CO$_2$ on Titan

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A sharp stratospheric emission feature at 667 cm^{-1} in the Voyager infrared spectra of Titan is associated with the ν_2 Q branch of CO$_2$. A coupling of photochemical and radiative transfer theory yields an average mole fraction above the 110 mbar level of $f_{CO_2} = 1.5 \pm {}^{1.5}_{0.8} \times 10^{-9}$, with most of the uncertainty being due to imprecise knowledge of the vertical distribution. CO$_2$ is found to be in a steady state, with its abundance being regulated principally by the ~72 K cold trap near the tropopause and secondarily by the rate at which water-bearing meteoritic material enters the top of the atmosphere. An influx of water about 0.4 times that at the top of the terrestrial atmosphere is consistent with a combination of the observed CO$_2$ abundance and a steady state CO mole fraction of 1.1×10^{-4}; the theoretical value for CO is close to the value observed by Lutz et al. (1983), although there are large margins for error in both numbers. If steady state conditions for CO prevail, little information is available regarding the evolution of Titan's atmosphere.

INTRODUCTION

Over sixteen separate molecular emission features have been observed in the stratosphere of Titan from spectra obtained by the Voyager 1 infrared spectrometer (IRIS) [cf. *Hanel et al.*, 1981; *Maguire et al.*, 1981; *Kunde et al.*, 1981]. The great majority have sharp Q branches associated with the hydrocarbons CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_3$H$_4$, C$_3$H$_8$, C$_4$H$_2$, and nitriles HCN, HC$_3$N, C$_2$N$_2$. An exception is the broad ν_9 band of C$_2$H$_6$ centered at 821 cm^{-1}. Of these organic species, the five least abundant (C$_3$H$_4$, C$_4$H$_2$, HCN, HC$_3$N, C$_2$N$_2$) all show a rapid decrease in abundance in progressing from high to mid-northern latitudes. HC$_3$N and C$_2$N$_2$, in fact, fall below detection limits by about latitude 60°N. Emission features of HCN and the two hydrocarbons become steadily weaker down to about 60°S, beyond which reliable data are not available.

With one exception, the few remaining unidentified sharp line features in the spectra also display the same decreasing strength from north to south. This is physically inevitable if they are signatures of products chemically derived from the higher hydrocarbons and nitriles that exhibit the latitudinal behavior described above. The single exception is a weak but well-defined sharp feature at 667 cm^{-1} (Figure 1), the latitudinal variation of strength of which closely mimics that of the 1304 cm^{-1} ν_4 band of CH$_4$. Because CH$_4$ should be uniformly mixed, the molecule responsible for the 667 cm^{-1} feature should also be uniformly distributed globally, and any variation of appearance of the two bands with latitude would be the result of latitudinal temperature variations. This apparent uniformity across the disk, implied by the 667 cm^{-1} feature, is inexplicable if the associated molecule is chemically derived from either the higher hydrocarbons or nitriles. Thus the 667 cm^{-1} feature cannot correspond to an organic molecule of low abundance.

It is equally improbable that the feature is the signature of a high abundance organic. Photochemical studies by *Strobel* [1974] and Y. L. Yung et al. (unpublished manuscript, 1982) do not predict any organic molecule with a feature at 667 cm^{-1}. Our own laboratory spectra of hydrocarbons and nitriles have included all the identified species as well as CH$_3$CN (methyl cyanide), C$_3$H$_6$ (propene), C$_4$H$_6$ (bivinyl), C$_4$H$_8$ (1-butene), and C$_4$H$_{10}$ (butane). None exhibits a feature near 667 cm^{-1}. Laboratory simulation studies by *Chang et al.* [1978] and *Gupta et al.* [1981] have reproduced the molecules identified in the IRIS spectra, but little else. The latter group had the advantage of knowing the correct initial conditions from the Voyager 1 results [*Hanel et al.*, 1981; *Tyler et al.*, 1981; *Broadfoot et al.*, 1981], enabling them to restrict their simulated Titan atmospheres to 1–4% CH$_4$, with N$_2$ comprising the remainder. They carried out experiments using UV radiation, electric discharges, an electron beam, γ ray radiation, and a proton beam as energy sources. In addition to the molecular species identified by IRIS, they found only two other molecules in trace amounts: CH$_3$CN and C$_3$H$_6$; neither has a feature at 667 cm^{-1}.

IDENTIFICATION AND RATIONALE

By this process of elimination we have been led to consider seriously the identification of the 667 cm^{-1} feature as the ν_2 Q branch of CO$_2$. The position of the feature is correct to within the accuracy of reading the data (see Figure 2). The band is very strong and readily observable for concentrations as low as 10^{-9} (mole fraction). On the other hand, CO$_2$ cannot be vertically homogeneous throughout the atmosphere with an abundance regulated solely by the ~72 K cold trap at the tropopause. Radiative transfer calculations indicate that the strength of the 667 cm^{-1} feature would be below the detection threshold under these conditions. If the cold trap does operate to condense CO$_2$, there must also be a relatively effective means of chemically producing CO$_2$ in the stratosphere or above. The resulting stratospheric enhancement of CO$_2$ requires a source of oxygen in a basically reducing atmosphere.

Two plausible sources suggest themselves. One is primordial CO trapped in the lattice structure of a water ice clathrate as it formed from the solar nebula. According to *Prinn and Fegley* [1981], the primordial CO/N$_2$ ratio predicted for such a clathrate at Jovian distances from the sun is

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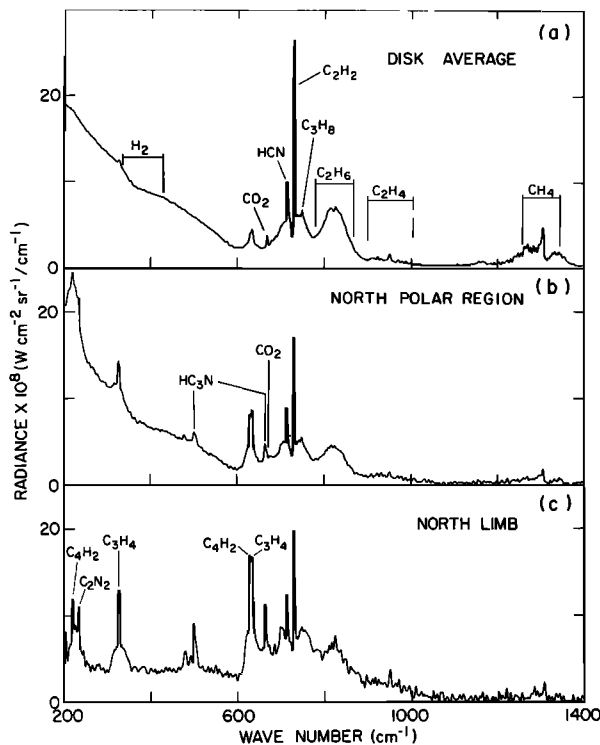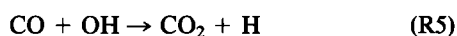
Fig. 1. Averages of (a) 346 low latitude, (b) 30 north polar region, and (c) three north limb spectra, showing the various identifications of stratospheric emission features. The 667 cm⁻¹ feature can be seen as a minor shoulder to the 663 cm⁻¹ HC₃N feature in the lower two panels, although it is completely unblended in the disk average because of the low abundance of HC₃N at low latitudes.
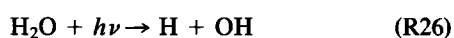
between 0.007 and 0.3, depending upon whether there was, respectively, negligible or extensive radial mixing of the circumplanetary nebula at the time of clathrate formation. Comparable ratios should be valid at Saturnian distances. If a significant fraction of the N_2 presently found in Titan's atmosphere is primordial in origin [*Owen*, 1982; *Strobel*, 1982] (as opposed to photochemically derived from NH_3, for example, *Atreya et al.* [1978]), it is probable that significant amounts of CO would also be contained in the present atmosphere, even after allowing for photochemical and charged-particle destruction of both N_2 and CO over geologic time. Because of the high vapor pressure, a CO mole fraction as large as 0.2 could exist, despite the cold trap at the tropopause, and the gas would become uniformly mixed throughout the atmosphere. The recent detection of CO on Titan by *Lutz et al.* [1983] demonstrates its availability and provides further support for our identification of CO_2.

A second potential source of oxygen is associated with a steady state water influx from outside the atmosphere. In addition to the water contained in chondritic meteorites, a certain amount might also be available from sputtering and collisions connected with the icy satellites and rings.
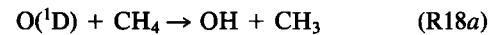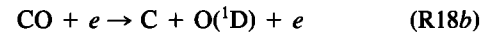
These two sources are expected to contribute to the production of CO_2, mainly through the reaction

$$CO + OH \rightarrow CO_2 + H \qquad (R5)$$

where the OH radical is produced in part from

$$H_2O + h\nu \rightarrow H + OH \qquad (R26)$$

and partly from

$$CO + e \rightarrow C + O(^1D) + e \qquad (R18b)$$

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (R18a)$$

where $O(^1D)$ is the excited state of atomic oxygen.

In order to test these ideas quantitatively it is necessary to adopt an iterative procedure: first, guessing the abundance of CO (and the H_2O influx rate) and then calculating the vertical distribution of CO_2 with the aid of a photochemical model. This distribution is then used in conjunction with the IRIS data and a radiative transfer model to infer a total CO_2 abundance, after which the photochemical model is iterated to derive the corresponding abundances of CO and H_2O. Fortunately, the CO_2 vertical distribution is not particularly sensitive to its total abundance, and further iteration is not required.

ABUNDANCE DETERMINATION

Because the P and R branches blend into the observed continuum, only that part of the Q branch of the ν_2 band that projects above the tops of the P and R branches is available for a radiative transfer analysis. Synthetic spectra were generated from a line-by-line program for isothermal atmospheres of 140 K and 170 K, with an underlying base at 75 K to provide contrast. About 85% of the Q branch projected above the P and R branch 'continuum.' The inferred reduced band strength was $S^Q = 3.4 \times 10^{-18}$ cm mol⁻¹ at 140 K and about 23% greater at 170 K.

A model atmosphere was then constructed by using the temperature profile shown in Figure 3 and the shape of the CO_2 abundance profile derived from our photochemical model, discussed in the following section. The weak line approximation formulated by *Maguire et al.* [1981] was adopted for preliminary radiative transfer calculations. An iterative procedure for repeated solution of the transfer equation was constructed along lines developed by *Samuelson et al.* [1981]; each iteration produces a multiplier by which the assumed vertical distribution of CO_2 is adjusted until convergence to the observed band intensity is reached. The weak line solution was then corrected to the exact solution with the complete line-by-line program [*Kunde and Maguire*, 1974]. The mole fraction derived for CO_2 is

$$f_{CO_2} = 1.5 \pm {}^{1.5}_{0.8} \times 10^{-9} \text{ (estimated error)}$$

where f_{CO_2} is averaged over a column extending from the tropopause at about 110 mbar (cf. Figure 3) to the top of the atmosphere. The corresponding column density of CO_2 is 2.9 $\times 10^{16}$ molecules cm⁻². Most of the error is due to uncertain-
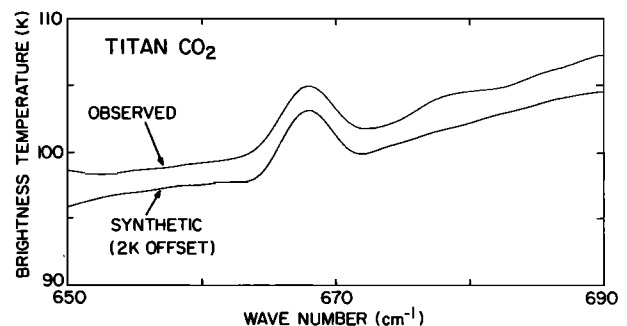

Fig. 2. Position comparison of observed 667-cm⁻¹ feature and computed ν_2 Q branch of CO_2.
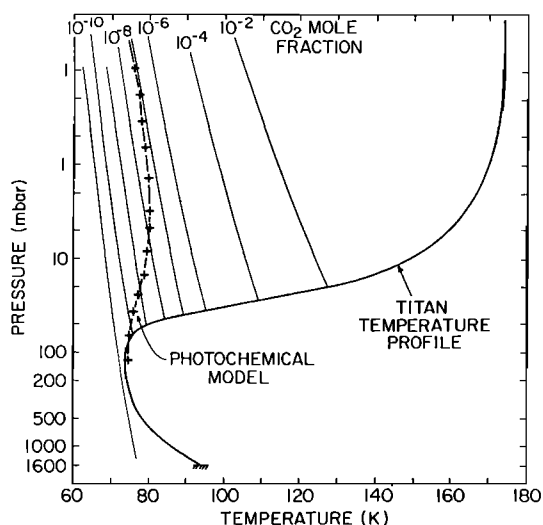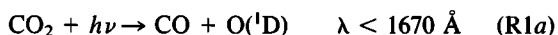
Fig. 3. CO_2 abundance profile (dashed curve) and temperature profile (solid curve) of Titan's atmosphere. The CO_2 mole fraction f_{CO_2} at any pressure level can be inferred by interpolating among curves of constant mole fraction. The weighted average above 110 mbar is $f_{CO_2} \sim 1.5 \times 10^{-9}$, obtained by dividing the column number density of CO_2 above that level by the corresponding atmospheric column density. Tangency of the temperature and abundance curves near the tropopause implies a CO_2 steady state regulated by (1) chemical production and (2) loss through condensation and attendant precipitation.

ties in the vertical distribution and cannot be determined with precision.

PHOTOCHEMISTRY OF CO_2

In the presence of ultraviolet radiation, carbon dioxide readily dissociates, according to the reactions [*Okabe*, 1978; *Yung and DeMore*, 1982]

$$CO_2 + h\nu \rightarrow CO + O(^1D) \qquad \lambda < 1670 \text{ Å} \qquad (R1a)$$

$$\rightarrow CO + O \qquad 1670 \text{ Å} < \lambda < 2060 \text{ Å} \qquad (R1b)$$

where $O(^1D)$ and O denote the excited (^1D) and ground (^3P) states of oxygen, respectively. In addition to photolysis, CO_2 can also be removed by reaction with the ground-state methylene radical

$$CO_2 + CH_2 \rightarrow H_2CO + CO \qquad (R19)$$
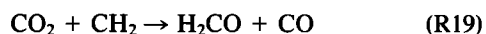
[*Laufer*, 1981]. The primary fate of $O(^1D)$ produced in (R1a) is either quenching by N_2

$$O(^1D) + N_2 \rightarrow O + N_2 \qquad (R17)$$
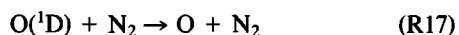
or reaction with a hydrocarbon

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \qquad (R8a)$$
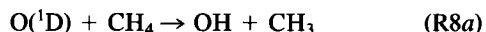
Thus the oxygen atom derived from CO_2 photolysis either remains as an oxygen atom (in the ground state) or is converted into a hydroxyl radical OH.

The most likely fate of an oxygen atom in the upper atmosphere of Titan is to participate in the formation of CO. Abstraction of a hydrogen atom from either H_2 or an alkane by an oxygen atom is possible in principle, as is illustrated by

$$O + CH_4 \rightarrow OH + CH_3 \qquad (R10)$$

$$O + H_2 \rightarrow OH + H \qquad (R11)$$

but these reactions have high activation energies and are exceedingly slow at temperatures appropriate for Titan. Abstraction of a hydrogen atom by oxygen from the alkenes and alkynes is endothermic. The oxygen atom, however, reacts rapidly with the hydrocarbon radicals via

$$O + CH_2 \rightarrow CO + 2H \qquad (R12)$$

$$O + CH_3 \rightarrow H_2CO + H \qquad (R13)$$
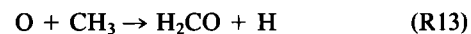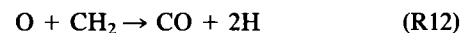
Formaldehyde is not stable and dissociates by absorption of visible sunlight in accordance with the reactions

$$H_2CO + h\nu \rightarrow H_2 + CO \qquad (R3a)$$

$$\rightarrow H + HCO \qquad (R3b)$$

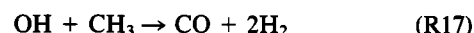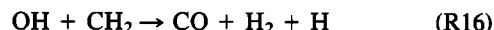$$HCO + h\nu \rightarrow H + CO \qquad (R4)$$
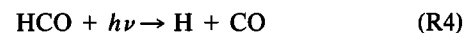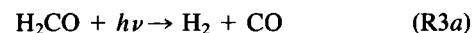
A search for a pathway to convert O to OH via reactions with the hydrocarbons and their radicals has been made (see the more extended table of reactions in Y. L. Yung et al., unpublished manuscript, 1982), but no simple and convincing reaction has been discovered. This conclusion is in essential agreement with those of *Herron and Huie* [1973], *Strobel and Yung* [1979], and *Prather et al.* [1978].

The chemistry of OH is crucial for restoring CO_2. The radical reacts readily with CO to form CO_2 via

$$CO + OH \rightarrow CO_2 + H \qquad (R5)$$
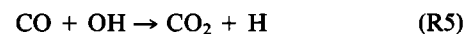
If the OH radical in (R5) is derived from (R1a) followed by (R8a), the net result of (R5) is to mitigate the impact of CO_2 photolysis. However, for (R5) to be important, CO must be abundant enough to compete with reactions such as
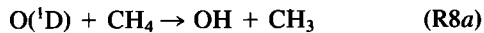
$$OH + CH_4 \rightarrow H_2O + CH_3 \qquad (R14)$$

$$OH + C_2H_2 \rightarrow CH_2CO + H \qquad (R15)$$

$$OH + CH_2 \rightarrow CO + H_2 + H \qquad (R16)$$

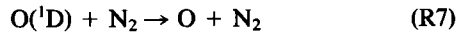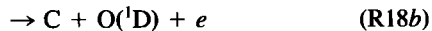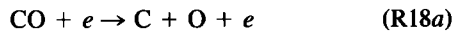$$OH + CH_3 \rightarrow CO + 2H_2 \qquad (R17)$$

Note that reaction (R5) offers a simple scheme for generating CO_2 if an independent source of oxygen is provided in the form of OH.

The above discussion shows that carbon dioxide is not stable in the atmosphere of Titan. There is a strong tendency for the molecule to lose an oxygen atom. Reactions (R1a), (R1b), (R10), (R12), (R13), (R16), (R17), and (R19) can be summarized by the overall reaction

$$CO_2 + \text{hydrocarbon} \rightarrow 2CO + \text{products}$$

The oxygen atom derived from CO_2 photolysis ultimately ends up in CO, an extremely stable molecule. In the absence of a comparable chemical source, the observed CO_2 on Titan would be destroyed in as short as 5×10^4 years, an insignificant period of time compared to the age of the solar system. For initially large amounts of CO_2 the depletion rate would only be exacerbated by continuous condensation at the tropopause, leading to even shorter depletion times. Thus to maintain the observed abundance of CO_2 in steady state, a photochemical source must be invoked. Production of CO_2 by (1) requires two conditions: (a) the abundance of CO in the atmosphere must be sufficiently high, and (b) a source of oxygen in the form of OH must be provided. We shall defer the question of the origin of CO until later and briefly address the source of OH.

Destruction of CO by electron impact could lead to the production of OH by

$$CO + e \rightarrow C + O + e \tag{R18a}$$

$$\rightarrow C + O(^1D) + e \tag{R18b}$$

$$O(^1D) + N_2 \rightarrow O + N_2 \tag{R7}$$

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \tag{R8a}$$

According to *Strobel and Shemansky* [1982], electron impact dissociation of N_2 occurs readily in the thermosphere of Titan, the energetic electrons being most probably of magnetospheric origin. The rate of N_2 destruction was estimated to be 1×10^9 molecules cm^{-2} s^{-1} (referred to the planetary surface). The rate of destruction of CO in relation to that of N_2 in a dominantly N_2 atmosphere is 1.2 (J. Fox, private communication, 1982). The quantum yield for $O(^1D)$ is unknown, but based on analogy with dissociation of N_2 [*Strobel and Shemansky*, 1982; *Lee and McKoy*, 1982], we estimate the value to be 50%. The flux of OH can be expressed by

$$\phi_{OH} = q_1 \times q_2 \times f_{CO} \times 1.2 \times 1 \times 10^9 \text{ molecules } cm^{-2} s^{-1}$$

where q_1 is the quantum yield of $O(^1D)$ in (R18) (0.50 in the standard model); f_{CO} is the mixing ratio of CO relative to N_2 in the bulk atmosphere; and q_2, the quantum yield of deriving an OH radical from $O(^1D)$, is given by

$$q_2 = \frac{k_{8_a}[CH_4] + k_9[H_2]}{(k_{8_a} + k_{8_b})[CH_4] + k_9[H_2] + k_7[N_2]}$$

where the numerator consists of reactions that produce OH from $O(^1D)$, and the denominator includes all the major reactions that destroy $O(^1D)$. The numerical value of q_2 is ~0.47. Because the atmosphere is mostly N_2, we shall henceforth treat f_{CO} as the mole fraction of CO with little loss of accuracy.

Another potential source of OH is H_2O derived from the abrasion of micrometeoroids in the upper atmosphere. Dissociation of H_2O yields OH radicals from the reaction

$$H_2O + h\nu \rightarrow H + OH \tag{R2b}$$

Meteorites have been postulated to be an important source of oxygen on Jupiter [*Prather et al.*, 1978]. On Titan there is no direct observation of the flux of meteoritic material. However, the Saturnian system abounds in icy bodies and particles, and the limited observations by Pioneer 11 suggested that the Saturnian environment is quite dusty, especially near the E ring [*Humes*, 1980]. Visual evidences for impact craters on the surface of smaller satellites testify to the high probability and frequency of impacting events [*Smith et al.*, 1982]. The mean flux of meteoritic material into the earth's atmosphere is 44 metric tons day^{-1} [*Hunten et al.*, 1980]. Assuming a H_2O content of 20% by weight, typical of C1 chondrites [*Mason*, 1971], we arrive at a flux of 6.8×10^5 molecules cm^{-2} s^{-1} for the terrestrial mesosphere. It is convenient to parameterize the flux of H_2O (referred to the surface) into the upper atmosphere of Titan by

$$\phi_{H_2O} = F_{H_2O} \times g \times 6.8 \times 10^5 \text{ molecules } cm^{-2} s^{-1}$$

where g is a geometric correction factor caused by the extended atmosphere (~2), and F_{H_2O} is an adjustable param-

eter to be varied in the model; $F_{H_2O} = 1$ corresponds to the terrestrial case.

The choice for F_{H_2O} appropriate for Titan is uncertain. Pioneer 10 and 11 measurements [*Humes*, 1980] showed a general decline in the flux of micrometeoroids as the spacecraft left the inner solar system, except at times of close encounter with Jupiter and Saturn. If the environment near Saturn is typical of the interplanetary medium at 10 AU, the proper choice for F_{H_2O} is 0.1. However, if there is a component of meteoroid flux dominated by contributions from the ring particles, the value of F_{H_2O} could be significantly higher. For reasons to be discussed below we choose $F_{H_2O} = 0.42$ for our standard model.

RESULTS AND DISCUSSION

A qualitative overview is useful for revealing the essential physics. Meteoritic H_2O provides OH through photolysis, which in turn reacts with the CO available to produce CO_2. Some CO_2 is destroyed, principally by photolysis and by reaction with the methylene radical, but at a combined rate that is insufficient to overcome CO_2 production. However, once the CO_2 vapor pressure reaches saturation near the tropopause, condensation and attendant precipitation will occur, effectively halting a further CO_2 buildup.
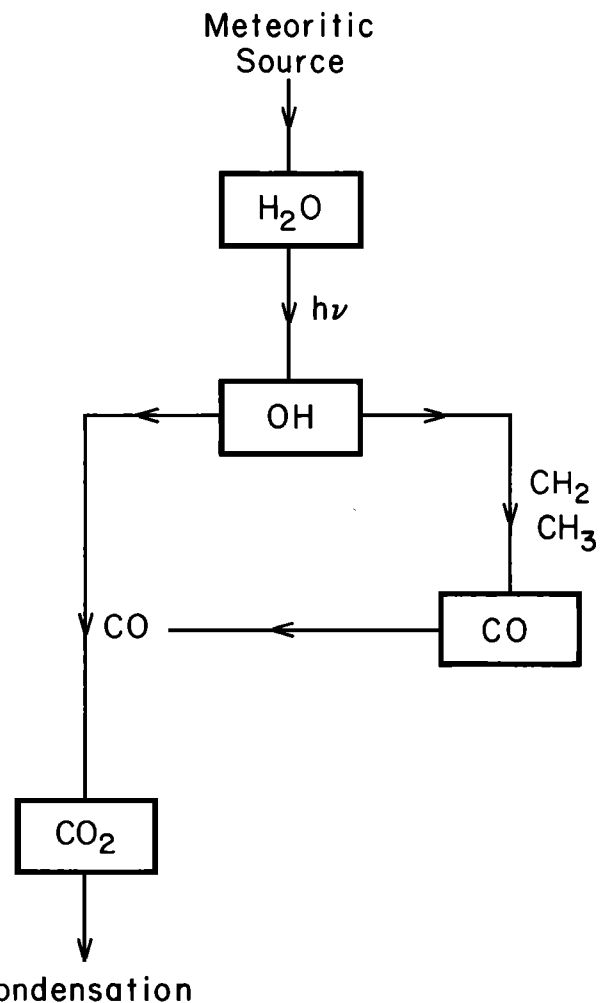

Fig. 4. Schematic diagram showing the reaction pathways and ultimate fate of the oxygen atom derived from meteoritic H_2O.

TABLE 1. Simplified List of Reactions Related to Photochemistry of CO$_2$ on Titan

	Reaction	Rate Coefficient	Reference
(R1a)	$CO_2 + h\nu \rightarrow CO + O(^1D)$	$J_{1_a} = 5.5 \times 10^{-9}$	Shemansky [1972]
(R1b)	$\rightarrow CO + O$	$J_{1_b} = 7.4 \times 10^{-11}$	
(R2a)	$H_2O + h\nu \rightarrow H_2 + O(^1D)$	$J_{2_a} = 2.0 \times 10^{-8}$	Allen et al. [1981]
(R2b)	$\rightarrow H + OH$	$J_{2_b} = 5.1 \times 10^{-8}$	
(R3a)	$H_2CO + h\nu \rightarrow H_2 + CO$	$J_{3_a} = 2.5 \times 10^{-7}$	Pinto et al. [1980]
(R3b)	$\rightarrow H + HCO$	$J_{3_b} = 1.8 \times 10^{-7}$	
(R4)	$HCO + h\nu \rightarrow H + CO$	$J_4 = 1.0 \times 10^{-4}$	Pinto et al. [1980]
(R5)	$CO + OH \rightarrow CO_2 + H$	$k_5 = 1.4 \times 10^{-13}$	DeMore et al. [1982]
(R6)	$H + HCO \rightarrow H_2 + CO$	$k_6 = 3.0 \times 10^{-10}$	Pinto et al. [1980]
(R7)	$O(^1D) + N_2 \rightarrow O + N_2$	$k_7 = 1.8 \times 10^{-11} e^{107/T}$	DeMore et al. [1982]
(R8a)	$O(^1D) + CH_4 \rightarrow OH + CH_3$	$k_{8_a} = 1.4 \times 10^{-10}$	DeMore et al. [1982]
(R8b)	$\rightarrow H_2CO + H_2$	$k_{8_b} = 1.4 \times 10^{-11}$	
(R9)	$O(^1D) + H_2 \rightarrow OH + H$	$k_9 = 1.0 \times 10^{-10}$	DeMore et al. [1982]
(R10)	$O + CH_4 \rightarrow OH + CH_3$	$k_{10} = 3.5 \times 10^{-11} e^{-4550/T}$	Hampson [1980]
(R11)	$O + H_2 \rightarrow OH + H$	$k_{11} = 1.6 \times 10^{-11} e^{-4570/T}$	Baulch et al. [1980]
(R12)	$O + CH_2 \rightarrow CO + 2H$	$k_{12} = 8.3 \times 10^{-11}$	Homann and Schweinfurth [1981]
(R13)	$O + CH_3 \rightarrow H_2CO + H$	$k_{13} = 1.3 \times 10^{-10}$	Baulch et al. [1980]
(R14)	$OH + CH_4 \rightarrow H_2O + CH_3$	$k_{14} = 2.4 \times 10^{-12} e^{-1710/T}$	Baulch et al. [1980]
(R15)	$OH + C_2H_2 \rightarrow CH_2CO + H$	$k_{15} = 1.2 \times 10^{-12} e^{-164/T} f*$	Perry and Williamson [1982]
(R16)	$OH + CH_2 \rightarrow CO + H_2 + H$	$k_{16} = 5.0 \times 10^{-12}$	estimated
(R17)	$OH + CH_3 \rightarrow CO + 2H_2$	$k_{17} = 6.7 \times 10^{-12}$	Fenimore [1968]
(R18a)	$CO + e \rightarrow C + O + e$	see text	
(R18b)	$\rightarrow C + O(^1D) + e$	see text	
(R19)	$CO_2 + CH_2 \rightarrow CO + H_2CO$	$k_{19} = 3.9 \times 10^{-14}$	Laufer [1981]

Taken from a more complete compilation in Y.L. Yung et al. (unpublished manuscript 1982). The units for mean photolysis rates (J) and two-body rate coefficients (k) are s^{-1} and cm^3 s^{-1}, respectively. Photolysis rates are computed by using the solar flux of Mount et al. [1980]. The numerical values quoted in this table refer to optically thin regions of the atmosphere.

$*f = \dfrac{M}{M + 1.7 \times 10^{18}}$, where M = number density (cm^{-3}) of ambient atmosphere.

These ideas appear to be borne out by the observed abundance of CO$_2$. According to Figure 3 the CO$_2$ abundance curve is very nearly tangent to the temperature profile at the point where condensation should occur. This suggests the CO$_2$ abundance is in a steady state. Any increase in CO$_2$ would lead immediately to supersaturation and removal by condensation, the major sink under these circumstances. On the other hand a decrease in CO$_2$ would lead to undersaturation and eliminate condensation as a sink altogether. In this case our photochemical model predicts a net increase in CO$_2$ production. Thus, as long as the meteoritic influx rate is constant, the CO$_2$ abundance will return to its steady state value. The response time for the system is about 4×10^3 yr.

The situation with respect to the evolution of CO is somewhat different. Because CO does not condense, it should be uniformly mixed throughout the troposphere and lower stratosphere where photochemistry is relatively unimportant. In the absence of a steady state the influx of meteoritic H$_2$O could be either a source or sink of CO, depending on the relative magnitudes of the production (P_{CO}) and loss (L_{CO}) rates. Explicitly,

$$\frac{d}{dt} \int_0^\infty [CO] \, dz = P_{CO} - L_{CO} \quad (1)$$

where

$$P_{CO} \sim \int_0^\infty [OH] \, \{k_{16}[CH_2] + k_{17}[CH_3]\} \, dz \quad (2)$$

and

$$L_{CO} \sim \int_0^\infty k_5 \, [CO] \, [OH] \, dz \quad (3)$$

where $[x]$ denotes the concentration of species x in molecules cm^{-3}, and the approximate expressions for P_{CO} and L_{CO} are valid for $F_{H_2O} > 0.3$. These relations are illustrated schematically in Figure 4.

From the above equations it is seen that the CO production rate is independent of the abundance of CO, whereas the CO loss rate is proportional to it. As a result the system acts as a negative feedback loop, with P_{CO} remaining constant (for a given H$_2$O influx rate) and L_{CO} increasing or decreasing as [CO] increases or decreases, respectively. The system tends toward a steady state ($P_{CO} \sim L_{CO}$) with f_{CO} approaching an asymptotic limit.

On the other hand both P_{CO} and L_{CO} are proportional to [OH] (and hence to F_{H_2O}) as long as $F_{H_2O} > 0.3$. It follows from (1)–(3) that the rate at which f_{CO} approaches its limit is porportional to the influx rate of H$_2$O, whereas the limiting value itself is essentially independent of this latter rate.

These ideas can be quantified by using our photochemical model. A simplified set of reactions related to the chemistry of carbon dioxide in the atmosphere of Titan is summarized in Table 1, and a schematic diagram showing the fate of oxygen derived from H$_2$O is shown in Figure 4. The concentrations of the hydrocarbons have been calculated in a more detailed model described by Y. L. Yung et al. (unpublished manuscript, 1982). Because the concentrations of the active
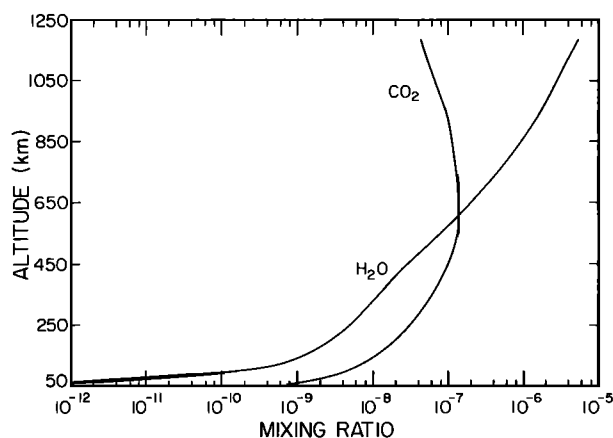
Fig. 5. Altitude profiles for the mixing ratios of the most important oxygen containing compounds (CO_2 and H_2O) computed in the standard model, for which $q_1 = 0.50$, $q_2 = 0.47$, $F_{H_2O} = 0.42$, and $f_{CO} = 1.1 \times 10^{-4}$.

oxygen species O, O(^{1}D), and OH are low it should not be necessary to modify the hydrocarbon abundances.

The discussion here is limited to the most important oxygen species: CO, CO_2, and H_2O. The emphasis is on the overall budget and evolution of CO and CO_2 in the atmosphere. A discussion of the detailed photochemical model and the chemistry of H_2CO and CH_2CO is deferred to Yung et al.

Requiring CO to be in a steady state yields $f_{CO} = 1.1 \times 10^{-4}$, a value which, as previously indicated, is largely independent of the H_2O influx rate. Once the CO mole fraction is established the observed value for f_{CO_2} determines this rate unambiguously. In particular a value $f_{CO_2} = 1.5 \times 10^{-9}$ yields $F_{H_2O} = 0.42$. This defines our standard model. Figure 5 presents altitude profiles for the important oxygen-containing species CO_2 and H_2O in this steady state model. The concentrations of the important radicals O, OH, CH_2, and CH_3 are shown in Figure 6, while the production and loss rates relevant to the chemistry of CO_2 are indicated in Figure 7. As noted earlier, the production of CO, mainly by (R16) and (R17), roughly balances the major loss of CO by (R5), leading to the formation of CO_2. The net source of oxygen is meteoritic water, with an input rate $\sim 6.1 \times 10^5$
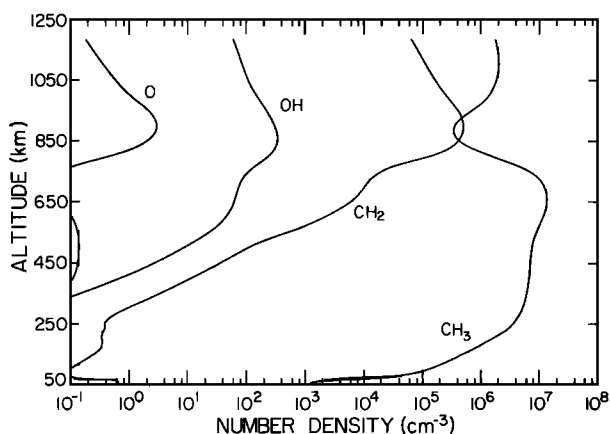

Fig. 6. Altitude profiles of the number densities of the most important radical species in the model. Note that CH_2 and CH_3 are assumed to be fixed in this model.
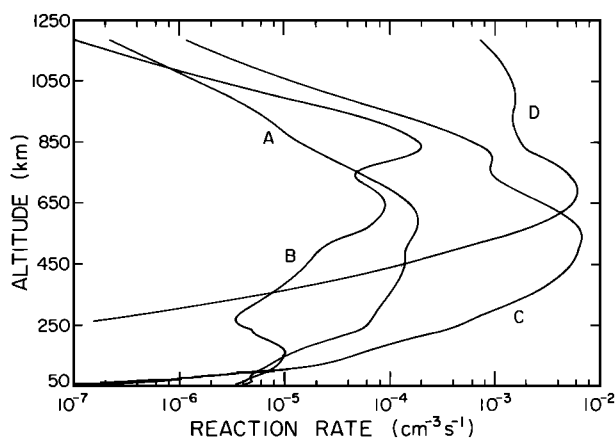

Fig. 7. Major reaction rates leading to the destruction and production of CO_2 and CO. Destruction of CO_2: curve A = (R1a) + (R1b), CO_2 + $h\nu$; curve B = (R19), CO_2 + CH_2. Production of CO_2: curve C = (R5), CO + OH. The source of OH in (R5) is electron impact dissociation of CO at high altitude (as shown by the small secondary peak in curve C) and by photolysis of meteoritic H_2O at lower altitudes. Note that curve C also represents the primary loss mechanism for CO. Production of CO: curve D = (R16) + (R17), OH + CH_2, OH + CH_3. The principal loss of CO_2 (and hence of oxygen) in the model is downward transport at the tropopause, where an eddy velocity of 6.5×10^{-5} cm s^{-1} is assumed.

atoms cm^{-2} s^{-1} (referred to the surface). The atmosphere loses oxygen through downward transport of CO_2 and H_2CO at the tropopause and escape of oxygen from the exosphere, with rates equivalent to 5.8×10^5, 0.1×10^5, and 0.2×10^5 O atoms cm^{-2} s^{-1}.

An important check of the model is provided by comparing the steady state calculation of f_{CO} with the observed value. Lutz et al. [1983] have inferred a value between 6×10^{-5} and 1.5×10^{-4} that brackets our theoretical value of 1.1×10^{-4}. The good agreement is probably fortuitous, as neither the model nor the observations are certain to within a factor of 3. Furthermore, we must entertain the possibility that CO is not in a steady state on Titan, as its doubling time in the model is $\sim 10^9$ years. We would also like to add a word of caution about the preliminary results of the hydrocarbon model used in the calculations. There are indications that the concentration of CH_3 radicals shown in Figure 6 are probably too high by a factor of 2–3. A downward revision of CH_3 would result in a lower concentration of CO in the steady state model.

Our current understanding implies that there may be little information available regarding the original CO content of Titan's atmosphere. If the water influx rate has been approximately constant ($F_{H_2O} \sim 0.4$) over a substantial fraction of the age of the solar system, an initial CO abundance of zero would have increased by now to its steady state value, $f_{CO} \sim 1.1 \times 10^{-4}$. On the other hand, if the conversion of CO to CH_4 and N_2 to NH_3 was inhibited during the time of formation of Saturn's circumplanetary nebula [as is true for certain of *Prinn and Fegley*'s [1981] models for the Jovian system], Titan might have accreted substantial quantities of CO and N_2. Thus, if most of the present N_2 in Titan's atmosphere is primordial in origin, large amounts of CO should also have been in the initial atmosphere [*Owen*, 1982].

This initially large amount would have been depleted over geologic time, however. For example, a CO mole fraction of

0.2 implies a CO destruction rate of $\sim 10^8$ molecules cm^{-2} s^{-1}. This would generate a CO_2 vapor pressure at the tropopause greatly in excess of saturation, and rapid removal by condensation would result. Depletion to the present steady state value would be accomplished well within the time frame available. A tenth of a Titan atmosphere of CO could be irreversibly destroyed over the age of the solar system, converted to about a meter of CO_2 ice on the surface. This compares with about a kilometer of heavy hydrocarbons deposited on the surface over the same time scale.

The identification of CO_2 on Titan opens up a new vista in the chemistry of reducing atmospheres. A complete understanding of this chemistry may ultimately be as significant as the chemistry of reduced compounds such as CH_4 and H_2 in an oxidizing atmosphere [cf. Logan et al., 1978, 1981; Aikin et al., 1982]. Abundance determinations of such gases as H_2O, CH_2CO, and H_2CO will provide crucial tests in further developments of the theory. Additionally, if the large influx of water postulated for Titan is borne out by further observation, H_2O vapor would have to be considered a potentially important source of oxygen for Saturn as well. Thus a search for CO in Saturn's upper atmosphere might yield positive results.

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