PHOTOCHEMISTRY OF THE ATMOSPHERE OF TITAN: COMPARISON BETWEEN MODEL AND OBSERVATIONS[1]

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ABSTRACT

The photochemistry of simple molecules containing carbon, hydrogen, nitrogen, and oxygen atoms in the atmosphere of Titan has been investigated using updated chemical schemes and our own estimates of a number of key rate coefficients. Proper exospheric boundary conditions, vertical transport, and condensation processes at the tropopause have been incorporated into the model. It is argued that the composition, climatology, and evolution of Titan's atmosphere are controlled by five major processes: (*a*) photolysis and photosensitized dissociation of CH_4; (*b*) conversion of H to H_2 and escape of hydrogen; (*c*) synthesis of higher hydrocarbons; (*d*) coupling between nitrogen and hydrocarbons; (*e*) coupling between oxygen and hydrocarbons. Starting with N_2, CH_4, and H_2O, and invoking interactions with ultraviolet sunlight, energetic electrons, and cosmic rays, the model satisfactorily accounts for the concentrations of minor species observed by the *Voyager* IRIS and UVS instruments. Photochemistry is responsible for converting the simpler atmospheric species into more complex organic compounds, which are subsequently condensed at the tropopause and deposited on the surface. Titan might have lost 5.6×10^4, 1.8×10^3, and 4.0 g cm^{-2}, or the equivalent of 8, 0.25, and 5×10^{-4} bars of CH_4, N_2, and CO, respectively, over geologic time. Implications of abiotic organic synthesis on Titan for the origin of life on Earth are briefly discussed.

Subject headings: planets: abundances — planets: atmospheres — planets: satellites — planets: Saturn

I. INTRODUCTION

Titan, a satellite with a massive atmosphere, has attracted considerable attention in recent years. Early work on observations and modeling of Titan was discussed and summarized in two NASA workshop reports (Hunten 1974*a*, 1978) and in several articles by Hunten (1972, 1974*b*, 1977), Caldwell (1977, 1978), and Trafton (1981). Notable progress was made in understanding Titan's geochemistry (Lewis 1971; Lewis and Prinn 1973), atmospheric radiation (Danielson, Caldwell, and Larach 1973), atmospheric dynamics (Leovy and Pollack 1973), and evolution (Hunten 1973; Atreya, Donahue, and Kuhn 1978). The early studies were aware of the fact that the CH_4-to-H_2 ratio on Titan must be large, rendering the atmosphere ideally suited for the synthesis of organic compounds. However, ground-based observations were unable to identify nitrogen as the major atmospheric constituent; instead, they indicated that methane was dominant. Because of this, the theoretical work by Strobel (1974) and Allen, Pinto, and Yung (1980) was restricted to hydrocarbon chemistry. It was in the laboratory where bold and imaginative experiments were performed with varying mixtures of hydrocarbons, nitrogen,

sulfur, and water vapor, on the supposition that gases other than methane were present (Khare and Sagan 1973; Sagan 1974; Scattergood and Owen 1977; Chang *et al.* 1979). These experiments yielded a host of interesting compounds such as alkanes, nitriles, and aldehydes, and anticipated the subsequent detection or inference of some of these compounds by the *Voyager* missions.

The recent *Voyager* missions to Saturn resulted in major advances in our knowledge of Titan and its immediate environment. It has now been established that the principal constituent of the atmosphere of Titan is nitrogen. The minor constituents that have been identified to date include CH_4, H_2, C_2H_2, C_2H_4, C_2H_6, CH_3C_2H, C_3H_8, C_4H_2, HCN, HC_3N, C_2N_2, CH_3D, CO, and CO_2. In addition observations of several haze layers at high altitude in the atmosphere and an extensive hydrogen torus in the vicinity of Titan's orbit have been reported. Table 1A summarizes the most important recent measurements relevant to our modeling effort. Most of the data are derived from the UVS (ultraviolet spectrometer), IRIS (infrared interferometer spectrometer), and radio occultation experiments on *Voyager* 1 and 2, as reported in the special issues, *Science*, **212** (1981), *Nature*, **292** (1981), and *J. Geophys. Res.*, **87** (1982). The detection of CH_3D and CO are based on post-Voyager ground-based observations. See Table 1A for detailed listing of appropriate references.

TABLE 1A

PHYSICAL PARAMETERS AND CHEMICAL COMPOSITION MEASUREMENTS FOR PHOTOCHEMICAL MODEL

Physical or Chemical Data	Reference and Remarks
At the Surface (altitude $z = 0$):	
r_0 = distance to center = 2575 km	Lindal et al. 1983
g_0 = gravity = 135 cm s^{-2}	Lindal et al. 1983
P_0 = total pressure = 1.50 bar	Lindal et al. 1983
T_0 = temperature = 94 K	Lindal et al. 1983
n_0 = number density = 1.2×10^{20} cm^{-3}	Lindal et al. 1983
Composition of the Troposphere (volume mixing ratio):	
$N_2 > 0.97$	Lindal et al. 1983
$CH_4 < 0.03$	Lindal et al. 1983
$H_2 = 0.002$	Samuelson et al. 1981
At the Tropopause ($z = 45$ km):	
$P = 130$ mbar	Lindal et al. 1983
$T = 71.4$ K	Lindal et al. 1983
$n = 1.1 \times 10^{19}$ cm^{-3}	Lindal et al. 1983
Composition of the Stratosphere (volume mixing ratio):	
$CH_4 = 1-3 \times 10^{-2}$	Hanel et al. 1981; see text
$H_2 = 2.0 \times 10^{-3}$	Samuelson et al. 1981
$C_2H_6 = 2 \times 10^{-5}$	Hanel et al. 1981
$C_2H_2 = 2 \times 10^{-6}$	Hanel et al. 1981
$C_2H_4 = 4 \times 10^{-7}$	Kunde et al. 1982
$C_3H_8 = 2-4 \times 10^{-6}$	Maguire et al. 1981
$CH_3C_2H = 3 \times 10^{-8}$	Maguire et al. 1981
$C_4H_2 = 10^{-8}-10^{-7}$	Kunde et al. 1981
$HCN = 2 \times 10^{-7}$	Hanel et al. 1981
$HC_3N = 10^{-8}-10^{-7}$	Kunde et al. 1981
$C_2N_2 = 10^{-8}-10^{-7}$	Kunde et al. 1981
$CO = 6 \times 10^{-5}$	Lutz, de Bergh, and Owen 1983; Muhleman, Berge, and Clancy 1984
$CO_2 = 1.5 \times 10^{-9}$	Samuelson et al. 1983
$H_2O < 1 \times 10^{-9}$	Kunde (1982, private communication)
CH_3D detected, abundance not available	de Bergh et al. 1981
Composition of Mesosphere and Thermosphere:	
$N_2 = 2.7 \times 10^8$ cm^{-3} at $z = 1280$ km	Smith et al. 1982a
$CH_4 = 1.2 \times 10^8$ cm^{-3} at $z = 1140$ km (mixing ratio = 0.08)	Smith et al. 1982a
C_2H_2 mixing ratio 1%–2% at $z = 840$ km	Smith et al. 1982a
H atoms: disk-averaged Lyα airglow ~ 500 R[a]	Strobel and Shemansky 1982
Haze Layers:	
optical haze $z = 300$ km	Smith et al. 1982b
UV haze $z = 400$ km	Smith et al. 1982a

[a] The observed airglow on the dayside is ~ 1 kR. However, based on our knowledge of the Lyα nightglow and other emissions, we conclude that the dayglow consists of roughly equal contributions from resonance scattering of solar radiation and excitation by electron impact. The value quoted here refers to the component of Lyα airglow arising from resonance scattering (Shemansky 1982, private communication).

In bulk chemical composition, Titan's atmosphere is reducing, with an oxidation state intermediate between that of the terrestrial planets and that of the Jovian planets. The abundance of organic compounds in the stratosphere offers an important clue to the type of chemistry that prevails on Titan. Table 1B presents an estimate of the maximum concentrations of select compounds consistent with saturation at the tropopause and the surface. Comparison of Tables 1A and 1B suggests that the abundances of most minor species exceed their saturated vapor pressures and should condense at the tropopause, or even at the surface. Thus, the lower atmosphere

cannot be the source of complex molecules to the upper atmosphere, even though some molecules such as HCN might be abundant on the surface and in the interior of Titan (Prinn and Fegley 1981). It is generally accepted that most of the observed compounds are derived from a few parent molecules via photochemical processes. In this sense the atmosphere of Titan is conceptually simple like the Martian atmosphere, whose present composition and past evolution can be adequately explained by photochemistry (McElroy and Donahue 1972; McElroy 1972; Nier, McElroy, and Yung 1976). In contrast, the atmospheres of Venus and the Jovian planets are

more complex, and require for a complete description the interaction between photochemistry in the upper atmosphere and thermochemistry in the lower atmosphere (Prinn 1975; Lewis and Kreimendahl 1980; Yung and DeMore 1982; Strobel 1973; Barshay and Lewis 1978). The terrestrial atmosphere is further complicated by interaction with the biosphere (Lovelock and Margulis 1974; Holland 1978). All existing evidence suggests that the atmosphere of Titan is like that of Mars in the sense that we expect photochemistry to provide a fundamental understanding of the present atmosphere and possibly its past evolution.

The purpose of this paper is to explore and develop this theme. We assume, without further inquiry, that the atmosphere contains the primitive parent molecules N_2, CH_4, and H_2O. The origin of N_2 and CH_4 can probably be traced to the initial endowment of volatiles acquired by Titan at the time of its formation (Owen 1982). H_2O is probably continuously replenished by a small but steady meteoritic source (Samuelson et al. 1983). Interaction between the parent molecules and ultraviolet radiation, energetic electrons, and cosmic rays leads to the production of reactive radicals, which can combine to form more complex molecules. The aim of the photochemical model is to invoke known reaction pathways to quantitatively explain the abundances of minor constituents listed in Table 1A. Unfortunately, the task is handicapped by the lack of appropriate laboratory kinetics data and uncertainties in defining the vertical mixing parameters of the atmosphere. The totality of currently available information is not sufficient for building a definitive photochemical model of Titan. This work must be considered as a preliminary attempt to provide a framework for integrating the extensive (but incomplete) set of observations, and the fragmentary (and often inconsistent) chemical kinetics data.

TABLE 1B[a]
MAXIMUM MIXING RATIOS OF SELECTED SPECIES AT TROPOPAUSE AND SURFACE OF TITAN

Molecule	Tropopause	Surface
CH_4	3.0×10^{-2}	1.2×10^{-1}
C_2H_6	5.1×10^{-7}	4.0×10^{-5}
C_2H_4	4.1×10^{-6}	1.9×10^{-4}
C_2H_2	6.9×10^{-10}	8.0×10^{-7}
CH_3C_2H	3.8×10^{-11}	4.3×10^{-8}
CH_2CCH_2	1.8×10^{-12}	5.3×10^{-9}
C_3H_6	6.8×10^{-10}	3.3×10^{-7}
C_3H_8	1.3×10^{-9}	4.8×10^{-7}
C_4H_2	7.4×10^{-18}	1.2×10^{-12}
C_4H_4	2.6×10^{-15}	5.4×10^{-11}
$1-C_4H_6$	3.5×10^{-15}	6.2×10^{-11}
$1,2-C_4H_6$	3.2×10^{-15}	5.1×10^{-11}
$1,3-C_4H_6$	6.0×10^{-13}	1.9×10^{-9}
C_4H_{10}	3.0×10^{-13}	1.2×10^{-9}
HCN	2.3×10^{-17}	1.7×10^{-12}
CO	1.5	2.1
CO_2	5.6×10^{-11}	1.4×10^{-7}
H_2O	0	6.5×10^{-20}
H_2CO	4.1×10^{-13}	2.0×10^{-9}

[a] Temperature and number density of the ambient atmosphere at the tropopause assumed in the computations are 70 K and 1.1×10^{19} cm^{-3}, respectively; at the surface, 95 K and 1.2×10^{20} cm^{-3}, respectively. Vapor pressure data are taken from Schlessinger 1970, and should be regarded as order of magnitude estimates.

II. OVERVIEW

While the complete chemical model is somewhat elaborate, we must emphasize its underlying simplicity. It is possible to understand the overall photochemistry on Titan in terms of a small number of chemical cycles or schemes, which are similar in principle to the ones that operate in the atmospheres of the terrestrial planets. The discussion in this section, with emphasis on concepts and atmospheric processes, should be regarded as parallel to that in § III, which emphasizes the mechanistic details of photolytic and chemical reactions.

It is convenient, for purposes of discussion, to divide the photochemistry of Titan's atmosphere into two regions, characterized by primary and photosensitized processes, respectively. In the thermosphere and mesosphere, dissociation of N_2, H_2O, and CH_4 occurs by direct photolysis or electron impact. This, as we shall show, leads to the production of the important species HCN, CO, CO_2, C_2H_2, C_2H_4, and CH_3C_2H. With the subsequent downward transport of these species, some of the molecules, notably C_2H_2, can now act as precursors of stratospheric chemistry by catalyzing the dissociation of CH_4. It will be shown that photosensitized processes in the stratosphere are responsible for producing C_2H_6 and

TABLE 1C
COMPARISON OF C_2H_6 AND C_2H_2 AND OTHER STRATOSPHERIC PARAMETERS ON TITAN, JUPITER, AND SATURN

Parameter	Titan[a]	Jupiter[b]	Saturn[c]
Mixing ratio of C_2H_6	2×10^{-5}	5×10^{-6}	4.8×10^{-6}
Mixing ratio of C_2H_2	2×10^{-6}	2×10^{-8}	1.1×10^{-7}
Mixing ratio of CH_4	$1-3 \times 10^{-2}$	1.75×10^{-3}	1.76×10^{-3}
Tropopause pressure (mb)	130	113	100
Tropopause temperature (K)	71	128	85
C_2H_6 (max)[d]	5×10^{-7}	1.1×10^{-1}	6.2×10^{-5}
C_2H_2 (max)[d]	6.9×10^{-10}	1.7×10^{-2}	5.1×10^{-7}

[a] Taken from Table 1A.

[b] Kunde et al. 1982, Gautier et al. 1982, Maguire (1983, private communication); Kostiuk et al. 1983 reported a much lower C_2H_6 abundance of 1.2×10^{-6} in the South Polar Region.

[c] Hanel et al. 1981; Courtin 1982.

[d] Maximum mixing ratio consistent with saturation vapor pressure at the tropopause.

C_3H_8. Stratospheric chemistry can also successfully account for the presence of C_4H_2, HC_3N, and C_2N_2. While the primary processes in the thermosphere and mesosphere are relatively well-defined in the photochemical model, the secondary photochemical processes in the stratosphere are currently rather ill-defined. So the first important problem addressed in this work is an assessment of the importance of stratospheric chemistry relative to mesospheric chemistry.

The second important problem in the photochemical model is related to the stability of unsaturated carbon compounds. Table 1A includes seven carbon species with unsaturated bonds, C_2H_2, C_2H_4, CH_3C_2H, C_4H_2, HCN, HC_3N, and C_2N_2, all extremely reactive toward H atoms. With the possible exception of C_2H_2 and HCN, most of these compounds can be destroyed by reactions with H. Since CH_4 is the ultimate source of all carbon atoms, the production of the more complex carbon species must be accompanied by comparable quantities of H or H_2. One way to guarantee the survival of the unsaturated species in the stratosphere is to convert H into H_2 by some hitherto unknown catalytic processes.

To what extent can the composition of Titan's atmosphere be explained by thermospheric and mesospheric chemistry alone? What is the compelling evidence for the existence of an active stratospheric chemistry? How are hydrogen atoms removed in the stratosphere? What are the consequences if the hydrogen atoms are not removed? These and related questions will be raised and examined in the following subsections. The models of Strobel (1974) and Allen, Pinto, and Yung (1980) provide a convenient starting point of our inquiry. Where the old ideas are useful, they will be appraised and incorporated into the new model. Where the old concepts prove inadequate, we shall advance new hypotheses, which are necessarily more speculative. It is hoped that this discussion serves to focus our attention on the critical issues of photochemistry on Titan, and that some of the new ideas proposed here are useful at least for guiding future laboratory investigations or for planning missions and observations.

### a) Primary Processes in the Thermosphere and Mesosphere

The observations of extensive airglow associated with N_2, N, and N^+ emissions led Strobel and Shemansky (1982) to conclude that dissociation of N_2 occurs readily in the thermosphere as the result of interactions with energetic electrons of magnetospheric origin (reaction number n in Rn refers to identifying reaction index in Tables 3A–3C and 7):

$$N_2 + e \rightarrow N + N(^2D) + e,$$
$$N_2^+ + e \rightarrow N + N(^2D), \qquad (R1)$$
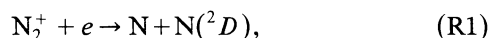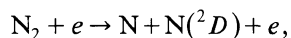
where N and $N(^2D)$, respectively, denote the ground (^4S) and excited (^2D) states of the nitrogen atom, and the products have been deduced on the basis of Oran, Julienne, and Strobel (1975), and Yung et al. (1977). Since the quenching of $N(^2D)$ by N_2 is not efficient, $N(^2D)$ most probably reacts with CH_4:
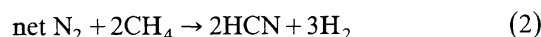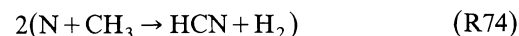
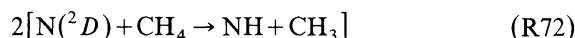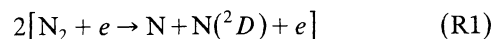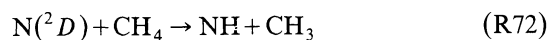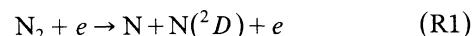$$N(^2D) + CH_4 \rightarrow NH + CH_3. \qquad (R72)$$
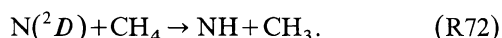
The probability of inserting the $N(^2D)$ atom into CH_4 with subsequent formation of the CN bond is not ruled out, but considered unlikely. The fate of NH in the thermosphere depends on the relative importance of the reactions

$$NH + H \rightarrow N + H_2, \qquad (R75)$$

$$NH + N \rightarrow N_2 + H. \qquad (R76)$$
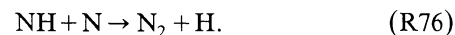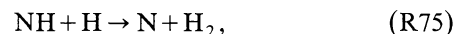
Since R76 is more important than R75, most of N_2 dissociation leads back to combination. Only a small fraction of N atoms will react with hydrocarbons. Based on analogy with the reaction N + CH (Messing et al. 1981), M. Lin (1982, private communication) suggested that an N atom attacks a CH_3 radical with the formation of HCN:

$$N + CH_3 \rightarrow HCN + H_2. \qquad (R74)$$
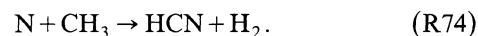
The overall nitrogen chemistry in the thermosphere can be summarized by two schemes (scheme number n refers to identifying scheme index in Table 2B):

$$N_2 + e \rightarrow N + N(^2D) + e \qquad (R1)$$

$$N(^2D) + CH_4 \rightarrow NH + CH_3 \qquad (R72)$$

$$\underline{N + NH \rightarrow N_2 + H} \qquad (R76)$$

$$\text{net } CH_4 \rightarrow CH_3 + H \qquad (1)$$

$$2[N_2 + e \rightarrow N + N(^2D) + e] \qquad (R1)$$

$$2[N(^2D) + CH_4 \rightarrow NH + CH_3] \qquad (R72)$$

$$N + NH \rightarrow N_2 + H \qquad (R76)$$

$$NH + H \rightarrow N + H_2 \qquad (R75)$$

$$\underline{2(N + CH_3 \rightarrow HCN + H_2)} \qquad (R74)$$

$$\text{net } N_2 + 2CH_4 \rightarrow 2HCN + 3H_2 \qquad (2)$$

Scheme (1) is a catalytic cycle for dissociating CH_4. The CH_3 radicals produced can further react with N, OH, or other hydrocarbon radicals. Scheme (2) is the major source of HCN on Titan and is much more important than a similar scheme driven by the absorption of cosmic rays in the lower stratosphere. HCN formed in the thermosphere is ultimately removed by transport to the stratosphere followed by condensation at the tropopause.

The influx of micrometeoroids into Titan's atmosphere provides a net source of oxygen to this reducing atmosphere. On Earth, the ablation of meteoroids occurs in the mesosphere with subsequent release of metallic atoms (Hunten, Turco, and Toon 1980). On Titan the incoming material is probably of more icy nature and would sublime in the thermosphere, delivering a source of H_2O molecules. H_2O is destroyed by
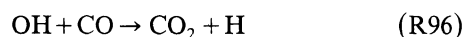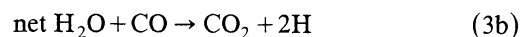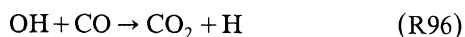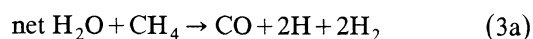
photolysis:

$$H_2O + h\nu \rightarrow H + OH. \tag{R21a}$$
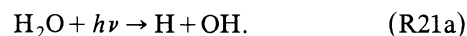
The OH radical can react with CH_3:

$$OH + CH_3 \rightarrow CO + 2H_2 \tag{R95}$$
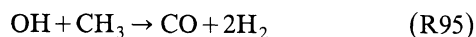
(Fenimore 1969), or further react with CO:

$$OH + CO \rightarrow CO_2 + H \tag{R96}$$

(DeMore *et al.* 1982). Thus, the fate of meteoritic H_2O can be summarized by two schemes:

$$H_2O + h\nu \rightarrow H + OH \tag{R21a}$$
$$OH + CH_3 \rightarrow CO + 2H_2 \tag{R95}$$
$$\underline{CH_4 \rightarrow CH_3 + H} \tag{1}$$
$$\text{net } H_2O + CH_4 \rightarrow CO + 2H + 2H_2 \tag{3a}$$

$$H_2O + h\nu \rightarrow H + OH \tag{R21a}$$
$$\underline{OH + CO \rightarrow CO_2 + H} \tag{R96}$$
$$\text{net } H_2O + CO \rightarrow CO_2 + 2H \tag{3b}$$

where in scheme (3a) the critical step $CH_4 \rightarrow CH_3 + H$ is driven by scheme (1). Scheme (3a) produces CO; scheme (3b) converts CO into CO_2. The two schemes offer a simple mechanism for regulating the abundances of CO and CO_2 on Titan. In steady state, the production and destruction of CO by schemes (3a) and (3b), respectively, must nearly balance. We have
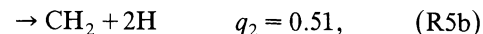
$$\int_0^\infty k_{95}[OH][CH_3]\,dz \approx \int_0^\infty k_{96}[OH][CO]\,dz.$$

Since H_2O influx and condensation of CO_2 are, respectively, the major source and sink of oxygen, we have

$$\phi(H_2O) \approx 2\phi(CO_2),$$

where $\phi(H_2O)$ is the meteoritic H_2O flux and $\phi(CO_2)$ is the downward flux of CO_2 into the troposphere. It is clear that these two expressions uniquely determine the abundances of CO and CO_2 in the atmosphere. It is of interest to note that to first order, abundances of CO and CO_2 are not related to each other. CO is proportional to CH_3, CO_2 to the flux of H_2O.

The bulk of CH_4 photolysis takes place in the mesosphere. The absorption cross sections for CH_4 reported in early work (Watanabe, Zelikoff, and Inn 1953) were shown to be in error at long wavelengths by Mount, Warden, and Moos (1977). The latter experiment demonstrated that the molecule does not absorb beyond 1450 Å. The products of CH_4 photolysis

were studied by McNesby and Okabe (1964), Laufer and McNesby (1968), Gorden and Ausloos (1967), Rebbert and Ausloos (1972), and Slanger (1982), with good agreement, in general, between the results of the various experiments. The principal branches and their quantum yields (q) at Lyα are

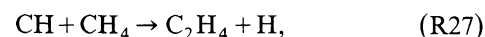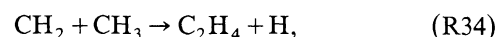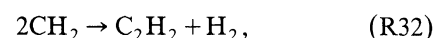$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2 \qquad q_1 = 0.41, \tag{R5a}$$
$$\rightarrow CH_2 + 2H \qquad q_2 = 0.51, \tag{R5b}$$
$$\rightarrow CH + H + H_2 \qquad q_3 = 0.08, \tag{R5c}$$
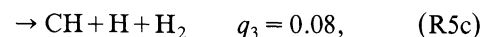
where ${}^1CH_2$ and CH_2 refer to the excited (singlet) and ground (triplet) states of methylene, respectively The branch $CH_4 + h\nu \rightarrow CH_3 + H$ is considered unimportant, and Slanger (1982) has placed an upper limit $q < 0.1$. At longer wavelengths, the only one of the above branches allowed by energy and spin conservation is
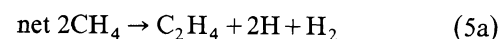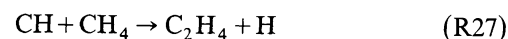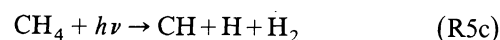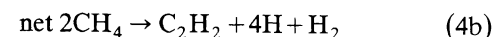
$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2, \tag{R5a}$$
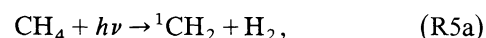
to which a quantum yield of unity is usually assigned. ${}^1CH_2$ is efficiently quenched to the ground state by N_2:

$${}^1CH_2 + N_2 \rightarrow CH_2 + N_2 \tag{R28}$$
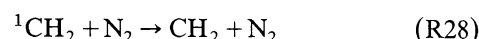
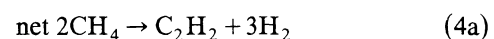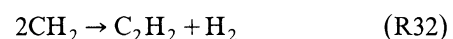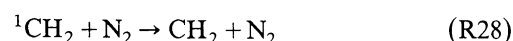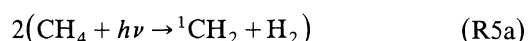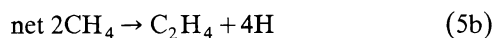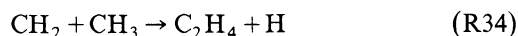(Ashfold *et al.* 1980; Laufer 1981*a*). The CH_2 and CH radicals are removed by reactions leading to the formation of C_2H_2 and C_2H_4:

$$2CH_2 \rightarrow C_2H_2 + H_2, \tag{R32}$$
$$CH_2 + CH_3 \rightarrow C_2H_4 + H, \tag{R34}$$
$$CH + CH_4 \rightarrow C_2H_4 + H, \tag{R27}$$

(Banyard *et al.* 1980; Laufer 1981*a*; Gorden and Ausloos 1967; Butler *et al.* 1981). The net results of CH_4 photolysis can be summarized by the following schemes:

$$2(CH_4 + h\nu \rightarrow {}^1CH_2 + H_2) \tag{R5a}$$
$${}^1CH_2 + N_2 \rightarrow CH_2 + N_2 \tag{R28}$$
$$\underline{2CH_2 \rightarrow C_2H_2 + H_2} \tag{R32}$$
$$\text{net } 2CH_4 \rightarrow C_2H_2 + 3H_2 \tag{4a}$$

$$2(CH_4 + h\nu \rightarrow CH_2 + 2H) \tag{R5b}$$
$$\underline{2CH_2 \rightarrow C_2H_2 + H_2} \tag{R32}$$
$$\text{net } 2CH_4 \rightarrow C_2H_2 + 4H + H_2 \tag{4b}$$

$$CH_4 + h\nu \rightarrow CH + H + H_2 \tag{R5c}$$
$$\underline{CH + CH_4 \rightarrow C_2H_4 + H} \tag{R27}$$
$$\text{net } 2CH_4 \rightarrow C_2H_4 + 2H + H_2 \tag{5a}$$

$$CH_4 + h\nu \rightarrow CH_2 + 2H \qquad (R5b)$$

$$CH_4 \rightarrow CH_3 + H \qquad (1)$$

$$\underline{CH_2 + CH_3 \rightarrow C_2H_4 + H} \qquad (R34)$$

$$net\ 2CH_4 \rightarrow C_2H_4 + 4H \qquad (5b)$$
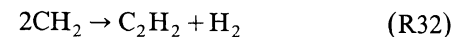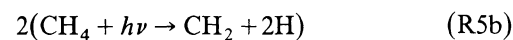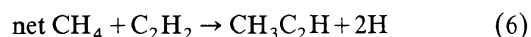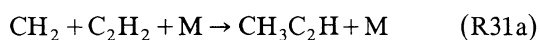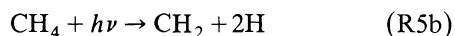
where in scheme (5b) the CH_3 radical is derived from scheme (1). Further reaction between CH_2 and C_2H_2 leads to the formation of methylacetylene

$$CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M \qquad (R31a)$$

(Laufer 1981a), and we have the scheme

$$CH_4 + h\nu \rightarrow CH_2 + 2H \qquad (R5b)$$

$$\underline{CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M} \qquad (R31a)$$

$$net\ CH_4 + C_2H_2 \rightarrow CH_3C_2H + 2H \qquad (6)$$

The chemistry summarized by schemes (4)–(6) is essentially what was proposed by Strobel (1974). It successfully accounts for the production of the observed species C_2H_2, C_2H_4, and CH_3C_2H. But the beautifully simple theory fails to explain the high abundance of C_2H_6 on Titan.
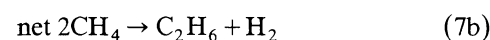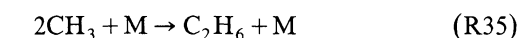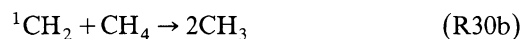
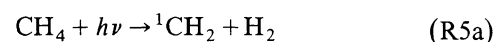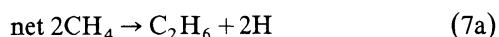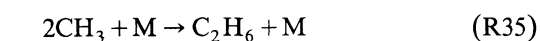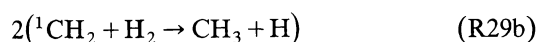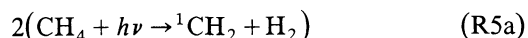### b) C_2H_6 and Photosensitized Dissociation of CH_4

Our understanding of the hydrocarbon photochemistry on Titan is closely related to that on Jupiter and Saturn. Table 1C presents a comparison of C_2H_6 and C_2H_2, and other relevant atmospheric parameters for Titan, Jupiter, and Saturn. The abundance of C_2H_6 in the stratosphere of Titan is high relative to C_2H_2, and when compared with C_2H_6 abundance in the stratosphere of Jupiter or Saturn. Comparison of the physical parameters of the atmospheres in Table 1C reveals no obvious explanation by simple physical processes such as condensation. We shall argue that this is an indication of a fundamental difficulty with the photochemical model of CH_4, as described by Strobel (1974).

Although no (or few) methyl radicals are produced in the direct photolysis of CH_4, the reactions of $^1CH_2$ with H_2 and CH_4 produce CH_3:

$$^1CH_2 + H_2 \rightarrow CH_3 + H, \qquad (R29b)$$

$$^1CH_2 + CH_4 \rightarrow 2CH_3 \qquad (R30b)$$
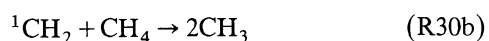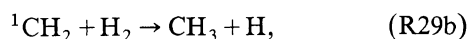
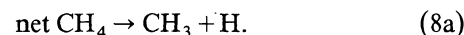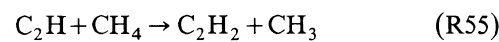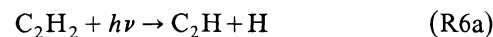(Laufer 1981a). This gives rise to two schemes for converting CH_4 into C_2H_6:

$$2\left(CH_4 + h\nu \rightarrow {}^1CH_2 + H_2\right) \qquad (R5a)$$

$$2\left({}^1CH_2 + H_2 \rightarrow CH_3 + H\right) \qquad (R29b)$$

$$\underline{2CH_3 + M \rightarrow C_2H_6 + M} \qquad (R35)$$

$$net\ 2CH_4 \rightarrow C_2H_6 + 2H \qquad (7a)$$

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2 \qquad (R5a)$$

$$^1CH_2 + CH_4 \rightarrow 2CH_3 \qquad (R30b)$$

$$\underline{2CH_3 + M \rightarrow C_2H_6 + M} \qquad (R35)$$

$$net\ 2CH_4 \rightarrow C_2H_6 + H_2 \qquad (7b)$$

Scheme (7a) is primarily responsible for producing C_2H_6 on Jupiter and Saturn, where H_2 is abundant (Strobel 1973; Yung and Strobel 1980). Strobel (1974) invoked schemes (7a) and (7b) to produce C_2H_6 on Titan under the assumption that the atmosphere was either pure CH_4 or 50% CH_4 and 50% H_2. In view of the *Voyager* discovery that N_2 is the dominant constituent of the atmosphere of Titan, we face a dilemma. Ninety-five percent of $^1CH_2$ produced in CH_4 photolysis is quenched by N_2; only 5% leads to production of CH_3. Indirect processes involving energetic electrons or cosmic rays such as scheme (1) provide a relatively small rate of production of CH_3 compared with the overall rate of CH_4 photolysis (see Table 2A for quantitative comparison). Thus, on the basis of primary photolysis of CH_4 we would not expect the abundance of C_2H_6 on Titan to exceed that of C_2H_2, or that there should be more C_2H_6 on Titan than on Jupiter and Saturn, in conflict with the observations summarized in Table 1C. We accept this as sufficient evidence for additional processes for driving CH_4 photochemistry on Titan.

Although the CH_3-H bond is only 102 kcal mole^{-1}, and photons with wavelengths shortward of 2768 Å are energetically capable of dissociating CH_4, the observed absorption threshold is at 1600 Å, and the absorption cross section does not become appreciable until $\lambda < 1450$ Å (Mount, Warden, and Moos 1977; Mount and Moos 1978). What is the fate of the soft ultraviolet photons longward of 1600 Å in the atmospheres of the outer planets and satellites? Recent observations of Jupiter and Saturn show that the ultraviolet albedos of these planets between 1500 and 2000 Å are dominated by acetylene absorption (Owen *et al.* 1980; Clarke, Moos, and Feldman 1982; McClintock *et al.* 1982; Moos and Clarke 1979; Gladstone and Yung 1983). Albedo measurements in this spectral range for Titan are not available, but C_2H_2 absorption is expected to be even more important because of the higher mixing ratio of C_2H_2 on Titan compared with that on Jupiter or Saturn (see Table 1C). Since most of the photons around 2000 Å are energetically capable of dissociating CH_4, molecular absorption could lead to an indirect path for destroying CH_4. Following the laboratory work by Payne and Stief (1976) and Laufer and Bass (1979), Allen, Pinto, and Yung (1980) proposed that the photolysis of C_2H_2 could lead to additional dissociation of CH_4 on Titan:

$$C_2H_2 + h\nu \rightarrow C_2H + H \qquad (R6a)$$

$$\underline{C_2H + CH_4 \rightarrow C_2H_2 + CH_3} \qquad (R55)$$

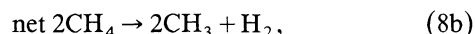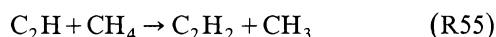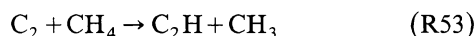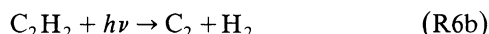$$net\ CH_4 \rightarrow CH_3 + H. \qquad (8a)$$

An extensive laboratory study by Okabe (1981, 1983a) has definitively established the existence of two important branches
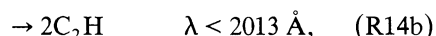
of C_2H_2 photolysis:

$$C_2H_2 + h\nu \rightarrow C_2H + H \qquad q_1, \qquad \text{(R6a)}$$

$$\rightarrow C_2 + H_2 \qquad q_2, \qquad \text{(R6b)}$$
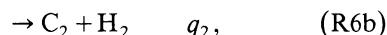
with quantum yields $q_1 = 0.3$ and 0.06 at 1470 and 1849 Å, respectively, and $q_2 \approx 0.1$ at both wavelengths. The first branch is crucial for scheme (8a). The second branch can give rise to another scheme for dissociating CH_4:
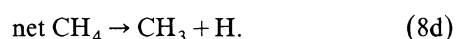
$$C_2H_2 + h\nu \rightarrow C_2 + H_2 \qquad \text{(R6b)}$$

$$C_2 + CH_4 \rightarrow C_2H + CH_3 \qquad \text{(R53)}$$

$$\underline{C_2H + CH_4 \rightarrow C_2H_2 + CH_3} \qquad \text{(R55)}$$

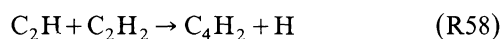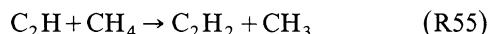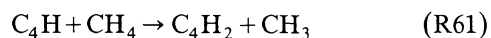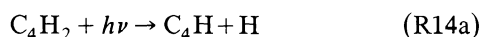$$\text{net } 2CH_4 \rightarrow 2CH_3 + H_2, \qquad \text{(8b)}$$

where the products in the reaction $C_2 + CH_4$ are based on the analysis of Pitts, Pasternack, and McDonald (1982). Note that two CH_4 molecules are destroyed for each C_2 radical produced.

There are obviously other possibilities. Diacetylene (C_4H_2), hydrogen cyanide (HCN), cyanoacetylene (HC_3N), and cyanogen (C_2N_2) have been detected on Titan. We shall first discuss C_4H_2. This molecule has an absorption spectrum that extends beyond that of C_2H_2 (Georgieff and Richard 1958). The products of photolysis include C_4H and C_2H (Graham, Dismuke, and Weltner 1974), but no quantitative study has been made. The primary processes are most probably
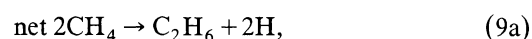
$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad \lambda < 2300 \text{ Å}, \qquad \text{(R14a)}$$

$$\rightarrow 2C_2H \qquad \lambda < 2013 \text{ Å}, \qquad \text{(R14b)}$$

where the threshold wavelengths (λ) have been estimated using heats of formation. The reactivity of C_4H toward CH_4 is not known. We postulate that it attacks CH_4 like C_2H. Photolysis of C_4H_2 gives rise to two schemes:

$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad \text{(R14a)}$$

$$\underline{C_4H + CH_4 \rightarrow C_4H_2 + CH_3} \qquad \text{(R61)}$$

$$\text{net } CH_4 \rightarrow CH_3 + H \qquad \text{(8c)}$$

$$C_4H_2 + h\nu \rightarrow 2C_2H \qquad \text{(R14b)}$$

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \qquad \text{(R55)}$$

$$\underline{C_2H + C_2H_2 \rightarrow C_4H_2 + H} \qquad \text{(R58)}$$

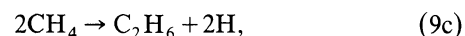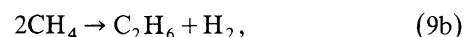$$\text{net } CH_4 \rightarrow CH_3 + H. \qquad \text{(8d)}$$

The schemes (8a)–(8d) share one common feature: they are catalytic cycles for decomposing CH_4 into CH_3 and hydrogen. The compounds C_2H_2 and C_4H_2 act as catalysts for collecting the solar energy needed for breaking CH_4 apart. The CH_3

radicals can now readily combine to form C_2H_6 as in

$$2CH_3 + M \rightarrow C_2H_6 + M \qquad \text{(R35)}$$

$$\underline{2(CH_4 \rightarrow CH_3 + H)} \qquad \text{(8a)}$$

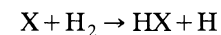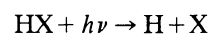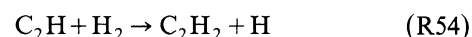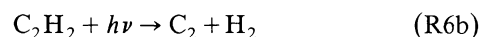$$\text{net } 2CH_4 \rightarrow C_2H_6 + 2H, \qquad \text{(9a)}$$

where the source of CH_3 is scheme (8a). Making similar use of schemes (8b)–(8d), we obtain the following schemes for converting CH_4 into C_2H_6:

$$2CH_4 \rightarrow C_2H_6 + H_2, \qquad \text{(9b)}$$

$$2CH_4 \rightarrow C_2H_6 + 2H, \qquad \text{(9c)}$$

$$2CH_4 \rightarrow C_2H_6 + 2H. \qquad \text{(9d)}$$

The efficiency of the new schemes is ultimately limited by the availability of photons. An estimate of the flux of photons that can be used to drive schemes (9a)–(9d) is given in Table 2A. Since the solar flux increases rapidly from 1000 to 2300 Å, it is clear that photosensitized dissociation of CH_4 could be significantly more important than direct photolysis and could provide a simple explanation for the high C_2H_6/C_2H_2 ratio on Titan.

The new chemistry is not expected to produce significant amounts of C_2H_6 on Jupiter and Saturn as a result of the scavenging of the reactive radicals by H_2. On the basis of Laufer and Bass (1979), Okabe (1981), and Pasternack and McDonald (1979), it is most likely that photolysis of C_2H_2 and C_4H_2 in a predominantly H_2 atmosphere results in the following schemes:

$$C_2H_2 + h\nu \rightarrow C_2 + H_2 \qquad \text{(R6b)}$$

$$\overset{\cdot}{C}_2 + H_2 \rightarrow C_2H + H \qquad \text{(R52)}$$

$$\underline{C_2H + H_2 \rightarrow C_2H_2 + H} \qquad \text{(R54)}$$

$$\text{net } H_2 \rightarrow 2H \qquad \text{(10a)}$$

$$HX + h\nu \rightarrow H + X$$

$$\underline{X + H_2 \rightarrow HX + H}$$

$$\text{net } H_2 \rightarrow 2H \qquad \text{(10b)}$$

where $X = C_2H$ or C_4H. In this case H_2 but not CH_4 is decomposed. Thus, the lower abundance of C_2H_6 on Jupiter and Saturn relative to that on Titan appears as a natural consequence of the predominance of H_2 on these planets.

The photochemistry of the observed nitrile compounds HCN, HC_3N, and C_2N_2 is similar to that of C_2H_2 and C_4H_2. Photolysis leads to the production of the reactive CN radical:

$$HCN + h\nu \rightarrow H + CN \qquad \lambda < 2200 \text{ Å}, \qquad \text{(R17)}$$

$$HC_3N + h\nu \rightarrow C_2H + CN \qquad \lambda < 1924 \text{ Å}, \qquad \text{(R18)}$$

$$C_2N_2 + h\nu \rightarrow 2CN \qquad \lambda < 2132 \text{ Å} \qquad \text{(R19)}$$
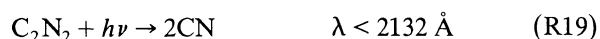
TABLE 2A

ESTIMATED MAXIMUM RATES OF DISSOCIATION OF SIMPLE MOLECULES IN
ATMOSPHERE OF TITAN BY INTERACTION WITH ULTRAVIOLET SUNLIGHT,
ENERGETIC ELECTRONS, AND COSMIC RAYS

Wavelength (Å)	πF^a $(cm^{-2} s^{-1})$	Potential Absorber	Quantum Yield	Maximum Dissociation Rate[b] $(cm^{-2} s^{-1})$
Solar flux				
Lyα (1216)	5.6×10^{11}	CH_4	1	2.2×10^9
1250–1600	6.0×10^{11}	CH_4	1	2.7×10^9
1600–2000	1.1×10^{13}	C_2H_2	0.16^c	8.0×10^9
2000–2300	1.2×10^{14}	C_4H_2	0.3^d	1.6×10^{11}
Energetic electrons[e]		N_2	1	1×10^9
Cosmic rays[f]		N_2	1	4×10^7

[a] Overhead Sun at 1 a.u. (Mount and Rottman 1981).
[b] $\pi F \times q \times f_1 \times f_2 \times f_3$, where q = quantum yield, f_1 = attenuation due to distance from Sun = 0.011, f_2 = global averaging factor = 0.25, and f_3 = sphericity correction factor = 1.6.
[c] Sum of C_2H and C_2 branches at 1849 Å (Okabe 1983a).
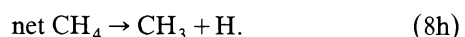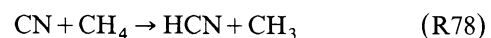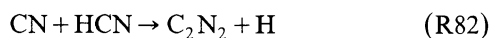[d] Estimated: see text.
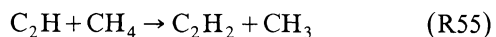[e] Strobel and Shemansky 1982.
[f] Capone et al. 1980.

TABLE 2B

SUMMARY OF IMPORTANT CHEMICAL CYCLES AND SCHEMES IN PHOTOCHEMICAL MODEL

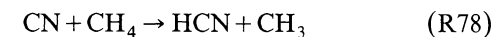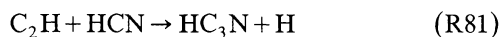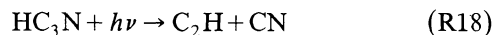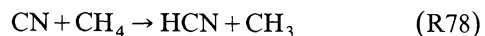| Scheme	Net Chemical Reaction	Region of Importance	Remarks
1	$CH_4 \rightarrow CH_3 + H$	thermosphere	catalyzed by N_2
2	$N_2 + CH_4 \rightarrow 2HCN + 3H_2$	thermosphere	driven by energetic electrons
3a	$H_2O + CH_4 \rightarrow CO + 2H + 2H_2$	thermosphere and mesosphere	major source of CO
3b	$H_2O + CO \rightarrow CO_2 + 2H$	thermosphere and mesosphere	major source of CO_2
4a	$2CH_4 \rightarrow C_2H_2 + 3H_2$	mesosphere	photolysis of CH_4
3b	$2CH_4 \rightarrow C_2H_2 + 4H + H_2$	mesosphere	photolysis of CH_4
5a	$2CH_4 \rightarrow C_2H_4 + 2H + H_2$	mesosphere	photolysis of CH_4
5b	$2CH_4 \rightarrow C_2H_4 + 4H$	mesosphere	photolysis of CH_4
6	$CH_4 + C_2H_2 \rightarrow CH_3C_2H + 2H$	mesosphere	photolysis of CH_4
7a	$2CH_4 \rightarrow C_2H_6 + 2H$	...	important on Jupiter but not on Titan
7b	$2CH_4 \rightarrow C_2H_6 + H_2$	...	important in Strobel 1974 model but not in current model
8a, 8c–8h ..	$CH_4 \rightarrow CH_3 + H$	stratosphere	catalyzed by C_2H_2, C_4H_2, HCN, HC_3N, C_2N_2
8b	$2CH_4 \rightarrow 2CH_3 + H_2$	stratosphere	catalyzed by C_2H_2
9a, 9c–9d ..	$2CH_4 \rightarrow C_2H_6 + 2H$	stratosphere	catalyzed by C_2H_2, C_4H_2
9b	$2CH_4 \rightarrow C_2H_6 + H_2$	stratosphere	catalyzed by C_2H_2
10a, 10b ...	$H_2 \rightarrow 2H$	...	quenching of C_2, C_2H, C_4H by H_2; important on Jupiter but not on Titan
11a–11c ...	$C_2H_6 \rightarrow C_2H_5 + H$	stratosphere	catalyzed by C_2H_2, C_4H_2
12	$CH_4 + C_2H_6 \rightarrow C_3H_8 + 2H$	stratosphere	driven by photosensitized dissociation of CH_4 and C_2H_6
13	$2C_2H_2 \rightarrow C_4H_2 + 2H$	stratosphere	major source of C_4H_2
14	$C_2H_2 + HCN \rightarrow HC_3N + 2H$	stratosphere	major source of HC_3N
15	$2HCN \rightarrow C_2N_2 + 2H$	stratosphere	major source of C_2N_2
16a–16c ...	$2H \rightarrow H_2$	stratosphere	catalyzed by C_2H_2 and HCN
17a	$C_2H_4 + 2H \rightarrow C_2H_6$	stratosphere	destruction of C_2H_4 by H
17b	$2CH_3C_2H + 2H \rightarrow C_2H_6 + 2C_2H_2$	stratosphere	cracking of CH_3C_2H by H
17c	$C_4H_2 + 2H \rightarrow 2C_2H_2$	stratosphere	cracking of C_4H_2 by H
17d	$C_2N_2 + 2H \rightarrow 2HCN$	stratosphere	cracking of C_2N_2 by H
17e	$HC_3N + 2H \rightarrow C_2H_2 + HCN$	stratosphere	cracking of HC_3N by H
18	$2H \rightarrow H_2$	stratosphere	catalyzed by C_4H_2

(Lee 1980; Connors, Roebber, and Weiss 1974). The following schemes are obvious analogs of schemes (8a)–(8d)

$$HCN + h\nu \rightarrow H + CN \qquad (R17)$$

$$\underline{CN + CH_4 \rightarrow HCN + CH_3} \qquad (R78)$$

$$net\ CH_4 \rightarrow CH_3 + H \qquad (8e)$$

$$HC_3N + h\nu \rightarrow C_2H + CN \qquad (R18)$$

$$C_2H + HCN \rightarrow HC_3N + H \qquad (R81)$$

$$\underline{CN + CH_4 \rightarrow HCN + CH_3} \qquad (R78)$$

$$net\ CH_4 \rightarrow CH_3 + H \qquad (8f)$$

$$HC_3N + h\nu \rightarrow C_2H + CN \qquad (R18)$$

$$CN + C_2H_2 \rightarrow HC_3N + H \qquad (R80)$$

$$\underline{C_2H + CH_4 \rightarrow C_2H_2 + CH_3} \qquad (R55)$$

$$net\ CH_4 \rightarrow CH_3 + H \qquad (8g)$$

$$C_2N_2 + h\nu \rightarrow 2CN \qquad (R19)$$

$$CN + HCN \rightarrow C_2N_2 + H \qquad (R82)$$

$$\underline{CN + CH_4 \rightarrow HCN + CH_3} \qquad (R78)$$

$$net\ CH_4 \rightarrow CH_3 + H. \qquad (8h)$$
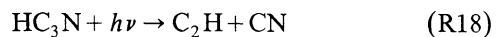
The overall additional contribution to the photosensitized dissociation of CH_4 is, however, small, because of the overlap of the spectral regions of absorption by C_2H_2 and C_4H_2 and the lower abundances of the nitrile compounds.

It should be pointed out that the importance of photosensitized dissociation in atmospheric chemistry is the rule rather than the exception. A notable example is the generation of hydroxyl radicals in the terrestrial troposphere by
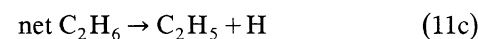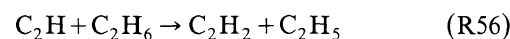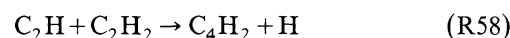
$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$\underline{O(^1D) + H_2O \rightarrow 2OH}$$

$$net\ O_3 + H_2O \rightarrow O_2 + 2OH$$
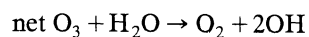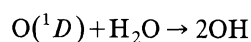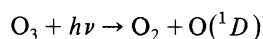
(Levy 1971; McConnell, McElroy, and Wofsy 1971). Direct photolysis of H_2O

$$H_2O + h\nu \rightarrow H + OH$$
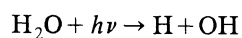
requires photons with wavelengths $\lambda < 2420$ Å and is negligible except in the mesosphere and thermosphere (see Allen, Yung, and Waters 1981). The photosensitized dissociation of

H_2O is initiated by absorption of photons with wavelength $\lambda < 3100$ Å and is the major source of the important OH radical in the troposphere (see Logan et al. 1978).

Pursuing the analogy with the terrestrial atmosphere, we note that Strobel (1974) had only mesospheric chemistry; the stratosphere in his model is an inert reservoir. The *Voyager* observations provide compelling evidence for the existence of stratospheric photochemistry, initiated by photosensitized processes. Acetylene plays a role in the stratosphere of Titan similar to that of ozone in the terrestrial troposphere. The similarity can be extended even further. The reactive radicals C_2H and C_4H are like $O(^1D)$ and OH, and are capable of abstracting H from C_2H_6:

$$C_2H_2 + h\nu \rightarrow C_2H + H \qquad (R6a)$$

$$\underline{C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5} \qquad (R56)$$

$$net\ C_2H_6 \rightarrow C_2H_5 + H \qquad (11a)$$

$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad (R14a)$$

$$\underline{C_4H + C_2H_6 \rightarrow C_4H_2 + C_2H_5} \qquad (R62)$$

$$net\ C_2H_6 \rightarrow C_2H_5 + H \qquad (11b)$$

$$C_4H_2 + h\nu \rightarrow 2C_2H \qquad (R14b)$$

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \qquad (R58)$$

$$\underline{C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5} \qquad (R56)$$

$$net\ C_2H_6 \rightarrow C_2H_5 + H \qquad (11c)$$
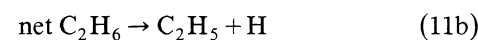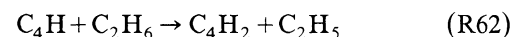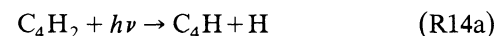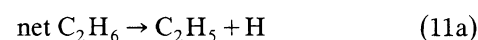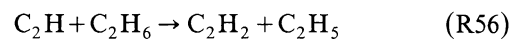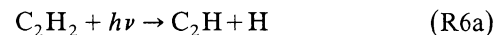
Note that the photosensitized dissociation of C_2H_6 ([11a]–[11c]) differs from the direct photolysis, which proceeds preferentially by molecular elimination:

$$C_2H_6 + h\nu \rightarrow C_2H_4 + H_2 \qquad (R8a)$$

$$\rightarrow C_2H_2 + 2H_2. \qquad (R8c)$$
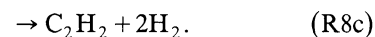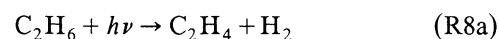
The production of the ethyl radical by schemes (11a)–(11c) opens a number of pathways for producing propane in the atmosphere. Combining the schemes (8a) and (11a) we have

$$2(C_2H_2 + h\nu \rightarrow C_2H + H) \qquad (R6a)$$

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \qquad (R55)$$

$$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5 \qquad (R56)$$

$$\underline{CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M} \qquad (R40b)$$

$$net\ CH_4 + C_2H_6 \rightarrow C_3H_8 + 2H. \qquad (12)$$
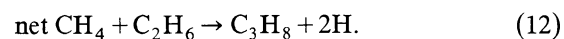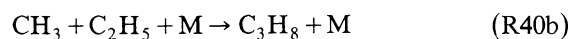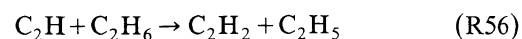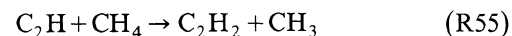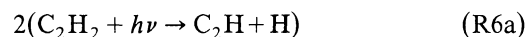
Obviously the combination of any one of the schemes (8a)–(8h) with any one of the schemes (11a)–(11c) results in the formation of C_3H_8. It is satisfying to note that the high abundance

of propane on Titan, as observed by the *Voyager*, is an inexorable consequence of the photosensitized processes in the stratosphere, but otherwise has no simple explanation.

c) Unsaturated Carbon Compounds and Scavenging of H Atoms

The production of the unsaturated carbon compounds listed in Table 1A poses no difficulty for the photochemical model. HCN, C_2H_2, C_2H_4, and CH_3C_2H are readily produced in the thermosphere and mesosphere by schemes (2), (4a)–(4b), (5a)–(5b), and (6), respectively. Production of C_4H_2, HC_3N, and C_2N_2 appears to be a natural consequence of stratospheric chemistry described in the previous subsection using C_2H_2 and HCN originally formed in the upper atmosphere, as illustrated by the following schemes:

$$C_2H_2 + h\nu \rightarrow C_2H + H \tag{R6a}$$

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H \tag{R58}$$

$$\text{net } 2C_2H_2 \rightarrow C_4H_2 + 2H \tag{13}$$

$$C_2H_2 + h\nu \rightarrow C_2H + H \tag{R6a}$$

$$C_2H + HCN \rightarrow HC_3N + H \tag{R81}$$

$$\text{net } C_2H_2 + HCN \rightarrow HC_3N + 2H \tag{14}$$

$$HCN + h\nu \rightarrow H + CN \tag{R17}$$

$$CN + HCN \rightarrow C_2N_2 + H \tag{R82}$$

$$\text{net } 2HCN \rightarrow C_2N_2 + 2H. \tag{15}$$
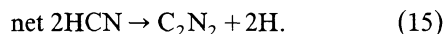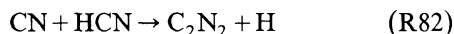
The kinetics for schemes (13)–(15) has been fairly well established by recent studies (Laufer 1981b; Okabe 1981; Schacke, Wagner, and Wolfrum 1977; Becker and Hong 1983).

To explain the high abundances of the unsaturated compounds on Titan, it is, of course, not sufficient that the molecules are easily produced. It is essential also that the destructive processes are somehow rendered impotent. Shielding against photolysis is provided to a large extent by C_2H_2 and C_4H_2. Most of the absorbed photons are converted into thermal energy. The small fraction that leads to dissociation of C_2H_2, C_4H_2, HCN, HC_3N, and C_2N_2 ultimately results in photosensitizing the dissociation of CH_4, as in schemes (8a)–(8h). Another way to view these schemes is that the unstable compounds that are photolyzed are restored at the expense of CH_4. Thus, the impact of ultraviolet radiation on the unsaturated compounds in the stratosphere is greatly mitigated. Unfortunately, the schemes (8a) and (8c)–(8h) produce a hydrogen atom for each photolysis event. Since carbon species with unsaturated bonds are extremely reactive toward H atoms, the stability of these compounds is not insured until the hydrogen atoms are removed.

Since hydrogen atoms cannot easily escape from the stratosphere, they must react with other stratospheric species. We shall first discuss the interaction between H and the most abundant unsaturated species C_2H_2. The reaction produces C_2H_3 (Payne and Stief 1976):

$$C_2H_2 + H + M \rightarrow C_2H_3 + M. \tag{R25}$$
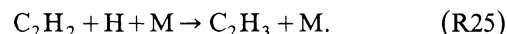
The vinyl radical can react again with H, or undergo disproportionation:

$$C_2H_3 + H \rightarrow C_2H_2 + H_2, \tag{R36}$$

$$2C_2H_3 \rightarrow C_2H_2 + C_2H_4. \tag{R38}$$

The ultimate fate of the hydrogen atoms tied up by C_2H_4 depends on the pathway of C_2H_4 photolysis:

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \tag{R7a}$$

$$\rightarrow C_2H_2 + 2H. \tag{R7b}$$
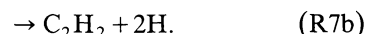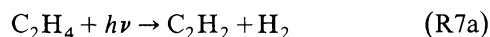
Only the first branch leads to net destruction of H. The results can be summarized in two schemes:
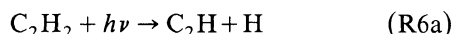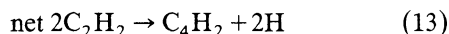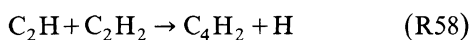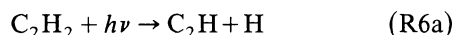
$$C_2H_2 + H + M \rightarrow C_2H_3 + M \tag{R25}$$

$$C_2H_3 + H \rightarrow C_2H_2 + H_2 \tag{R36}$$

$$\text{net } 2H \rightarrow H_2 \tag{16a}$$

$$2(C_2H_2 + H + M \rightarrow C_2H_3 + M) \tag{R25}$$

$$2C_2H_3 \rightarrow C_2H_2 + C_2H_4 \tag{R38}$$

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \tag{R7a}$$

$$\text{net } 2H \rightarrow H_2. \tag{16b}$$
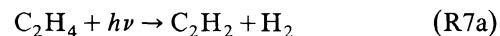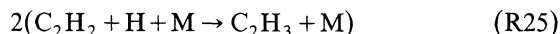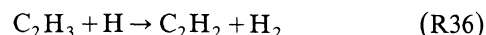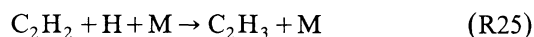
Schemes (16a) and (16b) convert hydrogen atoms into molecular hydrogen. Once it is formed, H_2 is practically inert in the atmosphere, and it eventually escapes from the exosphere.

The rate limiting step in the catalytic cycles (16a) and (16b) for removing H atoms is the reaction forming the vinyl radical. From the experiments of Payne and Stief (1976) we deduce the low and high pressure limit for the rate coefficient to be $k_0 = 9.5 \times 10^{-33}$ cm^6 s^{-1} and $k_\infty = 3.1 \times 10^{-15}$ cm^3 s^{-1} at 150 K. This is a slow reaction, and the catalytic cycles (16a) and (16b) are not capable of rapidly removing the copious amounts of H atoms produced by schemes (8a) and (8c)–(8h). Reaction between HCN and H has not been studied, but we can invoke an analogy with C_2H_2 and propose the following scheme for removing hydrogen atoms:

$$H + HCN + M \rightarrow H_2CN + M \tag{R83}$$

$$H + H_2CN \rightarrow H_2 + HCN \tag{R84}$$

$$\text{net } 2H \rightarrow H_2 \tag{16c}$$
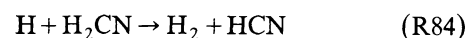
We do not expect cycle (16c) to be more important than cycles (16a) or (16b).

The reaction of ethylene with H has been extensively studied (see Kurylo, Peterson, and Braun 1970; Lee *et al.* 1978) and can be summarized by

$$C_2H_4 + H + M \rightarrow C_2H_5 + M, \qquad (R26)$$

$$C_2H_5 + H \rightarrow 2CH_3. \qquad (R39)$$
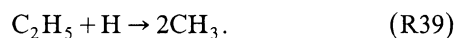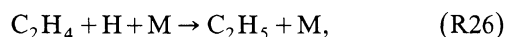
The branch restoring C_2H_4:

$$C_2H_5 + H \rightarrow C_2H_4 + H_2,$$

is considered unlikely with a maximum branching ratio of 5% relative to the cracking branch (Camilleri, Marshall, and Purnell 1974). Hence, the net result of H on C_2H_4 is the scheme:

$$C_2H_4 + H + M \rightarrow C_2H_5 + M \qquad (R26)$$

$$C_2H_5 + H \rightarrow 2CH_3 \qquad (R39)$$

$$\underline{2CH_3 + M \rightarrow C_2H_6 + M} \qquad (R35)$$

$$\text{net } C_2H_4 + 2H \rightarrow C_2H_6. \qquad (17a)$$

Once it is formed, C_2H_6 is fairly stable and represents a nearly permanent sink for C_2H_4. Laboratory studies have demonstrated that H atoms can destroy CH_3C_2H (von Wagner and Zellner 1972*a*; Whytock, Payne, and Stief 1976; Niedzielski, Gawlowski, and Gierczak 1983), C_4H_2 (Schwanebeck and Warnatz 1975), and C_2N_2 (Phillips 1978), as in the following schemes:

$$2(CH_3C_2H + H \rightarrow CH_3 + C_2H_2) \qquad (R45a)$$

$$\underline{2CH_3 + M \rightarrow C_2H_6 + M} \qquad (R35)$$

$$\text{net } 2CH_3C_2H + 2H \rightarrow C_2H_6 + 2C_2H_2 \qquad (17b)$$

$$C_4H_2 + H + M \rightarrow C_4H_3 + M \qquad (R68)$$

$$\underline{C_4H_3 + H \rightarrow 2C_2H_2} \qquad (R69a)$$

$$\text{net } C_4H_2 + 2H \rightarrow 2C_2H_2 \qquad (17c)$$

$$C_2N_2 + H + M \rightarrow HC_2N_2 + M \qquad (R87)$$

$$\underline{HC_2N_2 + H \rightarrow 2HCN} \qquad (R88)$$

$$\text{net } C_2N_2 + 2H \rightarrow 2HCN. \qquad (17d)$$
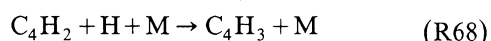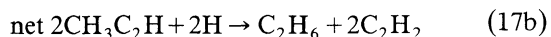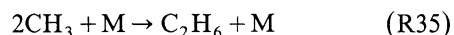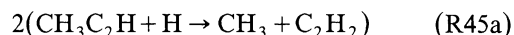
The reaction between H and HC_3N has not been studied, but we expect the result to be similar to that of H on C_4H_2 or C_2N_2, and we have the following analogous scheme:

$$HC_3N + H + M \rightarrow H_2C_3N + M \qquad (R85)$$

$$\underline{H_2C_3N + H \rightarrow C_2H_2 + HCN} \qquad (R86)$$

$$\text{net } HC_3N + 2H \rightarrow C_2H_2 + HCN. \qquad (17e)$$
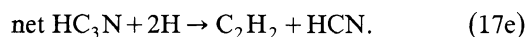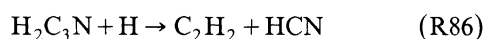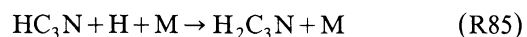
It is of interest to note that the net results of schemes (17c), (17d), and (17e) are exactly the reverse of that of schemes (13), (15), and (14), respectively.

We have arrived at a fundamental difficulty that is largely independent of the details of the model. The production of hydrogen is an inevitable consequence of using CH_4, a hydrogen-rich molecule, as the ultimate source of carbon in the synthesis of the more complex compounds, C_2H_6, C_3H_8, C_4H_2, HC_3N, and C_2N_2, that are deficient in hydrogen. A similar situation was encountered in Strobel's (1974) model. But the bulk of Strobel's chemistry takes place in the mesosphere, and the problem is alleviated by the escape of hydrogen. Unfortunately, stratospheric chemistry occurs much too deep in the atmosp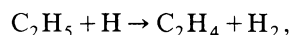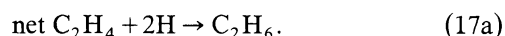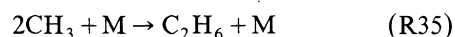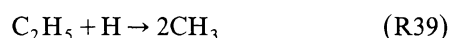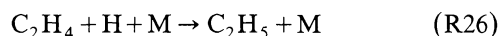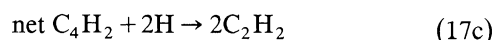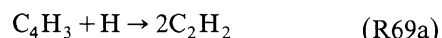here for escape of H atoms to occur. It is conceivable to find the equivalents of schemes (9a), (9c)–(9d), and (12)–(15) which all produce H_2 but not H. But this is forsaking a large body of known laboratory results in favor of the unknown. Instead we shall take a more conservative position of postulating just one catalytic scheme for removing H atoms:

$$C_4H_2 + H + M \rightarrow C_4H_3 + M \qquad (R68)$$

$$\underline{C_4H_3 + H \rightarrow C_4H_2 + H_2} \qquad (R69b)$$

$$\text{net } 2H \rightarrow H_2. \qquad (18)$$
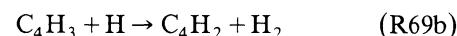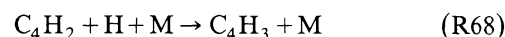
Scheme (18) is based on obvious analogy with (16a). According to H. Okabe (1983, private communication), the radical C_4H_3 is analogous to C_2H_3, and consequently scheme (18) could be several times more important than (17c). Postulating a kinetic rate coefficient for (R69b) equal to 1.2×10^{-11} cm^3 s^{-1} would be sufficient to resolve the hydrogen problem. For comparison, we note that the analogous reaction

$$C_2H_3 + H \rightarrow C_2H_2 + H_2$$
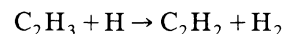
was measured by Keil *et al.* (1976) to have a rate coefficient between 1 and 2×10^{-11} cm^2 s^{-1}. Scheme (18) is supposed to include minor variations of the scheme, such as the following:

$$C_4H_2 + H + M \rightarrow C_4H_3 + M \qquad (R68)$$

$$C_4H_3 + H + M \rightarrow C_4H_4 + M \qquad (R69c)$$

$$\underline{C_4H_4 + h\nu \rightarrow C_4H_2 + H_2} \qquad (R103b)$$

$$\text{net } 2H \rightarrow H_2.$$
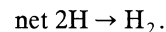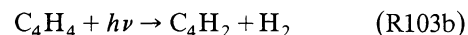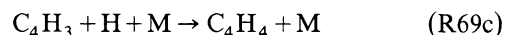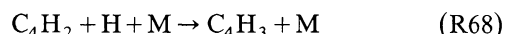
In an experiment studying the impact of H on C_4H_2, the intermediate species, vinyl acetylene (C_4H_4), has actually been observed (Schwanebeck and Warnatz 1975). It should be noted that scheme (18) is the simplest and the most plausible that we can think of. Any other process, such as recombination of H on the surface of aerosol grains, would serve the same purpose, and would be consistent with all the existing observations.

d) Outline of Approach

We have briefly discussed the photochemistry of Titan's atmosphere in terms of 18 major chemical cycles and schemes
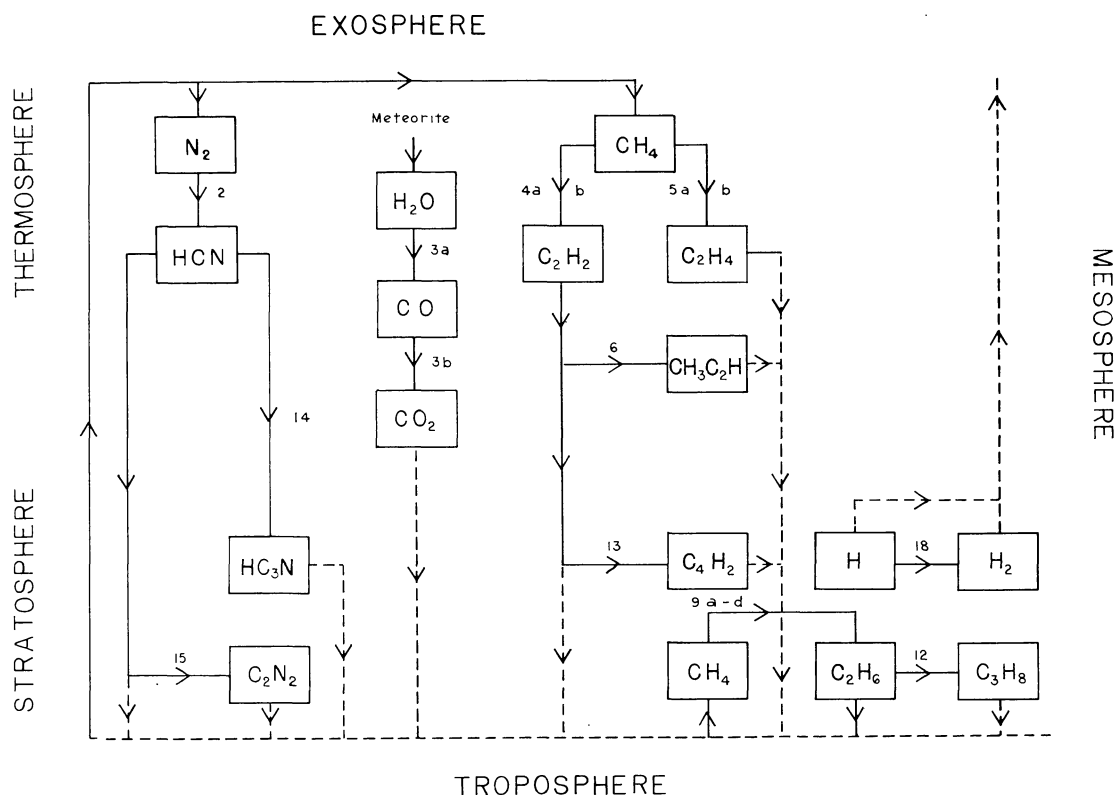
FIG. 1.—Schematic diagram showing how the observed species are related to the parent molecules N_2, H_2O, and CH_4, and to each other. Numbers refer to the chemical cycles or schemes discussed in § II and summarized in Table 2B.

summarized in Table 2B. A schematic diagram showing how the observed species relate to the parent molecules and to each other via the chemical schemes is presented in Figure 1. Table 2B and Figure 1 together provide a broad perspective of the chemistry of the Titanian atmosphere. This simple picture probably contains the essential ingredients of a successful model, although many details remain to be defined or refined. Our discussion reveals a number of deficiencies in our understanding of the reactions of $N(^2D)$, $N(^4S)$, and NH with hydrocarbons and their radicals, the photochemistry of C_4H_2, the chemical kinetics of the radicals C_2 and C_4H, and the interaction between H atoms and the unsaturated carbon species. These will be elaborated in the following section, which consists of an updated treatment of the photochemistry and chemical kinetics of hydrocarbons, nitrogen, and oxygen compounds. A photochemical model will be presented, along with comparisons between theory and observations. The implications of the model for the composition of the troposphere, the origin and evolution of Titan's atmosphere, Titan's geochemistry, and chemical evolution in the primitive terrestrial atmosphere will be discussed. The emphasis of this work is neutral chemistry. Ion chemistry, aerosol chemistry, and the strong coupling between thermal structure and chemistry will be explored in separate papers. Our work focuses on detailed photochemical modeling and should be regarded as complementary to recent work which addresses the formation of Titan (Prinn and Fegley 1981), the origin of its atmosphere (Owen 1982), airglow (Strobel and Shemansky 1982), thermal

structure (Friedson and Yung 1983), and general aeronomy (Strobel 1982; Hunten et al. 1983).

III. PHOTOCHEMISTRY AND CHEMICAL KINETICS

The photochemistry of hydrocarbons containing one or two carbon atoms has been studied in previous work (see Strobel 1974) and will not be discussed in detail here, except where revision or updating is needed. The photochemistry of polyacetylenes (these compounds are also known as polyynes; the nomenclature here follows that of combustion literature) has been briefly discussed by Allen, Pinto, and Yung (1980). The photochemistry of nitrogen compounds in a reducing atmosphere has not been investigated, except for a qualitative discussion by Strobel (1982). The photochemistry of oxygen compounds in a mildly reducing atmosphere has been investigated by Pinto, Gladstone, and Yung (1980). Tables 3A–3C list the essential reactions, related to dissociations, hydrocarbons, and nitrogen and oxygen, respectively. Speculative reactions involving the more complex hydrocarbons are discussed in the Appendix. Our tables include most of the reactions considered in previous work, as well as new reactions. Most of the material in this section has been assembled, with critical evaluation, from previous papers on related subjects and the extensive compilations or reviews by Calvert and Pitts (1966), Johnston, Cuff, and Price (1977), Okabe (1978), Allara and Shaw (1980), Laufer (1981a), Ashihara (1983), Brown and Winkler (1970), Safrany (1971), and DeMore et al. (1982).

TABLE 3

A.

MOLECULAR DISSOCIATION REACTIONS

Reaction[a]			Quantum Yield Ly α	Other	Photodissociation[b] Coefficient (J)	Reference
R1	$N_2 + e$	$\rightarrow$	$N + N\,(^2D) + e$	see text	—	Strobel and Shemansky 1982
R2	$N_2 + CR$	$\rightarrow$	$N + N(^2D)$	' '	—	Capone et al. 1980
R3a	$CO + e$	$\rightarrow$	$C + O + e$	' '	—	Lee and McKay 1982;
b		$\rightarrow$	$C + O(^1D) + e$	' '	—	See text
R4	$CH_3 + h\nu$	$\rightarrow$	$^1CH_2 + H$	1.0	1.0×10^{-6}	Parkes et al. 1973
R5a	$CH_4 + h\nu$	$\rightarrow$	$^1CH_2 + H_2$	0.41	1.0	2.2×10^{-8}	Watanabe et al. 1953;
b		$\rightarrow$	$CH_2 + 2H$	0.51	0	2.0×10^{-8}	Strobel 1973; Mount
c		$\rightarrow$	$CH + H + H_2$	0.08	0	3.2×10^{-9}	and Moos 1978
R6a	$C_2H_2 + h\nu$	$\rightarrow$	$C_2H + H$	0.3	0.06	4.5×10^{-8}	Nakayama and Watanabe 1964;
b		$\rightarrow$	$C_2 + H_2$	0.10	0.10	2.5×10^{-8}	Okabe 1981, 1983a
R7a	$C_2H_4 + h\nu$	$\rightarrow$	$C_2H_2 + H_2$	0.51		1.4×10^{-7}	Zelikoff and Watanabe 1953;
b		$\rightarrow$	$C_2H_2 + 2H$	0.49		1.2×10^{-7}	Back and Griffiths 1967
R8a	$C_2H_6 + h\nu$	$\rightarrow$	$C_2H_4 + H_2$	0.13	0.56	1.1×10^{-8}	Akimoto et al. 1965;
b		$\rightarrow$	$C_2H_4 + 2H$	0.30	0.14	9.1×10^{-9}	Hampson and McNesby 1965;
c		$\rightarrow$	$C_2H_2 + 2H_2$	0.25	0.27	9.9×10^{-9}	Lias et al. 1970;
d		$\rightarrow$	$CH_4 + {}^1CH_2$	0.25	0.02	6.1×10^{-9}	Mount and Moos 1978
e		$\rightarrow$	$2CH_3$	0.08	0.01	3.5×10^{-9}	
R9	$C_3H_3 + h\nu$	$\rightarrow$	$C_3H_2 + H$	1.0		1.2×10^{-7}	Poole and Anderson 1959; Ramsay and Thistlewaithe 1966; Jacox and Milligan 1974
R10a	$CH_3C_2H + h\nu$	$\rightarrow$	$C_3H_3 + H$	0.40		9.0×10^{-8}	Stief et al. 1971;
b		$\rightarrow$	$C_3H_2 + H_2$	0.15		2.4×10^{-8}	Hamai and Hirayama 1979;
c		$\rightarrow$	$CH_3 + C_2H$	0.02		4.5×10^{-9}	Heller and Milne 1978
R11a	$CH_2CCH_2 + h\nu$	$\rightarrow$	$C_3H_3 + H$	0.40		3.2×10^{-7}	Sutcliffe and Walsh 1952;
b		$\rightarrow$	$C_3H_2 + H_2$	0.15		1.2×10^{-7}	Rabalais et al. 1971;
c		$\rightarrow$	$C_2H_2 + CH_2$	0.06		4.9×10^{-8}	Heller and Milne 1978
R12a	$C_3H_6 + h\nu$	$\rightarrow$	$CH_2CCH_2 + H_2$	0.57		3.5×10^{-7}	Calvert and Pitts 1966;
b		$\rightarrow$	$C_2H_4 + CH_2$	0.02		1.2×10^{-8}	Borrell et al. 1971;
c		$\rightarrow$	$C_2H_2 + CH_3 + H$	0.34		2.0×10^{-7}	Collin et al. 1979
d		$\rightarrow$	$C_2H + CH_4 + H$	0.05		3.0×10^{-8}	
R13a	$C_3H_8 + h\nu$	$\rightarrow$	$C_3H_6 + H_2$	0.33	0.94	4.6×10^{-8}	Calvert and Pitts 1966
b		$\rightarrow$	$C_2H_6 + {}^1CH_2$	0.09	0.0	7.6×10^{-9}	
c		$\rightarrow$	$C_2H_5 + CH_3$	0.39	0.0	3.3×10^{-8}	
d		$\rightarrow$	$C_2H_4 + CH_4$	0.20	0.06	1.8×10^{-8}	
R14a	$C_4H_2 + h\nu$	$\rightarrow$	$C_4H + H$	0.30		2.6×10^{-7}	Georgieff and Richard 1958;
b		$\rightarrow$	$2C_2H$	0.30		1.7×10^{-7}	Okabe 1981; Heller and Milne 1978
R15a	$C_6H_2 + h\nu$	$\rightarrow$	$C_6H + H$	0.30		2.6×10^{-7}	Kloster-Jensen et al. 1974;
b		$\rightarrow$	$C_4H + C_2H$	0.30		1.7×10^{-7}	estimated, based on $C_4H_2 + h\nu$
R16a	$C_8H_2 + h\nu$	$\rightarrow$	$C_6H + C_2H$	0.30		2.6×10^{-7}	Kloster-Jenson et al. 1974;
b		$\rightarrow$	$2C_4H$	0.30		1.7×10^{-7}	estimated, based on $C_4H_2 + h\nu$
R17	$HCN + h\nu$	$\rightarrow$	$H + CN$	1.0		1.1×10^{-7}	West 1975; Lee 1980
R18	$HC_3N + h\nu$	$\rightarrow$	$C_2H + CN$	0.3		4.0×10^{-7}	Connors et al. 1974
R19	$C_2N_2 + h\nu$	$\rightarrow$	$2CN$	0.3		2.7×10^{-7}	Connors et al. 1974; Nuth and Glicker 1982
R20a	$CO_2 + h\nu$	$\rightarrow$	$CO + O$	c		7.4×10^{-11}	Shemansky 1972;
b		$\rightarrow$	$CO + O(^1D)$	c		5.5×10^{-9}	DeMore and Patapoff 1972
R21a	$H_2O + h\nu$	$\rightarrow$	$H + OH$	c		5.1×10^{-8}	Allen et al. 1981
b		$\rightarrow$	$H_2 + O(^1D)$	c		2.0×10^{-8}	
R22a	$H_2CO + h\nu$	$\rightarrow$	$H_2 + CO$	0.60		2.5×10^{-7}	Pinto et al. 1980
b		$\rightarrow$	$H + HCO$	0.40		1.8×10^{-7}	
R23	$HCO + h\nu$	$\rightarrow$	$H + CO$	1		1.0×10^{-4}	Pinto et al. 1980
R24	$CH_2CO + h\nu$	$\rightarrow$	$CH_2 + CO$	1		1.3×10^{-6}	Okabe 1978

[a] Excited atom or molecule: $N(^2D)$, $O(^1D)$, $^1CH_2 = CH_2(\tilde{a}^1A_1)$; CR = cosmic rays.

[b] The values for diurnally averaged dissociation coefficient refer to the top of the atmosphere in units of s^{-1}.

[c] See Allen, Yung, and Waters 1981; quantum yields wavelength dependent.

B.
ESSENTIAL HYDROCARBON REACTIONS

Reaction	Rate Coefficient[a] (k)	Reference
R25 $H + C_2H_2 + M \rightarrow C_2H_3 + M$	$k_0 = 6.4 \times 10^{-25} \, T^{-2} \, e^{-1200/T}$ $k_\infty = 9.2 \times 10^{-12} \, e^{-1200/T}$	Payne and Stief 1976; b
R26 $H + C_2H_4 + M \rightarrow C_2H_5 + M$	$k_0 = 1.1 \times 10^{-23} \, T^{-2} \, e^{-1040/T}$ $k_\infty = 3.7 \times 10^{-11} \, e^{-1040/T}$	Michael et al. 1973; Lee et al. 1978; c
R27 $CH + CH_4 \rightarrow C_2H_4 + H$	1.0×10^{-10}	Butler et al. 1981; products assumed
R28 $^1CH_2 + N_2 \rightarrow CH_2 + N_2$	7.9×10^{-12}	Ashfold et al. 1980
R29a $^1CH_2 + H_2 \rightarrow CH_2 + H_2$	1.0×10^{-12}	Laufer 1981a
b $\rightarrow CH_3 + H$	7.0×10^{-12}	
R30a $^1CH_2 + CH_4 \rightarrow CH_2 + CH_4$	1.6×10^{-12}	''
b $\rightarrow 2CH_3$	1.9×10^{-12}	
R31a $CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M$	$k_0 = 3.8 \times 10^{-25}$ $k_\infty = 2.2 \times 10^{-12}$	Laufer et al. 1983; Laufer 1981a
b $\rightarrow CH_2CCH_2 + M$	$k_0 = 3.8 \times 10^{-25}$ $k_\infty = 3.7 \times 10^{-12}$	
R32 $2CH_2 \rightarrow C_2H_2 + H_2$	5.3×10^{-11}	Banyard et al. 1980; Laufer 1981a
R33 $CH_3 + H + M \rightarrow CH_4 + M$	$k_0 = 1.7 \times 10^{-27}$ $k_\infty = 1.5 \times 10^{-10}$	Laufer et al. 1983; Patrick et al. 1980
R34 $CH_3 + CH_2 \rightarrow C_2H_4 + H$	7.0×10^{-11}	Laufer 1981a
R35 $2CH_3 + M \rightarrow C_2H_6 + M$	$k_0 = 1.3 \times 10^{-23}$ $k_\infty = 5.5 \times 10^{-11}$	Laufer et al. 1983; Callear and Metcalfe 1976
R36 $C_2H_3 + H \rightarrow C_2H_2 + H_2$	1.5×10^{-11}	Keil et al. 1976; d
R37a $C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4$	9.1×10^{-12}	estimated from Takita et al. 1968 Laufer et al. 1983
b $(+ M) \rightarrow C_3H_6 + M$	$k_0 = 1.3 \times 10^{-22}$ $k_\infty = 9.1 \times 10^{-12}$	
R38 $2C_2H_3 \rightarrow C_2H_4 + C_2H_2$	5.3×10^{-12}	MacFadden and Currie 1973
R39 $C_2H_5 + H \rightarrow 2CH_3$	$1.9 \times 10^{-10} \, e^{-440/T}$	Teng and Jones 1972
R40a $C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4$	$1.7 \times 10^{-12} \, e^{-200/T}$	Teng and Jones 1972 Laufer et al. 1983
b $(+ M) \rightarrow C_3H_8 + M$	$k_0 = 5.6 \times 10^{-22}$ $k_\infty = 4.2 \times 10^{-11} \, e^{-200/T}$	
R41a $C_2H_5 + C_2H_3 \rightarrow C_2H_6 + C_2H_2$	6.0×10^{-12}	Laufer et al. 1983
b $\rightarrow 2C_2H_4$	3.0×10^{-12}	
R42a $2C_2H_5 \rightarrow C_2H_6 + C_2H_4$	$1.7 \times 10^{-12} \, e^{-90/T}$	Teng and Jones 1972 Laufer et al. 1983
b $(+ M) \rightarrow C_4H_{10} + M$	$k_0 = 2.9 \times 10^{-21}$ $k_\infty = 1.3 \times 10^{-11} \, e^{-95/T}$	
R43 $C_3H_2 + H + M \rightarrow C_3H_3 + M$	$k_0 = 1.7 \times 10^{-26}$ $k_\infty = 1.5 \times 10^{-10}$	Laufer et al. 1983 based on analogy with $CH_3 + H$
R44a $C_3H_3 + H + M \rightarrow CH_3C_2H$	$k_0 = 1.7 \times 10^{-26}$ $k_\infty = 1.5 \times 10^{-10}$	''
b $\rightarrow CH_2CCH_2 + M$	same as branch (a)	''
R45a $CH_3C_2H + H + M \rightarrow (C_3H_5^* + M)$ $\rightarrow CH_3 + C_2H_2 + M$	$k_0 = 8.0 \times 10^{-24} \, T^{-2} \, e^{-1225/T}$ $k_\infty = 9.7 \times 10^{-12} \, e^{-1550/T}$	Whytock et al. 1976; e Wagner and Zellner 1972a
b $\rightarrow C_3H_5 + M$	same as branch (a)	
R46a $CH_2CCH_2 + H + M \rightarrow (C_3H_5^* + M)$ $\rightarrow CH_3 + C_2H_2 + M$	$k_0 = 8.0 \times 10^{-24} \, T^{-2} \, e^{-1225/T}$ $k_\infty = 9.7 \times 10^{-13} \, e^{-1550/T}$	Based on analogy with $CH_3C_2H + H$; Wagner and Zellner 1972b
b $\rightarrow C_3H_5 + M$	$k_0 = 8.0 \times 10^{-24} \, T^{-2} \, e^{-1225/T}$ $k_\infty = 1.4 \times 10^{-11} \, e^{-1000/T}$	
R47a $C_3H_5 + H \rightarrow CH_3C_2H + H_2$	1.5×10^{-11}	Based on analogy with $C_2H_3 + H$ and estimates based on Wagner and Zellner 1972a,b
b $\rightarrow CH_2CCH_2 + H_2$	1.5×10^{-11}	

TABLE 3B—*Continued*

	Reaction	Rate Coefficient[a] (k)	Reference
c	(+ M) $\rightarrow$ C_3H_6 + M	$k_0 = 1.0 \times 10^{-28}$ $k_\infty = 1.0 \times 10^{-11}$	
d	$\rightarrow$ CH_4 + C_2H_2	1.5×10^{-11}	
R48	C_3H_6 + H + M $\rightarrow$ C_3H_7 + M	$k_0 = 1.5 \times 10^{-29}$ $k_\infty = 3.7 \times 10^{-11}\ e^{-1040/T}$	Laufer et al. 1983 Based on analogy with C_2H_4 + H
R49	C_3H_7 + H $\rightarrow$ C_2H_5 + CH_3	$1.9 \times 10^{-10}\ e^{-440/T}$	Based on analogy with C_2H_5 + H
R50a	C_3H_5 + CH_3 $\rightarrow$ CH_3C_2H + CH_4	4.5×10^{-12}	Based on analogy with C_2H_3 + CH_3
b	$\rightarrow$ CH_2CCH_2 + CH_4	4.5×10^{-12}	
R51a	C_3H_7 + CH_3 $\rightarrow$ C_3H_6 + CH_4	$2.5 \times 10^{-12}\ e^{-200/T}$	Based on analogy with C_2H_5 + CH_3
b	(+ M) $\rightarrow$ C_4H_{10} + M	$k_0 = 2.5 \times 10^{-19}$ $k_\infty = 4.2 \times 10^{-11}\ e^{-200/T}$	Laufer et al. 1983
R52	C_2 + H_2 $\rightarrow$ C_2H + H	1.4×10^{-12}	Pasternack and McDonald 1979
R53	C_2 + CH_4 $\rightarrow$ C_2H + CH_3	1.9×10^{-11}	''
R54	C_2H + H_2 $\rightarrow$ C_2H_2 + H	$1.9 \times 10^{-11}\ e^{-1450/T}$	Laufer 1981b; Brown and Laufer 1981
R55	C_2H + CH_4 $\rightarrow$ C_2H_2 + CH_3	$2.8 \times 10^{-12}\ e^{-250/T}$	''
R56	C_2H + C_2H_6 $\rightarrow$ C_2H_2 + C_2H_5	6.5×10^{-12}	''
R57	C_2H + C_3H_8 $\rightarrow$ C_2H_2 + C_3H_7	1.4×10^{-11}	Okabe 1983b
R58	C_2H + C_2H_2 $\rightarrow$ C_4H_2 + H	3.1×10^{-11}	Laufer 1981b; Brown and Laufer 1981
R59	C_2H + C_4H_2 $\rightarrow$ C_6H_2 + H	3.1×10^{-11}	Estimated, see text
R60	C_2H + C_6H_2 $\rightarrow$ C_8H_2 + H	3.1×10^{-11}	''
R61	C_4H + CH_4 $\rightarrow$ C_4H_2 + CH_3	$9.3 \times 10^{-13}\ e^{-250/T}$	''
R62	C_4H + C_2H_6 $\rightarrow$ C_4H_2 + C_2H_5	2.2×10^{-12}	''
R63	C_4H + C_2H_2 $\rightarrow$ C_6H_2 + H	1.0×10^{-11}	''
R64	C_4H + C_4H_2 $\rightarrow$ C_8H_2 + H	1.0×10^{-11}	''
R65	C_6H + CH_4 $\rightarrow$ C_6H_2 + CH_3	$3.1 \times 10^{-13}\ e^{-250/T}$	''
R66	C_6H + C_2H_6 $\rightarrow$ C_6H_2 + C_2H_5	6.5×10^{-12}	''
R67	C_6H + C_2H_2 $\rightarrow$ C_8H_2 + H	3.3×10^{-12}	''
R68	H + C_4H_2 + M $\rightarrow$ C_4H_3 + M	$k_0 = 1.0 \times 10^{-28}$ $k_\infty = 2.0 \times 10^{-12}$	Schwanebeck and Warnatz 1975
R69a	H + C_4H_3 $\rightarrow$ $2C_2H_2$	3.3×10^{-12}	''
b	$\rightarrow$ C_4H_2 + H_2	1.2×10^{-11}	See text; branch c is not considered separately
c	(+ M) $\rightarrow$ C_4H_4 + M		
R70	H + CH_2CCH_2 $\rightarrow$ CH_3C_2H + H	$1.0 \times 10^{-11}\ e^{-1000/T}$	See text

[a] Units for two-body and three-body rate coefficients are $cm^3\ s^{-1}$ and $cm^6\ s^{-1}$, respectively; the effective two-body rate coefficient for a three-body reaction is given by $k = k_0 k_\infty M/(k_0 + k_\infty M)$, where k_0, k_∞, and M are, respectively, the rate coefficients in the low pressure and high pressure limits, and the number density of ambient atmosphere in molecules cm^{-3}.

[b] k_0 is obtained by fitting the data of Payne and Stief 1976 between 10 and 700 torr; the temperature dependence T^{-2} is assumed.

[c] k_0 is obtained using the data of Michael, Osborne, and Suess 1973 between 3 and 300 torr; products assumed.

[d] Based on Keil *et al.*'s 1976 conclusion that this rate coefficient must be between 1 and $2 \times 10^{-11}\ cm^3\ s^{-1}$.

[e] T^{-2} temperature dependence assumed.

In general, the chemistry of compounds containing two or less carbon atoms is fairly well established (see Strobel 1973, 1974); that of the more complex compounds is poorly understood. Fortunately, most of the reactions in Tables 3A–3C belong to certain recognizable types, and their behavior can be at least qualitatively predicted by semiempirical theories or by analogy with known reactions (Laufer *et al.* 1983). In § II we emphasize the conceptual similarity between the chemistry of the Titanian and the terrestrial atmospheres. It will become clear in the following discussion that this similarity is deeply rooted at the more fundamental level of chemical kinetics. The radicals CH, $^1CH_2$, CH_3, C_2H and CN are remarkably similar in character to the radicals $O(^1D)$, O, OH, and Cl. Since the chemistry of the latter species is well defined because of their importance in the terrestrial atmosphere (see Hudson, Reed, and Bojkov 1982; DeMore *et al.* 1982), it serves as a useful comparison. The discussion in this section is organized according to reaction types and should be regarded as a supplement to § II. Some subjects, such as CH_4 photolysis, have been addressed in the previous section. Others, such as

TABLE 3
C.
NITROGEN AND OXYGEN COMPOUND REACTION

	Reaction	Rate Coefficient[a] (k)	Reference
R71a	$N(^2D) \rightarrow N + h\nu$	2.3×10^{-5}	Okabe 1978
b	$N(^2D) + N_2 \rightarrow N + N_2$	$< 6 \times 10^{-15}$	Black et al. 1969
R72	$N(^2D) + CH_4 \rightarrow NH + CH_3$	3.0×10^{-12}	''
R73	$N + CH_2 \rightarrow HCN + H$	$5.0 \times 10^{-11} e^{-250/T}$	Estimated, see text
R74	$N + CH_3 \rightarrow HCN + H_2$	$5.0 \times 10^{-11} e^{-250}$	''
R75	$NH + H \rightarrow N + H_2$	$1.7 \times 10^{-12} T^{0.68} e^{-950/T}$	Mayer et al. 1966
R76	$NH + N \rightarrow N_2 + H$	$1.1 \times 10^{-11} \sqrt{T}$	Westley 1980
R77	$2NH + M \rightarrow N_2 + H_2 + M$	1.0×10^{-33}	Estimated, see text
R78	$CN + CH_4 \rightarrow HCN + CH_3$	$1.0 \times 10^{-11} e^{-857/T}$	Schacke et al. 1977
R79	$CN + C_2H_6 \rightarrow HCN + C_2H_5$	2.0×10^{-11}	Estimated
R80	$CN + C_2H_2 \rightarrow HC_3N + H$	5.0×10^{-11}	Schacke et al. 1977
R81	$HCN + C_2H \rightarrow HC_3N + H$	2.2×10^{-12}	Becker and Hong 1983; b
R82	$CN + HCN \rightarrow C_2N_2 + H$	3.1×10^{-11}	Estimated by analogy with $C_2H + C_2H_2$
R83	$HCN + H + M \rightarrow H_2CN + M$	$k_0 = 6.4 \times 10^{-25} T^{-2} e^{-1200/T}$ $k_\infty = 9.2 \times 10^{-12} e^{-1200/T}$	Estimated by analogy with $H + C_2H_2$
R84	$H_2CN + H \rightarrow HCN + H_2$	1.5×10^{-11}	''
R85	$HC_3N + H + M \rightarrow H_2C_3N + M$	$k_0 = 6.4 \times 10^{-25} T^{-2} e^{-1200/T}$ $k_\infty = 9.2 \times 10^{-12} e^{-1200/T}$	''
R86	$H_2C_3N + H \rightarrow C_2H_2 + HCN$	1.5×10^{-11}	''
R87	$C_2N_2 + H + M \rightarrow HC_2N_2 + M$	$k_0 = 6.4 \times 10^{-25} T^{-2} e^{-1200/T}$ $k_\infty = 1.5 \times 10^{-15}$	'' Phillips 1978
R88	$HC_2N_2 + H \rightarrow 2HCN$	$1.7 \times 10^{-13} e^{-110/T}$	Albers 1969
R89a	$O(^1D) \rightarrow O + h\nu$	6.7×10^{-3}	Okabe 1978
b	$O(^1D) + N_2 \rightarrow O + M$	$1.8 \times 10^{-11} e^{107/T}$	DeMore et al. 1982
R90a	$O(^1D) + CH_4 \rightarrow OH + CH_3$	1.4×10^{-10}	''
b	$\rightarrow H_2CO + H_2$	1.4×10^{-11}	
R91	$O + CH_2 \rightarrow CO + 2H$	8.3×10^{-11}	Homann and Schweinfurth 1981
R92	$O + CH_3 \rightarrow H_2CO + H$	1.3×10^{-10}	Hampson 1980
R93	$OH + CH_4 \rightarrow H_2O + CH_3$	$2.4 \times 10^{-12} e^{-1710/T}$	Baulch et al. 1980
R94	$OH + CH_2 \rightarrow CO + H_2 + H$	5.0×10^{-12}	Estimated, based on analogy with $OH + CH_3$
R95	$OH + CH_3 \rightarrow CO + 2H_2$	6.7×10^{-12}	Fenimore 1969
R96	$OH + CO \rightarrow CO_2 + H$	1.4×10^{-13}	DeMore et al. 1982
R97	$OH + C_2H_2 + M \rightarrow CH_2CO + H + M$	$k_0 = 5.8 \times 10^{-31} e^{1258/T}$ $k_\infty = 1.4 \times 10^{-12} e^{388/T}$	Perry and Williamson 1982
R98	$CH_2 + CO_2 \rightarrow CO + H_2CO$	3.9×10^{-14}	Laufer 1981a
R99	$H + CO + M \rightarrow HCO + M$	$2.0 \times 10^{-33} e^{-850/T}$	Pinto et al. 1980
R100	$H + HCO \rightarrow H_2 + CO$	3.0×10^{-10}	''
R101	$2HCO \rightarrow H_2CO + CO$	6.3×10^{-11}	''
R102	$CH_2 + CO + M \rightarrow CH_2CO + M$	$k_0 = 1.0 \times 10^{-28}$ $k_\infty = 1.0 \times 10^{-15}$	estimated Laufer 1981a

[a]Units for unimolecular reactions are s^{-1}; for bimolecular and termolecular reactions, see note (a) of Table 3B.
[b]On the basis of Becker and Hong 1983, we obtained the ratio $k_{81}/k_{58} = 0.07$.

H_2O and CO_2 photochemistry, are well understood from our experience with the terrestrial planets. These subjects will not be further discussed.

a) Dissociation

The molecules N_2 and CO are sufficiently stable (bond energy = 226, 257 kcal mole^{-1}, respectively) that photolysis is negligible. As discussed in § IIa, dissociation of these molecules can occur as a result of impact by energetic electrons of magnetospheric origin. The analysis of Strobel and Shemansky (1982) suggested an integrated dissociation rate of N_2 equal to 1×10^9 cm^{-2} s^{-1}. (Unless otherwise stated, all fluxes refer to the surface.) The product is an even mixture of N and $N(^2D)$. A small fraction of the nitrogen atoms will react with hydrocarbons to form CN compounds (see § IIIb). Most recombine to restore N_2 (see § IIIe). Based on the similarity in the molecular properties of CO and N_2, Samuelson et al. (1983) inferred an integrated dissociation rate of CO equal to $1.2 \times 10^9 f_{CO}$ cm^{-2} s^{-1}, where f_{CO} is the mixing ratio of CO. The destruction of CO by this mechanism is not important in the present atmosphere, but could be important if CO were more abundant in the past. Dissociation of N_2 can also occur in the stratosphere by absorption of cosmic rays, but the integrated rate is much smaller $\sim 4 \times 10^7$ cm^{-2} s^{-1} (Capone et al. 1980). The impact of cosmic rays on CO is negligible and is not considered.

Four absorption bands of CH_3 are listed in Okabe (1978). Of these, the $B - X$ band at 2160 Å is the most important for dissociating CH_3:

$$CH_3(X^2A_2) + h\nu \rightarrow CH_2(\tilde{a}^1A_1) + H(^2S_{1/2}). \quad (R4)$$
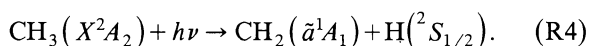
We assume that the quantum yield is unity. The products have been deduced by the present authors, on the basis of spin conservation. Photolysis of CH_3 is marginally important compared with removal by chemical reactions. Photolysis of CH_2 (Okabe 1978) and C_2H_5 (Adachi, Basco, and James 1979) is relatively unimportant.

As discussed in § IIb, the photolysis of C_2H_2 provides a source of the important radicals C_2H and C_2 in the stratosphere. Okabe's study at 1470 and 1849 Å has been extended to 1933 Å by Irion and Kompa (1982), with generally consistent results. Three important questions remain unanswered regarding the photochemistry of C_2H_2: (a) What is the fate of the major fraction of the excited C_2H_2 molecules which do not dissociate? (b) Are they related to vinylidene radicals (Laufer 1982; Laufer and Yung 1983)? (c) Why is the quantum yield (q) for C_2H_2 disappearance at 1470 Å so high (Okabe 1981)? Question (c) is profoundly disturbing. Okabe reported a quantum yield $q \approx -1.5$. For comparison, $q \approx -0.4$ due to direct photolysis, and $q \approx -0.8$ if we assume, in addition, complete removal of C_2H and C_2 by C_2H_2. Okabe's puzzling result is consistent with that of Zelikoff and Aschenbrand (1956) at 1849 Å at low pressure. The latter work gave $q \approx -2$ and further showed that the loss of C_2H_2 cannot be explained by converting it into the species C_2H_4, C_4H_2, C_4H_4, and C_6H_6, which were measured in the experiment. So there is the intriguing possibility that a hitherto unknown mechanism can photosensitize the destruction of

C_2H_2 at low pressure, perhaps by converting it into a polymer. This may offer a simple explanation for the low abundances of C_2H_2 on Jupiter and Saturn and the existence of Axel-Danielson dust (Axel 1972) on these planets (see Table 1C and Gladstone 1983). However, in this work the interesting possibilities regarding excited C_2H_2, vinylidene, and C_2H_2 polymerization will not be pursued.

We have little information on the photofragmentation pattern of some of the higher hydrocarbons. There is, however, a close relation between fragmentation processes due to photons and those due to energetic electrons of comparable energies (Brion et al. 1979; Hitchcock, Brion, and van der Wiel 1980; Trajmar 1980a, b). Excitation of a molecule by a photon or an energetic electron can be described by a dipole transition. The decay of the excited state into the allowed product channels is essentially a statistical phenomenon. This implies some limited usefulness of the mass spectral data based on electron impact for suggesting the pattern of photodissociation. The photolysis branches of C_4H_2, CH_3C_2H, and CH_2CCH_2 are estimated on the basis of the electron mass spectroscopy data taken from Heller and Milne (1978).

The absorption cross sections for C_4H_2 have been measured by Georgieff and Richard (1958) and Okabe (1981). Although the observed absorption spectrum extends as far as 2700 Å. we note that the processes

$$C_4H_2 + h\nu \rightarrow C_4H + H \qquad q_1 = 0.3, \quad (R14a)$$

$$\rightarrow 2C_2H \qquad q_2 = 0.3, \quad (R14b)$$
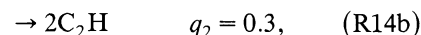
are energetically possible only with the absorption of photons with wavelengths below 2300 and 2013 Å, respectively. The quantum yields for dissociation have not been measured. Based on analogy with C_2H_2 dissociation, and discussion in the previous paragraph, we estimate quantum yields of 0.30 for the above two branches. Pontrelli (1966) suggested that photolysis of C_4H_2 at 2537 Å can proceed by molecular elimination of C_2 from a bent excited molecule. However, no quantitative information is available. Okabe (1983, private communication) did not consider this branch to be important. Until further experiments are performed, the results of Pontrelli will be ignored. Inspection of the relative spectra of higher polyacetylenes obtained by Kloster-Jensen, Haink, and Christen (1974) suggests that the cross sections for C_6H_2 and C_8H_2 are similar to those of C_4H_2.

The absorption cross sections of methylacetylene are taken from Hamai and Hirayama (1979). The quantum yields at 1470 Å for the branches

$$CH_3C_2H + h\nu \rightarrow C_3H_3 + H \qquad q_1 = 0.40, \quad (R10a)$$

$$\rightarrow C_3H_2 + H_2 \qquad q_2 = 0.15, \quad (R10b)$$
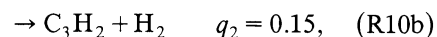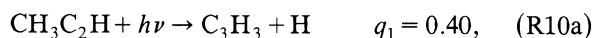
were measured by Stief, DeCarlo, and Payne (1971). Note that these two branches do not result in a net loss of C_3 compounds. The branch

$$CH_3C_2H + h\nu \rightarrow CH_3 + C_2H \qquad q_3 = 0.02, \quad (R10c)$$
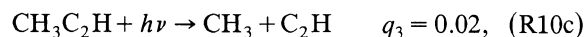
which destroys C_3 compounds, has not been measured, and we

estimate a conservative quantum yield of 0.02 by analogy with its fragmentation pattern by electron impact (Heller and Milne 1978). The absorption spectrum for allene was measured by Sutcliffe and Walsh (1952). However, this reference contains only a photographic plate and a qualitative description of the major absorption features. The actual cross sections used in our model are taken from Rabalais et al. (1971), who apparently had access to Sutcliffe and Walsh's original data. The computed photolysis rate for allene is only 3 times higher than that for methylacetylene. Thus, photolysis alone may not account for the absence of allene on Titan. Photoisomerization of allene into cyclopropene and methylacetylene has been suggested by Steinmetz, Mayes, and Yang (1982), but no quantitative data are available, and we do not include this reaction in our model. A preferred mechanism for converting allene to methylacetylene is proposed in § IIIe. A recent investigation by Collin, Deslauriers, and Deschenes (1979) suggested that allene is readily produced by photolysis of propene

$$C_3H_6 + h\nu \rightarrow CH_2CCH_2 + H_2. \qquad (R12a)$$
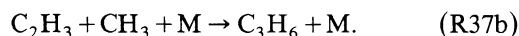
The primary source of C_3H_6 in the atmosphere of Titan is the reaction

$$C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M. \qquad (R37b)$$

This provides a source of C_3 compounds in the stratosphere (see § IIId).

Photodissociation of HCN shortward of 1500 Å has been studied by Lee (1980). But the absorption continuum certainly extends as far as 1950 Å (West 1975). Photolysis of HCN leads to the production of the important CN radical

$$HCN + h\nu \rightarrow H + CN. \qquad (R17)$$

On the basis of the absence of fluorescence following the absorption of a photon by HCN, L. Lee (1981, private communication) concluded that the quantum yield for dissociation is unity. The absorption cross sections for HC_3N and C_2N_2 are taken from Connors, Roebber, and Weiss (1974). Estimates for the quantum yields are based on analogy with that for C_4H_2.
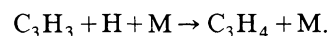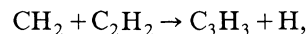
b) Insertion

Methylacetylene and allene are formed by insertion of methylene into acetylene, as first suggested by Strobel (1974):

$$CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M, \qquad (R31a)$$

$$\rightarrow CH_2CCH_2 + M. \qquad (R31b)$$
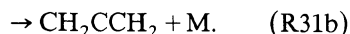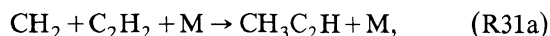
At room temperature, in the two-body limit, Laufer and Bass (1974) obtained $k_{31} = k_{31a} + k_{31b} = 7.5 \times 10^{-12}$ cm^3 s^{-1}, a value which should be compared with 4.0×10^{-12} cm^3 s^{-1}, as reported by Pilling and Robertson (1977). Laufer (1981a) proposed an average value for $k_{31} = 5.8 \pm 1.8 \times 10^{-12}$ cm^3 s^{-1}. The ratio of the two channels k_{31a}/k_{31b} is 0.50 and 0.59, according to Laufer and Bass (1974) and Pilling and Robertson (1977), respectively, in marked contrast to the value 1.5 re-

ported by Terao, Sakai, and Shida (1963). The difference could be attributed to the presence of $^1CH_2$ in the experiment by Terao et al. (Laufer 1981a). Recent work (Banyard et al. 1980) claimed that k_{31} could be 15 times smaller than the value obtained by Laufer and Bass (1974). However, since these authors did not publish a detailed account of their work, we do not include their results in this paper. Homann and Schweinfurth (1981) argued that C_3H_4 (methylacetylene or allene) is actually produced in two steps:

$$CH_2 + C_2H_2 \rightarrow C_3H_3 + H,$$

$$C_3H_3 + H + M \rightarrow C_3H_4 + M.$$

The new mechanism leads to the same result as (R31), since the propargyl radical C_3H_3 most likely reacts with atomic hydrogen in our model.

The rate coefficients for the insertion reactions leading to the formation of higher polyacetylenes ($n \geq 2$)

$$C_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H,$$
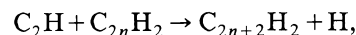
have not been measured, but in view of the simple insertion mechanism it is reasonable to assume that these reactions have rate coefficients similar to

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H. \qquad (R58)$$
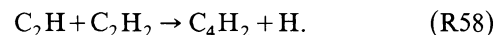
The higher polyacetylene radicals are probably less reactive than C_2H, and their rate coefficients have been adjusted according to

$$k(C_{2n}H) = 3^{1-n}k(C_2H),$$

where $n = 1, 2, 3$ (see Table 3B).

The mechanism for polymerization of acetylene on Titan proposed by Allen, Pinto, and Yung (1980) is a crucial part of our hydrocarbon theory. The experimental and theoretical basis of this mechanism will be briefly discussed. The existence of long-chain cyanopolyacetylenes in the interstellar medium is well established (see Watson 1976; Green 1981), and a scheme for producing long-chain carbon compounds using ion-neutral reactions has been proposed by Mitchell and Huntress (1979). This mechanism bears striking resemblance to ours. The only difference is in the use of ions rather than radicals to drive polymerization. The ion scheme has probably limited applications to planetary atmospheres, except perhaps in the auroral zones of Jupiter (Gladstone 1983).

The problem of building complex long-chain carbon compounds from simpler hydrocarbons is an outstanding one in the theory of combustion. It is now known that polyacetylenes are produced in the combustion of acetylene-rich fuel, and it has been further suggested that polyacetylenes are precursors of soot (Bonne, Homann, and Wagner 1965; Homann 1967; Homann and Wagner 1968; Homann, Warnatz, and Wellmann 1976). A number of schemes for producing polyacetylenes from acetylene have been suggested. All these schemes must address a crucial issue, described in the words of Homann, Warnatz, and Wellmann (1976): "For polyacetylenes to form from C_2H_2, the molecule must gain carbon

in some form and release hydrogen atoms, if one excludes the addition of free carbon... However, after the first addition of C_2H or CH to C_2H_2 a comparatively inert H_3-species is formed and further rapid addition of C_2H_2 is blocked if the radical cannot release some of its hydrogen by action of O atoms." Our scheme is modeled after Homann *et al.*, but with the important modification that we use ultraviolet radiation instead of O atoms to produce active radicals and ensure the buildup of long chains by a series of insertion reactions. We can now see that the long-chain carbon chemistry in three diversely different systems—interstellar medium, combustion, and Titan's atmosphere—are complementary, and much of our theory is based on empirical combustion data.

A small fraction of odd nitrogen derived from the thermosphere survives self-destruction to react with hydrocarbon radicals. Formation of HCN in our model occurs primarily via the insertion reactions:

$$N + CH_2 \rightarrow HCN + H, \qquad (R73)$$

$$N + CH_3 \rightarrow HCN + H_2. \qquad (R74)$$
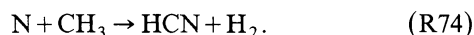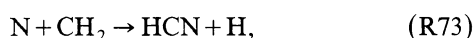
Based on the discussion by Safrany (1971) and the experiment by Froben (1974), reaction (R74) is probably the net result of two reactions

$$N + CH_3 \rightarrow H_2CN + H$$

$$\underline{H + H_2CN \rightarrow HCN + H_2}$$

$$\text{net } N + CH_3 \rightarrow HCN + H_2.$$
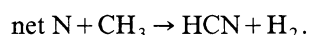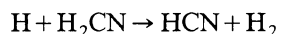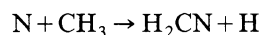
The overall rate coefficient k_{74} has been estimated by Armstrong and Winkler (1955) to lie between $(5.0 \times 10^{-11} - 5.0 \times 10^{-13})e^{-250/T}$. We have chosen a high value for Table 3C. Reaction (R73) was suggested by Safrany (1971). We assume that its rate coefficient is the same as that for (R74). For comparison, we note that the reaction CH + N has been measured by Messing *et al.* (1981) to be fast, with rate coefficient $k = 2.1 \times 10^{-11}$ cm^3 s^{-1}. According to M. Lin (1982, private communication), the most likely products are CN + H, and the reactions $CH_2 + N$ and $CH_3 + N$ should behave like CH + N in rates and products.

Following the arguments of Michael (1980), we reject the results of all previous work on the formation of HCN by direct insertion of N atoms into alkanes, alkenes, and alkynes (Miyazaki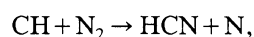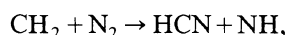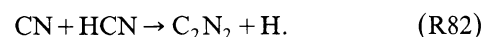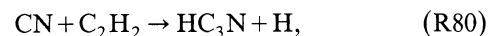 and Takahashi 1968; Solomon, Homann, and Warnatz 1970; Sato, Suguwara, and Ishikawa 1979), since the results might have been due to contamination by trace quantities of excited states of nitrogen, $N_2(A^3\Sigma_u^+)$ and $N(^2D)$. Nor do we include possible new channels for the formation of HCN by

$$CH_2 + N_2 \rightarrow HCN + NH,$$

$$CH + N_2 \rightarrow HCN + N,$$

since the results of the experiments of Braun, McNesby, and Bass (1967) and Laufer and Bass (1978) cannot be simply interpreted in terms of the above endothermic reactions. A recent high temperature study by Berman, Fleming, and Lin

(1982) showed that the reaction $CH + N_2 \rightarrow HCN + N$ has an activation energy of 11 kcal mole^{-1}, making it totally unimportant for Titan. Direct reaction between NH and hydrocarbons in solution leads to the formation of HCN (Kitamura, Tsunashima, and Sato 1981), but there is no basis for putting together even a speculative scheme for similar processes in the gas phase.

The major pathway for reactions involving CN and C_2H with compounds containing unsaturated bonds is probably insertion, followed by ejection of a hydrogen atom. This can lead to the production of new nitrile compounds, cyanoacetylene (HC_3N) and cyanogen (C_2N_2):

$$CN + C_2H_2 \rightarrow HC_3N + H, \qquad (R80)$$

$$C_2H + HCN \rightarrow HC_3N + H, \qquad (R81)$$

$$CN + HCN \rightarrow C_2N_2 + H. \qquad (R82)$$

The alternative pathway, abstraction of a hydrogen atom, most probably has a high activation energy. Some of the products in reactions (R80)–(R82) have been identified in experiments by Herron, Franklin, and Bradt (1959) and Schacke, Wagner, and Wolfrum (1977). The appropriate rate coefficients listed in Table 3C have been estimated using Schacke, Wagner, and Wolfrum (1977), Becker and Hong (1983), and analogy with similar reactions involving the ethynyl radical.

We have excluded from one discussion the possibility of insertion of CN into alkanes such as

$$CH_4 + CN \rightarrow CH_3CN + H.$$
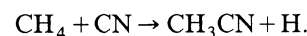
This reaction is exothermic by 12 kcal mole^{-1} and could have been responsible for the production of CH_3CN in the experiments of Haggart and Winkler (1960) and Gupta, Ochiai, and Ponnamperuma (1981). However, unless further experimental data demonstrate the contrary, we consider the insertion of CN into an alkane as slow when compared with abstraction, consistent with the absence of CH_3CN in the atmosphere of Titan.

Given a source of oxygen in the forms of O and OH, CO can be readily produced by the insertion reactions with the radicals CH_2 and CH_3:

$$O + CH_3 \rightarrow CO + 2H, \qquad (R91)$$

$$O + CH_3 \rightarrow H_2CO + H, \qquad (R92)$$

$$OH + CH_2 \rightarrow CO + H_2 + H, \qquad (R94)$$

$$OH + CH_3 \rightarrow CO + 2H_2. \qquad (R95)$$
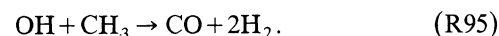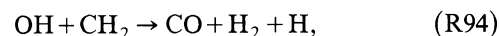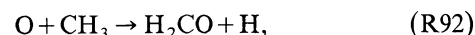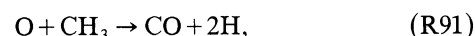
Since H_2CO rapidly dissociates via (R22a), (R22b), and R23, the end product is CO. Reaction (R91) has been postulated by Shaub and Lin (1980) and Shaub *et al.* (1981) to be a major laser pumping reaction. The authors concluded that the other branch:

$$O + CH_2 \rightarrow CO + H_2,$$
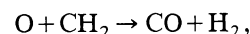
is also possible, but the difference is immaterial for our model. The rate coefficient for (R91) has not been measured in an isolated experiment. The value quoted in Table 3C, $k_{91} = 8.3 \times 10^{-11}$, was inferred indirectly by Homann and Schweinfurth (1981). This choice is consistent with the rate coefficient of a similar reaction that was recently studied by Messing *et al.* (1981):

$$O + CH \rightarrow CO + H \qquad k = 9.5 \times 10^{-11},$$

where the products have been assumed. Reaction (R92) has been extensively studied, with good agreement between the various experiments (Morris and Niki 1972; Washida and Bayes 1976). Reaction (R95) has been studied only once by Fenimore (1969), but the result appears to be reliable. Reaction (R94) has not been studied, and its rate coefficient and products are based on analogy with (R95).

Insertion reactions between O and OH and the unsaturated hydrocarbons can occur such as in the following (units for two-body and three-body reactions are $cm^3 \ s^{-1}$ and $cm^6 \ s^{-1}$, respectively):

$$O + C_2H_2 \rightarrow CO + CH_2,$$
$$k = 2.0 \times 10^{-11} e^{-2400/T}; \qquad (a)$$

$$O + C_2H_4 \rightarrow CH_3 + HCO,$$
$$k = 5.3 \times 10^{-12} e^{-640/T}, \qquad (b)$$

$$\rightarrow CH_2CO + H_2$$
$$k = 2.8 \times 10^{-13} e^{-640/T}; $$

$$OH + C_2H_2 + M \rightarrow CH_2CO + H + M,$$
$$k_0 = 7.1 \times 10^{-31} e^{-164/T}, \qquad (R97)$$
$$k_\infty = 1.2 \times 10^{-12} e^{-164/T}$$

$$OH + C_2H_4 + M \rightarrow C_2H_4OH + M,$$
$$k_0 = 5.8 \times 10^{-31} e^{1258/T}, \qquad (c)$$
$$k_\infty = 1.4 \times 10^{-12} e^{388/T};$$

where references for (a) are Herron and Huie (1973); Shaub and Lin (1980); for (b), Hampson (1980); for (c) Prather, Logan, and McElroy (1978). These reactions are generally unimportant, since the bulk of oxygen chemistry occurs in the mesosphere and thermosphere under conditions of low temperature and low pressure.

c) Hydrogen Abstraction

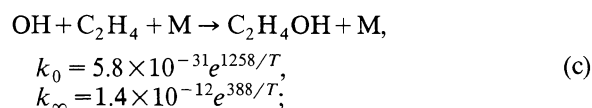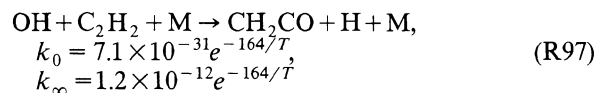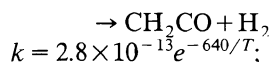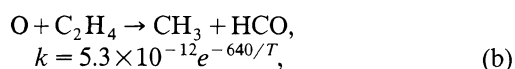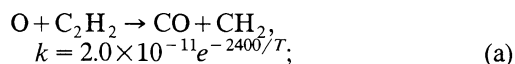The most important abstraction reactions in the atmosphere of Titan are the ones involving the C_2, C_2H, and C_4H radicals (see § II*b*). The rate coefficients for the key reactions with ethynyl radicals have been measured by Lange and Wagner (1975), Laufer and Bass (1979), Laufer (1981*b*), Okabe (1981), and Renlund *et al.* (1981) at room temperature. The last reference reported rate coefficients for $C_2H + CH_4$ and $C_2H + H_2$ that are significantly faster than those obtained by the previous workers. The discrepancy is attributed to the existence of excited C_2H radicals in the experiments of Renlund *et al.* (1982, private communication). Consequently, the results of Renlund *et al.* (1981) are not used. Extrapolation of the rate coefficients for ethynyl radicals to the lower temperatures appropriate for Titan can be made using estimates of activa-

tion energies by Brown and Laufer (1981), whose expressions we adopt:

$$k_{54} = 1.9 \times 10^{-11} e^{-1450/T},$$

$$k_{55} = 2.8 \times 10^{-12} e^{-250/T}.$$

The activation energies have been estimated by comparing the measured values for k_{54} and k_{55} at room temperature with the preexponential factors in the rate coefficients calculated by the BEBO (bond-energy-bond-order) method. Laufer (1982, private communication) stated that his estimate for the activation energies for C_2H reactions is accurate to 1 kcal mole^{-1}. The rate coefficients between C_2H and C_2H_6, and C_3H_8 are close to the gas kinetic rate (Laufer 1981*b*; Okabe 1983*b*), and no temperature dependence is assumed. C_2 can readily react with a large number of hydrocarbons (Pasternack and McDonald 1979; Reisler, Mangir, and Wittig 1980). According to Pitts, Pasternack, and McDonald (1982), the primary path for the reaction of C_2 with CH_4 is

$$C_2 + CH_4 \rightarrow C_2H + CH_3. \qquad (R53)$$

The initial step may actually be an insertion, but the product will dissociate:

$$C_2 + CH_4 \rightarrow CH_3C_2H^*$$

$$\rightarrow C_2H + CH_3.$$
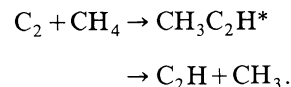
The net result result is equivalent to the abstraction reaction. The abstraction reactions involving C_4H are based on analogy with C_2H reactions.

The most abundant radicals in the model H, CH_2, CH_3, C_2H_3, and C_2H_5 do not appreciably abstract hydrogen from the alkanes. The reason is the high activation energies associated with these reactions, as can be seen from the following examples (units for k are $cm^3 \ s^{-1}$):

$$H + CH_4 \rightarrow CH_3 + H_2,$$
$$k = 3 \times 10^{-10} e^{-6560/T}; \qquad (a)$$

$$H + C_2H_6 \rightarrow C_2H_5 + H_2,$$
$$k = 2.2 \times 10^{-10} e^{-4760/T}; \qquad (b)$$

$$CH_2 + CH_4 \rightarrow products,$$
$$k < 3 \times 10^{-19}; \qquad (c)$$

$$C_2H_3 + C_2H_6 \rightarrow C_2H_4 + C_2H_5,$$
$$k = 9.3 \times 10^{-13} e^{-5840/T}; \qquad (d)$$

$$C_2H_3 + CH_4 \rightarrow C_2H_4 + CH_3,$$
$$k = 1.3 \times 10^{-13} e^{-2250/T}; \qquad (e)$$

$$C_2H_5 + CH_4 \rightarrow C_2H_6 + CH_3,$$
$$k = 2.9 \times 10^{-13} e^{-5030/T}; \qquad (f)$$
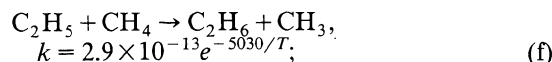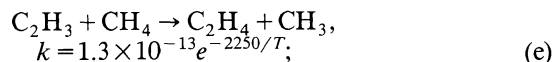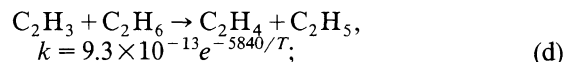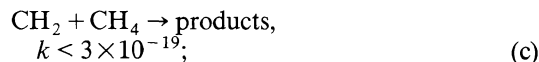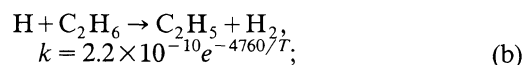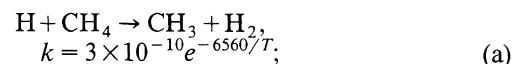
where references for (a) are Sepehrad, Marshall, and Purnell (1979); for (b), Camilleri, Marshall, and Purnell (1974); for (c), Lee, Russell, and Rowland (1970); for (d), Kerr and Parsonage (1972); (e) was estimated using reverse reaction (Holt and Kerr 1977) and equilibrium constant; (f) was esti-

mated using reverse reaction (Snow 1966) and equilibrium constant. The reactions between oxygen atoms and alkanes:

$$O + RH \rightarrow OH + R,$$
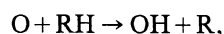
have activation energies of 6–10 kcal mole^{-1} (Andresen and Luntz 1980; Luntz and Andresen 1980) and are consequently not important for Titan. It is difficult, if not impossible, for NH to abstract a hydrogen atom from the hydrocarbons to form NH$_2$. The reaction

$$NH + CH_4 \rightarrow NH_2 + CH_3,$$
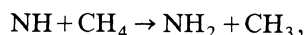
suggested by Capone *et al.* (1980) is endothermic by ~ 5 kcal mole^{-1} for NH in the ground state. It is conceivable that the difficulty could be overcome by using the excited states of NH, but then we must postulate a large source of excited NH and a slow rate coefficient for quenching the excited states. In this work such remote possibilities are not considered.

The radicals in their excited states $^1CH_2$ and $O(^1D)$ readily abstract H from CH$_4$:

$$^1CH_2 + CH_4 \rightarrow 2CH_3, \tag{R30b}$$

$$O(^1D) + CH_4 \rightarrow OH + CH_3. \tag{R90a}$$
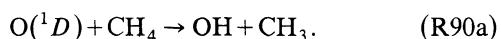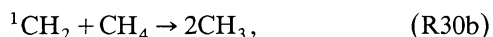
The major quenching reactions are

$$^1CH_2 + N_2 \rightarrow CH_2 + N_2, \tag{R28}$$

$$O(^1D) + N_2 \rightarrow O + N_2. \tag{R89b}$$

The ratios k_{30b}/k_{28} and k_{90a}/k_{89b} are 0.24 and 4.1, respectively. Since the ratio CH$_4$/N$_2$ is ~ 0.1 in the thermosphere (Table 1A), it is clear that (R30b) is not important in our model (see § IIb). Reaction (R90a) represents a major sink of $O(^1D)$. While not important in the present atmosphere because of the small source of $O(^1D)$, reaction (R90a) could be important if the abundance of CO were higher in the past. The scheme

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

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

$$\underline{OH + CO \rightarrow CO_2 + H}$$

$$\text{net } 2CO + CH_4 \rightarrow CO_2 + C + CH_3 + H$$
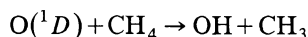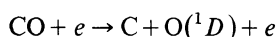
could be an efficient process for removing primordial CO.

The rate coefficient for the reaction N(^2D) with CH$_4$ has been measured by Black *et al.* (1969) to be 3×10^{-12} cm^3 s^{-1} at room temperature. The products are unknown. T. Slanger (1983, private communication) favored abstraction:

$$N(^2D) + CH_4 \rightarrow NH + CH_3, \tag{R72}$$
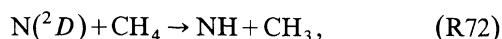
for at least two reasons. First, (R72) is too fast to be a straightforward quenching reaction, which is typically much slower:

$$N(^2D) + N_2 \rightarrow N + N_2,$$
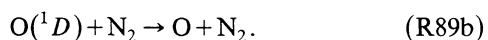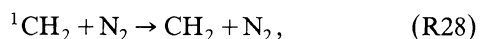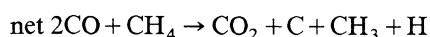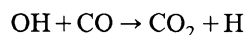$$k_{71b} \leq 6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1};$$

$$N(^2D) + Ar(He) \rightarrow N + Ar(He),$$
$$k \leq 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}.$$
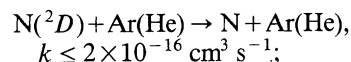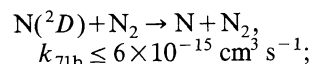
Second, the analogous reaction

$$N(^2D) + H_2 \rightarrow NH + H, \qquad k = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1};$$
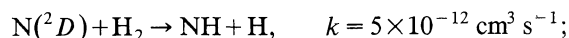
was considered to be an H abstraction reaction by Donovan and Husain (1970) on the basis of adiabatic correlation between the states of N and H$_2$ and NH + H. Note that the rate coefficients for N(^2D) with CH$_4$ and H$_2$ are within a factor of 2 of each other. The production of NH by this reaction has major impact on the odd nitrogen budget of the atmosphere (see §§ IIa and IIIe).

d) Combination and Disproportionation

Interesting compounds are synthesized in Titan's atmosphere by radical-radical combination under conditions which are usually described as the low-pressure limit in the laboratory. The efficiency of such reactions will now be discussed. There is a fundamental difference between association reactions involving simple systems such as

$$O + O + M \rightarrow O_2 + M,$$
$$k = 4.8 \times 10^{-33}; \tag{a}$$

$$H + H + M \rightarrow H_2 + M,$$
$$k = 8.1 \times 10^{-33}; \tag{b}$$
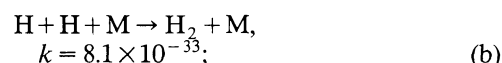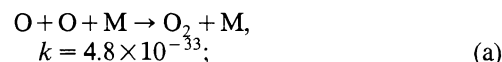
and reactions involving more complex molecules such as

$$CH_3 + H + M \rightarrow CH_4 + M,$$
$$k = 5.6 \times 10^{-29}; \tag{c}$$

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M,$$
$$k = 1.8 \times 10^{-25}; \tag{d}$$
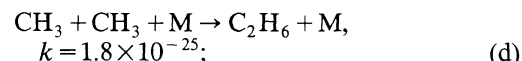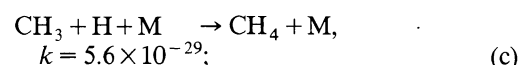
where the references are (a) Baulch *et al.* (1980); (b) Trainor, Ham, and Kaufman (1973); (c) Cheng and Yeh (1977); (d) MacPherson, Pilling, and Smith (1983). The rate coefficients have been evaluated in the low-pressure limit at room temperature in units of cm^6 s^{-1}. We note that the experimentally determined rate coefficients for these two classes of reactions differ by many orders of magnitude at room temperature. The reason is quite simple in the framework of RRKM theory (Rice-Ramsperger-Kassel-Marcus; see text book on the subject by Robinson and Holbrook 1972). Three-body association reactions involving the reactants A and B, and the product AB may be described as

$$A + B \rightarrow AB^* \qquad k_a,$$

$$AB^* \rightarrow A + B \qquad k_b,$$

$$AB^* + M \rightarrow AB + M \qquad k_c,$$
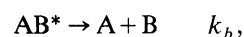
where AB* is an excited complex, and k_a, k_b, and k_c are the appropriate rate coefficients for association, dissociation, and stabilization, respectively. The overall reaction can be summarized as

$$A + B + M \rightarrow AB + M \qquad k_{eff},$$

with an effective three-body rate given by

$$k_{eff} = \frac{k_a k_c}{k_b + k_c M},$$

which, in the low-pressure limit, reduces to

$$\lim_{M \rightarrow 0} k_{eff} \equiv k_0 = \frac{k_a k_c}{k_b},$$

Hence, a critical parameter in determining the value of k_{eff} is the lifetime k_b^{-1} of the activated complex AB*, which is unstable and tends to dissociate. Excited molecules like O_2^* and H_2^* have only one vibrational mode, and all the excess energy in the activated complex is available for breaking the bond. On the other hand, excited molecules like CH_4^* and $C_2H_6^*$ have eight and 18 degrees of vibrational freedom, respectively. It takes many thousands of vibrations before the excess energy (which is most likely widely distributed among all possible modes) can be all concentrated into one particular bond that breaks. Consequently, CH_4^* and $C_2H_6^*$ have lifetimes many orders of magnitude longer than those for O_2^* and H_2^*. The rate coefficients are accordingly larger.

Of all three-body reactions in Table 3B, only the following have been measured in the low-pressure or falloff region:

$$H + C_2H_2 + M \rightarrow C_2H_3 + M, \qquad (R25)$$

$$H + C_2H_4 + M \rightarrow C_2H_5 + M, \qquad (R26)$$

$$H + CH_3 + H \rightarrow CH_4 + M, \qquad (R33)$$

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M, \qquad (R35)$$

$$H + CH_3C_2H + M \rightarrow C_3H_5 + M. \qquad (R45b)$$

Estimates for other important three-body reactions have been made using Williams (1971) and Troe (1977a, b) by Laufer et al. (1983). The computed three-body rate coefficients are about a factor of 10 different from the available measurements of a number of reactions at 300 K. For simplicity and self-consistency, in our model we use calculated rate coefficients at 200 K for most of the three-body synthesis reactions.

The consequence of such high values for the three-body rate coefficients is that the formation of higher hydrocarbons is extremely efficient and proceeds like two-body reactions even in the mesosphere. In the two-body limit, the most important parameter that characterizes these reactions is the disproportionation-to-combination ratio. This ratio seems to fit a simple pattern for the entire class of alkyl-alkyl reactions and has been extrapolated to cases involving alkyl-vinyl and alkyl-propargyl reactions by Laufer et al. (1983). It is largely a consequence of the smallness of this ratio that combination of radicals is so efficient on Titan, leading to the production of

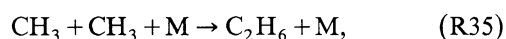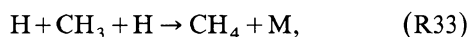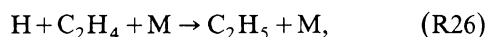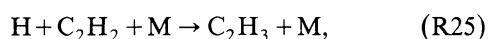more complex compounds. Hydrocarbons containing four carbon atoms (besides diacetylene) are readily synthesized by radical-radical combination, as shown in the Appendix.

e) Exchange and Transfer

Conversion of CH_2CCH_2 to CH_3C_2H in the presence of H atoms was reported by von Wagner and Zellner (1972b), but no detailed mechanism was suggested. Since the heat of formation for allene is 1.3 kcal mole^{-1} higher than that for methylacetylene, R. K. Sparks (1981, private communication) suggested an interesting exchange reaction:

$$H + CH_2CCH_2 \rightarrow CH_3C_2H + H. \qquad (R70)$$

This reaction, however, involves converting a pair of double bonds into a single bond and a triple bond. The activation energy could be high, but is expected to be about equal to that required for breaking the double bond of C_2H_4 by H in (R26) (Laufer 1982, private communication). We estimate k_{70} to be $1 \times 10^{-11} e^{-1000/T}$, based on $k_{26}(\infty) = 3.7 \times 10^{-11} e^{-1040/T}$. Since the two principal reactions that produce C_3H_4 ([R31], [R12a]) both favor CH_2CCH_2 over CH_3C_2H, it is difficult to explain the detection of CH_3C_2H and the absence of CH_2CCH_2 on Titan. Preferential destruction of CH_2CCH_2 by photolysis does not appear to be the answer (see § IIIa). Reaction (R70) provides a satisfactory resolution of the apparent difficulty in our model. Needless to say, laboratory work is needed to establish the validity of this reaction.

As shown in § IIa, a critical reaction that destroys odd nitrogen is the transfer reaction

$$NH + N \rightarrow N_2 + H, \qquad (R76)$$
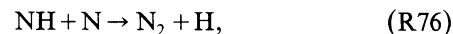
and this reaction must compete with another transfer reaction

$$NH + H \rightarrow N + H_2 \qquad (R75)$$
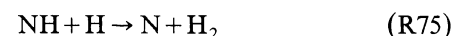
which restores N. Neither k_{76} nor k_{75} has been measured. Our estimate for k_{76} is based on Westley's (1980) compilation and the reaction

$$N + NO \rightarrow N_2 + O, \qquad k = 8.2 \times 10^{-11} e^{-410/T};$$

(Hampson and Garvin 1978). Our estimate for k_{75} is based on a theoretical calculation by Mayer, Schieler, and Johnston (1966) for high temperatures. Strobel (1982) suggested the probable importance of the reaction

$$2NH \rightarrow N_2 + 2H.$$
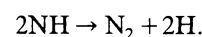
Meaburn and Gordon (1968) reported a nearly useless upper limit of 2.3×10^{-9} cm^3 s^{-1} for the rate coefficient of this reaction. In Back and Salahub's (1967) experiment using ^{14}N and $^{15}NH_3$, only $^{14}N^{15}N$ was produced, and the authors concluded that the above reaction is unlikely. There is another pathway for self-reaction of NH:

$$NH + NH + M \rightarrow N_2H_2 + M$$

$$\underline{N_2H_2 + h\nu \rightarrow N_2 + H_2}$$

$$\text{net } 2NH \rightarrow N_2 + H_2.$$
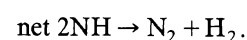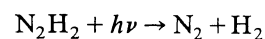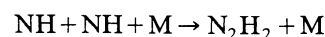
The intrinsic instability of N_2H_2 toward photolysis (Okabe 1978) suggests that the association reaction is the rate limiting step in the above scheme. Even if the three-body rate coefficient were as low as 1×10^{-33} cm^6 s^{-1}, this would imply an effective two-body rate coefficient of order 1×10^{-14} cm^3 s^{-1} in the lower stratosphere. In this work we adopt an overall reaction:

$$NH + NH + M \rightarrow N_2 + H_2 + M, \qquad (R77)$$
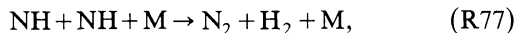
with a conservative estimate for the rate coefficient $k_{77} = 1 \times 10^{-33}$ cm^6 s^{-1}.

Our knowledge of the reactions (R75), (R76), and (R77) is extremely poor. In the thermosphere only (R75) and (R76) are important, and our choice of the rate coefficients (Table 3C) implies $k_{76}/k_{75} \approx 620$. Thus, most of the dissociation of N_2 leads back to recombination. A small fraction ($\sim 10\%$) of dissociation results in irreversible formation of nitrile compounds. We should regard the ill-defined ratio k_{76}/k_{75} as an additional assumption of the model that remains to be established by future laboratory studies.

f) Cracking and Hydrogen Scavenging

Since scheme (18) employing C_4H_2 as a scavenger for H atoms in the stratosphere is crucial for the model (see § IIc), we will now briefly examine the circumstantial evidence in support of this scheme, based on reactions related to CH_3C_2H. In its reaction toward H atoms, C_4H_2 (H—C≡C—C≡C—H) is remarkably similar to CH_3C_2H (CH_3—C≡C—H). The first hydrogen atom can insert into the triple C≡C bond:

$$C_4H_2 + H + M \rightarrow C_4H_3 + M, \qquad (R68)$$

$$CH_3C_2H + H + M \rightarrow C_3H_5 + M. \qquad (R45b)$$
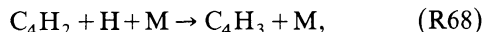
This leaves the single C—C bond vulnerable to cracking by the second hydrogen atom:

$$C_4H_3 + H \rightarrow 2C_2H_2, \qquad (R69a)$$

$$C_3H_5 + H \rightarrow CH_4 + C_2H_2. \qquad (R47d)$$
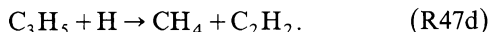
However, there are other possibilities. The second hydrogen atom can strip off the first hydrogen atom:

$$C_4H_3 + H \rightarrow C_4H_2 + H_2, \qquad (R69b)$$

$$C_3H_5 + H \rightarrow CH_3C_2H + H_2 \qquad (R47a)$$

$$\rightarrow CH_2CCH_2 + H_2. \qquad (R47b)$$

The net result in this case is scavenging of H atoms; the molecules C_4H_2 and CH_3C_2H are not cracked. The second hydrogen can also be added to the system:

$$C_4H_3 + H + M \rightarrow C_4H_4 + M, \qquad (R69c)$$

$$C_3H_5 + H + M \rightarrow C_3H_6 + M. \qquad (R47c)$$
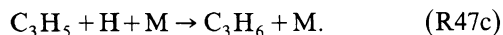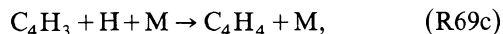
But the products C_4H_4 and C_3H_6 are readily destroyed by

photolysis, with the most probable branches being

$$C_4H_4 + h\nu \rightarrow C_4H_2 + H_2, \qquad (R103b)$$

$$C_3H_6 + h\nu \rightarrow CH_2CCH_2 + H_2. \qquad (R12a)$$
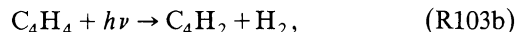
The result in this case is equivalent to scavenging of H atoms.

von Wagner and Zellner (1972a, b) and Niedzielski, Janusz, and Gierczak (1983) have studied the interaction between H atoms and CH_3C_2H and its isomer CH_2CCH_2. It is of interest to note that the experiments yielded comparable amounts of C_2H_2, C_3H_6, and H_2 at low pressure. In terms of the simple reaction pathways we have discussed, this implies that (R47d), (R47a), (R47b), and (R47c) are comparable in importance. Drawing on the analogy between C_4H_2 and CH_3C_2H, we deduce that reactions (R69a), (R69b), and (R69c) are comparable in rates. Indeed, in the experime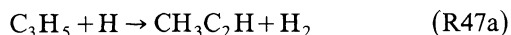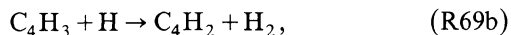nt studying $H + C_4H_2$ performed by Schwanebeck and Warnatz (1975), nearly equal amounts of C_2H_2 and C_4H_4 were produced at low pressure, implying $k_{69a} \approx k_{69c}$. Unfortunately, the yield of H_2 was not reported in the experiment, and we could not obtain a quantitative assessment of k_{69b}. In our model, we assume that $k_{69b} + k_{69c}$ equals a few times k_{69a}, a most reasonable conclusion in view of this discussion. It is unfortunate that (R47a) and (R47b), which have been studied in the laboratory, are not important for removing hydrogen atoms, because the rate limiting reaction (R45b) is too slow in the three-body limit. This puts almost all the burden of H removal in the stratosphere on C_4H_2.

IV. MODEL ASSUMPTIONS

A model atmosphere for Titan, consistent with the information given in Table 1A, has been constructed by solving the hydrostatic equation in spherical coordinates. The altitude profiles for total number density $n(z)$ and temperature $T(z)$ are shown in Figure 2a. For simplicity, a pure N_2 atmosphere is assumed. The choice of the thermal profile $T(z)$ presents a difficult problem. The temperatures in the thermosphere above 800 km, in the stratosphere below 1 mb, and in the troposphere can be inferred from the ultraviolet, infrared, and radio occultation experiments on the *Voyager* mission. However, the upper stratosphere and mesosphere constitute a "most inaccessible region" for which there are no data. Comparison with the terrestrial atmosphere may be illuminating. The most significant radiative processes in the terrestrial thermosphere, mesosphere, and stratosphere are absorption of EUV radiation by O_2, cooling by CO_2, and absorption of near-ultraviolet sunlight by ozone, respectively. On Titan analogous roles are played by EUV and electron impact heating in the thermosphere, cooling by C_2H_2 in the mesosphere, and absorption of solar radiation by Axel-Danielson dust in the stratosphere. As in the case of the Earth, cooling in the mesosphere of Titan must be significant, since the mixing ratio of C_2H_2 on Titan is much higher than that of CO_2 on Earth, and the band intensity for the 13.6 μm band of C_2H_2 responsible for cooling off the mesosphere is ~ 4 times stronger than that for the 15 μm band of CO_2. Modeling of the thermal structure of the atmosphere of Titan suggests that the mesopause temperature could be as low as 100 K (Friedson and Yung 1984). Since the exosphere is ~ 190 K, one conse-
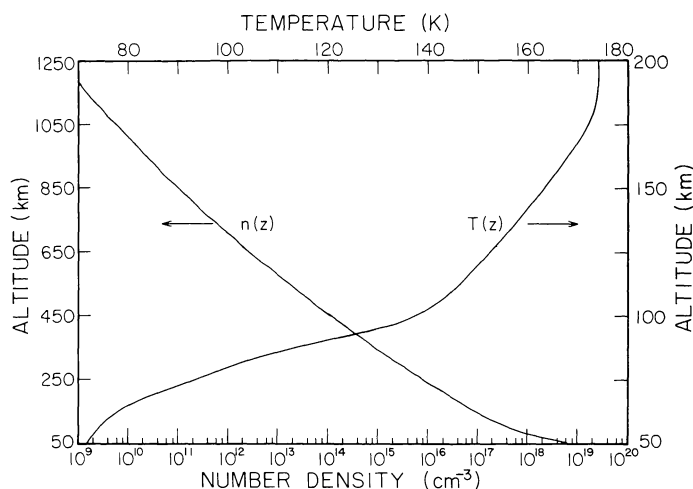
FIG. 2a
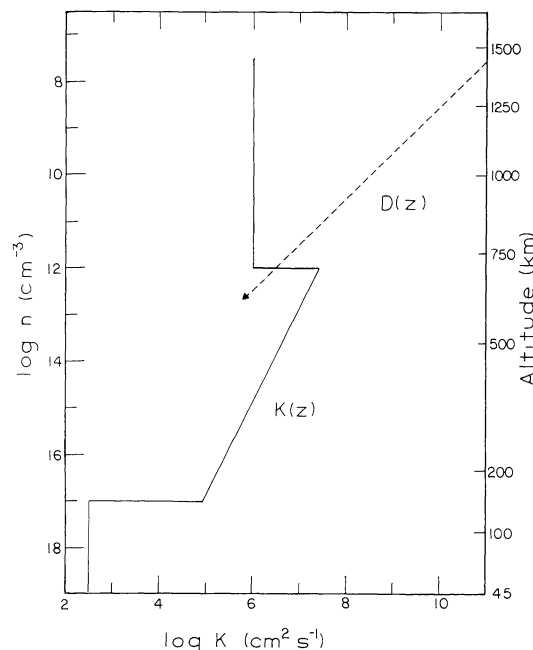
FIG. 2b

FIG. 2.—(a) Altitude profile for total number density $n(z)$ and temperature $T(z)$. $T(z) = 174$ K for $z > 200$ km. (b) Eddy diffusivity profile, $K(z)$ cm^2 s^{-1}. Molecular diffusivity profile for CH_4 in N_2, $D(z)$ cm^2 s^{-1}, is given for comparison (dotted line).

quence of the cold mesopause is the existence of a positive temperature gradient, which could inhibit vertical mixing. For simplicity, in our model we assume a constant temperature for the entire upper stratosphere and mesosphere.

The choice of the eddy diffusion coefficient is based on the analysis of Smith et al. (1982a) and by our own effort to refine their results. We adopt the expression

$$K(z) = \begin{cases} 1 \times 10^6 \text{ cm}^2 \text{ s}^{-1}, \\ \quad n < 1 \times 10^{12} \text{ cm}^{-3}; \\ 2.5 \times 10^{13}/\sqrt{n} \text{ cm}^2 \text{ s}^{-1}, \\ \quad 1 \times 10^{17} > n > 1 \times 10^{12} \text{ cm}^{-3}; \\ 3 \times 10^2 \text{ cm}^2 \text{ s}^{-1}, \\ \quad 1 \times 10^{19} > n > 1 \times 10^{17} \text{ cm}^{-3}; \end{cases}$$

where n is the number density of ambient atmosphere in molecules per cm^3. The quantity $K(z)$ is shown in Figure 2b, along with $D(z)$, the molecular diffusion coefficient for CH_4 in N_2. It is clear that molecular diffusion is more important above $n = 1 \times 10^{12}$ cm^{-3} level; eddy diffusion dominates beneath this level. The profile for $K(z)$ exhibits two regions of stagnancy, in the lower thermosphere and the lower stratosphere, due to thermal inversion (Friedson and Yung 1984; Lindal et al. 1983). Our choice of the somewhat artificial $K(z)$ is partially motivated by the work of Allen, Yung, and Waters (1981) on deriving the eddy transport in the terrestrial upper atmosphere. The magnitudes of the eddy diffusion coefficient in the stagnant regions have been adjusted so that the model provides satisfactory simulation of the Voyager UVS and IRIS observations. In the bulk of the stratosphere our $K(z)$ profile

is based on the result of Fricke et al. (1982), who first pointed out the remarkable similarity for the magnitude of the eddy diffusion coefficient in the Jovian stratosphere with that in the atmospheres of the terrestrial planets, as summarized by the simple expression:

$$K(z) = A/\sqrt{n} \text{ cm}^2 \text{ s}^{-1},$$

where $A = 1-3 \times 10^{13}$ cm$^{1/2}$ s^{-1}. Molecular diffusion coefficients are taken from the standard references Mason and Marrero (1970) and Banks and Kockarts (1973).

The solar flux below 2000 Å is taken from Mount and Rottman (1981). Above 2000 Å we use Ackerman (1971). Diurnally averaged values for photodissociation appropriate for a plane parallel atmosphere at 30° latitude are adopted. (For optically thick absorption, this is equivalent to global averaging.) In the lower stratosphere the solar radiation field is attenuated by aerosol absorption in addition to molecular absorption. This is roughly accounted for by reducing the incident solar flux at all wavelengths below 3000 Å by a transmission factor defined as

$$Tm(z) = e^{-(240-z)/Ha} \qquad 45 < z < 240 \text{ km}$$

$$Tm(z) = 1 \qquad z > 240 \text{ km},$$

where the scale height Ha for aerosol absorption equals 50 km. This particular choice of $Tm(z)$ is consistent with Caldwell et al.'s (1981) measurement of 0.03 for the geometric albedo of Titan between 2000 and 2500 Å, and Pollack et al.'s (1980) aerosol model for Titan (Rages 1981, private communication). The adoption of the transmission factor is obviously a crude

approximation. Self-consistent calculations involving aerosol scattering and photochemical modeling will be deferred to a future publication.

In the lower stratosphere near the tropopause, the calculated number density of some species, n, often exceeds its saturated number density, n_s. In this case condensation must occur to keep the model n close to n_s. A somewhat arbitrary scheme is devised as follows. Let S be the fractional supersaturation;

$$S = \begin{cases} (n - n_s)/n_s & n > n_s \\ 0 & n < n_s \end{cases}.$$

The removal rate is then parameterized as

$$\text{loss rate} = 1 \times 10^{-9} \frac{S}{1+S} n \ (\text{cm}^{-3} \ \text{s}^{-1}).$$

In our model condensation removal is important for all species except C_2H_4, H_2, CO, and the extremely short-lived radicals. Fortunately, the integrated rate of removal is limited primarily by the small eddy diffusion coefficient in the lower stratosphere and is consequently not sensitive to the particular choice of parameterization for the loss rate.

The one-dimensional continuity equations in spherical coordinates are solved for all major species with appropriate boundary conditions. Photochemical equilibrium (flux = 0) is assumed for all short-lived species. For long-lived species we assume loss by diffusion through the lower boundary with maximum deposition velocity given by

$$v_d = \frac{K_0}{H_0},$$

where H_0 is the atmospheric scale height and K_0 is the eddy diffusion coefficient at the tropopause. Molecular hydrogen has no known sink in the troposphere, and hence its deposition velocity is zero. At the upper boundary, most species cannot escape, and zero flux is assumed. Escape of H and H_2 can readily occur, and we set the escape velocities equal to the Jeans escape velocities at 190 K. The species $N(^2D)$, C_2, C_4H_3, H_2CN, H_2C_3N, and HC_2N_2 are not explicitly solved, but their effects on the model are implicitly taken into account. The effect of CO dissociation by energetic electron is simulated by a flux of OH at the upper boundary. Table 4 provides a summary of the essential assumptions and boundary conditions in the model.

The complete set of continuity equations is solved using a finite-difference iterative algorithm with a resolution of three vertical steps for every scale height (Allen, Yung, and Waters 1981). The large number of species in the model is divided into groups. The first group consists of C_1 and C_2 compounds, hydrogen, and polyacetylenes and is the most important. The other groups are composed separately of C_3 and nitrogen and oxygen species. Each group, which is usually strongly coupled internally, is solved rigorously. Convergence is considered established when successive iterations yield solutions differing by less than one part in 10^4. The different groups are solved in succession and are allowed to interact with each other until a

TABLE 4
BOUNDARY CONDITIONS[a] FOR SELECTED SPECIES IN PHOTOCHEMICAL MODEL

Species	Lower Boundary[b]	Upper Boundary[c]
H	$\phi = 0$	$v = 2.5 \times 10^4$
H_2	$\phi = 0$	$v = 6.1 \times 10^3$
CH_4	$f = 2.0 \times 10^{-2}$	$\phi = 1.0 \times 10^{9d}$
N	$\phi = 0$	$\phi = -1.0 \times 10^9$
NH	$\phi = 0$	$\phi = -1.0 \times 10^9$
CH_3	$\phi = 0$	$\phi = -1.0 \times 10^9$
OH......	$\phi = 0$	$\phi = 3.3 \times 10^4$
H_2O	$v = 2.0 \times 10^{-4}$	$\phi = -6.1 \times 10^5$
CO......	$\phi = 0$	$\phi = 8.8 \times 10^4$

[a] For species not given here, their boundary conditions are stated in § IV. The symbols f, ϕ, and v refer to mixing ratio, flux (cm^{-2} s^{-1}), and velocity (cm s^{-1}), respectively. The sign convention for ϕ and v is positive for upward flow.

[b] At tropopause $z = 45$ km ($n = 1.1 \times 10^{19}$ cm^{-3}).

[c] At $z = 1160$ km ($n = 1.2 \times 10^9$ cm^{-3}) for all species except H and H_2, for which the upper boundary is at 1425 km ($n = 4.9 \times 10^7$ cm^{-3}).

[d] All fluxes refer to the surface.

final self-consistent solution is obtained. The overall accuracy for species in the first group is $\sim 10\%$, for species in the other groups, about a factor of 2, adequate for present purposes.

V. MODEL RESULTS

The results of the photochemical model will now be discussed in some detail. The discussion deals separately with C_1 and C_2 hydrocarbons, H and H_2, polyacetylenes, C_3 hydrocarbons, and nitrogen and oxygen compounds. The discussion of C_4 compounds and long-chain polymers is deferred to the Appendix. The emphasis is on the more abundant species that have been observed and the major processes which control their abundances. As we will show, the model is successful in accounting for the abundances of most of the minor species listed in Table 1A.

Figure 3 presents altitude profiles for the major diurnally averaged photodissociation coefficients in the chemical model. More detailed information on photodissociation is listed in Table 3A. The major absorber in the atmosphere below 1450 Å is CH_4. Beyond 1600 Å, absorption by C_2H_2, C_2H_4, polyacetylenes, and HCN become important. Aerosol opacity provides significant attenuation of solar radiation below 240 km.

a) C_1 and C_2 Family

The mixing ratios of H_2 and the major hydrocarbon species CH_4, C_2H_2, C_2H_4, and C_2H_6 are given in Figure 4a. To facilitate comparison between model and observation, we define the column-averaged mixing ratio for species i by

$$\bar{f}_i = \frac{\int_{45 \, \text{km}}^{\infty} [i] \, dz}{\int_{45 \, \text{km}}^{\infty} [n] \, dz},$$
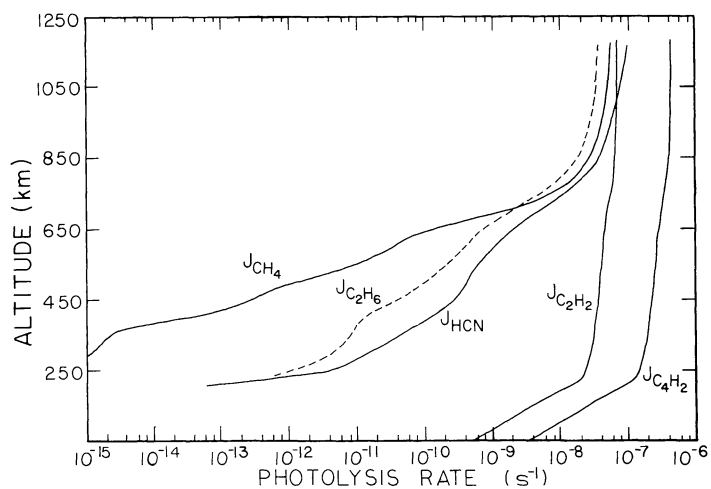
FIG. 3.—Altitude profiles for selected photodissociation coefficients. Total rates (sum of all branches) are given for CH_4, C_2H_2, C_2H_6, C_4H_2, and HCN.
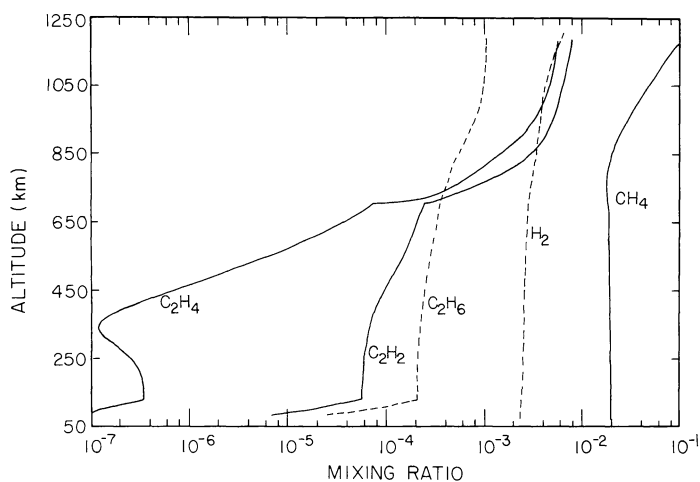
FIG. 4a
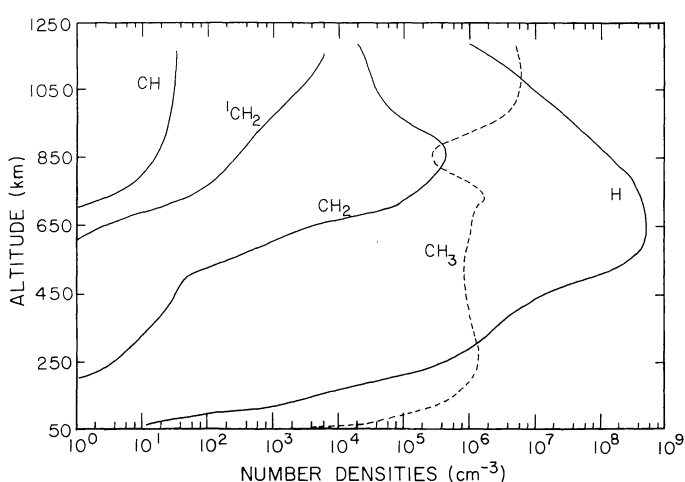
FIG. 4b
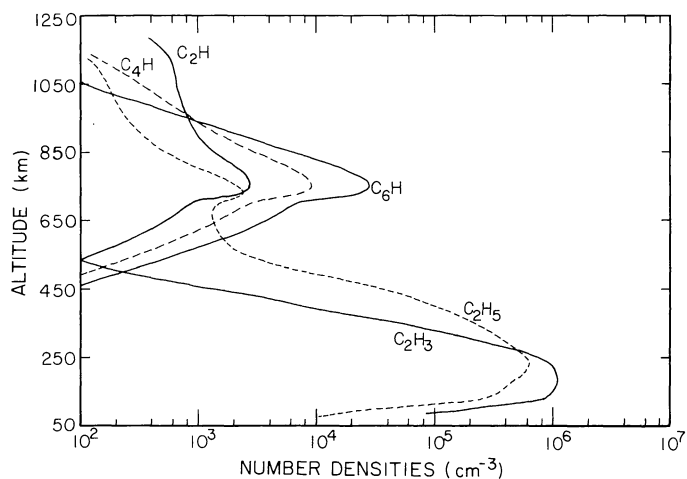
FIG. 4c
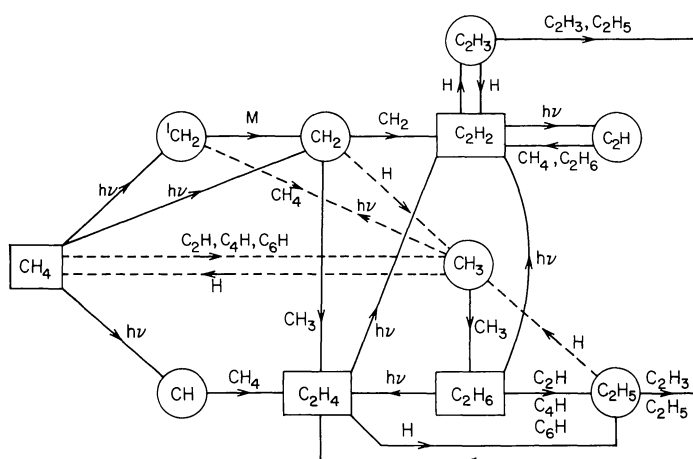
FIG. 4d

FIG. 4.—(a) Altitude profiles for the mixing ratios of CH_4, C_2H_2, C_2H_4, C_2H_6, and H_2. (b) Altitude profiles for the number densities of H, CH, $^1CH_2$, CH_2, and CH_3. (c) Altitude profiles for the number densities of C_2H_3, C_2H_5, C_2H, C_4H, and C_6H. (d) Schematic diagram showing the major pathways for the interconversion of major C_1 and C_2 species.

where $[i]$ and $[n]$, respectively, denote the number density of the species i and the ambient atmosphere. Comparison with the observed mixing ratios by IRIS, as listed in Table 1A, indicates that, except for C_2H_4, the model successfully accounts for all the major C_1 and C_2 species and H_2. The number densities of the important radicals H, CH, $^1CH_2$, CH_2, CH_3, C_2H_3, C_2H_5, C_2H, C_4H, and C_6H are shown in Figures 4b and 4c. The concentrations of the radical species except H are, in general, too small to be detected by spacecraft or ground-based detectors. A schematic diagram showing the pathways for the interconversion of major C_1 and C_2 species is given in Figure 4d.

b) CH_4

The mixing ratio of CH_4 at the tropopause is fixed to be 2.0×10^{-2}. The computed mixing ratio of CH_4 at 1140 km is

8.1%, in good agreement with the value $8 \pm 3\%$ deduced by the *Voyager* UVS experiment (Table 1A). The driving force for hydrocarbon photochemistry is destruction of CH_4. The rates for major reactions destroying CH_4, viz., (R5) = (R5a)+(R5b) +(R5c) $CH_4 + h\nu$; (R55) $CH_4 + C_2H \rightarrow CH_3 + C_2H_2$; (R61) $CH_4 + C_4H \rightarrow CH_3 + C_4H_2$; and (R65) $CH_4 + C_6H \rightarrow CH_3 + C_6H_2$, and the most important reaction reforming CH_4, viz., (R33) $CH_3 + H \rightarrow CH_4$, are shown in Figure 5a. Primary photolysis of CH_4 occurs at an altitude ~ 800 km, but the bulk of CH_4 destruction occurs via secondary processes in the stratosphere ~ 250 km. Few hydrogen atoms recombine with methyl radicals by (R33). Consequently, the efficiency for converting CH_4 into higher hydrocarbons (per dissociation) is 96%, a value similar to the corresponding value of 95% in Strobel (1974). The column integrated rates for (R5), (R53), (R55), (R61), (R65), and (R33) are 2.9×10^9, 3.0×10^9, $5.1 \times$
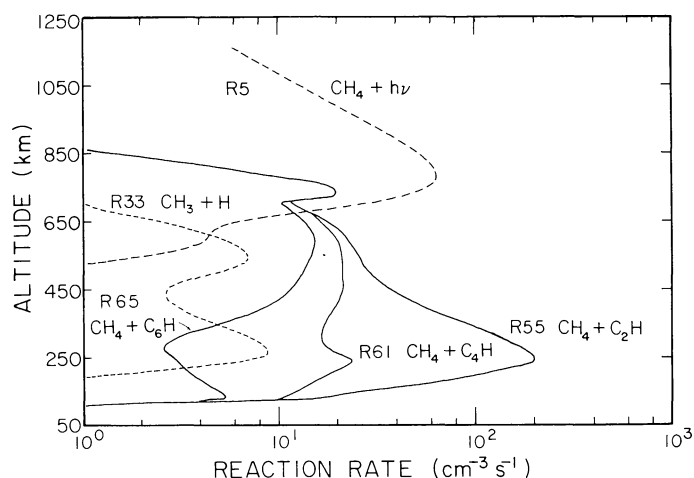
FIG. 5a
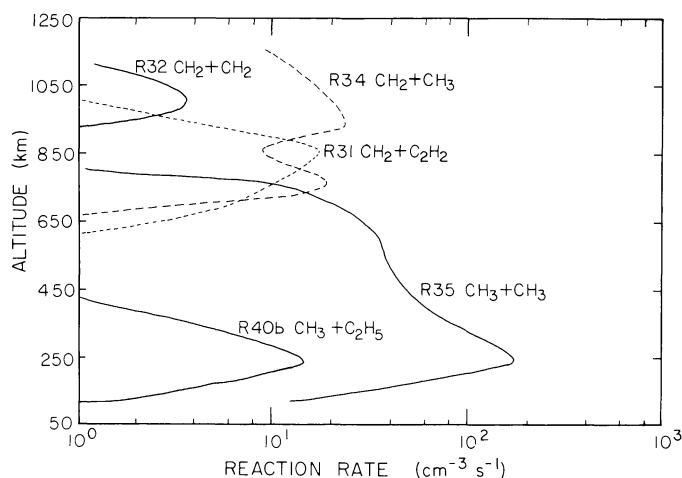
FIG. 5b
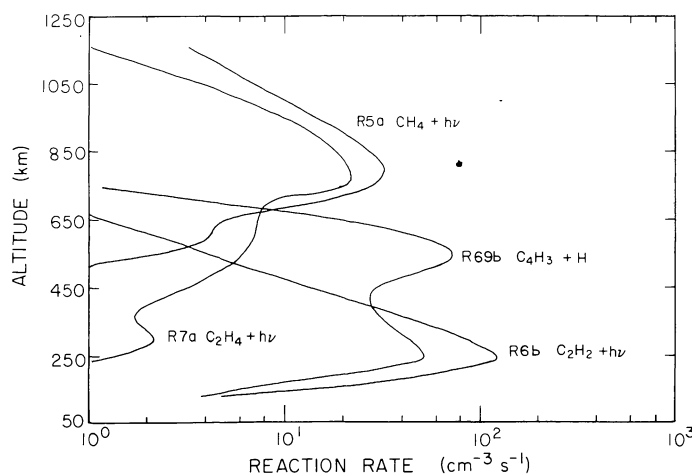
FIG. 5c

FIG. 5.—(a) Reaction rates for major reactions destroying and producing CH_4: (R5) $CH_4 + h\nu \rightarrow$ products; (R55) $CH_4 + C_2H \rightarrow CH_3 + C_2H_2$; (R61) $CH_4 + C_4H \rightarrow CH_3 + C_4H_2$; (R65) $CH_4 + C_6H \rightarrow CH_3 + C_6H_2$; and (R33) $CH_3 + H \rightarrow CH_4$. (b) Reaction rates for important synthesis reactions: (R31) $CH_2 + C_2H_2 \rightarrow CH_3C_2H$ and CH_2CCH_2 (the sum is shown here); (R32) $2CH_2 \rightarrow C_2H_2 + H_2$; (R34) $CH_2 + CH_3 \rightarrow C_2H_4 + H$; (R35) $2CH_3 \rightarrow C_2H_6$; and (R40b) $CH_3 + C_2H_5 \rightarrow C_3H_8$. (c) Reaction rates for major reactions that produce H_2: (R5a) $CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$; (R6b) $C_2H_2 + h\nu \rightarrow C_2 + H_2$; (R7a) $C_2H_4 + h\nu \rightarrow C_2H_2 + H_2$; and (R69b) $C_4H_3 + H \rightarrow C_4H_2 + H_2$.

10^9, 1.7×10^9, 1.0×10^9, and 4.0×10^7 $cm^{-2}s^{-1}$, respectively. The net destruction rate of CH_4, which must be balanced by an equivalent upward flux at the tropopause, is 1.5×10^{10} $cm^{-2}s^{-1}$.

The character of CH_4 destruction in the upper atmosphere is somewhat different from that in the lower atmosphere. In the upper atmosphere, primary photolysis breaks CH_4 into the radicals CH, $^1CH_2$, and CH_2. CH_3 is produced indirectly by (R72) $N(^2D) + CH_4 \rightarrow CH_3 + NH$. In the lower atmosphere the net result of photosensitized dissociation is breaking CH_4 into CH_3 and hydrogen. CH_2 is now produced by (R4) $CH_3 + h\nu \rightarrow ^1CH_2 + H$, followed by quenching of $^1CH_2$ by N_2. As illustrated in Figure 4b, the concentration of CH_2 is comparable with that of CH_3 at 850 km, whereas CH_3 completely dominates over CH_2 elsewhere. Figure 5b summarizes the reaction rates for the major synthesis reactions: (R31) $CH_2 + C_2H_2 \rightarrow CH_3C_2H$ (and CH_2CCH_2); (R32) $2CH_2 \rightarrow C_2H_2 + H_2$; (R34) $CH_2 + CH_3 \rightarrow C_2H_4 + H$; (R35) $2CH_3 \rightarrow C_2H_6$; and (R40b) $CH_3 + C_2H_5 \rightarrow C_3H_8$. It is clear that synthesis of alkenes and alkynes (except polyacetylenes) occurs mainly in the mesosphere, where CH_2 is abundant. Synthesis of alkanes occurs preferentially in the stratosphere, where alkyl radicals are readily produced by photosensitized dissociation (see also Figs. 4b and 4c).

c) C_2H_6

Ethane is produced primarily by the association reaction (R35) $2CH_3 + M \rightarrow C_2H_6 + M$, as shown in Figure 5$b$. As discussed in § II$b$, most of C_2H_6 production occurs in the lower stratosphere as a result of the photosensitized dissociation of CH_4. Ethane can be destroyed by photolysis (R8) $C_2H_6 + h\nu \rightarrow$ products and by abstraction reactions such as (R56) $C_2H_6 + C_2H \rightarrow C_2H_5 + C_2H_2$. However, the rate of photolytic destruction is small, as a result of effective shielding by CH_4 and C_2H_2. Most of the abstraction reactions do not lead to a net destruction of ethane, as illustrated by the following sequence of reactions

$$C_2H_6 + C_2H \rightarrow C_2H_5 + C_2H_2 \qquad (R56)$$

$$C_2H_5 + H \rightarrow 2CH_3 \qquad (R39)$$

$$\underline{2CH_3 + M \rightarrow C_2H_6 + M \qquad (R35)}$$

$$\text{net} \quad C_2H + H \rightarrow C_2H_2.$$
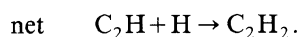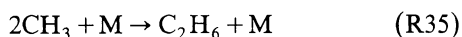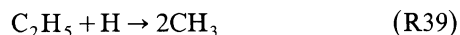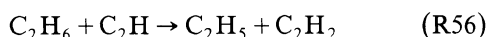
Ethane condenses near the tropopause and is ultimately deposited on the surface. The equivalent downward flux at the tropopause is 5.8×10^9 molecules cm^{-2} s^{-1} and represents the principal loss of atmospheric C_2H_6. The chemical losses are about an order of magnitude less efficient. The column averaged abundance 1.7×10^{-5} is in good agreement with the observed value of 2×10^{-5}. The vertical mixing ratio profile shown in Figure 4a is nearly constant in the upper atmosphere, but falls off in the lower stratosphere, so that the abundance of C_2H_6 does not exceed that allowed by the saturated vapor pressure. Thus, the condensation removal mechanism postulated in this model is crucial for predicting a C_2H_6 profile that satisfies *both* constraints of IRIS observations and saturation vapor pressure.

d) C_2H_4

In the upper atmosphere, the major reactions producing ethylene are (R27) $CH + CH_4 \rightarrow C_2H_4 + H$ and (R34) $CH_2 + CH_3 \rightarrow C_2H_4 + H$, with minor contributions from photolysis of C_2H_6, i.e., (R8a) and (R8b). The altitude profile for (R34) is given in Figure 5b. The column integrated production rate by (R34) is $2.1 \times 10^9 cm^{-2}$ s^{-1}. The corresponding rates due to (R27), (R8a), and (R8b) (not shown in Fig. 5b) are 1.8×10^8, 6.4×10^7, and $2.4 \times 10^7 cm^{-2}$ s^{-1}, respectively. Ethylene in the upper atmosphere is destroyed by photolysis ([R7a], [R7b]), which is apparently so efficient that few molecules survive to the lower altitudes. Figure 4a shows the drastic decrease in the mixing ratio of C_2H_4 with decreasing altitude. The secondary peak in C_2H_4 mixing ratio near 200 km is produced by disproportionation and exchange reactions:

$$2C_2H_3 \rightarrow C_2H_4 + C_2H_2, \qquad (R38)$$

$$C_2H_5 + CH_3 \rightarrow C_2H_4 + CH_4, \qquad (R40a)$$

$$C_2H_5 + C_2H_3 \rightarrow 2C_2H_4, \qquad (R41b)$$

$$2C_2H_5 \rightarrow C_2H_4 + C_2H_6. \qquad (R42a)$$
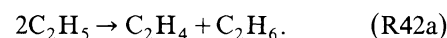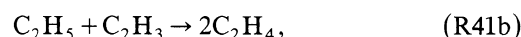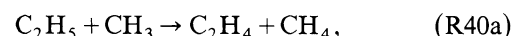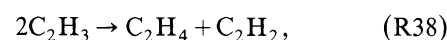
The ultimate source of C_2H_4 in these reactions is C_2H_2 and C_2H_6. Although the total production rates due to the above reactions are comparable to that of (R34), ethylene in the stratosphere is rapidly removed by

$$C_2H_4 + H + M \rightarrow C_2H_5 + M, \qquad (R26)$$

followed by

$$C_2H_5 + H \rightarrow 2CH_3, \qquad (R39)$$

$$2CH_3 + M \rightarrow C_2H_6 + M \qquad (R35)$$
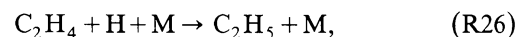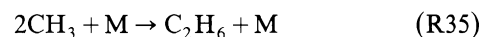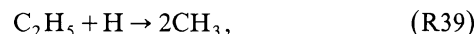
Consequently, the abundance of C_2H_4 in the stratosphere remains rather low. The column-averaged mixing ratio for C_2H_4, 3.3×10^{-8}, is much lower than the observed value 4.0×10^{-7}. The ratios of appropriate column abundance $[C_2H_4]/[C_2H_6]$ and $[C_2H_4]/[C_2H_2]$ are 1.9×10^{-3} and 8.3×10^{-3}, respectively. The corresponding observed values are 2.0×10^{-2} and 2.0×10^{-1}, respectively. Thus, the model prediction for ethylene is too low by an order of magnitude. A resolution of this difficulty is not easy. We can suggest three possibilities: (*a*) the quantum yield for photolysis ([R7a], [R7b]) might have been overestimated, (*b*) the abundance of hydrogen atoms in the stratosphere is too high, and (*c*) the IRIS observation of C_2H_4 has not been correctly analyzed.

e) C_2H_2

The primary sources of acetylene are (R7) $C_2H_4 + h\nu \rightarrow C_2H_2 + H_2$ (or 2H) and (R32) $2CH_2 \rightarrow C_2H_2 + H_2$, with minor contributions from (R8c) $C_2H_6 + h\nu \rightarrow C_2H_2 + 2H_2$. Altitude profile for (R32) is shown in Figure 5b. The column integrated production rates due to (R7), (R32), and (R8c) are

1.4×10^9, 4.6×10^8, and 3.6×10^7 cm^{-2} s^{-1}, respectively. Once it is formed, acetylene is extremely stable against chemical destruction. Photolysis of C_2H_2:

$$C_2H_2 + h\nu \rightarrow C_2H + H, \qquad (R6a)$$
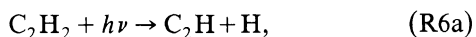
is usually followed by hydrogen abstraction reactions that restore C_2H_2;

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3, \qquad (R55)$$

$$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5. \qquad (R56)$$
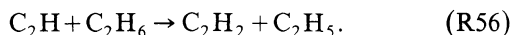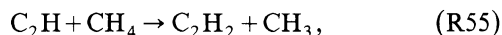
The vinyl radical disproportionation reaction, (R38) $2C_2H_3 \rightarrow C_2H_4 + C_2H_2$, does not result in a net loss of C_2H_2, since C_2H_4 readily dissociates to yield C_2H_2 again. Even addition reactions such as

$$C_2H_2 + CH_2 + M \rightarrow CH_3C_2H + M \qquad (R31a)$$

$$\rightarrow CH_2CCH_2 + M, \qquad (R31b)$$

$$C_2H_3 + CH_3 + M \rightarrow C_3H_6 + M \qquad (R37b)$$

only transform C_2H_2 temporarily into CH_3C_2H, CH_2CCH_2, and C_3H_6, since these molecules are not stable and easily break up into fragments from which C_2H_2 can be retrieved. The only significant mechanism for destroying C_2H_2 appears to be condensation at the tropopause, with a column integrated rate of 1.2×10^9 cm^{-2} s^{-1}. The profile of acetylene shown in Figure 4a is consistent with IRIS. The column-averaged mixing ratio, 4×10^{-6}, is somewhat higher than the observed value of 2×10^{-6}, but is probably within the limits of uncertainties of the observations. However, in the mesosphere the calculated concentrations of C_2H_2 are in serious conflict with observations. UVS deduced a mixing ratio 1%–2% for C_2H_2 a 840 km, where our model predicts a mixing ratio of 2.7×10^{-3}. This discrepancy of a factor of 10 is somewhat disturbing since our column-averaged abundance (which is heavily weighted by the lower stratosphere) is close to the abundance reported by IRIS. We propose an alternative interpretation of the UVS observation. We argue that the ultraviolet opacity attributed to C_2H_2 in the UVS experiment was actually caused by absorption due to other molecules. Consider the opacity at 1550 Å along a straight line tangent to Titan at a radial distance of $R = 3300$ km. The optical depth due to species $[i]$ can be approximately computed by

$$\tau_i = \sqrt{2\pi R H}\, \sigma_i n_i,$$

where σ_i and n_i denote cross section and number density, respectively, and H is atmospheric scale height (~ 63 km at this altitude). Using relevant data from our model we estimate optical depths of 0.02, 0.01, 0.02, 0.01, 0.60, 0.60, and 0.60 for C_2H_2, HCN, HC_3N, C_2H_4, C_4H_2, C_6H_2, and C_8H_2, respectively. Unfortunately, the combined opacity now exceeds that observed by Smith *et al.* (1982a). Condensation of the polyacetylenes near the mesopause could resolve the difficulty.

f) H

Hydrogen atoms are produced in the upper atmosphere mainly by (R5b) $CH_4 + h\nu \rightarrow CH_2 + 2H$, (R7b) $C_2H_4 + h\nu \rightarrow C_2H_2 + 2H$, and (R34) $CH_2 + CH_3 \rightarrow C_2H_4 + H$, and in the lower atmosphere by photolysis of acetylene and polyacetylenes, i.e., (R6a), (R14a), and (R15a). The combined production rate is 1.1×10^{10} cm^{-2} s^{-1}. All hydrogen atoms produced below 600 km are effectively scavenged by the C_4H_2 catalytic cycle. However, hydrogen atoms produced above this level readily escape from the atmosphere. The escape flux calculated in our model is 5.5×10^9 cm^{-2} s^{-1}. This is somewhat larger than the value of 1–3×10^9 cm^{-2} s^{-1} deduced by Smyth's (1981) modeling of *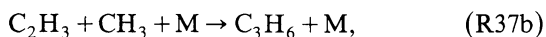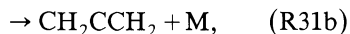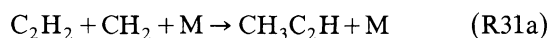Pioneer 11* and *IUE* observations of the Saturnian system. But a quantitative comparison is not possible until Smyth's model has been updated to simulate the Voyager observations.

There is another observational constraint on the concentration of hydrogen atoms in the upper atmosphere. The UVS instrument reported a disk-averaged Lyα emission of 1 kR, of which about half may be attributed to resonance scattering of solar radiation (see discussion in footnote of Table 1A). The column abundance of hydrogen above 750 km (where absorption of Lyα by CH_4 starts to dominate) is 3×10^{15} cm^{-2}. Radiative calculations, similar to those described in Yung and Strobel (1980), using the profiles of H and CH_4 presented in Figures 4b and 4a, yield an airglow of 600 R. Within limits of the uncertainties of the observations, these results are consistent. In the Lyα calculations we used a solar flux of 5.6×10^{11} photons cm^{-2} s^{-1} Å^{-1} at 1 a.u. (Mount and Rottman 1981), close to the value 5.1×10^{11} photons cm^{-2} s^{-1} Å^{-1} used by Yung and Strobel (1980).

g) H_2

The most important reactions for producing H_2 in the model are shown in Figure 5c. The column integrated rates for (R5a) $CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$, (R7a) $C_2H_4 + h\nu \rightarrow C_2H_2 + H_2$, (R6b) $C_2H_2 + h\nu \rightarrow C_2 + H_2$, and (R69b) $C_4H_3 + H \rightarrow C_4H_2 + H_2$ are 1.4×10^9, 1.2×10^9, 1.8×10^9, and 2.7×10^9 cm^{-2} s^{-1}, respectively. The reaction (R36) $C_2H_3 + H \rightarrow C_2H_2 + H_2$ is relatively unimportant, with an integrated production rate of 7×10^7 cm^{-2} s^{-1}. Once it is formed, H_2 is chemically very stable. The fate of more than 99% of H_2 produced in our model is escape from the exosphere. The flux is 7.2×10^9 cm^{-2} s^{-1}. The predicted H_2 abundance 2.1×10^{-3} is in good agreement with the IRIS observation of $2 \pm 1 \times 10^{-3}$. The H_2 abundance in the model depends on the rate of production and the rate of escape from the exosphere. Since the temperature of the exosphere is known, the rate of production of H_2 must be close to that computed in our model. This result, which is independent of the uncertainties in the choice of the eddy diffusivity profile (as long as the eddy diffusion coefficient at the homopause exceeds a certain critical value) and the details of the atmospheric chemistry, suggests that the minimum rate of CH_4 destruction is many times larger than the primary photolysis rate. This provides the most direct confirmation of the importance of photosensitized processes in the stratosphere.
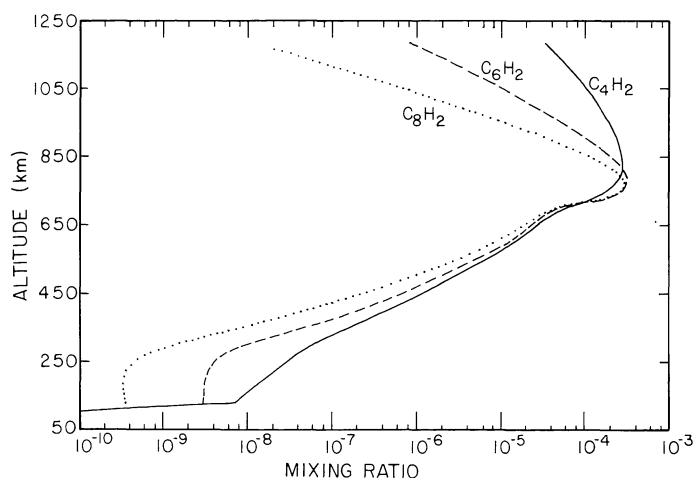
FIG. 6a
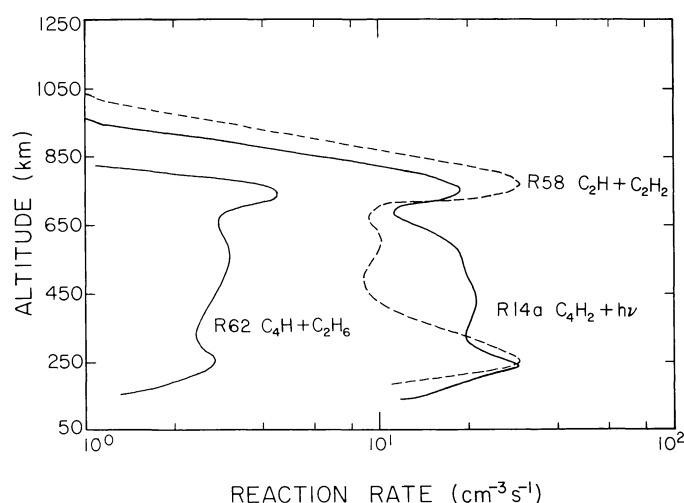
FIG. 6b

FIG. 6.—(a) Altitude profiles for the mixing ratios of C_4H_2, C_6H_2, and C_8H_2. (b) Reaction rates for selected important reactions producing, destroying, and recycling C_4H_2: (R58) $C_2H_2 + C_2H \rightarrow C_4H_2 + H$; (R14a) $C_4H_2 + h\nu \rightarrow C_4H + H$; and (R62) $C_4H + C_2H_6 \rightarrow C_4H_2 + C_2H_5$.

h) Polyacetylenes

Altitude profiles for the mixing ratios of polyacetylenes C_4H_2, C_6H_2, and C_8H_2 are presented in Figure 6a. Only C_4H_2 has been observed by IRIS. The reported column-averaged, $10^{-8}-10^{-7}$, is higher than our model value of 7.8×10^{-10}. The polyacetylenes are an order of magnitude less than acetylene in the mesosphere, but since their cross sections are ~ 10 times higher than that of acetylene, they contribute to the observed atmospheric opacity in the vacuum ultraviolet (see discussion in § Ve on UVS observations). The polyacetylenes are produced by the insertion reactions (R58) $C_2H + C_2H_2 \rightarrow C_4H_2 + H$; (R63) $C_4H + C_2H_2 \rightarrow C_6H_2 + H$; (R67) $C_6H + C_2H_2 \rightarrow C_8H_2 + H$; (R59) $C_2H + C_4H_2 \rightarrow C_6H_2 + H$; (R60) $C_2H + C_6H_2 \rightarrow C_8H_2 + H$; and (R64) $C_4H + C_4H_2 \rightarrow C_8H_2 + H$, with column-integrated production rates equal to 1.7×10^9, 1.2×10^9, 8.4×10^7, 1.5×10^8, 1.9×10^8, and 1.7×10^8 cm^{-2} s^{-1}, respectively. The polyacetylenes undergo rapid photolysis and recycling in the atmosphere, resulting in the photosensitized dissociation of CH_4 and other alkanes. As an illustration of this discussion, Figure 6b presents a selected set of reactions involving C_4H_2. Diacetylene is produced by (R58) $C_2H_2 + C_2H \rightarrow C_4H_2 + H$, recycled by (R14a) $C_4H_2 + h\nu \rightarrow C_4H + H$ and (R62) $C_4H + C_2H_6 \rightarrow C_4H_2 + C_2H_5$ (the net result of this cycle is breaking C_2H_6 into $C_2H_5 + H$). Another recycling reaction, (R61) $C_4H + CH_4 \rightarrow C_4H_2 + CH_3$, has been shown in Figure 5a.

The predicted concentrations of polyacetylenes in the present model are less than those in our previous study (Allen, Pinto, and Yung 1980). There are at least three differences between these models. First, we have now adopted Brown and Laufer's (1981) high rate coefficient for (R55) $C_2H + CH_4 \rightarrow C_2H_2 + CH_3$, $k_{55} = 2.5 \times 10^{-12} e^{-750/T}$, whereas Allen, Pinto, and Yung used $k_{55} = 3.0 \times 10^{-11} e^{-1400/T}$. Since (R55) tends to suppress the formation of long-chain compounds by quenching the C_2H radical, we might expect less $C_{2n}H_2$. Second, we have included the new scheme (17a) for cracking

C_4H_2 by H. Lately, we have revised the dissociation pathways for $C_{2n}H_2$. The dominant dissociation of $C_{2n}H_2$ is by $C_{2n}H_2 + h\nu \rightarrow C_{2n}H + H$, and does not lead to a loss of C_{2n} compounds. The net result of all these changes is a decrease in the abundances of polyacetylenes in the present model. Note that we can drastically increase C_4H_2 in the stratosphere by postulating a faster (R69b) or by invoking another mechanism for removal of H atoms.

In our model we do not deal with polyacetylenes beyond C_8H_2. It is mildly embarrassing that the calculated abundances of the polyacetylenes, $C_4H_2 = 7.8 \times 10^{-10}$, $C_6H_2 = 3.6 \times 10^{-10}$, and $C_8H_2 = 1.5 \times 10^{-10}$, do not fall off rapidly with increasing carbon atoms. Thus, our cutoff of the long-chain compounds appears somewhat arbitrary. However, we do not regard this as a fundamental weakness of the model. The cross sections and quantum yields for dissociation for the higher polyacetylenes could be larger than our estimates, and the rate of condensation could increase with molecular weight. Inclusion of any of these considerations would result in lower concentrations for the higher polyacetylenes, but unfortunately at the expense of more model parameters. Alternatively, the high abundance of the long-chain compounds may be real. The early experiments of Lasaga, Holland, and Dwyer (1971) and more recent ones by Sagan and Thompson (1983) all produce considerable amounts of organic compounds of high molecular weights. A small fraction of the polyacetylenes produced can be irreversibly removed as long-chain polymers. This ultimately represents a net loss of acetylene from the atmosphere (see Appendix).

i) C_3 Hydrocarbons

Altitude profiles for the major C_3 species CH_3C_2H, CH_2CCH_2, C_3H_6, and C_3H_8, and their associated radicals C_3H_2, C_3H_3, C_3H_5, and C_3H_7 are shown in Figures 7a and 7b, respectively. A schematic diagram showing the major pathways connecting the important C_3 species is presented in
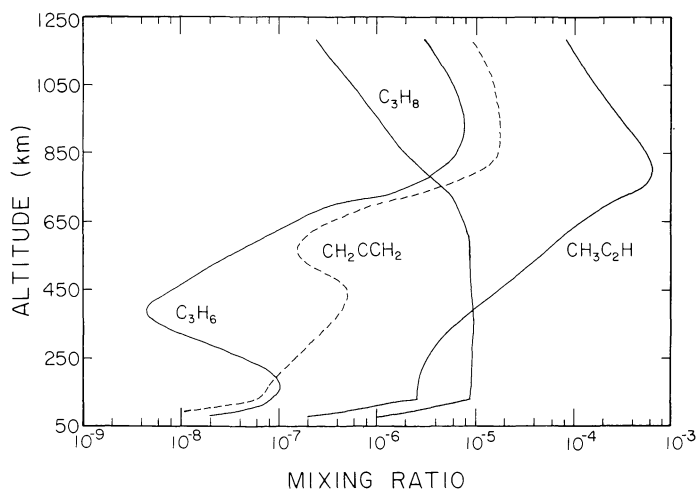
Fig. 7a
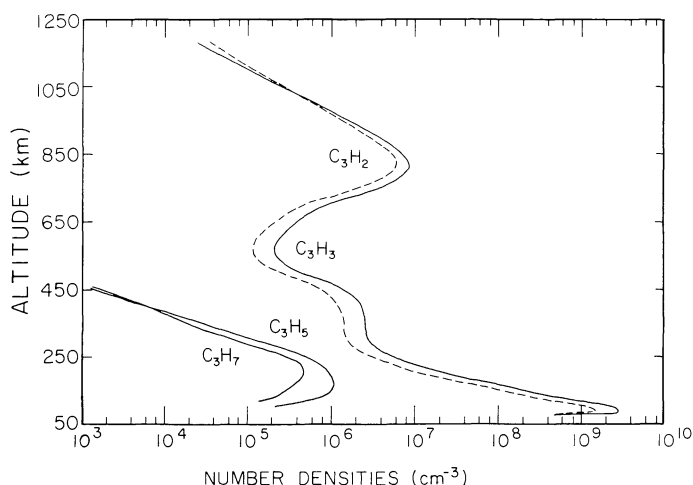
Fig. 7b
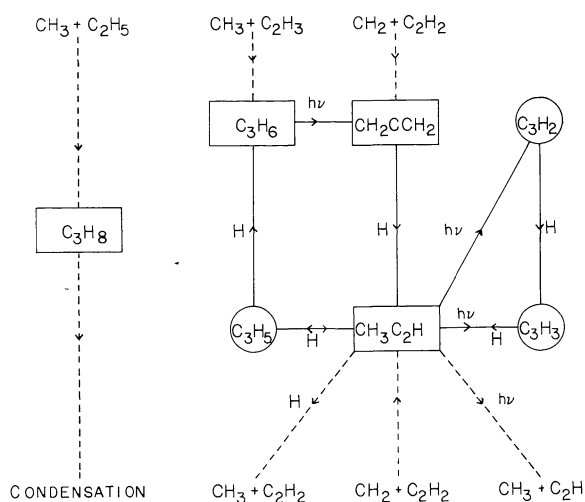
Fig. 7c

Fig. 7.—(a) Altitude profiles for the mixing ratios of CH_3C_2H, CH_2CCH_2, C_3H_6, and C_3H_8. (b) Altitude profiles for the number densities of C_3H_2, C_3H_3, C_3H_5, and C_3H_7. (c) Schematic diagram showing the major pathways connecting C_3 compounds.

Figure 7c. The computed column-averaged mixing ratio for CH_3C_2H is 1.8×10^{-7}, a value higher than the IRIS observation of 3×10^{-8}. The concentrations of CH_3C_2H and the radicals C_3H_3 and C_3H_2 are unrealistically high in the model. One reason is that we have omitted the speculative reactions that convert C_3 into C_4, viz., (R111a) $CH_3 + C_3H_3 \rightarrow 1, 2\text{-}C_4H_6$ or $1\text{-}C_4H_6$, and (R112) $CH_3 + C_3H_5 \rightarrow C_4H_8$. Inclusion of these reactions (see Appendix) brings the model abundance for CH_3C_2H to 3×10^{-8}, and the number densities of C_3H_3 and C_3H_2 to below 10^6 cm^{-3} in the lower stratosphere. The major reactions producing CH_3C_2H and CH_2CCH_2 are (R31a) $CH_2 + C_2H_2 \rightarrow CH_3C_2H$, (R31b) $CH_2 + C_2H_2 \rightarrow CH_2CCH_2$, and (R12a) $C_3H_6 + h\nu \rightarrow CH_2CCH_2 + H_2$, with integrated column rates equal to 4.0×10^8, 4.9×10^8, and 8.5×10^7 cm^{-2} s^{-1}, respectively. CH_2CCH_2 is rapidly con-

verted into CH_3C_2H by the H exchange reaction (R70) $CH_2CCH_2 + H \rightarrow CH_3C_2H + H$. The main reactions that result in a net loss of CH_3C_2H are photolysis and the cracking by H, viz., (R45a) $CH_3C_2H + H \rightarrow CH_3 + C_2H_2$.

The column-averaged mixing ratio of propane in the model is 7.9×10^{-7}, in fair agreement with the observed abundance of $2\text{-}4 \times 10^{-6}$. C_3H_8 is formed almost entirely by the association reaction (R40b) $CH_3 + C_2H_5 \rightarrow C_3H_8$, as shown in Figure 5b. The high three-body rate coefficient, derived on the basis of Troe's theory, is essential for predicting a high C_3H_8 abundance in the model. C_3H_8 is destroyed by photolysis R13 and abstraction by C_2H, R57. Like ethane, propane is sufficiently stable against chemical destruction that most of the C_3H_8 produced in the model is lost by condensation in the lower stratosphere. The net downward flux of C_3H_8 is 1.4×10^8 cm^{-2} s^{-1}.

j) Nitrogen Compounds

Figure 8a summarizes the altitude profiles of the important nitrile compounds HCN, HC_3N, and C_2N_2. The concentrations of odd nitrogen radicals N, NH, and CN are shown in Figure 8b. A schematic diagram showing the relation between the nitrogen compounds is given in Figure 8c. The predicted column averaged abundances for HCN, HC_3N, and C_2N_2 are 5.6×10^{-7}, 5.6×10^{-8}, and 1.9×10^{-8}, respectively. The corresponding observations reported by IRIS are 2.0×10^{-7}, $10^{-8}\text{-}10^{-7}$, and $10^{-8}\text{-}10^{-7}$, respectively. So the theory agrees well with observation. The major source of odd nitrogen is downward flow from the thermosphere, with a flux of 2×10^9 cm^{-2} s^{-1} for the sum of N and NH. Cosmic-ray dissociation of N_2 contributes an additional flux of N+NH equal to 7.4×10^7 cm^{-2} s^{-1} in the lower stratosphere. The lifetime of odd nitrogen in the atmosphere is sufficiently short, so that the vertical profiles of the radicals N and NH exhibit large gradients in the vicinity of the sources. As shown in Figure 9a, most of odd nitrogen is destroyed by (R76) $NH + N \rightarrow N_2 + H$. Only ~10% of the total odd nitrogen produced is converted into HCN by reactions (R73) $N + CH_2 \rightarrow HCN + H$ and (R74) $N + CH_3 \rightarrow HCN + H_2$. The column production rates for

FIG. 8a

FIG. 8b

FIG. 8c

FIG. 8.—(*a*) Altitude profiles for the mixing ratios of HCN, HC$_3$N, and C$_2$N$_2$. (*b*) Altitude profiles for the number densities of N, NH, and CN. (*c*) Schematic diagram showing the major pathways connecting the nitrogen compounds.

(R73) and (R74) are 4.6×10^6 and 2.6×10^8 cm^{-2} s^{-1}, respectively. The formation of the extremely stable CN bond represents a net sink of atmospheric nitrogen $\sim 2 \times 10^8$ N cm^{-2} s^{-1}, as the ultimate sink of nitrile compounds is condensation. Recycling of the CN radical between HCN, HC$_3$N, and C$_2$N$_2$ determines their relative abundances. A sampling of the important recycling reactions are shown in Figure 9*b*: (R17) HCN + $h\nu \rightarrow$ H + CN; (R79) CN + C$_2$H$_6 \rightarrow$ HCN + C$_2$H$_5$; (R81) HCN + C$_2$H $\rightarrow$ HC$_3$N + H; (R82) HCN + CN $\rightarrow$ C$_2$N$_2$ + H; and (R87) C$_2$N$_2$ + 2H $\rightarrow$ 2HCN. Another important recycling reaction is (R78) CH$_4$ + CN $\rightarrow$ HCN + CH$_3$, but this reaction is not as important as (R87). As shown in Figure 9*b*, the reaction (R87) C$_2$N$_2$ + 2H $\rightarrow$ 2HCN, first postulated in this work, is an important sink for C$_2$N$_2$ in the lower stratosphere, comparable in magnitude to photolysis (R19). This suggests that a low concentration of H in the lower stratosphere is required to be consistent with the concentration of C$_2$N$_2$.

k) Oxygen Compounds

Altitude profiles for the mixing ratios of CO, CO$_2$, H$_2$O, H$_2$CO, and CH$_2$CO, and the number densities of O(^{1}D), O, OH, and HCO are presented in Figures 10*a* and 10*b*, respectively. A schematic diagram showing the relation between the oxygen compounds is given in Figure 10*c*. The computations have been performed with a downward flux of H$_2$O equal to 6.1×10^5 cm^{-2} s^{-1}, a value that has been chosen to reproduce the observed CO$_2$ abundance of 1.5×10^{-9}. The predicted abundance of CO is 1.8×10^{-4}, somewhat higher than the value 6×10^{-5} deduced from radio observations by Muhleman, Berge, and Clancy (1984), and infrared observations by Lutz, de Bergh, and Owen (1983).

As shown in Figure 11*a*, the chemical reactions that destroy CO$_2$ are (R20a) CO$_2$ + $h\nu \rightarrow$ CO + O, (R20b) CO$_2$ + $h\nu \rightarrow$ CO + O(^{1}D), and (R98) CO$_2$ + CH$_2 \rightarrow$ CO + H$_2$CO. The integrate rates for (R20a), (R20b), and (R98) are 4.3×10^4, 1.0×10^5, and 2.1×10^4 cm^{-2} s^{-1}. Downward transport through the tropopause introduces an additional loss of 2.8×10^5 cm^{-2} s^{-1}, respectively. In the absence of chemical sources, it would take only 2×10^3 yr to deplete the stratosphere of CO$_2$. The only reaction that acts to restore CO$_2$ is (R96) CO + OH $\rightarrow$ CO$_2$ + H, as shown in Figure 11*a*. The integrated rate for (R96) is 4.4×10^5 cm^{-2} s^{-1}. As shown in Figure 11*b*, CO is mainly formed in the thermosphere by (R95) OH + CH$_3 \rightarrow$ CO + 2H$_2$. The other interesting compounds such as H$_2$CO and CH$_2$CO are formed primarily in the stratosphere. However, because of the instability of these compounds toward photolysis, they are all below current detection levels (see Fig. 10*a*).

l) Summary of Model

An overall comparison of the model results and observations is given in Table 5A. It can be seen that the model correctly accounts for the order of magnitude of most of the observations. It is possible to obtain better agreement between model and observation by adjusting the model parameters. But in view of the uncertainties of the observations and laboratory data such exercise is probably not meaningful. The
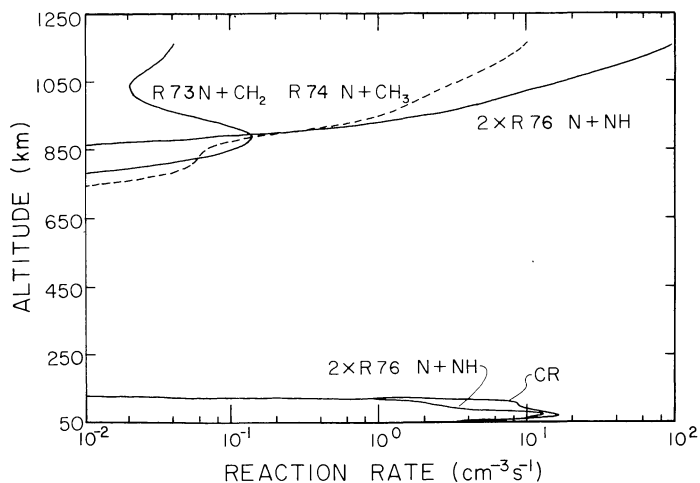
FIG. 9a
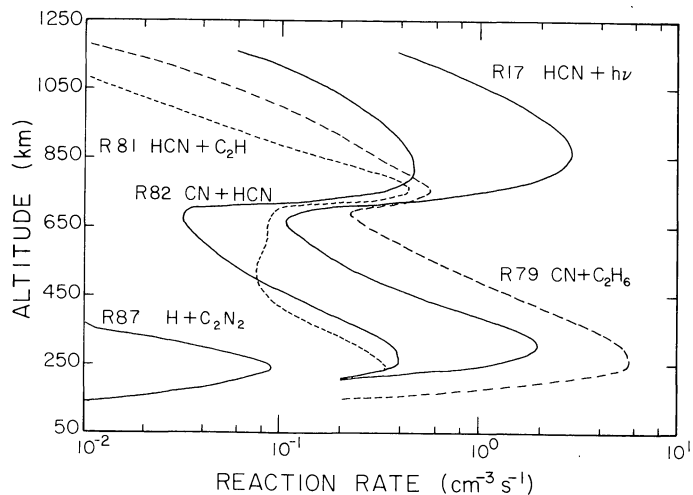
FIG. 9b

FIG. 9.—(a) Reaction rates for reactions producing and destroying odd nitrogen and those forming the CN bond: CR = production of odd nitrogen (N + NH) by cosmic rays; (R76) $N + NH \rightarrow N_2 + H$; (R73) $N + CH_2 \rightarrow HCN + H$; (R74) $N + CH_3 \rightarrow HCN + H_2$. The major source of odd nitrogen is downward fluxes of N and NH at the upper boundary, as discussed in the text. (b) Reaction rates for selected important reactions recycling nitrile species: (R17) $HCN + h\nu \rightarrow H + CN$; (R79) $CN + C_2H_6 \rightarrow HCN + C_2H_5$; (R81) $C_2H + HCN \rightarrow HC_3N + H$; (R82) $CN + HCN \rightarrow C_2N_2 + H$; (R87) $C_2N_2 + 2H \rightarrow 2HCN$.
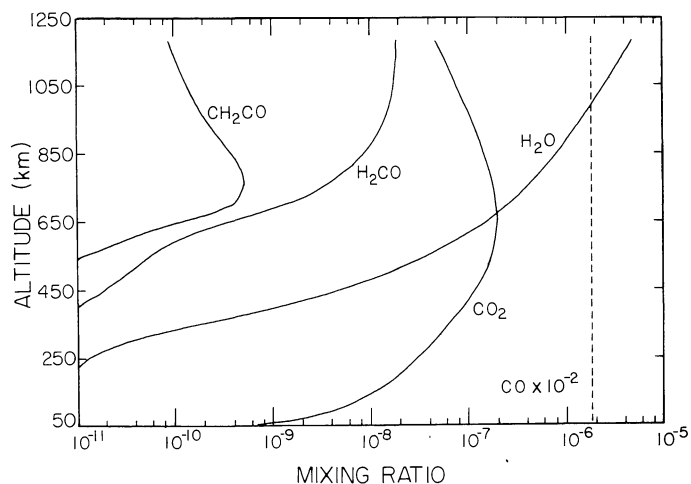
FIG. 10a
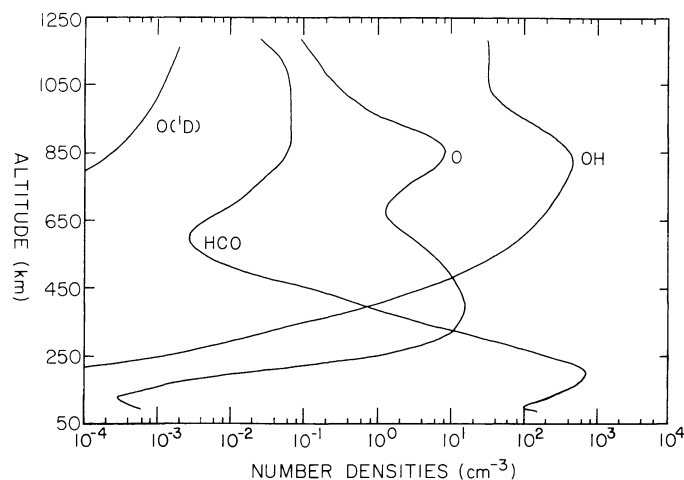
FIG. 10b
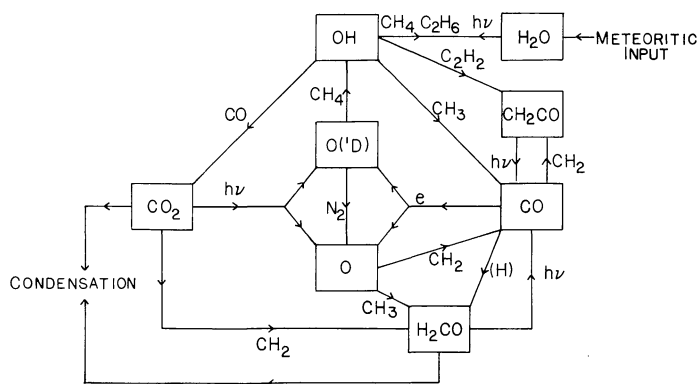
FIG. 10c

FIG. 10.—(a) Altitude profiles for the mixing ratios of CO, CO_2, H_2O, H_2CO, and CH_2CO. (b) Altitude profiles for the number densities of O, $O(^1D)$, OH, and HCO. (c) Schematic diagram showing the interaction between the oxygen species.
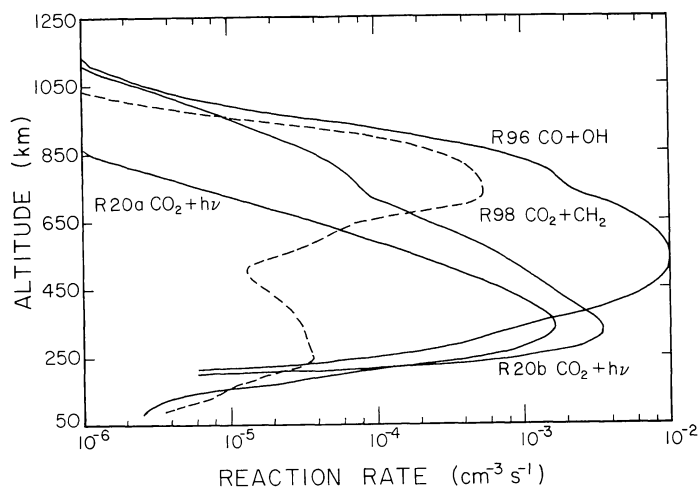
FIG. 11a
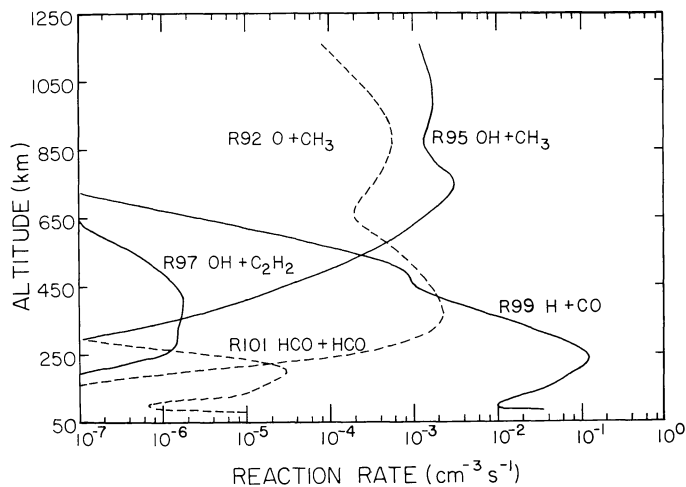
FIG. 11b

FIG. 11.—(a) Reaction rates for major reactions destroying CO_2: (R20a) $CO_2 + h\nu \rightarrow CO + O$; (R20b) $CO_2 + h\nu \rightarrow CO + O(^1D)$; (R98) $CO_2 + CH_2 \rightarrow CO + H_2CO$, and producing CO_2: (R96) $CO + OH \rightarrow CO_2 + OH$. (b) Reaction rates for selected important reactions involving O, OH, and HCO: (R92) $O + CH_3 \rightarrow H_2CO + H$; (R97) $OH + C_2H_2 \rightarrow CH_2CO + H$; (R95) $OH + CH_3 \rightarrow CO + 2H_2$; (R99) $H + CO \rightarrow HCO$; (R101) $2HCO \rightarrow H_2CO + CO$.

TABLE 5A

SUMMARY OF IMPORTANT MODEL RESULTS AND COMPARISON WITH OBSERVATIONS IN TABLE 1A

Species	Model[a] Abundance	Observed[a] Abundance	Remarks
CH_4	2.0×10^{-2}	$1-3 \times 10^{-2}$	{ model value imposed as boundary condition at 45 km
H_2	2.1×10^{-3}	$2 \pm 1 \times 10^{-3}$	...
C_2H_6	1.7×10^{-5}	2×10^{-5}	...
C_2H_4	3.3×10^{-8}	4×10^{-7}	...
C_2H_2	4.0×10^{-6}	2×10^{-6}	...
CH_3C_2H	1.8×10^{-7} (3×10^{-8})	3×10^{-8}	b,c
CH_2CCH_2	5.0×10^{-9}	...	{ searched for but not observed by IRIS
C_3H_8	7.9×10^{-7}	$2-4 \times 10^{-6}$	...
C_4H_2	7.8×10^{-10}	$10^{-8} - 10^{-7}$	b
HCN...........	5.6×10^{-7}	$2 \times 10^{-7} - 10^{-7}$	b
HC_3N..........	5.6×10^{-8}	$10^{-8} - 10^{-7}$	b
C_2N_2	1.9×10^{-8}	$10^{-8} - 10^{-7}$	b
CO	1.8×10^{-4}	6×10^{-5}	d
CO_2............	1.5×10^{-9}	1.5×10^{-9}	{ flux of meteoritic H_2O has been adjusted to yield the correct CO_2 abundance

[a]Unless otherwise stated concentrations are given in column-averaged mixing ratios above 45 km. To convert mixing ratios into column integrated abundances above 45 km, multiply the appropriate mixing ratios by 1.9×10^{25} molecules cm^{-2}.

[b]Strong latitudinal asymmetry; more abundant at the north pole to which the observations refer.

[c]The value of CH_3C_2H in parenthesis refers to the case when speculative reactions in Table 7 are included (see Appendix).

[d]The observed abundance for CO quoted here is from Lutz, de Bergh, and Owen 1983 and Muhleman, Berge, and Clancy 1984.

TABLE 5B

BUDGET FOR PARENT MOLECULES CH_4, N_2, AND H_2O[a]

Reaction	Flux	Reaction	Flux
Destruction of CH_4 (sum total =	1.5×10^{10})	Destruction of N_2:	
R72 $N(^2D) + CH_4$	1.0×10^9	$N_2 + e$	1.0×10^9
R5 $CH_4 + h\nu$	2.9×10^9	N_2 + cosmic rays	3.7×10^7
R53 $CH_4 + C_2$	3.0×10^9	escape[c]...................................	1.6×10^8
R55 $CH_4 + C_2H$	5.1×10^9		
R61 $CH_4 + C_4H$	1.7×10^9	Production of N_2:	
R65 $CH_4 + C_6H$	1.0×10^9	R76 $N + NH$	8.9×10^8
R78 $CH_4 + CN$	4.0×10^7		
		Downward Flux of Nitrile Compounds:	
Production of CH_4 (sum total =	5.9×10^8):	HCN	2.0×10^8
R33 $CH_3 + H$	3.5×10^8	HC_3N	1.7×10^7
R37a $CH_3 + C_2H_3$	2.1×10^8	$2 \times C_2N_2$	1.2×10^7
Escape Fluxes of H and H_2:		Influx of meteoritic H_2O:	6.1×10^5
H	5.5×10^9	Escape of O:[c]	3.3×10^4
H_2	7.2×10^9		
		$2 \times$ downward flux of CO_2:[b]	5.7×10^5
Downward Fluxes of Hydrocarbons:[b]			
C_2H_6	5.8×10^9	Net loss of parent molecules from atmosphere:	
C_2H_2	1.2×10^9	CH_4	1.5×10^{10}
CH_3C_2H	5.7×10^7	N_2	2.8×10^8
C_3H_8	1.4×10^8	H_2O	6.1×10^5
C_4H_{10}	2.3×10^7		

[a] Integrated reaction rates and fluxes (normalized to the surface) are in units of $cm^{-2} s^{-1}$.
[b] At the tropopause; the species transported downward are assumed to be irreversibly lost.
[c] Taken from Strobel and Shemansky 1982.

most important implication of Table 5A is that the composition of minor constituents of Titan's atmosphere can be understood in terms of a simple photochemical model. A summary of the important reactions and processes that affect the global budget of atmospheric carbon, hydrogen, nitrogen, and oxygen is given in Table 5B. As pointed out in § II, the most significant processes are photosensitized destruction of CH_4, hydrogen escape, and organic synthesis. The atmosphere is not in equilibrium, but continuously evolving and losing material at rates listed in Table 5B.

How realistic are these computations? The model has achieved a moderate degree of success in accounting for most of the observations. However, caution must be exercised in intepreting our results for nitrogen and oxygen species, since we are now compounding the uncertainties of hydrocarbon chemistry with that of nitrogen and oxygen. We are least confident about the mechanism that regulates the abundance of CO in the atmosphere. The time constant for photochemical adjustment under current conditions is $\sim 10^9$ yr. Over such a long time scale other processes, such as planetary degassing, could be more important than photochemical processes. Thus, the apparent agreement between the observed and predicted CO abundance may be fortuitous. We have no illusions that the quantitative details of the model are all correct. We only hope that the model has been useful for identifying the problems of Titan chemistry, providing a framework to digest recent observations and suggesting guidelines for future work. As an overview, our present knowledge of atmospheric chemistry in the outer solar system is probably at the stage of the terrestrial atmosphere three decades ago (Bates and Nicolet 1950), or the Cytherean and Martian atmospheres more than a decade ago (Jastrow and Rasool 1969; McElroy and Hunten 1970).

VI. IMPLICATIONS OF THE MODEL

The atmosphere can be simply viewed as a chemical system that processes the simpler molecules into more complex ones. At the upper boundary of the model, the exobase, H and H_2 escape from Titan to become part of the extensive torus around Saturn. The ultimate source of the starting material such as CH_4 and N_2 is the surface or the interior of Titan. The complex molecules produced in the model affect the composition of the troposphere and the geochemistry of the surface, as well as planetary climatology and evolution. In our modeling effort, we have so far focused on the chemistry of the atmosphere. The model results presented in the previous section now provide a basis for discussing a number of important problems related to the upper and lower boundaries, and the past history of the satellite and the Earth.

a) Hydrogen Torus

Both H and H_2 can readily escape from Titan at the present exospheric temperature of 190 K. The significance of hydrogen escape for atmospheric stability and evolution was recognized by Kuiper (1944). Subsequently, the question of stability (or instability) of light gases on Titan led to the development of such fundamental concepts as the limiting flux (Hunten 1973) and the gaseous toroidal ring (McDonough and Brice 1973a, b). Both ideas transcended their original applications to Titan and are extremely useful for studying a wide class of planetary problems (Hunten and Strobel 1974; Liu and Donahue 1974; Carlson and Judge 1974; Fang, Smyth, and McElroy 1976).

We can now regard the escape of hydrogen from Titan as established on the basis of Lyα observations of the torus associated with Titan by *Pioneer 11* (Judge, Wu, and Carlson

1980) and *Voyager 1* and *2* (Broadfoot *et al.* 1981; Sandel *et al.* 1982). The torus is estimated to contain 7.3×10^{34} atoms of H. Assuming that all the hydrogen atoms originate from Titan at the rate of 5.5×10^9 cm^{-2} s^{-1}, we obtain a mean lifetime of 2×10^7 s for H atoms in the torus. This value is not unreasonable when compared with the lifetime of 5×10^7 s against charge transfer with protons (Bridge *et al.* 1982). Since the cross sections of H and H_2 toward charge transfer are similar (Allison 1958), we would expect the lifetime for H_2 in the torus to be close to that of H. Since the escape rates of H_2 and H are comparable according to our model, there should be nearly equal amounts of H and H_2 in the torus. Unfortunately, direct observation of H_2, a molecule without a convenient spectroscopic signature, is difficult.

b) Troposphere

Titan's troposphere, with column density of 2.5×10^{26} cm^{-2}, or ~ 10 times as massive as Earth's troposphere, is more like a shallow terrestrial ocean than an atmosphere. The radiative lifetime is ~ 140 yr (Flasar, Samuelson, and Conrath 1981). The time constant for troposphere-stratosphere exchange is, according to our model, ~ 600 yr. The order of magnitude of these time constants is characteristic of our oceans, but not of the atmospheres of terrestrial planets. In our model we have chosen the tropopause to be at 45 km, where the temperature is 70 K. Across this boundary CH_4 and N_2 are supplied to the stratosphere, and photochemical products are returned to the troposphere. The heavy hydrocarbons will probably sink to the surface. The more volatile compounds can reevaporate near the surface, where the temperature is much higher ~ 94 K. Thus, except for CO, the lower troposphere could acquire a composition close to the saturation composition described by Table 1B under the heading "surface." For example, the mixing ratios for C_2H_6, C_2H_2, C_3H_8, and CO_2 near the ground would be $\sim 4 \times 10^{-5}, 8 \times 10^{-7}, 5 \times 10^{-7}$, and 1×10^{-7}, respectively, and the atmosphere should arrive at steady state for these species in less than 6×10^4, 5×10^3, 3×10^4, and 3×10^6 yr, respectively. The presence of these molecules in the troposphere with abundances indicated here may contribute to the greenhouse effect, since they all have strong absorption bands in the infrared (Wang *et al.* 1976).

c) Climatology

How does the atmosphere arrive at the current state? Starting from a pure N_2 and CH_4 atmosphere, we can envision the following sequence of events:

1. Photolysis of CH_4 in the mesosphere leads to production of C_2H_2 and C_2H_4.

2. C_2H_2 abundance builds up in the stratosphere.

3. Photosensitized dissociation of CH_4 becomes important, producing C_2H_6, polymers, and aerosols.

4. Absorption of sunlight by aerosols leads to thermal inversion and dynamical stability.

5. Stratosphere becomes more stable, resulting in a further increase of the abundances of higher hydrocarbons and leading back to step 3.

Steps 3, 4, and 5 constitute a cycle with positive feedback and can, in principle, be catastrophic. In practice, the cycle is limited by the availability of ultraviolet photons. It is clear that the smoggy atmosphere solution which prevails at present "hangs together" by a delicate coupling between photochemistry, radiation, and dynamics. There is no *a priori* reason to believe that this is the only or even the most stable solution. A clear atmosphere solution is perfectly viable from the theoretical point of view. In fact, Strobel's (1974) model with $K_0 = 10^5$ cm^2 s^{-1} is representative of the clear atmosphere solution, characterized by low hydrocarbon content and absence of aerosols. That the atmosphere can have two fundamentally different states is perhaps a manifestation of the beauty and subtlety of a coupled geochemical and geophysical system. For comparison, we note the Earth's climate also has two states: clement like the present, and frigid in an ice age. Our experience in modeling Titan's atmosphere suggests that the fundamental challenge is to understand the complex polymer chemistry that leads to the formation of photochemical aerosols. Aerosol chemistry provides a linkage between ultraviolet radiation, photochemistry, and climatic change. The solar-planetary climate effect, which has proved so elusive to document on Earth (Eddy 1982), may be more amenable to verification on Titan (Suess and Lockwood 1980; Allen, Pinto, and Yung 1980; Sromovsky *et al.* 1981). More laboratory experiments, continued ground-based and spacecraft observations, and new theoretical insights are needed in this direction.

d) Evolution

There is evidence based on photochemical and isotopic studies that the atmospheres of the terrestrial planets have undergone extensive evolution (McElroy 1972; Nier, McElroy, and Yung 1976; McElroy, Prather, and Rodriguez 1982; Donahue *et al.* 1982; Craig and Lupton 1976; Pollack and Yung 1980). On Titan the tempo of evolution is much faster; the action, more vivid. Destruction of the atmosphere occurs by escape of gases, including nitrogen, from the exosphere and by conversion into condensable organic compounds which are then deposited on the surface. No other object in the solar system, with perhaps the exception of comets, offers such a dramatic demonstration of photochemistry as a driving force of atmospheric evolution. Hydrogen, extracted from methane, escapes and forms a torus around Saturn. The hydrogen-poor organic compounds form extensive aerosol layers that contribute to the remarkable visual appearance of Titan.

The column abundances of CH_4, N_2, and CO in the present atmosphere are, according to our model, 1.4×10^2, 1.2×10^4, and 2.2 g cm^{-2}, respectively. If the loss rates given in Table 5B were constant over the age of the solar system (4.5 billion yr), we would estimate accumulated losses of 5.6×10^4, 1.8×10^3, and 4.0 g cm^{-2}, respectively, for CH_4, N_2, and CO. Note that the total amount of CH_4 destroyed is ~ 400 times that in the atmosphere today and must be supplied from the surface. Since carbon does not escape from the exosphere at an appreciable rate, the surface must have acquired the equivalent of a kilometer of photochemical products. On the basis of our model, the composition of this material is 77% C_2H_6, 16% C_2H_2, with the rest composed of heavy hydrocarbons, polymers, and nitriles. Many questions about the impact of the photochemical products on Titan's geology and geochem-

istry may be quite interesting, such as: (*a*) How do they interact with a possible CH_4 or N_2 ocean on the surface? (*b*) How do they affect the noble gas contents of the atmosphere? (*c*) How do they interact with the interior of the satellite if Titan is tectonically active? Some of these issues were discussed by Lunine, Stevenson, and Yung (1983). The total amount of N_2 destroyed is ~17% of the present atmosphere, with roughly equal losses to space and to the ground. The total destruction of CO computed here is probably a lower limit. The rate of destruction in the past might have been much higher, in principle, as high as that for N_2 if the abundance of CO were comparable to that of N_2 (Samuelson *et al.* 1983). As pointed out by Samuleson *et al.* (1983), the abundance of CO in the atmosphere today is photochemically controlled and is consequently not diagnostic of its primordial origin.

The presence of large quantities of CH_4 on Titan is expected on the basis of Lewis' (1971) model. The theory of Prinn and Fegley (1981) allows for a primordial origin of N_2 and CO. But then to understand the low abundance of CO on Titan today, we have to invoke efficient destruction of CO in the past. The detailed photochemical model remains to be worked out. The alternative hypothesis that N_2 is derived from the photochemistry of ammonia (Atreya, Donahue, and Kuhn 1978) rests on the postulate of a prolonged period of warm climate on the satellite in the past (Strobel 1982). There is no compelling evidence or theoretical arguments in its favor. The photochemistry of NH_3 in the presence of CH_4 is probably more complicated than the description given by Atreya, Donahue, and Kuhn (1978) and should be further investigated.

e) Organic Synthesis

The modern era in prebiotic organic synthesis began with the experiments by Miller (1953, 1955, 1957) and Miller and Urey (1959) demonstrating the synthesis of complex organic compounds from mixtures of simple gases of reducing composition using electric discharges. The subject has recently been reviewed in depth by Chang *et al.* (1983), with emphasis on geochemistry and laboratory studies. For applications to planetary atmospheres, the Miller-Urey experiments suffer from a serious deficiency. The experiments are mainly concerned with analyzing the bulk composition of the reaction products. Without an understanding of the mechanisms and intermediate products, it is difficult to extrapolate from the laboratory to geophysical situations. Our modeling of Titan, based on chemical kinetics and a realistic atmosphere, provides a remedy and an extension of Miller-Urey type of work.

In our model, synthesis of organic compounds consists of two steps: dissociation of the more stable parent molecules into radicals by absorption of ultraviolet radiation, energetic electrons, or cosmic rays, followed by radical-radical or radical-molecule reactions producing organic compounds. The quantities of hydrocarbons, nitrogen, and oxygen compounds generated by the atmosphere over the age of the solar system are of order of 10^5, 10^3, and 1 g cm^{-2}, respectively, sufficient to be of biological interest (Margulis *et al.* 1977). For possible extrapolations to other systems, quantum yields are sometimes more useful. About 96% of CH_4 dissociation (mostly by

photosensitized processes) leads to production of higher hydrocarbons, ~10% of N_2 dissociation (mostly by electron impact) results in nitrile production. Since Titan is a specially favored place in the solar system for organic synthesis, it is unlikely that these quantum yields can be exceeded on primitive Earth.

Miller and Urey (1959) postulated a highly reducing prebiotic terrestrial atmosphere composed mainly of H_2, CH_4, NH_3, and H_2O, a viewpoint later followed by Sagan and Mullen (1972) for different reasons. Holland's (1962) work provides a framework for the possible successive evolution of the atmosphere from a highly reduced state to a more oxidized state. However, the stability of CH_4 and NH_3 in the primitive atmosphere, and indeed the very existence of this hypothetical reducing atmosphere, has been questioned (Abelson 1966; Kuhn and Atreya 1979; Kasting 1982; Walker 1977; Chang *et al.* 1982). Based on our own experience with modeling the early terrestrial atmosphere (Yung and McElroy 1979; Pinto, Gladstone, and Yung 1980) and the atmosphere of Titan, we favor a mildly reducing primitive terrestrial atmosphere composed primarily of N_2, CO_2, H_2O, and H_2. The major source of reduced carbon in this system is formaldehyde, and odd nitrogen is mainly derived from dissociation of N_2, as on Titan. CH_4 and perhaps NH_3 can be supplied in small quantities by nonequilibrium processes initiated in the planet's interior (Welhan and Craig 1979). Before the widespread appearance of oxygen producing organisms, the concentration of O_2 in the atmosphere must have been much lower than today's. The presence of ferrous ions in the early oceans indicates that they were much more highly reducing than today (Walker 1977). The synthesis of organic compounds followed by their accumulation in stable environments are necessary steps for the origin of life. The details of the scenario described above remain to be worked out, but it is clear that the hypothesis of a primitive atmosphere intermediate in composition between the present atmospheres of Mars and Titan is simple, attractive, and consistent with existing knowledge of the solar system.

VII. CONCLUSION

We have identified and extensively discussed the chemical cycles and schemes that are essential for photochemical modeling of Titan (see Table 2B for summary). A comprehensive set of chemical reactions relevant for photochemical studies of Titan and the outer solar system has been compiled in Tables 3A–3C and 7 (see Appendix). Using these reactions, together with a minimal number of other parameters, such as eddy diffusion coefficient, condensation loss rates, and flux of meteoritic material, we have constructed a photochemical model that can successfully account for the chemical composition of the atmposhere of Titan, within the uncertainties of observations and laboratory chemical kinetics. The comparison between model and observations is presented in Table 5A. The major processes that lead to the destruction of the simple parent molecules and the production of more complex species are given in Table 5B. Methane photochemistry is driven by photolysis and interaction between methane and active radicals derived from acetylene photochemistry. Electron impact dissociation of N_2 in the thermosphere provides the major

TABLE 6

RECOMMENDED LIST OF FUTURE CHEMICAL KINETICS EXPERIMENTS
RELEVANT TO TITAN AND JOVIAN STUDY

Reaction	Remarks
Photolysis	
R10 $CH_3C_2H + h\nu$	need cross sections, quantum yields and
R14 $C_4H_2 + h\nu$	branch ratios, especially at long
R15 $C_6H_2 + h\nu$	wavelength $\lambda \sim 2000$ Å
R16 $C_8H_2 + h\nu$	
R18 $HC_3N + h\nu$	
R19 $C_2N_2 + h\nu$	
Synthesis Reactions	
R31 $CH_2 + C_2H_2$	a new class of experiments needs to be
R37b $CH_3 + C_2H_3$	developed to study these reactions under
R40b $C_2H_5 + CH_3$	conditions of low pressure $\sim 10^{-2}$ torr
R42b $C_2H_5 + C_2H_5$	and low temperature ~ 150 K
R51b $CH_3 + C_3H_7$	
R109 $C_2H_3 + C_2H_3$	
R111 $CH_3 + C_3H_3$	
R112 $CH_3 + C_3H_5$	
Insertion Reactions	
R59 $C_2H + C_4H_2$	need low temperature studies
R63 $C_4H + C_2H_2$	
R73 $N + CH_2$	
R74 $N + CH_3$	
R80 $CN + C_2H_2$	
R81 $C_2H + HCN$	
R82 $CN + HCN$	
R91 $O + CH_2$	
R92 $O + CH_3$	
Miscellaneous Reactions	
R69 $C_4H_3 + H$	
R75 $NH + H$	
R76 $NH + N$	
R77 $NH + NH$	

NH reactions with hydrocarbons

source of odd nitrogen and nitrile compounds. A small flux of H_2O released by sublimation of micrometeoroids in the upper atmosphere may be important for determining the abundances of CO and CO_2 in the bulk atmosphere. A major obstacle to further progress in photochemical studies of Titan and the outer solar system is the lack of high-quality kinetics data. Table 6 identifies a list of reactions that most urgently need to be studied. Future missions and observations, using both ground-based and Earth-orbiting instrumentation, are expected to improve and extend our model. We strongly recommend observations refining our knowledge of the composition of Titan's atmosphere and the nature of Titan's surface, documentation of the variability of Titan's albedo and its possible correlation with solar activity, and the Lyα torus, and synoptic studies of the photometric asymmetry between the northern and southern hemispheres. The model presented here suffers from the restriction of being one-dimensional and time-independent. A two-dimensional model with realistic simulation of the seasonal cycle is required to interpret the wealth of IRIS data.

Three of the most outstanding problems concerning the Earth's atmosphere are as follows: (a) What is the impact of man-made chemical pollutants on ozone? (b) What is the climatic consequence of a doubling of atmospheric CO_2? (c) What are the conditions on primitive Earth leading to spontaneous generation of life? We note what appears to be three separate problems on Earth concerning chemistry, climate, and chemical evolution, is really only one on Titan. Photochemistry is the unified force that determines the composition of Titan's atmosphere, its evolution, climatology, and organic synthesis. The principles, concepts, and techniques we employ for modeling the atmosphere of Titan are the same as those used for Earth's atmosphere (Nicolet 1971; Logan et al. 1978, 1981). Our faith in this class of models, and indeed in this entire approach, is predicated upon its success in explaining a wide range of observations. We can now assert that this program has been fruitfully applied to Earth (Hudson, Reed, and Bojkov 1982), Mars (McElroy and Donahue 1972), Venus (Yung and DeMore 1982), Jupiter (Strobel 1973), and Titan. Photochemical aerosols in Titan's stratosphere, with positive feedback mechanisms, play a role similar to that of ice cover on Earth and dust on Mars, and provide insights into chemistry as a force for controlling and modulating climate. Finally, abiotic organic synthesis in the atmosphere of Titan offers a planetary scale demonstration of how the Miller-Urey synthesis works under favorable conditions. Even though Titan may not be a preserved record of pristine Earth, it serves as an idealization, inspiration, and yardstick for future studies of photochemical processes in the primitive Earth's atmosphere.

The chemical species and their interactions in the planetary atmospheres exhibit bewildering richness and variety. However, it is satisfying to note that beneath this apparent diversity there is a pattern of simplicity, order, and unity. Our work reveals and exploits the intimate connections, many hitherto unsuspected, between the chemistry of Titan's atmosphere and that of other planets. The fundamental concepts of photochemistry, such as catalytic cycle, photosensitized dissociation, photochemical regulation of atmospheric composition, climatology, and evolution, were originally developed to understand the atmospheres of the terrestrial planets. The successful application of these concepts to Titan reveals the deeper significance and the universal character of these ideas. It is as though the poetic glimpses that illuminated some past but now classic riddles were recaptured and recreated, and there emerged a vision more profound, an insight more penetrating, and a beauty more enduring than before. In the end we are rewarded with a new perspective of the terrestrial atmosphere that is more mature and complete because of its cosmic connections. No words can better describe the intellectual excitement and practical importance of the planetary experience than those of McElroy (1976): "It has become clear in recent years that we cannot expect to develop a detailed appreciation for the Earth in isolation. Earth is a planet and we can hope to understand it fully only by viewing it in context."

APPENDIX

C_4 HYDROCARBONS AND LONG CHAIN POLYMERS

The C_4 hydrocarbons C_4H_4, $1\text{-}C_4H_6$, $1,2\text{-}C_4H_6$, $1,3\text{-}C_4H_6$, C_4H_8, and C_4H_{10} can be synthesized using the reactions shown in Table 7. The column-averaged mixing ratio estimated with our model for the above species is, respectively, 2.5×10^{-12}, 5.8×10^{-9}, 3.3×10^{-11}, 3.8×10^{-13}, 6.3×10^{-9}, and 2.3×10^{-7}. None of these compounds have been detected to date. It is of interest to note the high abundance predicted for butane. This is a consequence of the same set of circumstances that bring about a high

TABLE 7
List of Speculative Reactions Related to More Complex Hydrocarbons

Reaction	Rate Coefficient	Reference
R103a $\quad C_4H_4 + h\nu \rightarrow 2C_2H_2$	2.6×10^{-6}	Braude 1945;
b $\quad\qquad\qquad \rightarrow C_4H_2 + H_2$	1.0×10^{-5}	Heller and Milne 1978
R104a $\quad 1,2\text{-}C_4H_6 + h\nu \rightarrow 1,3\text{-}C_4H_6$	2.0×10^{-7}	Calvert and Pitts 1966;
b $\quad\qquad\qquad \rightarrow C_4H_4 + H_2$	4.1×10^{-7}	Doepker and Hill 1969
c $\quad\qquad\qquad \rightarrow C_3H_3 + CH_3$	2.8×10^{-7}	
d $\quad\qquad\qquad \rightarrow C_2H_4 + C_2H_2$	1.4×10^{-7}	
R105a $\quad 1,3\text{-}C_4H_6 + h\nu \rightarrow 1,2\text{-}C_4H_6$	5.3×10^{-6}	Calvert and Pitts 1966;
b $\quad\qquad\qquad \rightarrow C_4H_4 + H_2$	1.3×10^{-6}	Doepker 1968
c $\quad\qquad\qquad \rightarrow C_3H_3 + CH_3$	2.8×10^{-6}	
d $\quad\qquad\qquad \rightarrow C_2H_4 + C_2H_2$	9.5×10^{-6}	
R106a $\quad 1\text{-}C_4H_6 + h\nu \rightarrow 1,2\text{-}C_4H_6$	1.3×10^{-8}	Calvert and Pitts 1966;
b $\quad\qquad\qquad \rightarrow C_4H_4 + H_2$	2.3×10^{-8}	Deslauriers et al. 1980
c $\quad\qquad\qquad \rightarrow C_3H_3 + CH_3$	4.0×10^{-8}	
d $\quad\qquad\qquad \rightarrow C_2H_4 + C_2H_2$	1.2×10^{-8}	
R107a $\quad C_4H_8 + h\nu \rightarrow C_3H_5 + CH_3$	3.4×10^{-7}	Calvert and Pitts 1966;
b $\quad\qquad\qquad \rightarrow CH_2CCH_2 + CH_4$	2.4×10^{-8}	Borrell and Cashmore 1968;
c $\quad\qquad\qquad \rightarrow C_2H_6 + C_2H_2$	4.7×10^{-9}	Collin 1973
d $\quad\qquad\qquad \rightarrow 2C_2H_4$	4.3×10^{-8}	
R108a $\quad C_4H_{10} + h\nu \rightarrow C_4H_8 + H_2$	8.5×10^{-9}	Calvert and Pitts 1966
b $\quad\qquad\qquad \rightarrow C_3H_7 + CH_3$	5.1×10^{-8}	
c $\quad\qquad\qquad \rightarrow C_3H_6 + CH_3 + H$	1.6×10^{-8}	
d $\quad\qquad\qquad \rightarrow C_2H_6 + C_2H_2 + H_2$	1.6×10^{-8}	
e $\quad\qquad\qquad \rightarrow 2C_2H_5$	1.4×10^{-8}	
f $\quad\qquad\qquad \rightarrow 2C_2H_4 + 2H$	2.5×10^{-8}	
R109 $\quad 2C_2H_3 + M \rightarrow 1,3\text{-}C_4H_6 + M$	$k_0 = 1.3 \times 10^{-22}$ $k_\infty = 1.5 \times 10^{-12}$	Christianson et al. 1975; Laufer et al. 1983
R110 $\quad C_2H_3 + C_2H_5 + M \rightarrow C_4H_8 + M$	$k_0 = 1.3 \times 10^{-22}$ $k_\infty = 9.1 \times 10^{-12}$	Estimated by analogy with $CH_3 + C_2H_3$; Laufer et al. 1983
R111a $\quad CH_3 + C_3H_3 + M \rightarrow 1,2\text{-}C_4H_6 + M$	$k_0 = 1.3 \times 10^{-22}$ $k_\infty = 5.5 \times 10^{-11}$	Estimated by analogy with $CH_3 + CH_3$
b $\quad\qquad\qquad \rightarrow 1\text{-}C_4H_6 + M$	same as branch (a)	
R112 $\quad C_3H_5 + CH_3 + M \rightarrow C_4H_8 + M$	$k_0 = 1.3 \times 10^{-22}$ $k_\infty = 9.1 \times 10^{-12}$	Estimated based on analogy with $C_2H_3 + CH_3$
R113 $\quad C_2H + C_8H_2 \rightarrow$ polymer	1.0×10^{-12}	Estimated
R114 $\quad C_4H + C_6H_2 \rightarrow$ polymer	3.0×10^{-13}	Estimated
R115 $\quad C_4H + C_8H_2 \rightarrow$ polymer	3.0×10^{-13}	Estimated
R116 $\quad C_6H + C_4H_2 \rightarrow$ polymer	1.0×10^{-14}	Estimated
R117 $\quad C_6H + C_6H_2 \rightarrow$ polymer	1.0×10^{-14}	Estimated
R118 $\quad C_6H + C_8H_2 \rightarrow$ polymer	1.0×10^{-14}	Estimated

concentration of C_3H_8 (see § V*i*). However, the reader should be cautioned that our C_4 photochemistry is very incomplete, and the results presented here probably represent order of magnitude estimates. Photolysis is the primary loss process for all C_4 compounds except C_4H_{10}, a major fraction of which is lost by condensation followed by transport through the tropopause.

Long-chain compounds beyond C_8H_2 can be produced by reactions (R113)–(R118), as shown in Table 7. The most likely fate of these compounds is probably condensation and could provide a source of material for Axel-Danielson dust. The integrated column production rate for the sum of (R113) to (R118) is estimated to be of order $1 \times 10^8 \, cm^{-2} \, s^{-1}$. The peak production occurs at ~ 800 km, and this material could contribute to the high-altitude haze layers observed by UVS and IRIS.

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