \quad (35)$$

or

$$h\nu + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}. \quad (36)$$

We did not explicitly treat possible catalysis of CO recombination by trace quantities of free chlorine. Prinn (1971) suggested that the dominant path for recombination of Venus CO$_2$ might be

$$\text{Cl} + \text{O}_2 + \text{CO}_2 \rightarrow \text{ClOO} + \text{CO}_2, \quad (37)$$

followed by

$$\text{ClOO} + \text{CO} \rightarrow \text{ClO} + \text{CO}_2, \quad (38)$$

and

$$\text{ClO} + \text{CO} \rightarrow \text{Cl} + \text{CO}_2. \quad (39)$$

Omission of these reactions in the present context should not be interpreted to reflect a judgment regarding their possible importance. They were omitted primarily due to the lack of relevant laboratory data.

5. Concluding remarks

We have presented a model for the photochemistry of the Venus atmosphere which satisfactorily accounts for the stability of CO$_2$. The recombination path is similar to that believed appropriate for Mars and is catalyzed by trace hydrogenous species such as H, OH, HO$_2$ and H$_2$O$_2$. Carbon monoxide is removed by

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}, \quad (34)$$

with OH formed either by

$$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2, \quad (35)$$

or

$$h\nu + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}. \quad (36)$$

We did not explicitly treat possible catalysis of CO recombination by trace quantities of free chlorine. Prinn (1971) suggested that the dominant path for recombination of Venus CO$_2$ might be

$$\text{Cl} + \text{O}_2 + \text{CO}_2 \rightarrow \text{ClOO} + \text{CO}_2, \quad (37)$$

followed by

$$\text{ClOO} + \text{CO} \rightarrow \text{ClO} + \text{CO}_2, \quad (38)$$

and

$$\text{ClO} + \text{CO} \rightarrow \text{Cl} + \text{CO}_2. \quad (39)$$

Omission of these reactions in the present context should not be interpreted to reflect a judgment regarding their possible importance. They were omitted primarily due to the lack of relevant laboratory data. Prinn's scheme could be important, however, and would proceed in addition to, but not in competition with, the hydrogenous scheme emphasized here. In particular, our estimates for the mixing ratio of O$_3$ could be too high if (37)-(39) are found to be important for Venus.

Free chlorine can also catalyze recombination of CO and O. The reaction sequence (37) followed by

$$\text{ClOO} + \text{O} \rightarrow \text{ClO} + \text{O}_2 \quad (40)$$

and (39) offers a recombination path which could proceed in addition to (1) and which might be important below about 10 km. Some indirect support for (37) and (40) can be obtained from a laboratory study of oxygen recombination in the presence of Cl$_2$. Kaufman (1958) concluded that his data could be understood if (40) were fast, and if the rate constant for (37) were of order $10^{-31}$ cm$^6$ sec$^{-1}$. There is, however, no direct evidence for the reactions with CO$_2$ and CO, although other chlorine reactions have been involved in a variety of contexts as discussed by Kaufman (1958). If it turns out that (37), (39) and (40) are indeed important, then densities of atomic oxygen and ozone will be less than values computed in the present paper at altitudes below about 10 km. Other features of the present work would be unaltered, however. In particular, dissociation of CO$_2$ above 20 km would still be expected to lead mainly to formation of O$_2$ which must be removed by (2) and its chlorine equivalent (37)-(39).

The mixing ratio of O$_3$ in the vicinity of the Venus cloud deck must be small, of order $10^{-7}$ or less. Otherwise, dissociation of HCl and subsequent chemistry would lead to production of unacceptably large quantities of H$_2$O. Our predictions for O$_3$ are consistent with the observational limit imposed by Traub and Carleton (1973). We noted, however, that O$_3$ may not be homogeneously mixed with CO$_2$ throughout the upper atmosphere of Venus.

The abundance of H$_2$O in the atmosphere of Venus is uncertain. We argued that H$_2$O must be at least as abundant as CO in the bulk of the atmosphere and most of the Venus H$_2$O could be formed as a by-product of upper atmospheric chemistry.

The present work should impose important constraints on attempts to model the chemistry of sulphur in the atmosphere of Venus, a matter of importance in
view of the recent suggestion by Young (1973) regarding the composition of the clouds. The rate for formation of H$_2$SO$_4$ may be limited by the available supply of O$_3$.

Acknowledgments. This work was supported by the Atmospheric Sciences Division of the National Science Foundation under Grant GA3390X to Harvard University. We thank the Harvard High Energy Group for permission to use their computer (on a low priority basis, of course) for the low energy research described here. The computer is supported by AEC Contract AT (11-1)-3064. We are indebted to Mark Rosen for helpful comments.

APPENDIX A

The Chemical Model

The detailed chemical model adopted for present purposes is summarized in Table 2. We assume that chemical equilibrium holds for Cl, Cl$_2$, H, OH, H$_2$O, H$_2$O$_2$, and O. Then

\[ J_{21}[\text{Cl}]+2J_{21}[\text{Cl}_2] = 2k_{16}[\text{Cl}][\text{CO}_2]+k_{11}[\text{Cl}][\text{H}_2], \]  
(A1)

\[ k_{16}[\text{Cl}][\text{CO}_2] = J_{21}[\text{Cl}_2], \]  
(A2)

\[ k_{6}[\text{CO}][\text{OH}]+k_6[\text{O}][\text{OH}] + 2J_{21}[\text{Cl}]+J_{21}[\text{H}_2] = k_6[\text{H}][\text{O}][\text{CO}_2]+(k_{10}+k_{12})[\text{H}][\text{H}_2][\text{O}_2] \]  
(A3)

\[ 2k_6[\text{H}_2][\text{O}]+J_{21}[\text{H}_2][\text{O}]+2k_{11}[\text{H}][\text{O}][\text{CO}_2] = k_6[\text{CO}][\text{OH}]+k_{11}[\text{H}][\text{O}][\text{H}_2] \]  
(A4)

\[ k_3[\text{H}][\text{O}][\text{H}_2][\text{O}_2] = (k_{10}+k_{12})[\text{H}][\text{H}_2][\text{O}_2]+k_{11}[\text{OH}][\text{H}_2][\text{O}_2] \]  
(A5)

\[ k_{17}[\text{H}][\text{H}_2][\text{O}_2][\text{O}_2] = 2k_4[\text{H}][\text{O}][\text{H}_2][\text{O}_2]+k_{11}[\text{OH}][\text{H}_2][\text{O}_2]+k_6[\text{O}][\text{OH}]. \]  
(A6)

We can combine (A1), (A2) to give (11), where

\[ p(\text{HCl}) = k_{16}[\text{Cl}][\text{H}_2]-J_{21}[\text{H}_2]. \]  
(A8)

\[ p(\text{H}^3) = k_{16}[\text{H}][\text{H}_2][\text{O}_2]+k_{17}[\text{H}][\text{H}_2][\text{O}_2]-J_{21}[\text{H}_2]. \]  
(A9)

\[ p(\text{H}_2)[\text{O}][\text{H}_2][\text{O}_2] = k_{16}[\text{H}][\text{H}_2][\text{O}_2]-J_{21}[\text{H}_2]. \]  
(A10)

In like manner (A4) and (A5) imply (10) with

\[ p(\text{CO}) = k_{16}[\text{CO}][\text{OH}]-J_{21}[\text{CO}_2]. \]  
(A11)

\[ p(\text{O}_2) = k_{16}[\text{O}][\text{O}][\text{CO}_2]+k_{17}[\text{O}][\text{OH}]-k_6[\text{O}][\text{OH}]. \]  
(A12)

Reactions involving O$_3$ are generally unimportant for Venus, and have been omitted in Eqs. (A1)-(A11). These reactions were, however, included in the detailed numerical calculations described earlier in this paper. We introduce here a number of additional approximations in order to provide a simple analytic framework for interpretation of the detailed numerical results. Below 6 km the relative concentrations of H, OH and H$_2$O are controlled by $k_5$, $k_7$, $k_9$, $k_{12}$ and $J_{21}$. Above 8 km, the relative concentrations of H, OH, H$_2$O and O are controlled by $k_5$, $k_7$, and $k_9$.

Below 20 km, we have

\[ \frac{[\text{OH}]}{[\text{H}]} = \frac{k_6[\text{O}][\text{CO}_2]+k_{17}[\text{H}_2][\text{O}_2]}{k_{16}[\text{CO}][\text{OH}]-k_6[\text{O}][\text{OH}].} \]  
(A13)

Below 6 km, we have

\[ k_{17}[\text{H}]+k_7[\text{O}][\text{OH}]. \]  
(A14)

Thus

\[ \frac{[\text{HO}_2]}{[\text{OH}]} \approx \frac{k_{17}[\text{H}]+k_7[\text{O}]}{2k_4}. \]  
(A15)

Above 6 km we have (A14) in the reverse direction and

\[ \frac{[\text{H}_2][\text{O}_2][\text{O}_2]}{[\text{OH}]} \approx \frac{k_{16}[\text{H}][\text{H}_2][\text{O}_2]}{k_{17}[\text{H}]+k_4[\text{O}]} \]  
(A15')

If $k_{17}[\text{OH}]/k_{16}[\text{H}] < 1$, that is, if

\[ \frac{f_{\text{OH}}}{f_{\text{CO}}} \approx \frac{k_{17}[\text{H}]}{k_6[\text{O}][\text{OH}]-k_6[\text{O}][\text{OH}].} \]  
(A16)

where $f_{\text{OH}}$ and $f_{\text{CO}}$ are mixing ratios of O$_2$ and CO, respectively, then the equation for odd H is simply

\[ k_{16}[\text{H}][\text{H}_2][\text{O}_2] \approx J_{21}[\text{H}_2][\text{O}][\text{H}_2]. \]  
(A17)

Expressions (14)-(16) can be readily derived using (A13), (A15) and (A17); expressions (17)-(20), which are appropriate in the height range 6-18 km, can be derived using (A13), (A15), (A17) and (A7). The bulk of the total CO recombination in the Venus atmosphere
occurs below 18 km and is satisfactorily approximated by (26) and (27). Note that recombination of CO below 20 km is essentially independent of the value for the mixing ratio of CO.

We consider now the alternate case in which H recombination leads to production of H$_2$O. In this case we have

$$k_1 k_{f0} [CO] \gg k_9 k_{f0} CO.$$  

(A22)

As before, the expressions for [H], [OH] and [HO$_2$] assume different limiting forms depending on whether HO$_2$ is cycled by $k_7$ or $k_4+k_{12}$. In the first case we have

$$[HO_2] = \left\{ \frac{k_3 [CO] (J_3 [H_2O] + J_4 [HCl])}{2 k_9 k_{11}} \right\}^{1/3},$$  

(A23)

$$[H] = \frac{2 k_9 k_{11} [CO] (J_3 [H_2O] + J_4 [HCl])^{1/3}}{k_1 J_1 [CO_2]},$$  

(A24)

$$[OH] = \frac{2 k_9 k_{11} [CO] (J_3 [H_2O] + J_4 [HCl])^{1/3}}{k_1 J_1 [CO_2]}.$$  

(A25)

In the second case

$$[HO_2] = \frac{k_3 [CO] (J_3 [HCl] + J_4 [H_2O])}{k_1 J_1 [CO_2]},$$  

(A26)

$$[H] = \frac{J_3 [CO]}{k_3 [CO_2]},$$  

(A27)

$$[OH] = \frac{J_4 [CO]}{k_3 [CO]},$$  

(A28)

$$[O] = \frac{k_1 \{J_3 [CO_2]\}^2}{k_3 \{J_3 [CO_2]\} (J_3 [HCl] + J_4 [H_2O])}.$$  

(A29)

As before, (A23)–(A25) are valid mainly below 6 km and (A26)–(A29) apply between 6 km and 18 km. The corresponding expressions for the CO recombination rate are

$$R(CO) = 2 k_9 k_{11}^3 k_{f0}^{-4} [CO]^{1/3} (J_3 [H_2O] + J_4 [HCl]),$$  

(A30)

$$R(CO) = J_3 [CO_2].$$  

(A30')

Above 20 km, $k_3 [CO] << k_8 [O]$, and the relative concentrations of H, OH and HO$_2$ are controlled by $k_3$, $k_4$ and $k_8$. Then

$$[OH] = \frac{k_3 [O_2] [CO_2]}{[H]},$$  

(A31)

$$[OH] = \frac{k_4}{[H_2O]},$$  

(A32)

and

$$k_9 [H] [CO_2] \approx J_3 [HCl] + J_3 [H_2O].$$  

(A33)

The photochemical equations can now be solved to give the approximate results given by (21)–(24) which are identical in both wet and dry models.

The rate for recombination of CO is given by (27) and

$$R(O_2) = \frac{1}{2} J_3 [CO_2].$$  

(A34)

**APPENDIX B**

**Time Constants**

The time constants for CO$_2$, CO, H$_2$O, O$_2$, H, OH, HO$_2$ and H$_2$O$_2$ can be calculated in the usual way. The time constants for O$_2$, H$_2$, odd O, odd H and Cl are calculated from the following expressions:

$$\tau_{O_2} = \frac{[O_2]}{k_9 [HO_2]^2 + k_{12} [H] [HO_2]},$$  

(B1)

$$\tau_{H_2} = \frac{[H_2]}{J_4 [HCl]},$$  

(B2)

$$\tau_{odd O} = \frac{[O] + [OH]}{2 k_9 [O] [CO_2] + k_3 [OH][CO] + 2 k_3 [OH][O] + k_1 [OH][HO_2]},$$  

(B3)

$$\tau_{odd H} = \frac{[H] + [OH] + [HO_2]}{2 k_9 [H][HO_2] + 2 k_1 [OH][HO_2] + 2 k_{12} [H][CO_2] + 1}{k_{14} [H_2]},$$  

(B4)

In these calculations $f_{H_2}$ is taken to be $7.5 \times 10^{-8}$ as estimated from thermodynamic equilibrium on the surface of Venus.
APPENDIX C

Molecular Oxygen

The concentration of O$_2$ is given by

$$\frac{d\phi}{dz} = p - Ln,$$

$$\phi = -K \left( \frac{dn}{dz} + \frac{dT}{dz} + \frac{n}{dz} \right)$$

where $\phi$, $n$ are the flux and number density of O$_2$.

In order to analytically approximate the solution we take

$$p = 0$$

$$L = \tau_e^{-1} = 5 \times 10^{-8} \text{ sec}^{-1}$$

where $\tau_e$ is the mean chemical time constant for O$_2$ in the height range 0–6 km where O$_2$ may not be well mixed. Little error is introduced by this procedure.

The boundary conditions appropriate for the present context are

$$\phi(z=6 \text{ km}) = -3 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$$

$$n(z=0 \text{ km}) = 10^{-7} \text{[CO}_2\text{]}$$

The condition on $\phi$ is set by the column production rate of O$_2$ above 18 km. The condition on $n$ is set by the requirement that we should have an overall balance for various species. Solutions for various $K$ are shown in Fig. 8. Acceptable solutions must have $\phi < 0$ or $df_{O_2}/dz > 0$ over the height range of interest. It follows that consistent O$_2$ profiles are obtained only for $K > 4 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$.

![Fig. 8. Mixing ratios of O$_2$ for various eddy coefficients.](image-url)

Schultz, E. D., and A. C. Holland, 1963: The solar flux incident at the top of the atmospheres of earth and neighboring planets for the spectral range 50 Å to 3000 Å. NASA CR-11, Washington, D. C.


