Photochemistry of the Reducing Atmospheres of Jupiter, Saturn and Titan

Darrell F. Strobel[a]

[a] Naval Research Laboratory, Washington, DC, USA

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PHOTOCHEMISTRY OF THE REDUCING ATMOSPHERES OF JUPITER, SATURN AND TITAN

DARRELL F. STROBEL

Naval Research Laboratory, Washington, DC 20375, USA

ABSTRACT

The photochemistry of atmospheric constituents in the cold atmospheres of Jupiter, Saturn and Titan is reviewed: H_2, CH_4, NH_3, PH_3, H_2O, N_2, etc. A detailed discussion of major dissociation paths and essential chemical reactions is given with the emphasis on a first-order description of the concentrations of simple molecules in the photochemical regions of these atmospheres. The composition as measured by Voyager spacecraft instruments, IUE and ground-based telescopes is compared with the predictions of aeronomical models and generally acceptable agreement is found for Jupiter, provided the C_2H_6 mixing ratio is $\sim 1 \times 10^{-6}$. More complex molecules do not exceed ppb mixing ratios as a consequence of large H-atom concentrations and the efficiency of H-atom cracking reactions. Even on Titan with lower H-atom concentrations these reactions are apparently effective in suppressing the concentrations of C_4H_2, C_3H_4, HC_3N, and C_2N_2.

1. INTRODUCTION

The Voyager encounters with the Jovian and Saturnian systems have produced significant advances in our understanding of the chemistry of reducing planetary atmospheres. For Titan, Saturn's largest satellite and the second largest satellite in the solar system after Ganymede, the Voyager data represent our first definitive knowledge of its atmospheric composition and structure. This review serves two purposes:

1. To integrate our knowledge from the Voyager encounters with previous ground-based, laboratory and Pioneer data.
2. As an update on the author's previous review of photochemistry written after the Pioneer spacecraft observations (Strobel, 1975).

Jupiter and Saturn are the largest planets in the solar system with respective radii in units of the earth's radius (6378 km) of 11.18 and 9.42 R_E. From the Voyager results Titan's radius is now known to be 2575 km (Lindal *et al.*, 1983), which may be compared to our own Moon's radius of 1738 km. Jupiter and Saturn orbit the Sun at 5.2 and 9.54 AU, respectively, where 1 AU is the semi-major axis of the Earth's orbit. Titan orbits Saturn at 20 R_s (1 R_s = 60,000 km = Saturn's radius) which, depending on solar wind pressure and longitudinal position along the orbit, may be inside Saturn's magnetosphere or fully exposed to the solar wind. The respective gravitational accelerations of Jupiter, Saturn and Titan are 2350, 950 and 136 cm s^{-2}.

The photochemistry of planetary atmospheres was first discussed by Wildt (1937) who

raised concern that substantial amounts of CH_4 in the H_2-dominated, cold $(T < 200°K)$ atmospheres of the major planets would be converted to polymers through the action of solar UV radiation. He suggested that the CH_3 radicals produced in CH_4 photolysis would react with the abundant H_2 to regenerate CH_4. But Cadle (1962) noted the large activation energy of the reaction, $CH_3 + H_2 \rightarrow CH_4 + H$, and concluded that CH_4 was irreversibly converted to heavier hydrocarbons. McNesby (1969) invoked hot molecule chemistry, in particular long-wavelength solar UV excitation of CH_3 radicals to react with H_2 and overcome the activation energy barrier, to recycle CH_4 efficiently on Jupiter. In a study of the stability of CH_4 in the presence of UV radiation, Strobel (1969) concluded that the CH_4 abundance could be maintained on Jupiter, provided that heavier hydrocarbons could be transported downward to the hot, dense interior where thermal decomposition and subsequent reaction with H_2 would form fresh CH_4, which would be transported upward to replenish the CH_4 lost in photolysis. In the atmosphere of Titan Strobel (1974b) concluded that CH_4 was irreversibly converted to heavier hydrocarbons by photolysis with an efficiency greater than 95%.

Wildt (1937) was more perplexed by the maintenance of NH_3 on the major planets; he offered no viable processes. Cadle (1962) invoked a slow photolysis of H_2 to maintain a large concentration of H atoms, which would react with the NH_3 photolysis products, NH_2 and N_2H_4, to regenerate NH_3. McNesby (1969) argued that solar excitation of NH_2 to the $\tilde{A}^2A_2$ state followed by reaction with H_2 would be the most efficient way to recycle NH_3 on Jupiter. However Strobel (1973b) noted that the photolysis of NH_3 is most important in the 0.05–0.5 bar region where the reaction $NH_2 + NH_2 \rightarrow N_2H_4$ is more probable than excitation of NH_2 to the $\tilde{A}$ state. To maintain NH_3, downward transport and thermal decomposition of N_2H_4 was invoked, with subsequent NH_3 formation by reaction with H_2 at the elevated temperatures in the interior.

Laboratory experiments have been performed to unravel the photochemistry of these atmospheres. Sagan and Miller (1960) sparked a mixture of CH_4 and NH_3 in an excess of H_2 and produced C_2H_6, C_2H_4, HCN and CH_3CN as the most abundant molecules. H_2S and H_2O were added in later experiments to simulate the photochemistry in the lower Jovian clouds. Although Lewis (1969a) and Owen and Mason (1969) have suggested that H_2S is an important constituent in this region, it has not yet been detected spectroscopically. The importance of these experiments for the outer solar system has been discussed by Sagan (1971).

The planets in the solar system are generally thought to be composed of material similar to the sun but modified in a variety of ways by subsequent evolution. The largest planets, Jupiter and Saturn, are massive enough to retain their original, solar composition by gravity. Reactive atoms such as C, N and O are primarily present in the form of saturated hydrides (e.g., CH_4, NH_3 and H_2O) at approximately the solar ratios of C, N and O. Condensable substances, e.g., H_2O and NH_3, are expected to form clouds at appropriate levels in the atmosphere when their saturation vapor pressures are reached.

A thermodynamic model constructed with an adiabatic temperature lapse rate is widely regarded as a correct first-order description of the deep atmosphere of Jupiter and Saturn. The more successful models have been those of Lewis (1969a,b) and Barshay and Lewis (1978). The presence of C_2H_6 and C_2H_2 far in excess of thermodynamic expectations for the major planets poses no problem, as photochemical processes occurring high in the atmosphere can readily account for their observed abundances as we shall shortly discuss (Strobel, 1975). The detection of PH_3 (Ridgway, 1974) also appeared to invalidate thermodynamic models, since according to Lewis (1969b) phosphorus is removed deep in the atmosphere by condensation as P_4O_6. Prinn and Lewis (1975) pointed out that rapid convection in Jupiter's interior could more than compete with chemical conversion of PH_3 to P_4O_6 and transport observable amounts to the upper troposphere and lower stratosphere.

Prinn and Barshay (1977) have argued that rapid convection is also required to explain observable amounts of CO detected by Beer (1975).

The massive N_2 atmosphere on Titan is consistent with the early, steady state, thermal models developed by Lewis (1971) for icy satellites. He suggested a surface composed of a mixture of H_2O ice and solid hydrates of CH_4 and NH_3. Over the age of the solar system, photolysis of gaseous NH_3 in equilibrium with these hydrates produced enough N_2 to accumulate to the present observed abundances (*see also* Hunten, 1972; Atreya *et al.*, 1978). An alternative view has been proposed by Owen (1982) and Strobel (1982) on the basis of a recent study by Prinn and Fegley (1981). Owen and Strobel argued for the possibility that the Saturnian nebula temperature at Titan's orbital distance was below $60°K$ and N_2 condensed preferentially as $N_2 \cdot 7H_2O$ during the formation of Titan. Subsequently, Titan's surface warmed up sufficiently to evaporate N_2 as the dominant component of the atmosphere. The cold surface temperature ($T \sim 95°K$) prevents significant abundances of gases other than CO, CH_4 and the noble gases. CO could also be liberated from a clathrate hydrate and then be photochemically converted to CO_2 which would precipitate out as a solid to form a thin (1 m) layer of dry ice on Titan's surface over geologic time (Samuelson *et al.*, 1983).

Given this framework with which to understand the basic composition and structure of the atmospheres of Jupiter, Saturn and Titan, we now focus on the photochemical departures driven by solar UV radiation. Our knowledge of these planetary atmospheres is primitive in comparison to what we have learned from a decade of intensive study of the earth's stratosphere motivated by predicted environmental pollution effects. While we certainly do not have a complete understanding at this time, we do believe that the basic photochemical processes in these atmospheres are understood. In the next section the composition and thermal structure of Jupiter's, Saturn's and Titan's atmospheres are reviewed. Then the basic photochemical and transport processes are discussed in Section 3 and followed by detailed reviews of the photochemistry of each atmosphere.

2. COMPOSITION AND THERMAL STRUCTURE

The composition and vertical temperature structure of a planetary atmosphere are fundamental quantities which are needed to acquire an understanding of photochemistry. Many chemical reactions are extremely sensitive to temperature. Some photochemically produced products are highly condensable at the cold temperatures encountered in the atmospheres under discussion. In *Figure 1* representative vertical temperature profiles as a function of pressure are given for Jupiter, Saturn and Titan. For the major planets this pressure range is limited to regions where photochemical processes are known to be important. On Jupiter the temperature profile starts at the transition level from a convectively controlled, adiabatic lapse rate to a radiatively controlled region above. The rapid temperature decrease to the 150 mb level is accompanied by rapid sublimation of NH_3. (The word sublimation is used to denote a phase transition between gas and solid in either direction.) The temperature minimum of $\sim 110°K$ is an effective cold trap which limits the NH_3 volume mixing ratio (mole fraction) to less than 10^{-7} in the upper atmosphere. Above the 1 mb level the temperature is approximately $200°K$ up to the 3×10^{-4} mb level where the temperature starts an increase to $\sim 1200°K$ at ionospheric heights (Broadfoot *et al.*, 1981b).

On Saturn the vertical temperature profile is similar to Jupiter's as the same physical processes are controlling it, but temperatures in the tropopause region are approximately $25°K$ colder. The cold trap temperature is $\sim 85°K$ which effectively prevents detectable NH_3 concentrations in the upper atmosphere. The quasi-isothermal stratosphere and
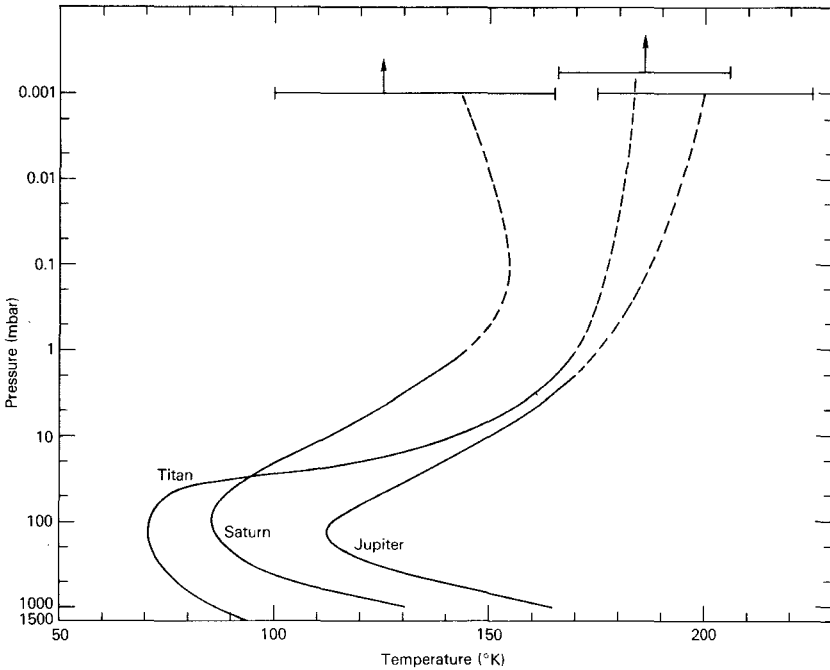
FIG. 1.   Representative vertical temperature profiles. For Jupiter based on Gautier *et al.* (1981) with the low pressure temperature from Broadfoot *et al.* (1981b). For Saturn based on Hanel *et al.* (1981) with the low pressure value at 10^{-5}mbar from Sandel *et al.* (1982). For Titan based on Lindal *et al.* (1983) and Hanel *et al.* (1981) with low pressure value at 7×10^{-9}mbar. From Smith *et al.* (1982).

mesosphere on Saturn is at $\sim 150°$K. Sandel *et al.* (1982) inferred T $\sim 125^{+40°}_{-25}$ °K at the 10^{-5} mbar level. At ionospheric heights the temperature rises to the $420 \pm 30°$K range (Smith *et al.*, 1983).

Titan, unlike Jupiter and Saturn, has a surface with temperature of $\sim 94°$K and a pressure of 1.5 bar (Lindal *et al.*, 1983). At the tropopause the temperature and pressure are $71.4°$K and ~ 130 mbar (Hanel *et al.*, 1981). The extremely cold temperatures on Titan result in CH_4 clouds in the upper troposphere. H_2O and NH_3 are limited to minuscule concentrations in the atmosphere and most photochemical products from N_2 and CH_4 precipitate out in the vicinity of the cold trap.

In *Table 1* the composition of Jupiter's atmosphere is given. The helium to hydrogen ratio is in agreement with solar abundance (Gautier *et al.*, 1981). However the CH_4/H_2 ratio in Jupiter's atmosphere is approximately 2.1 times the generally accepted solar equivalent value (Gautier *et al.*, 1982). The meaning of this result is open to debate since it is possible for Jupiter's bulk composition to be different from its atmospheric composition. Preliminary analysis of a variety of NH_3 data also leads to the conclusion that the N/H ratio is enhanced a factor of 2 over the solar ratio (Gautier *et al.*, 1982). The situation becomes even more puzzling when H_2O the predominant form of oxygen is used to infer the O/H ratio on Jupiter. Both aircraft measurements (Larson *et al.*, 1975) and Voyager IR measurements (Kunde *et al.*, 1982) indicate a strong depletion of oxygen ($\sim$ a factor of 50–150) on Jupiter. The mixing ratio of GeH_4 is also a factor of ~ 10 below the expected solar value (Kunde *et al.*, 1982). Taken at face value the C/H, N/H, Ge/H and O/H ratios on

Jupiter argue against the formation of the planetary system from a primitive, homogeneous nebula in favour of accretion of planetesimals from the primordial solar nebula.

TABLE 1. Composition of Jupiter's atmosphere

Constituent	Volume mixing ratio	Reference
H_2	0.89	Gautier et al. (1981)
He	0.11	Gautier et al. (1981)
CH_4	0.00175	Gautier et al. (1982)
C_2H_2	0.02 ppm	Maguire et al. (1982)
C_2H_4*	7 ppb	Kim et al. (1982)
C_2H_6	5 ppm	Maguire et al. (1982)
CH_3C_2H*	2.5 ppb	Kim et al. (1982)
C_6H_6*	2 ppb	Kim et al. (1982)
CH_3D	0.35 ppm	Kunde et al. (1982)
NH_3[†]	180 ppm	Kunde et al. (1982)
PH_3	0.6 ppm	Kunde et al. (1982)
H_2O[†]	1–30 ppm	Kunde et al. (1982)
GeH_4	0.7 ppb	Kunde et al. (1982)
CO	1–10 ppb	Beer and Taylor (1978); Larson et al. (1978)

* Tentative identification, polar region
† Value at 1–4 bar

In the stratosphere of Jupiter a number of minor hydrocarbons are seen in thermal emission, e.g., C_2H_6, C_2H_2, and C_2H_4. The abundance is usually given in terms of mixing ratio, which is an inferred quantity since independent information is needed on the altitude distribution of density. In addition the deduced column density is sensitive to the assumed temperature profile. For example, Kostiuk et al. (1983) find that the C_2H_6 mixing ratio is 1.2×10^{-6} above the 100 mbar level with a measured inversion temperature of $\sim 170°K$ in contrast to the Voyager inferred mixing ratio of $\sim 5 \times 10^{-6}$ at a lower effective temperature. Although Jupiter's atmosphere is reducing, oxygen in the form of CO is also present and will be discussed in connection with photochemistry.

The other species in Table 1 will be discussed in the photochemistry section. It should be noted that benzene and methyl acetylene are tentative identifications in Jupiter's polar regions (Kim et al., 1982).

In Table 2 the composition of Saturn is summarized. In contrast to Jupiter the He/H_2 ratio is one half the solar value and suggests that gravitational separation and/or condensation of helium at high pressures in the interior have removed helium from the atmosphere (Stevenson and Salpeter, 1977; Hanel et al., 1981). The analysis of Voyager infrared data by Courtin (1982) indicated that the C/H ratio on Saturn is also 2.1 times the solar value. The sublimation of most NH_3 in the upper troposphere makes a determination of the N/H ratio difficult. The C_2H_6 and C_2H_2 mixing ratios on Saturn are similar to Jupiter's ratios. In addition methylacetylene and propane have been tentatively identified (Hanel et al., 1981).

The composition of Titan is summarized in Table 3. The combined Voyager IR, UV and radio occultation data conclusively yield N_2 as the dominant constituent (Broadfoot et al., 1981a; Hanel et al., 1981; Tyler et al., 1981). The most controversial constituent is ^{36}Ar, whose presence has been argued by inference that a constituent heavier than N_2 is needed to give a mean molecular mass greater than 28, since CH_4 is known to be present at the 2% level (Samuelson et al., 1981; Smith et al., 1982; Lindal et al., 1983). Argon 40 is improbable, as Titan's rocky interior would have to be excessively enriched with potassium 40 (Owen, 1982; Strobel, 1982). Argon 36, if it were present, probably outgassed from clathrate hydrates in Titan's crust which were formed at a nebular temperature of $\sim 60°K$

TABLE 2.   Composition of Saturn's atmosphere

Constituent	Volume mixing ratio	Reference
H_2	0.94	Hanel *et al.* (1981)
He	0.06	Hanel *et al.* (1981)
CH_4	0.00176	Courtin (1982)
C_2H_2	0.11 ppm	Courtin (1982)
C_2H_6	4.8 ppm	Courtin (1982)
CH_3C_2H*	No estimate	Hanel *et al.* (1981)
C_3H_8*	No estimate	Hanel *et al.* (1981)
CH_3D	0.23 ppm	Courtin (1982)
PH_3	2 ppm	Courtin (1982)

*   Tentative identification

and contained also CO and N_2 (Owen, 1982; Strobel, 1982). Neon, of course, does not condense out until much colder temperatures and would not be retained. Lindal *et al.* (1983) in their analysis of the radio occultation data favor a pure N_2 atmosphere with only at most 2% CH_4 and trace amounts of heavier hydrocarbons; no argon 36 is required to obtain the temperature to mean molecular mass ratio deduced directly from their measurements.

TABLE 3.   Composition of Titan's atmosphere

Constituent	Volume mixing ratio		
N_2	0.76–0.98[d]		
	Surface	Stratosphere	Thermosphere (3900 km)
CH_4	0.02–0.08[d]	≤ 0.026[a]	0.08 ± 0.03[g]
Ar	< 0.16[d]		< 0.06[h]
Ne	< 0.002[h]		< 0.01[h]
CO	100 ± 50 ppm[j]		<0.05[h]
H_2	0.002 ± 0.001[f]		
C_2H_6		20 ppm[a]	
C_3H_8		1–5 ppm[c]	
C_2H_2		3 ppm[a]	~ 0.0015[g] (3400 km)
C_2H_4		0.4 ppm[c]	
HCN		0.2 ppm[a]	< 0.0005[g] (3500 km)
C_2N_2		0.01–0.1 ppm[b]	
HC_3N		0.01–0.1 ppm[b]	
C_4H_2		0.01–0.1 ppm[b] 0.03 ppm[e]	
CO_2		0.7–3 ppm[i]	

[a]   Hanel *et al.* (1981)
[b]   Kunde *et al.* (1981)
[c]   Kunde (1982)
[d]   Lindal *et al.* (1983)
[e]   Maguire *et al.* (1981)
[f]   Samuelson *et al.* (1981)
[g]   Smith *et al.* (1982)
[h]   Strobel and Shemansky (1982)
[i]   Samuelson *et al.* (1983)
[j]   Lutz *et al.* (1983)

The detection of CO_2 in Titan's atmosphere at the 10^{-9} mixing ratio level was surprising (Samuelson *et al.,* 1983). They have argued that its presence is due to either initial outgassing of CO from a mixed hydrate in the crust or meteoritic infall of water bearing material which is photochemically converted to CO_2 and CO. The latter has been recently detected spectroscopically at the 10^{-4} mixing ratio level by Lutz *et al.* (1983). To round out the list are a suite of hydrocarbons including those found on Saturn (C_2H_6, C_2H_2, C_3H_4, C_3H_8) plus C_2H_4, and nitrogen-containing compounds (HCN, C_2N_2, HC_3N). All of these compounds will be shown below to be photochemical products of CH_4 and N_2 photolysis and ion chemistry driven by magnetospheric interaction with Titan's exosphere (Strobel, 1982).

3. BASIC PRINCIPLES

A satisfactory theoretical description of an individual constituent in a planetary atmosphere initially requires an accurate calculation of its vertical density profile which is a solution of the continuity equation

$$\frac{d\phi_i}{dz} = P_i - L_i n_i \tag{1}$$

where ϕ_i is the vertical flux, P_i is the production rate per unit volume, L_i is the chemical loss rate, n_i is the number density, and z is the altitude. The usual representation of vertical transport includes molecular diffusion represented by an average diffusion coefficient, D_i, and an eddy diffusion coefficient, K, which is a parameterization of macroscopic vertical mixing in the atmosphere by dissipative waves and the mean wind systems

$$\phi_i = -D_i \left[\frac{dn_i}{dz} + \left(\frac{1}{T}\frac{dT}{dz} + \frac{1}{H_i} \right) n_i \right] - K \left[\frac{dn_i}{dz} + \left(\frac{1}{T}\frac{dT}{dz} + \frac{1}{H_a} \right) n_i \right] \tag{2}$$

where T is temperature, $H_i = kT/m_i g$ is the scale height of the individual constituent, $H_a = kT/m_a g$ is the scale height of the background atmosphere, m_i is the constituent's mass, m_a is the mean molecular mass of the atmosphere, and g is the gravitational acceleration. The concept of eddy diffusion can be put on a rigorous basis as Strobel (1981) has shown, but in practice it is difficult to calculate K from first principles for the atmospheres under consideration. The level at which $D_i = K$ is known as the homopause and is the level where these processes are competitive in transporting a constituent. At heights substantially above this level eddy diffusion may be neglected and constituents which do not readily escape the gravitational field of a planet have $\phi_i = 0$ at the top of the atmosphere. In the absence of chemistry above the homopause ($P_i = L_i = 0$) the density varies as

$$n_i \propto \exp(-z/H_i) \tag{3}$$

in an isothermal atmosphere and depends critically on the mass. In the opposite limit, at altitudes much below the homopause, molecular diffusion can be neglected and in the absence of chemistry and net transport through the atmosphere

$$n_i \propto \exp(-z/H_a) \tag{4}$$

Since the background atmospheric density is also proportional to $\exp(-zH_a)$ the constituent's mixing ratio (mole fraction), f_i, is

$$f_i = \text{constant} \tag{5}$$

It follows for any family of species whose net chemistry exactly cancels

$$\sum_i (P_i - L_i n_i) \equiv 0 \tag{6}$$

then

$$\sum_i \phi_i = \text{constant} = 0 \tag{7}$$

if their thermal escape or loss to the surface or interior is negligible. Since $\phi_i \propto df_i/dz$, Eq. (7) also implies

$$\sum_i f_i = \text{constant} \tag{8}$$

that is the mixing ratio of an element in all forms is conserved in the homosphere, the region below the homopause.

Another interesting solution is the case $d\phi_i/dz = 0$ and $D_i \ll K$, then Eqs. (1) and (2) give

$$n_i = c \cdot \exp\left(-z/H_a\right) + \frac{\phi_o}{K}\left[\frac{1}{H_a} - \frac{1}{H_k}\right]^{-1} \tag{9}$$

where K is assumed to have an altitude variation of $\exp(z/H_k)$, $H_k > H_a$, and ϕ_o is the downward flux which is equal to the net column production rate high in the atmosphere. If $\phi_o = 0$, the constituent is fully mixed, i.e., $f_i = \text{constant}$. If the integration constant is zero, then the constituent is being transported downward at the maximum rate $K[(1/H_a) - (1/H_k)]$ (Strobel, 1971). Since in Eq. (9) $n_i \propto 1/K$ when $c = 0$, the maximum density occurs where eddy transport is a minimum. This illustrates the reason why pollutants accumulate in the earth's stratosphere. Since ϕ_o is downward it also means if, for example on Jupiter, oxygen in all forms is preferentially concentrated in the tropopause region where K is a minimum the oxygen must have an external source, e.g., meteoritic infall.

The attenuation of solar radiation incident at the top of the atmosphere is proportional to $\exp(-N_i\sigma_i)$ where N_i is the column density of the absorber along the path of the solar radiation and σ_i is the cross section at the wavelength of interest. Thus the dominant constituent will remove most of the solar radiation at wavelengths where it absorbs strongly. Only at longer wavelengths will minor constituents absorb substantial solar radiation, and then provided their cross sections are not negligible. As a practical example H_2 absorbs the bulk of the solar radiation shortward of 845 Å in Jupiter's atmosphere. CH_4 and H_2 in the Lyman and Werner band systems compete in the wavelength region 845–1109 Å. Beyond 1109 Å CH_4 absorbs most of the solar radiation out to approximately 1450 Å, where C_2H_6 and C_2H_2 take over. Lower in the atmosphere NH_3 absorbs the bulk of the solar radiation between 1650 and 2300 Å.

4. PHOTOCHEMISTRY ON JUPITER AND SATURN

4.1 Hydrogen

The dominant constituent in the atmospheres of Jupiter and Saturn, molecular hydrogen, has a dissociation continuum below 845 Å and an ionization continuum below 804 Å (Cook and Metzger, 1964). Fluorescent dissociation of H_2 can occur after discrete

absorption in the Lyman and Werner bands (Field *et al.*, 1966; Stecher and Williams, 1967) as summarized by

$$H_2(X^1\Sigma_g^+, v = 0) + h\nu\,(\lambda < 1109\,\text{Å}) \rightarrow H_2(B^1\Sigma_u^+, v = v') \rightarrow H_2(X, v = v'') + h\nu \qquad (10)$$
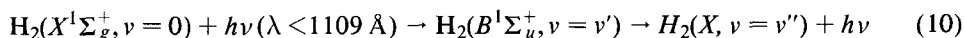
If $v'' > 14$, then Lyman band emission leaves H_2 in the vibrational continuum of the ground state and thus dissociated. If $\lambda < 1009\,\text{Å}$, excitation to the $C^1\Pi_u$ state and radiation in the Werner bands is possible.
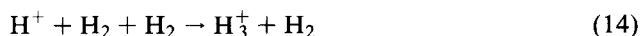
Ionization of H_2 leads to the formation of at least two H atoms by the reactions

$$H_2^+ + H_2 \rightarrow H_3^+ + H \qquad (11)$$

$$H_3^+ + e \rightarrow H_2 + H \text{ or } 3H \qquad (12)$$

The number of H atoms released in the dissociative recombination reaction is uncertain. Ionization of He also leads to H-atom formation by

$$He^+ + H_2 \rightarrow H_2^+ + He \qquad (13)$$

$$\rightarrow H^+ + H + He$$

followed by Eq. (11) and

$$H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2 \qquad (14)$$

with dissociative recombination of H_3^+ as indicated in Eq. (12). Since three-body recombination of H atoms is exceedingly slow at ionospheric pressures there is a net downward flux of H atoms from the ionosphere of Jupiter and Saturn to the lower atmosphere. The approximate magnitude of these fluxes is 10^8–$10^9\,\text{cm}^{-2}\text{s}^{-1}$, with the larger values applicable to Jupiter (Strobel, 1975; Yung and Strobel, 1980). Ionospheric chemistry on Jupiter has most recently been reviewed by Strobel and Atreya (1983).

4.2 Hydrocarbons

Methane photochemistry is driven primarily by CH_4 absorption of the intense solar Lyman α line, since CH_4 absorbs solar radiation only below $\sim 1450\,\text{Å}$ (Mount *et al.*, 1977). The primary dissociation paths at Lyman α are

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$$
$$\rightarrow {}^{1\text{ or }3}CH_2 + 2H \qquad (15)$$
$$\rightarrow CH + H + H_2$$
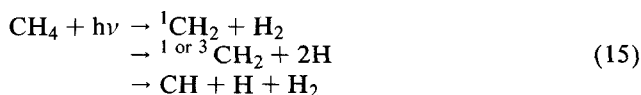
where the last-named path has a yield of ~ 0.08 and the other two are comparable with each other (Laufer and McNesby, 1968; Rebbert *et al.*, 1972; Black and Slanger, 1982). The experimental work of Welch and Judge (1972) indicates that ${}^1CH_2$ is unlikely to be formed in the $\tilde{b}\,{}^1B_1$ state. In an H_2-dominated atmosphere ${}^1CH_2$ reacts preferentially with H_2 to form CH_3

$$^1CH_2 + H_2 \rightarrow CH_3 + H \qquad (16)$$

with a minor quenching path of

$$^1CH_2 + H_2 \rightarrow {}^3CH_2 + H_2 \qquad (17)$$

Also CH forms CH_3 by

$$CH + H_2 + M \rightarrow CH_3 + M \qquad (18)$$

but could also react with CH_4

$$CH + CH_4 \rightarrow C_2H_4 + H \qquad (19)$$

The relative competition between Eqs. (18) and (19) is a function of the pressure at which CH_4 is photolyzed in the atmosphere as reaction Eq. (18) will be in the low pressure limit.

The $^3CH_2$ formed by Eqs. (15) and (17) has a number of possible reaction paths

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2 \text{ (or 2H)} \qquad (20)$$

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \qquad (21)$$

$$^3CH_2 + C_2H_2 + M \rightarrow C_3H_4 + M \qquad (22)$$

$$^3CH_2 + H + M \rightarrow CH_3 + M \qquad (23)$$
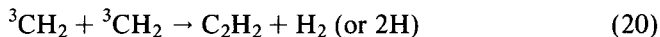
of which Eq. (21) is the most probable according to Gladstone (1982). The rapid photolysis of C_2H_4 leads to C_2H_2 formation

$$C_2H_4 + h\nu \rightarrow C_2H_2 + H_2 \qquad (24a)$$

$$\rightarrow C_2H_2 + 2H \qquad (24b)$$
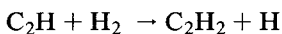
where these paths have comparable probability (Back and Griffiths, 1967).

Methyl radicals recombine to form ethane and methane

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \qquad (25)$$
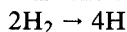
$$CH_3 + H + M \rightarrow CH_4 + M \qquad (26)$$
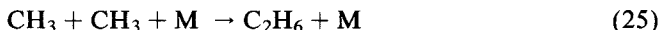
At low pressures the rate constant of Eq. (25) is 3000 times greater than the rate constant for Eq. (26) (Van den Bergh *et al.,* 1976; Patrick *et al.,* 1980). However at high pressures the rate constant of Eq. (26) is three times that of Eq. (25). The net result in the atmosphere of Jupiter is that Eq. (25) is in its high pressure limit where CH_3 is abundant and CH_3 recombines preferentially by Eq. (26) due to the large supply of H atoms from the ionosphere (Gladstone, 1982).

In the upper atmosphere where direct photolysis of CH_4 occurs, C_2H_2 is relatively stable, since its photolysis yields (Okabe, 1981, 1983)
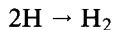
$$C_2H_2 + h\nu \rightarrow C_2H + H \qquad (27a)$$

$$\rightarrow C_2 + H_2 \qquad (27b)$$

$$C_2H + H_2 \rightarrow C_2H_2 + H \qquad (28)$$

$$C_2 + H_2 \rightarrow C_2H + H \qquad (29)$$

$$\underline{C_2H + H_2 \rightarrow C_2H_2 + H}$$

net $$2H_2 \rightarrow 4H$$

a net dissociation of H_2. On the other hand

$$H + C_2H_2 + M \rightarrow C_2H_3 + M \qquad (30)$$

$$\underline{H + C_2H_3 \rightarrow C_2H_2 + H_2} \qquad (31)$$

net $$2H \rightarrow H_2$$
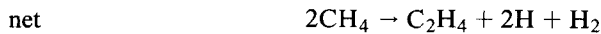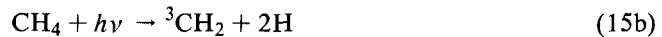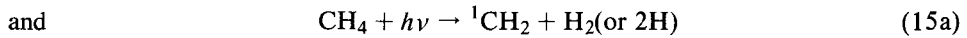
catalytically recombines the H atoms. Reactions (28) and (29) have a significant activation energy of 2.9 kcal mole^{-1} (Brown and Laufer, 1981; Pitts *et al.,* 1982). In the lower stratosphere the radicals C_2H and C_2 react preferentially with CH_4

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \qquad (32)$$

$$C_2 + CH_4 \rightarrow C_2H + CH_3 \qquad (33)$$
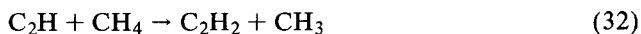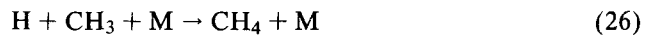
to form CH_3 and yield as a net result of C_2H_2 photolysis in this region the catalytic dissociation of CH_4 into $CH_3 + H$ (Allen *et al.,* 1980).

The respective quantum yields of C_2H and C_2 in Eq. (27) are 0.3, $\lesssim 0.1$ at 1470 Å (Okabe, 1981) and 0.06, 0.1 at 1849 Å (Okabe, 1983). Thus the major channel is either a metastable state of C_2H_2 (Okabe, 1981) or vinylidene ($H_2C{=}C$, Laufer and Yung, 1983) whose fates in planetary atmospheres are unknown, but certainly important as this is the principal process of C_2H_2 photochemistry.
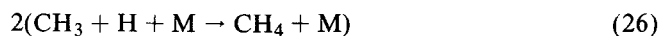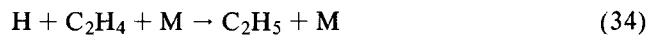
The net photochemistry of CH_4, initiated by solar radiation principally Lyman α, may be summarized by

$$2(CH_4 + h\nu \rightarrow {}^1CH_2 + H_2) \tag{15a}$$

$$2({}^1CH_2 + H_2 \rightarrow CH_3 + H) \tag{16}$$

$$2CH_3 + M \rightarrow C_2H_6 + M \tag{25}$$

net $\qquad\qquad 2CH_4 \rightarrow C_2H_6 + 2H$

and $\qquad\quad CH_4 + h\nu \rightarrow {}^1CH_2 + H_2(\text{or } 2H) \tag{15a}$

$$CH_4 + h\nu \rightarrow {}^3CH_2 + 2H \tag{15b}$$

$${}^1CH_2 + H_2 \rightarrow CH_3 + H \tag{16}$$

$${}^3CH_2 + CH_3 \rightarrow C_2H_4 + H \tag{21}$$

net $\qquad\qquad 2CH_4 \rightarrow C_2H_4 + 4H$

and $\qquad\quad CH_4 + h\nu \rightarrow CH + H + H_2 \tag{15c}$

$$CH + CH_4 \rightarrow C_2H_4 + H \tag{19}$$

net $\qquad 2CH_4 \rightarrow C_2H_4 + 2H + H_2$

(Gladstone, 1982). Acting in opposition to above production of heavier hydrocarbons are the cycles

$$H + CH_3 + M \rightarrow CH_4 + M \tag{26}$$

and

$$H + C_2H_4 + M \rightarrow C_2H_5 + M \tag{34}$$

$$H + C_2H_5 \rightarrow 2CH_3 \tag{35}$$

$$2(CH_3 + H + M \rightarrow CH_4 + M) \tag{26}$$

net $\qquad\qquad C_2H_4 + 4H \rightarrow 2CH_4$

The most recent calculations (Gladstone, 1982) indicate that $\sim 20\%$ of the photons absorbed by CH_4 produce C_2H_6, $\sim 10\%$ yield C_2H_4 and the remaining 70% initiate a 'do nothing' cycle as illustrated by Eqs. (34), (35) and (26).

Some C_2H_6 is lost by photolysis

$$C_2H_6 + h\nu \rightarrow C_2H_4 + H_2 \tag{36a}$$

$$\rightarrow C_2H_4 + 2H \tag{36b}$$

$$\rightarrow C_2H_2 + 2H_2 \tag{36c}$$

$$\rightarrow CH_4 + {}^1CH_2 \tag{36d}$$

$$\rightarrow 2CH_3 \tag{36e}$$

where the primary paths are discussed by Lias *et al.* (1970). As a consequence of photolysis and subsequent chemical reactions, C_2H_6 is partially converted to C_2H_2 and CH_4, and partially recycled. However the time constant for photolysis exceeds the time constant for vertical transport as shown in *Figure 2* and the bulk of the C_2H_6 is transported downward to the stagnant lower stratosphere where it accumulates. C_2H_2 is also transported down to the lower stratosphere because photolysis is followed by 'do nothing' cycles (Eqs. 27–29). Here C_2H_2 photolysis leads to a net dissociation of CH_4 at a rate which is comparable to the direct dissociation rate of CH_4 high in the atmosphere (Gladstone, 1982). Gladstone (1982) found that 20% of the photons absorbed by C_2H_2 resulted in C_2H_6 production and 80% led to in essence 'do nothing' cycles.
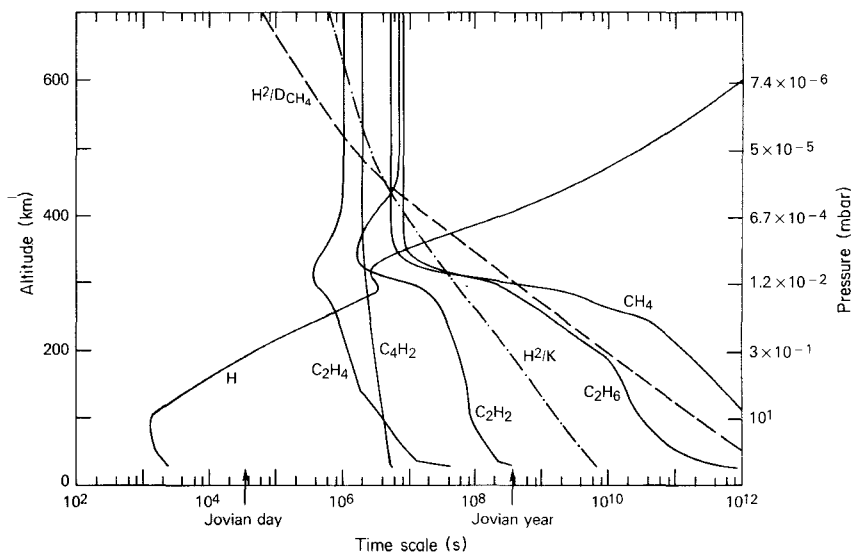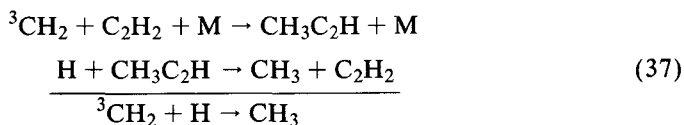

FIG. 2.   Photochemical loss time constants compared with transport time constants for molecular diffusion (H^2/D_{CH_4}) and eddy diffusion (H^2/K) on Jupiter, where $K = 1.3 \times 10^6 \, (2.17 \times 10^{13}/[M]^{0.6}) \, cm^2 s^{-1}$. Taken from Gladstone (1982).

Gladstone's (1982) work represents the most recent and up-to-date calculations of the pure hydrocarbon photochemistry in the atmosphere of Jupiter. His results should also be qualitatively applicable to Saturn's atmosphere, where the major differences would be lower temperature and more vigorous vertical mixing (Atreya, 1982; Sandel *et al.,* 1982). Gladstone's (1982) results are shown in *Figure 3* and are generally consistent with the available observational data. The data base includes thermal emission in the IR, UV reflection spectra measured by the International Ultraviolet Explorer (IUE), and Voyager UVS occultation data. After CH_4, C_2H_6 and C_2H_2 are the most abundant hydrocarbons followed by smaller amounts of C_2H_4, C_4H_2 and CH_3C_2H (compare with *Table 1*). The CH_3C_2H concentration should be regarded as an upper limit since the only reactions included by Gladstone (1982) were with C_2H_2 as a catalyst

$$^3CH_2 + C_2H_2 + M \rightarrow CH_3C_2H + M$$

$$\frac{H + CH_3C_2H \rightarrow CH_3 + C_2H_2}{^3CH_2 + H \rightarrow CH_3} \qquad (37)$$
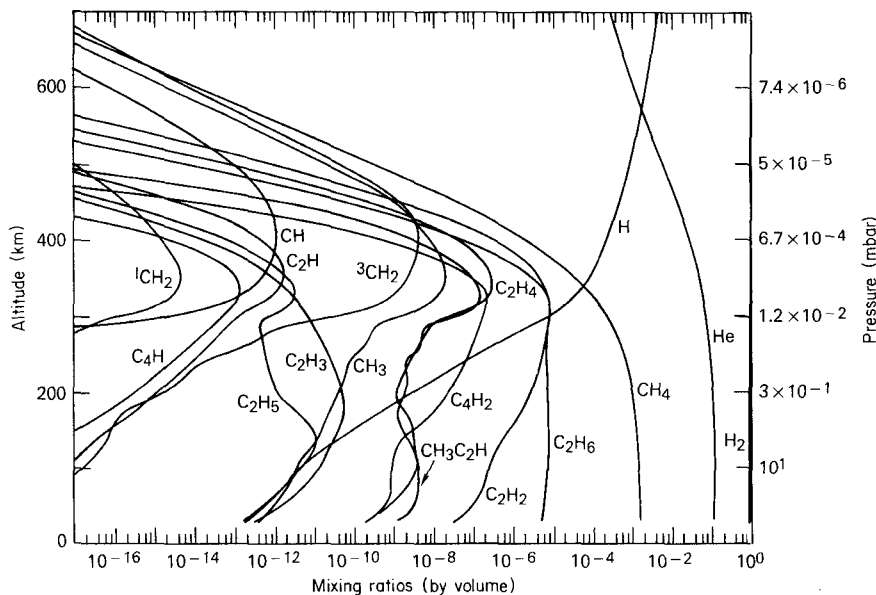
net

FIG. 3. Altitude profiles of the hydrocarbon mixing ratios computed by Gladstone. Taken from Gladstone (1982).

To achieve an C_2H_6 concentration in agreement with observations Gladstone (1982) had to specify a lower boundary condition that severely constrained the downward flux into the troposphere. It was substantially less than the maximum permitted flux (cf. Eq. 9 and discussion) which would seem to be required by the thermochemical conditions in the deep atmosphere (Yung and Strobel, 1980). It would appear that the model is incapable of producing the observed C_2H_6 abundance if a more appropriate lower boundary condition were used. An additional difficulty is that large H concentrations result from NH_3 photochemistry (*see* below) and cause more CH_3 radicals produced by C_2H_2 photolysis (Eqs. 27, 32, 33) to recombine with H (Eq. 26) instead of with another CH_3 (Eq. 25) (Kaye and Strobel, 1983b). In contrast to Gladstone (1982) who found approximately equal amounts of C_2H_6 produced by Lyman α photolysis of CH_4 high in the atmosphere and by catalytic dissociation of CH_4 initiated by C_2H_2 photolysis, Kaye and Strobel (1983b) find that the latter is approximately 1% of the former. Thus in the evolution of models (Strobel, 1973a, 1974a; Yung and Strobel, 1980; Gladstone, 1982) the improvements in input laboratory data have left us with a problem in accounting for one of the most abundant hydrocarbons. One possible resolution of the problem might be that the dissociation channel (Eq. 15)

$$CH_4 + h\nu \rightarrow {}^1CH_2 + 2H$$
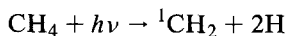
produces only $^1CH_2$, not $^3CH_2$ as Gladstone (1982) assumed. This would severely reduce the C_2H_4 and C_2H_2 production and significantly increase the C_2H_6 production perhaps by 50%. If the reaction (Eq. 35) yields ethane

$$H + C_2H_5 + M \rightarrow C_2H_6 + M$$

in its high pressure limit then the C_2H_6 yield from C_2H_2 photolysis would be increased. It is

important for hydrocarbon photochemistry on Jupiter and Saturn to know the product yields as a function of pressure and temperature for this class of reactions.

Alternatively the observed C_2H_6 mixing may be closer to 1×10^{-6} rather than 5×10^{-6} (*Table 1*) as Kostiuk *et al.* (1983) measured because the stratospheric inversion temperature has been systematically underestimated. The Kostiuk *et al.* (1983) measurements are probably the best combined temperature and C_2H_6 abundance data available. Yung and Strobel (1980) found it difficult for C_2H_6 to exceed 3×10^{-6} at the 10 mb level as a consequence of strong vertical transport into the troposphere and the number of solar photons available to initiate photolysis.
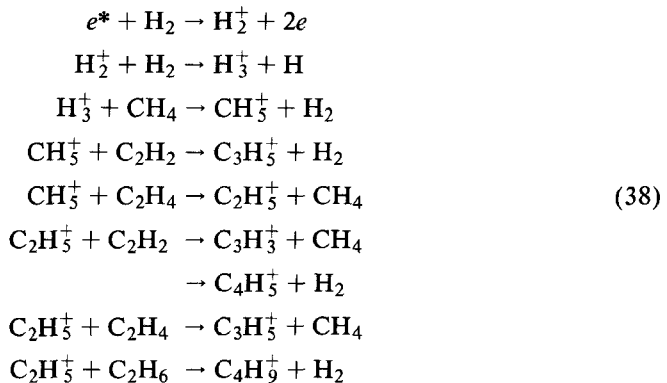
The observed C_2H_4 mixing ratio in the polar regions ($\sim 7 \times 10^{-7}$, *Table 1*) is consistent with the predicted abundance ($\lesssim 3 \times 10^{-9}$, *Fig. 3*) in the equatorial regions, where only an observational upper limit is available (Kim *et al.*, 1982). Both C_2H_4 and C_6H_6 are confined to the magnetic polar regions on Jupiter and their sources are probably related to energetic electrons and ions precipitating into the atmosphere from the extensive magnetosphere. So far C_2H_4 remains undetected on Saturn as models would predict (Strobel, 1978).

In laboratory photochemistry of C_2H_2 Okabe (1983) attributes C_6H_6 formation to a reaction of a metastable (triplet) state $C_2H_2^{**}$

$$C_2H_2^{**} + 2C_2H_2 \rightarrow C_6H_6$$
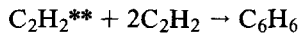
On Jupiter $C_2H_2^{**}$ would be preferentially deactivated by collisions with H_2, the rate ratio being inversely proportional to the C_2H_2/H_2 mixing ratio. Benzene production by this mechanism would be extremely small on Jupiter.

An additional source of complex hydrocarbons is auroral precipitation below the homopause (Yung and Strobel, 1980)

$$e^* + H_2 \rightarrow H_2^+ + 2e$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_3^+ + CH_4 \rightarrow CH_5^+ + H_2$$
$$CH_5^+ + C_2H_2 \rightarrow C_3H_5^+ + H_2$$
$$CH_5^+ + C_2H_4 \rightarrow C_2H_5^+ + CH_4 \qquad (38)$$
$$C_2H_5^+ + C_2H_2 \rightarrow C_3H_3^+ + CH_4$$
$$\rightarrow C_4H_5^+ + H_2$$
$$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4$$
$$C_2H_5^+ + C_2H_6 \rightarrow C_4H_9^+ + H_2$$

where e^* represents fast secondary electrons and the reactions are based on Munson and Field (1969) and Huntress (1977). Recombination of these complex ions will lead to the formation on non-methane hydrocarbons

$$C_xH_y^+ + e \rightarrow C_2H_2, C_2H_4, C_2H_6, \text{ etc.} \qquad (39)$$
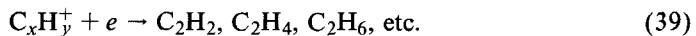
The available evidence from Voyager experiments indicates that the auroral processes are initiated by precipitating energetic ions which lose most of their energy above the homopause where the hydrocarbon densities are very low and most H^{3+} will dissociatively recombine rather than react with CH_4 and other hydrocarbons (Gehrels and Stone, 1983). On the other hand galactic cosmic ray ionization would occur preferentially in the lower stratosphere at high magnetic latitudes as a consequence of shielding by Jupiter's strong magnetic field (Capone *et al.*, 1979).

4.3 Ammonia and phosphine

As we have indicated before, CH_4, H_2 and C_2H_6 absorb the bulk of the solar radiation below 1600 Å. Therefore photolysis of NH_3 yields only

$$NH_3 + h\nu_2 \ NH \rightarrow (\tilde{X}\,^2B_1) + H \tag{40a}$$

$$\rightarrow NH\,(a^1\Delta) + H_2 \tag{40b}$$
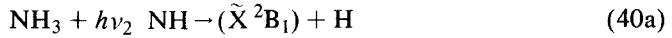
Upper limits on the quantum yield of (Eq. 40b) are 0.005 at 2062 Å and 0.04 at 1849 Å (McNesby *et al.*, 1962; Schurath *et al.*, 1969). However the reaction

$$NH\,(a^1\Delta) + H_2 \rightarrow NH_2 + H \tag{41}$$
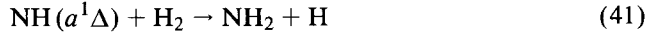
is probably very fast and (Eq. 40a) is effectively the only photolysis path. Due to the high activation energies of reactions with stable molecules in the Jovian atmosphere, NH_2 reacts preferentially with H and itself

$$NH_2 + NH_2 + M \rightarrow N_2H_4 + M \tag{42}$$

$$NH_2 + H + M \rightarrow NH_3 + M \tag{43}$$
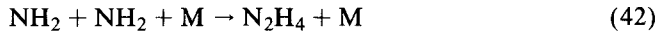
Unfortunately the rate constants for Eqs. (42) and (43) available from the literature are in some disagreement and for Jupiter they are needed for temperatures of ~ 100–$130°K$ in the transition region from low to high pressure limits with H_2 as the third body. Kaye and Strobel (1983a) used a statistical model (Keck and Kalelkar, 1968) to estimate the following rate constants (in $cm^3 s$ units)

$$k_{42} = \frac{1.6 \times 10^{-28}[H_2]}{1 + 10^{-17}[H_2]}$$
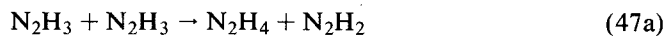
$$k_{43} = \frac{3.4 \times 10^{-30}[H_2]}{1 + 1.2 \times 10^{-19}[H_2]}$$

Clearly more accurate laboratory measurements are needed to alleviate this unsatisfactory state of affairs for these important reactions.

Once N_2H_4 is formed its most probable fate is sublimation at the cold temperatures on Jupiter (Strobel, 1973b; Atreya *et al.*, 1977). The few remaining N_2H_4 molecules are susceptible to photolysis and H-atom attack

$$N_2H_4 + h\nu \rightarrow N_2H_3 + H \tag{44}$$

$$H + N_2H_4 \rightarrow N_2H_3 + H_2 \tag{45}$$

(Schurath and Schindler, 1970; Lee *et al.*, 1976). The N_2H_3 reacts with H or itself to form N_2H_2

$$H + N_2H_3 \rightarrow N_2H_2 + H_2 \tag{46a}$$

$$\rightarrow 2NH_2 \tag{46b}$$

$$N_2H_3 + N_2H_3 \rightarrow N_2H_4 + N_2H_2 \tag{47a}$$

$$\rightarrow 2NH_3 + N_2 \tag{47b}$$

Paths Eqs. (46a) and (47a) are the preferred channels. N_2H_2 is unstable and decomposes into N_2 and H_2

$$N_2H_2 \rightarrow N_2 + H_2 \tag{48}$$

Thus if N_2H_4 did not sublime, N_2 would be the ultimate photolysis product of NH_3. However solid N_2H_4 particles probably descend to the troposphere where they evaporate. Here gaseous N_2H_4 is out of reach of dissociating solar UV radiation due to the strong attenuation by NH_3 absorption and H_2 Rayleigh scattering (Strobel, 1973b).

Strobel (1973b) showed that NH_3 underwent considerable photochemical destruction in the vicinity of the Jovian tropopause and thus explained the three orders of magnitude discrepancy in NH_3 abundances inferred from UV and IR data (Anderson *et al.,* 1969; Tomasko, 1974). As a consequence of irreversible photolysis Strobel (1973b) derived a convenient, approximate expression for the ammonia density profile

$$[NH_3] \propto \exp\left(-\frac{z}{H_m}\right) \tag{49}$$

where $H_m = \sqrt{K/\varepsilon J}$ is the 'photomechanical' scale height. Here J is the NH_3 dissociation rate and ε is the fraction of dissociation events that lead to irreversible. NH_3 destruction (~ 0.4 according to Strobel, 1973b). In conjunction with an analysis of Jupiter's UV albedo by Tomasko (1974) it was determined that $H_m \sim 3$ km and $K \sim 2 \times 10^4$ cm^{2}s^{-1}. The latter value is still in excellent agreement with the most recent model determination (Kaye and Strobel, 1983a). Note that H_m is significantly less than the atmospheric scale height (~ 15 km) and thus the NH_3 mixing ratio decreases rapidly with height (*Figure 4*).
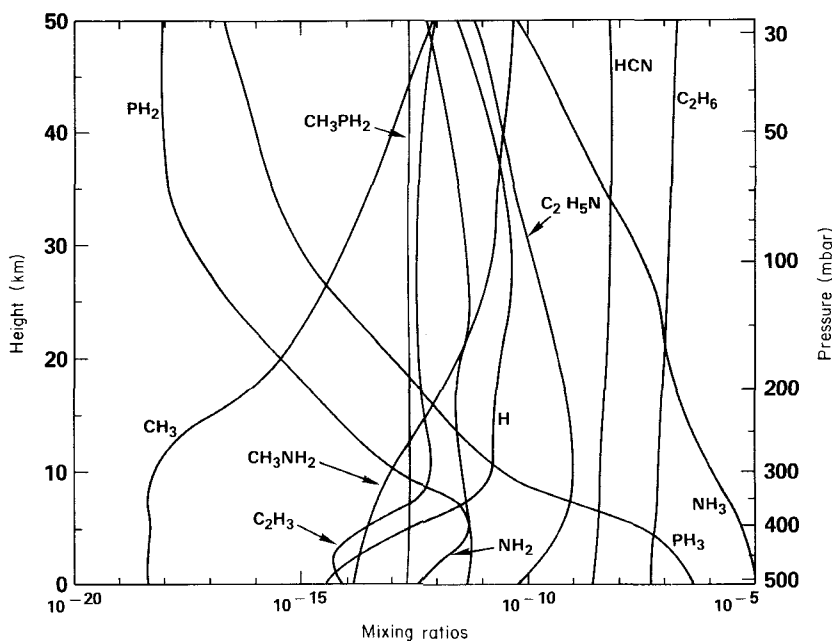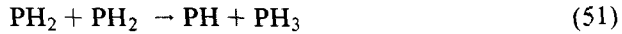

FIG. 4.   Calculated mixing ratios from the photochemical model of Kaye and Strobel (1983b).

The discovery of PH_3 in the atmosphere of Jupiter (Ridgway, 1974) considerably complicates NH_3 photochemistry since both constituents are photolyzed in the same region of the Jovian atmosphere by the same UV photons (Strobel, 1977). Prinn and Lewis (1975)

constructed a model of PH_3 photochemistry (in the absence of NH_3) which was based on the laboratory work by Norrish and Oldershaw (1961):

$$PH_3 + h\nu \rightarrow PH_2 + H \tag{50}$$

$$PH_2 + PH_2 \rightarrow PH + PH_3 \tag{51}$$

$$PH + PH \rightarrow P_2 + H_2 \tag{52}$$

$$P_2 + P_2 + M \rightarrow P_4 + M \tag{53}$$

$$H + H + M \rightarrow H_2 + M \tag{54}$$
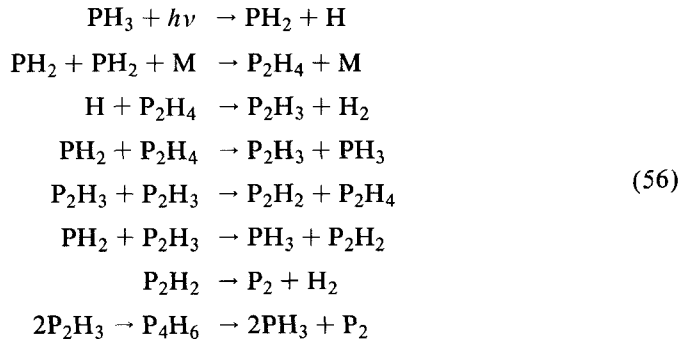
Prinn and Lewis (1975) argued that the P_4 formed in Eq. (53) is red phosphorus, which actually has an ill-defined structure (Shoemaker, 1981), and that it is the red coloring material observed on Jupiter, particularly in the Great Red Spot. In their model the Great Red Spot was assumed to be a region where PH_3 was mixed to higher altitudes and photolyzed. This led to the production and concentration of P_4 at higher altitudes with a larger, red phosphorus optical depth above the NH_3 cloud deck in contrast to adjacent regions. Actually the Prinn and Lewis model is only strictly applicable to Saturn where the NH_3 concentration is negligible in the photolysis region.

Norrish and Oldershaw (1961) argued that their laboratory results could be understood if the following reaction had a high activation energy

$$H + PH_3 \rightarrow PH_2 + H_2 \tag{55}$$
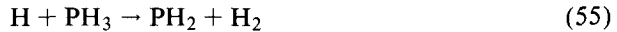
But Lee *et al.* (1976) found $k_{55} = 4.5 \times 10^{-11} \exp(-735/T) \text{ cm}^3\text{s}^{-1}$ and this activation energy of only ~ 1.5 kcal mole^{-1} necessitated a reassessment of the kinetics inferred from Norrish and Oldershaw (1961).

Ferris and Benson (1980, 1981) have shown that the photochemistry of PH_3 is essentially the same as NH_3

$$
\begin{aligned}
PH_3 + h\nu &\rightarrow PH_2 + H \\
PH_2 + PH_2 + M &\rightarrow P_2H_4 + M \\
H + P_2H_4 &\rightarrow P_2H_3 + H_2 \\
PH_2 + P_2H_4 &\rightarrow P_2H_3 + PH_3 \\
P_2H_3 + P_2H_3 &\rightarrow P_2H_2 + P_2H_4 \\
PH_2 + P_2H_3 &\rightarrow PH_3 + P_2H_2 \\
P_2H_2 &\rightarrow P_2 + H_2 \\
2P_2H_3 &\rightarrow P_4H_6 \rightarrow 2PH_3 + P_2
\end{aligned}
\tag{56}
$$

This mechanism does not account for the observation of PH (Norrish and Oldershaw, 1961) but at room temperature some PH_2 could recombine by reaction (51) as a minor channel.

There has been some controversy over the actual color of the phosphorus found during PH_3 photolysis. Noy *et al.* (1981) argued on the basis of their laboratory results that yellow, not red, phosphorus is formed in contradistinction to the work of Norrish and Oldershaw (1961), Ruiz and Rowland (1978) and Ferris and Bossard (1983). The latter argue that the red phosphorus formed in their experiments, which were authenticated by spectroscopy, was almost identical to the Noy *et al.* (1981) 'yellow' phosphorus and visually had a range of colors from yellow to violet (Donohue, 1974; Corbridge, 1980). Ruiz and Rowland (1978) found that the presence of C_2H_2 and C_2H_4 suppressed the formation of red
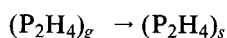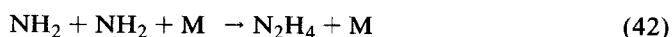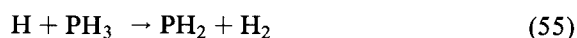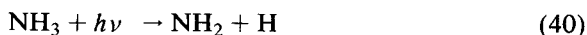
phosphorus during PH_3 photolysis at room temperature. It remains an open question whether at the cold temperatures of the outer planets and the small concentrations of C_2H_2 and C_2H_4 present, the scavenging effect of these molecules will be important.

In another development Bosco *et al.* (1983) have measured a very slow reaction rate for

$$NH_2 + PH_3 \rightarrow NH_3 + PH_2, \, k_{57} = 1.5 \times 10^{-12} e^{-928/T} \, cm^3 s^{-1} \qquad (57)$$
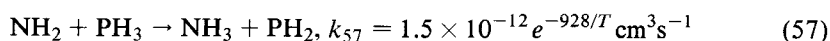
which had been inferred by Strobel (1977) to be much faster from a study of the radiation chemistry of an NH_3–PH_3 gas mixture (Buchanan and Hanrahan, 1970).

On the basis of the most recent calculations (Kaye and Strobel, 1983a, b) a first-order description of NH_3 and PH_3 photochemistry is given by

$$NH_3 + h\nu \ \rightarrow NH_2 + H \qquad (40)$$

$$PH_3 + h\nu \ \rightarrow PH_2 + H \qquad (50)$$

$$H + PH_3 \ \rightarrow PH_2 + H_2 \qquad (55)$$

$$PH_2 + H + M \ \rightarrow PH_3 + M$$

$$NH_2 + H + M \ \rightarrow NH_3 + M$$

$$NH_2 + NH_2 + M \ \rightarrow N_2H_4 + M \qquad (42)$$

$$PH_2 + PH_2 + M \ \rightarrow P_2H_4 + M$$

$$(N_2H_4)_g \ \rightarrow (N_2H_4)_s$$
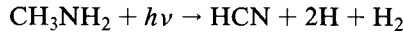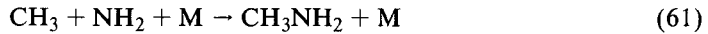$$(P_2H_4)_g \ \rightarrow (P_2H_4)_s \qquad (58)$$

The H liberated from NH_3 photolysis accelerates the photochemical destruction of PH_3 by Eq. (55) and produces the rapid density fall-off above 20 km shown in *Figure 4*. The rapid condensation of N_2H_4 and P_2H_4 terminates further photochemical reactions which would eventually lead to the formation of N_2 and P_n. The respective photomechanical scale heights of NH_3 and PH_3 are ~ 3 and 0.5 km in *Figure 3* (cf. Eq. (49)). This behaviour is consistent with the absence of a significant UV signature in albedo data; UV photons sample only the stratosphere because Rayleigh scattering by hydrogen prevents deeper penetration (Tomasko, 1974). As a consequence of its slow recombination (Eq. (54)) H is the most abundant radical in this region of the atmosphere. Note that in *Figure 4* NH_3 is saturated below 25 km and its density is controlled by the temperature profile.

Additional complications to the NH_3 photochemistry in the Jovian atmosphere were brought to light by the discovery of HCN. Tokunaga *et al.* (1981) obtained definitive evidence for HCN at a column density of $\sim 1.3 \times 10^{17} \, cm^{-2}$ and mixing ratio of $\sim 2 \times 10^{-9}$. Since HCN appeared in IR absorption rather than thermal IR emission, it must be concentrated in the vicinity of the tropopause or below. On Saturn only an upper limit of $6.5 \times 10^{17} \, cm^{-2}$ was obtained, but the absence of appreciable NH_3 in the upper atmosphere would preclude a local source of nitrogen atoms to produce HCN.

Since HCN can be a precursor of α-amino acids and nucleic acid bases (Mizutani *et al.*, 1975) the role of HCN in the photochemistry of reduced atmospheres and in the chemical evolution of the earth's prebiotic atmosphere has been of substantial interest in recent years. On the basis of the thermochemical models of Barshay and Lewis (1978) HCN cannot be convected out from the dense, hot interior at the required mixing ratio. The coupled photochemistry of CH_4 and NH_3 in the overlap region (where direct CH_4 photolysis trails off and NH_3 has been photochemically depleted), proposed by Kuhn *et al.* (1977) to produce CH_3NH_2 and to yield HCN by subsequent photolysis (Gardner, 1981), is also insufficient (Kaye and Strobel, 1983a). Even the formation of CH_3NH_2 by hot H-atom

chemistry and subsequent photolysis to HCN makes only a minor contribution (Kaye and Strobel, 1983b):

$$NH_3 + h\nu \rightarrow NH_2 + H^* \tag{59}$$

$$H^* + CH_4 \rightarrow H_2 + CH_3 \tag{60}$$

$$CH_3 + NH_2 + M \rightarrow CH_3NH_2 + M \tag{61}$$

$$CH_3NH_2 + h\nu \rightarrow HCN + 2H + H_2$$

This scheme is based on the work of Aronowitz *et al.* (1981) and Gardner (1981). Formation of HCN from rapid, local heating of the atmosphere by lightning discharges and subsequent equilibrium chemistry at high temperatures in the shocked atmosphere leads only to an absolute upper limit HCN mixing ratio of $\sim 3 \times 10^{-12}$ (Lewis, 1980a). The actual amount is probably $\lesssim 10^{-17}$. This limit is valid in spite of the confusion from the interpretation of the Voyager data on lightning discharges (Lewis, 1980b; Scarf *et al.*, 1981; Borucki *et al.*, 1982).

One possible pathway for HCN formation might be the addition of NH_2 directly to C_2H_2 to form the C_2H_4N radical, which could yield HCN by subsequent reactions. Essentially nothing is known about the photochemistry of C_2H_4N. The two rate constant measurements for

$$NH_2 + C_2H_2 \rightarrow products \tag{62}$$

differ substantially. Hack *et al.* (1979) found k_{62} to be $2.4 \times 10^{-8}T^{-2.7}\,cm^3s^{-1}$ whereas Bosco *et al.* (1983) obtained $1.1 \times 10^{-13}e^{-1852/T}\,cm^3s^{-1}$. At 130°K these rate constants differ by a factor of 7×10^5.

A more promising pathway is the ultraviolet photolysis of the C_2H_5N isomer aziridine, a plausible product of the recombination of NH_2 and C_2H_3 which originate respectively from NH_3 photolysis and addition of H atoms to acetylene (Kaye and Strobel, 1983a).

$$NH_2 + C_2H_3 + M \rightarrow C_2H_5N + M \tag{63}$$

$$C_2H_5N + h\nu \rightarrow HCN + CH_3 + H \tag{64}$$
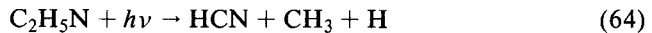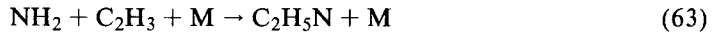
Vinylamine ($CH_2=CH-NH_2$) is also a highly probable product of Eq. (63). Kaye and Strobel argued that in the high pressure limit (Eq. (63)) has a non-zero yield of ~ 0.1. Of the four isomers of C_2H_5N, HCN can be obtained directly from aziridine photolysis (Eq. (64)) or by a two-step process from ethylidenimine ($CH_3-CN=NH_2$) and N-methylmethylene-imine ($H_2C=N-CH_3$)

$$C_2H_5N + h\nu \rightarrow H_2CN + CH_3 \tag{65}$$

$$H + H_2CN \rightarrow H_2 + HCN \tag{66}$$
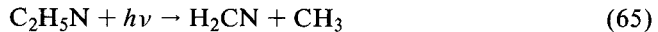
In their model a photolysis yield of ~ 0.33 for Eq. (64) produced a HCN concentration (*Fig. 4*) in reasonably good agreement with the Tokunaga *et al.* (1981) observations. This yield is less than the 0.41 and 0.47 obtained at 1470 Å by Kawasaki *et al.* (1973) and Scala and Salomon (1976) for CH_3 production. Although this mechanism is speculative it is entirely plausible on the basis of known laboratory processes.

In an extension of their work Kaye and Strobel (1983b) investigated CH_3NH_2 formation in the Jovian tropopause region. Hot H-atom chemistry maximizes CH_3NH_2 formation in the lowest 10 km of *Figure 4,* whereas catalytic dissociation of CH_4 (Eqs. (27), (28), (29), (32), (33)) and recombination of CH_3 by Eq. (61) maximizes at ~ 25 km. It is known that CH_3NH_2 photolysis yields HCN and is highly wavelength dependent (Gardner, 1981; Gardner and McNesby, 1982). For the wavelengths of interest, $\lambda > 1600$ Å, the principal processes are

$$CH_3NH_2 + h\nu \rightarrow CH_3NH + H$$

$$\rightarrow CH_2=NH + 2H \qquad (67)$$

$$\rightarrow HCN + 2H + H_2$$
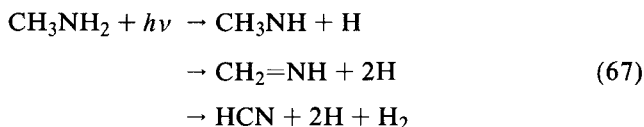
Methyleneimine probably decomposes to HCN + 2H whereas CH_3NH may recombine

$$CH_3NH + H + M \rightarrow CH_3NH_2 + M \qquad (68)$$
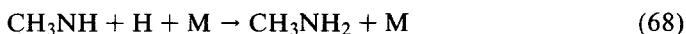
as it should be in its high pressure limit at the Jovian tropopause (p $\sim$ 0.1 bar), but could decompose to

$$CH_3NH \rightarrow CH_2=NH + H \qquad (69)$$

$$CH_2=NH \rightarrow HCN + 2H \qquad (70)$$

With the maximum HCN yield from CH_3NH_2 photolysis an HCN column density of $\sim 1 \times 10^{17}$ cm^{-2} is impossible although a column density of $\sim 4 \times 10^{16}$ cm^{-1} is more realistic when Eq. (68) occurs preferentially to Eq. (69) (Kaye and Strobel, 1983b). In comparison the recombination of NH_2 and C_2H_3 radicals to form C_2H_5N followed by photolysis to HCN yields an HCN column density of $\sim 2.2 \times 10^{17}$ cm^{-2} with the yields given above. To account for the observed amounts of HCN in the tropopause region of Jupiter slow mixing ($K \sim 10^4$ cm^{2}s^{-1}) above the ammonia clouds is required to accumulate HCN preferentially there (cf. Eq. (9)). This condition was also required by Massie and Hunten (1982) to explain the *ortho* and *para* hydrogen equilibration in the same region. Below the ammonia cloud tops rapid mixing in the convection zone of the troposphere will cause a sharp decrease in the HCN concentration.

The possibility of forming phosphirane, the P-containing analog of aziridine,

$$PH_2 + C_2H_3 + M \rightarrow C_2H_5P + M \qquad (71)$$
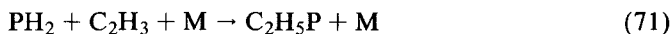
was considered by Kaye and Strobel (1983a). From *Figure 4* it can be inferred that C_2H_5P formation is restricted to the lowest 10 km, where photolysis of C_2H_5P might be inhibited, depending on its absorption cross sections and subsequent photochemistry. Since $[NH_2] > [PH_2]$ generally it is probable that the C_2H_5P column density is substantially less than that of C_2H_5N. Similarly the column density of HCP would be expected to be substantially less than the HCN column density if photolysis of C_2H_5P were the major source. Kaye and Strobel (1983b) estimated that the column density of CH_3PH_2 is at least an order of magnitude less than the CH_3NH_2 column density. Clearly further work is needed in the laboratory and in atmospheric modelling for phosphorus-containing compounds. In addition the photochemistry of phosphorus compounds in the absence of NH_3 need to be investigated for Saturn's atmosphere.

4.4 Oxygen compounds

Although it is common to think of the atmospheres of Jupiter and Saturn as totally reducing, the solar abundance of O and thermochemistry require substantial amounts of H_2O and other oxygen species in these atmospheres. Since most of the H_2O will condense out before reaching the photochemical regions, no oxygen compounds and no associated photochemistry would be expected. Beer's (1975) discovery of CO on Jupiter proved otherwise. More recent observations and further analysis by Beer and Taylor (1978) indicate a CO column density of $4.3^{+4.3}_{-2.2} \times 10^{17}$ cm^{-2} and a rotational temperature of $\sim 125 \pm 25°$ K. This low rotational temperature implies that CO accumulates in the Jovian tropopause region (Beer and Taylor, 1978). Since rapid outward convection from the hot interior cannot concentrate CO preferentially in the stratosphere, this observation implies an

extraplanetary source of oxygen (cf. Section 3). Larson *et al.* (1978) have reported similar observations at lower resolution but without the complications of telluric CO using the Kuiper Airborne Observatory. They estimated a column density of $8 \times 10^{17} \, \mathrm{cm}^{-2}$ and a rotational temperature of 150–300° K, due to probable detection of high J lines. Their observations would be consistent with rapid convection of CO from the hot ($\sim 1000°$ K) interior region, where the CO mixing ratio is $\sim 10^{-9}$, to the Jovian upper troposphere in spectroscopically detectable amounts (Prinn and Barshay, 1977). In the interior CH_4 and H_2O are thermochemically converted to CO. Until the CO rotational temperature issue can be resolved, the relative importance of this internal source as compared to extraplanetary sources can not be assessed.

Two extraplanetary sources have been proposed:

1. Ablation in Jupiter's atmosphere of meteoroidal material which contains substantial amounts of H_2O (Prather *et al.*, 1978).
2. Infall of material from the Galilean satellites of Jupiter, principally Io and Europa (Strobel and Yung, 1979).

Prather *et al.* (1978) have estimated the flux of H_2O to be in the range of $(1 - 200) \times 10^7 \, \mathrm{cm}^{-2}\mathrm{s}^{-1}$ on the basis of data reported by Humes (1976). The material flux of O into Jupiter's atmosphere associated with the Galilean satellites is approximately $(0.3–5) \times 10^7 \, \mathrm{cm}^{-2}\mathrm{s}^{-1}$ on the basis of Voyager data (*Science, 202*, 945–1008, 1979). As is well known from Voyager data Io is the site of intense volcanic activity (Morabito *et al.*, 1979), has an SO_2 atmosphere (Pearl *et al.*, 1979) and is the source of S and O ions that comprise the plasma torus (Bridge *et al.*, 1979; Broadfoot *et al.*, 1979). From expression (9) with $H_k = 2H_a$, $c = 0$, the CO column density from an extraplanetary source, N, is

$$N = \frac{4H_a^2 \, \phi_0}{K_{\min}} \qquad (72)$$

(Strobel and Yung, 1979) where $K_{\min}$ is the minimum value of K, generally between the tropopause and ammonia cloud tops. With $H_a \sim 2 \times 10^6 \, \mathrm{cm}$ and observed $N \sim 6 \times 10^{17} \, \mathrm{cm}^{-2}$, we find
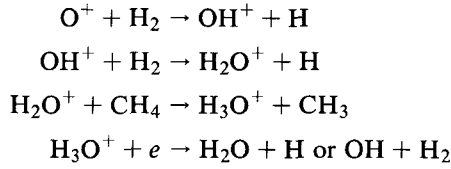
$$\frac{\phi_0}{K_{\min}} \sim 4 \times 10^4 \, \mathrm{cm}^{-4}$$

For constituents such as NH_3 with rapid chemistry Kaye and Strobel (1983b) inferred $K_{\min} \sim 10^4 \, \mathrm{cm}^2\mathrm{s}^{-1}$, but for C_2H_6 which has slow chemistry they required $K_{\min} \sim 10^3 \, \mathrm{cm}^2\mathrm{s}^{-1}$ in agreement with the theory of Strobel (1981). Since CO has exceedingly slow chemistry $K_{\min} \sim 10^3 \, \mathrm{cm}^2\mathrm{s}^{-1}$ is preferred and thus
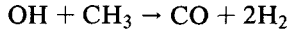
$$\phi_0 \sim 4 \times 10^7 \, \mathrm{cm}^{-2}\mathrm{s}^{-1}$$

is the required oxygen source rate. Ablation of meteoroidal material can comfortably supply this amount of oxygen whereas the Galilean satellite source requires an infall rate near its upper limit.

The ultimate conversion of oxygen in any form, e.g., O^+, O, H_2O, to CO in Jupiter's atmosphere is virtually certain although the detailed reaction paths are still somewhat uncertain. In *Figure 5* the essential reactions of Prather *et al.* (1978) and Strobel and Yung (1979) are schematically presented. For example $O^+ + H_2$ represents a sequence of reactions

$$O^+ + H_2 \rightarrow OH^+ + H$$

$$OH^+ + H_2 \rightarrow H_2O^+ + H$$

$$H_2O^+ + CH_4 \rightarrow H_3O^+ + CH_3$$

$$H_3O^+ + e \rightarrow H_2O + H \text{ or } OH + H_2$$

For

$$OH + CH_3 \rightarrow CO + 2H_2$$

the products may not be formed directly in a single reaction. The other reaction paths in *Figure 5* are straightforward.
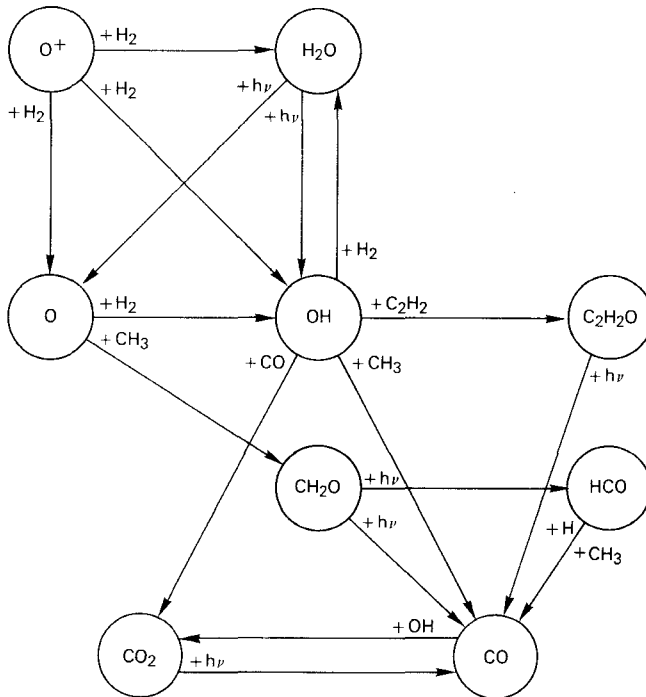

FIG. 5.   Schematic diagram of oxygen photochemistry on Jupiter. The oxygen sources are a flux of H_2O in the form of meteoroidal material and energetic O^+ ions from the magnetosphere. The sinks are H_2O sublimation and a downward CO flux to the troposphere.

CO is the predominant gaseous form of oxygen in the Jovian stratosphere since solar radiation above 1600 Å does not dissociate it and CO_2 and H_2O undergo rapid photolysis. For example the photolysis time constant for H_2O is $\sim 10^7$s, whereas the vertical transport time constant is $\sim 10^9$s. Thus even though OH may preferentially react with H_2, OH must react only once with C_2H_2 (or C_2H_4) in a cycle of repeated H_2O dissociation, as oxygen is mixed down to the tropopause, being irreversibly converted to CO. Once formed CO cannot be photolyzed and is not susceptible to chemical attack in the lower stratosphere because sublimation of H_2O removes the OH source to convert CO to CO_2.

    Fortunately there are observational tests to distinguish the two extraplanetary sources.

Meteoroidal material contains a significant amount of Si and observable amounts of SiO are predicted by Prather *et al.* (1978). Io's volcanoes, atmosphere, and torus contain substantial amounts of sulfur and the theory of Strobel and Yung (1979) would predict observable amounts of CS by analogy with CO chemistry. To date neither SiO nor CS have been detected on Jupiter.

On Saturn ablation of meteoroidal material should also be important and lead to observable amounts of CO. The predominant source of satellite material may be Saturn's rings which are mostly water ice. The infall rate to Saturn's atmosphere is not accurately known, but on the basis of the mass of Saturn's rings and the age of the Saturnian system it must be much less than $5 \times 10^6 [H_2O]$ $cm^{-2}s^{-1}$.
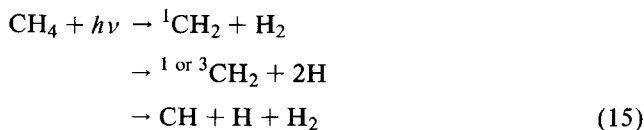
5. PHOTOCHEMISTRY OF TITAN'S ATMOSPHERE

In contrast to Jupiter and Saturn, Titan's atmosphere has only trace amounts of H_2 (cf. *Table 3*). With an extended atmosphere (exobase at 0.6 of a Titan radius from the surface, the level where the probability of thermal escape is 0.5) weak gravitational acceleration (g $\sim$ 55 cm^2s^{-1} at the exobase), and 'warm' exosphere ($T \geq 186°$ K), hydrogen in atomic and molecular form escapes rapidly from Titan's exosphere by thermal processes (Strobel, 1982). The hydrogen escape rate is governed by the CH_4 dissociation rate. The extensive hydrogen (atom) torus detected by the Voyager UVS around Saturn between 8 and 25 R_s (R_s = Saturn radius) is positive evidence of hydrogen loss from Titan (Broadfoot *et al.*, 1981a). As a result a photochemistry and hydrogen escape complex, heavy hydrocarbons are left behind to accumulate on the surface (Hunten, 1977). Titan's unique atmosphere is, thus, a favorable environment for chemical evolution as indicated by the suite of hydrocarbons discovered by the Voyager infrared experiment (IRIS, *Table 3*, Hanel *et al.*, 1981).
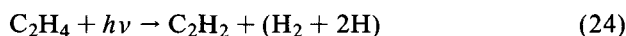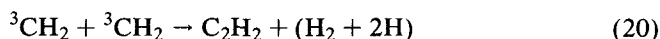
5.1 Hydrocarbons

The first study of Titan's hydrocarbon photochemistry was performed by Strobel (1974b) who concluded that C_2H_6 and C_2H_2 were the principal products which would eventually sublime in the tropopause region of Titan and fall to the surface. He considered model atmospheres of CH_4 and H_2, which were then regarded as the dominant atmospheric constituents. Allen *et al.* (1980) constructed an updated model which included catalytic dissociation of CH_4 (Eqs. (27), (32), (53)) and the formation of polyacetylenes as the precursor molecules for the extended haze on Titan.

On the basis of Voyager data N_2 is known to be the dominant constituent and has an important effect on the net photolysis of CH_4

$$CH_4 + h\nu \rightarrow {}^1CH_2 + H_2$$

$$\rightarrow {}^{1 \text{ or } 3}CH_2 + 2H$$

$$\rightarrow CH + H + H_2 \tag{15}$$

$${}^1CH_2 + N_2 \rightarrow {}^3CH_2 + N_2 \tag{73}$$

It ensures that ${}^3CH_2$ is the net product with only a minor pathway ($\sim$ 0.08) to CH (Strobel, 1973a). These radicals react to form primarily C_2H_2 and C_2H_4, prominent minor constituents on Titan (*Table 3*)

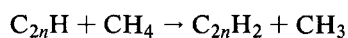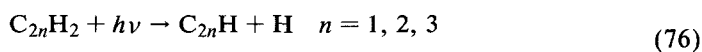$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + (H_2 + 2H) \tag{20}$$

$$^3CH_2 + C_2H_2 + M \rightarrow C_3H_4 + M \tag{22}$$

$$CH + CH_4 \rightarrow C_2H_4 + H \tag{19}$$

$$^1CH_2 + CH_4 \rightarrow 2CH_3 \tag{74}$$

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \tag{21}$$

$$C_2H_4 + h\nu \rightarrow C_2H_2 + (H_2 + 2H) \tag{24}$$

Although formation of CH_2CCH_2 is favored over CH_3C_2H in Eq. (22) (Laufer and Bass, 1974), Yung *et al.* (1983) argue that the former must isomerize rapidly to the latter because allene has not been detected on Titan, whereas methyl acetylene is present (*Table 3*). Methyl acetylene can be efficiently removed by

$$H + CH_3C_2H \rightarrow CH_3 + C_2H_2 \tag{75}$$
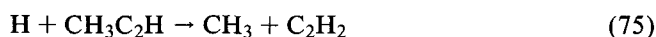
(Wagner and Zellner, 1972).

At lower altitudes on Titan the catalytic dissociation of CH_4 discussed earlier becomes important (Allen *et al.,* 1980)

$$\begin{aligned} C_{2n}H_2 + h\nu &\rightarrow C_{2n}H + H \quad n = 1, 2, 3 \\ \underline{C_{2n}H + CH_4 \rightarrow C_{2n}H_2 + CH_3} \end{aligned} \tag{76}$$

net $CH_4 \rightarrow H + CH_3$
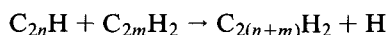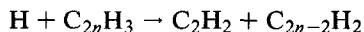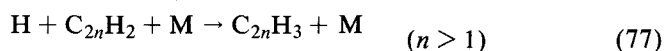
since polyacetylenes absorb solar radiation out to beyond 3000 Å, in contrast to $\lambda < 1450$ Å for CH_4.

The polyacetylenes are formed by

$$C_{2n}H + C_{2m}H_2 \rightarrow C_{2(n+m)}H_2 + H$$

A principal difficulty encountered by Yung *et al.* (1983) (and Allen *et al.,* 1980) in the synthesis of large molecules in Titan's atmosphere by this scheme is that polyacetylenes are susceptible to H-atom cracking (Schwanebeck and Warnatz, 1975),

$$\begin{aligned} H + C_{2n}H_2 + M &\rightarrow C_{2n}H_3 + M \\ H + C_{2n}H_3 &\rightarrow C_2H_2 + C_{2n-2}H_2 \end{aligned} \quad (n > 1) \tag{77}$$

just as methyl acetylene (Eq. (75)). Preliminary calculations by Yung *et al.* (1983) indicate that the H-atom concentration is sufficiently large that processes (75) and (77) inhibit accumulation to observed concentrations. If the haze on Titan is comprised of large, condensed hydrocarbon molecules, then a mechanism must be found to efficiently generate these aerosols.

The CH_3 formed in Eq. (76) can recombine via

$$CH_3 + CH_3 + M \rightarrow C_2H_6 + M \tag{25}$$

or recycle CH_4 by

$$CH_3 + H + M \rightarrow CH_4 + M \tag{26}$$
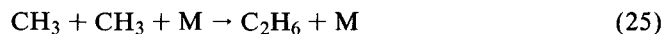
at a rate which can be important. The ethynyl radical can attack C_2H_6

$$C_2H + C_2H_6 \rightarrow C_2H_5 + C_2H_2 \tag{78}$$
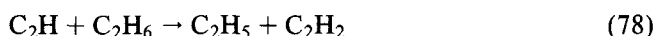
to subsequently form propane

$$CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M \tag{79}$$
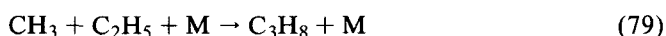
which has been observed (*Table 3*) and butane

$$2C_2H_5 + M \rightarrow C_4H_{10} + M \tag{80}$$
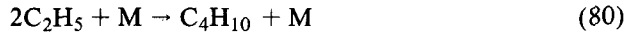
which has not been detected.

5.2 Nitrogen

It is well known that the N_2 bond is extremely difficult to break and on Titan energetic magnetospheric electrons interacting with Titan's upper atmosphere, solar radiation below 1000 Å, and secondary electrons generated in the lower stratosphere by cosmic rays are the principal means for dissociating N_2 in 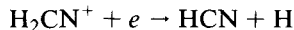the energy ratio of 10:1:2 (Capone *et al.*, 1980; Strobel and Shemansky, 1982). The ion chemistry of N_2^+ in the upper atmosphere preserves the N_2 bond (Strobel, 1982). Dissociative ionization of N_2 by electron impact or solar radiation is followed by reaction with CH_4
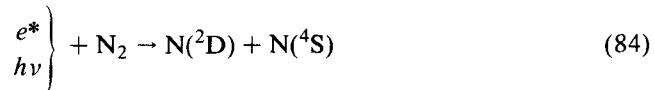
$$
\begin{aligned}
N^+ + CH_4 &\rightarrow CH_3^+ + N + H \\
&\rightarrow CH_4^+ + N \\
&\rightarrow H_2CN^+ + H + H \\
&\rightarrow HCN^+ + H_2 + H
\end{aligned}
\tag{81}
$$

$$
\begin{aligned}
HCN^+ + CH_4 &\rightarrow H_2CN^+ + CH_3 \quad 84\% \\
&\rightarrow C_2H_{+3} + NH_2 \quad 16\%
\end{aligned}
\tag{82}
$$
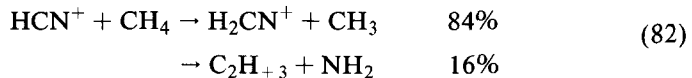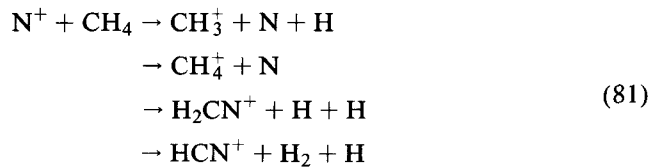
and then recombination

$$H_2CN^+ + e \rightarrow HCN + H$$
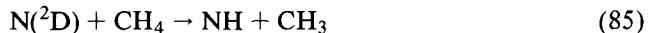
(Huntress *et al.*, 1980; McEwan *et al.*, 1981) for a net yield of HCN and N.
   Dissociation of N_2 by electron impact and solar radiation yields

$$\left.\begin{array}{c} e^* \\ h\nu \end{array}\right\} + N_2 \rightarrow N(^2D) + N(^4S) \tag{84}$$

The $N(^2D)$ reacts probably with CH_4 to form

$$N(^2D) + CH_4 \rightarrow NH + CH_3 \tag{85}$$

rather than HCN

$$N(^2D) + CH_4 \rightarrow HCN + H + H_2 \tag{86}$$
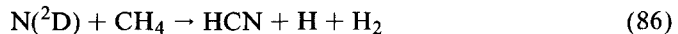
as Capone *et al.* (1980) assumed. The fate of $N(^4S)$ is more problematical. Michael (1980) has argued that the vast literature on reaction rates of $N(^4S)$ with hydrocarbons is spurious because in active nitrogen $[N_2(A^3\Sigma)]$ rather than $N(^4S)$ was the initial reactant. If this is true, then $N(^4S)$ most probably reacts with radicals such as

$$N(^4S) + {}^3CH_2 \rightarrow HCN + H \tag{87}$$

$$N(^4S) + CH_3 \rightarrow HCN + 2H \text{ or } H_2CN + H \tag{88}$$

$$H + H_2CN \rightarrow HCN + H_2 \tag{89}$$

$$N + NH \rightarrow N_2 + H \tag{90}$$
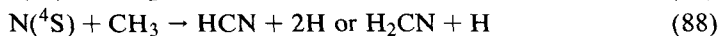
Reaction (90) represents self destruction of odd nitrogen as would the reaction

$$NH + NH \rightarrow N_2 + 2H \tag{91}$$

if it were fast. Solar excitation of $N_2(A^3\Sigma)$ on Titan may occur as it does on the earth (Zipf, 1980) and subsequent reactions with hydrocarbons may yield HCN if Michael's (1980) interpretation is correct. The detailed mechanisms are unknown.

Dissociation of HCN yields CN which can react with CH_4 to recycle HCN

$$CN + CH_4 \rightarrow HCN + CH_3 \tag{92}$$

and other hydrocarbons

$$CN + C_2H_2 \rightarrow HC_3N + H \tag{93}$$

$$CN + C_2H_4 \rightarrow C_2H_3CN + H \tag{94}$$

$$CN + HCN \rightarrow (CN)_2 + H \tag{95}$$
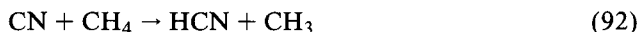
to generate some products (HC_3N, $(CN)_2$) which have been detected on Titan (*Table 3*). These nitrile compounds are readily dissociated to CN and HCN and are also subject to cracking by H atoms. A preliminary quantitative attempt by Yung *et al.* (1983) has been made to model these chemical processes on Titan. The principal difficulty encountered was that the cracking efficiency of H atoms was too high; this leads to an underestimate in the abundance of nitrile compounds. A similar problem was encountered for polyacetylenes.

5.3 CO and CO₂

The recent discoveries of CO_2 and CO in Titan's atmosphere are evidence for either the initial formation of the atmosphere with significant amounts of CO or a constant input of meteoroidal material (Lutz *et al.*, 1983; Samuelson *et al.*, 1983). The photochemistry of these species in Titan's reducing atmosphere has important implications.

For an initial atmosphere with appreciable CO, precipitation of magnetospheric electrons could initiate the chemical destruction of CO by

$$e^* + CO \rightarrow C + O(^1D) + e \tag{96}$$

$$e^* + N_2 \rightarrow N_2(A^3\Sigma) + e \tag{97}$$
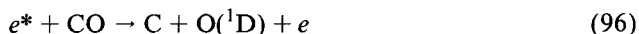
Solar radiation could also excite $N_2(A^3\Sigma)$ (Zipf, 1980). The $O(^1D)$ reacts with CH_4

$$O(^1D) + CH_4 \rightarrow OH + CH_3 \tag{98}$$

followed by

$$CO + OH \rightarrow CO_2 + H \tag{99}$$
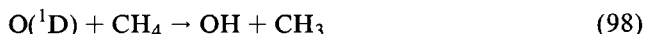
to convert CO to CO_2. The energy of $N_2(A^3\Sigma)$ can be transferred almost resonantly to CO

$$N_2(A^3\Sigma) + CO \rightleftharpoons CO(a^3\Pi) + N_2 \tag{100}$$

followed by

$$CO(a^3\Pi) + CO \rightarrow CO_2 + C \tag{101}$$
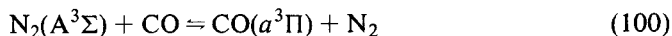
In Titan's cold atmosphere the resultant CO_2 will become supersaturated whenever there is more than a trace amount of oxygen species, sublime, and produce a layer of dry ice on the surface (Samuelson *et al.*, 1983). They estimated an initial CO mixing ratio of 0.1 translates into $\sim$ 1 m of dry ice over geologic time.

Meteoroidal H_2O is photolyzed

$$H_2O + h\nu \rightarrow H + OH \qquad (102)$$

$$\rightarrow H_2 + O(^1D, {}^1S)$$

The OH radical reacts with either CO or hydrocarbon radicals (Samuelson *et al.*, 1983)

$$CO + OH \rightarrow CO_2 + H \qquad (103)$$
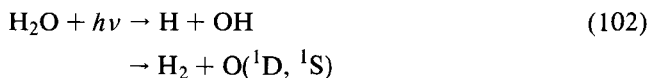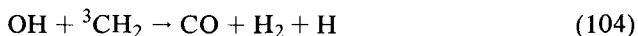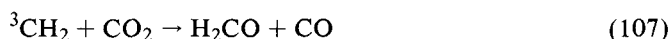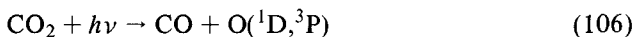
$$OH + {}^3CH_2 \rightarrow CO + H_2 + H \qquad (104)$$

$$OH + CH_3 \rightarrow CO + 2H_2 \qquad (105)$$

The latter two reactions need to be studied in the laboratory. CO_2 will either sublime or be readily converted back to CO by reactions such as

$$CO_2 + h\nu \rightarrow CO + O(^1D,{}^3P) \qquad (106)$$

$${}^3CH_2 + CO_2 \rightarrow H_2CO + CO \qquad (107)$$

$$H_2CO + h\nu \rightarrow H_2 + CO \qquad (108)$$

$$\rightarrow H + HCO \qquad (109)$$

$$HCO + h\nu \rightarrow H + CO \qquad (110)$$

$$H + HCO \rightarrow H_2 + CO \qquad (111)$$

According to Samuelson *et al.* (1983) the present CO abundance on Titan is in an approximate balance between meteoroidal H_2O input, sublimation loss of CO_2 and H_2CO to the surface and escape of O from the exosphere. An increasing meteoroidal H_2O source strength implies a smaller CO abundance as a consequence of Eqs. (102) and (103). The observed CO abundance (*Table 3*) implies a meteoroidal H_2O input rate ($2.9 \times 10^5 \, cm^{-2}s^{-1}$) which is 0.4 times the terrestrial rate, according to their calculations. Alternatively the present CO abundance may represent the evolution of an initially large CO mixing ratio (e.g., 0.1) to the accumulation of a meter of CO_2 and H_2CO ice on Titan's surface (Samuelson *et al.*, 1983).

6. FORMATION OF COMPLEX MOLECULES AND AEROSOLS

In the previous sections the emphasis has been on relatively simple molecules. The outer solar system displays a variety of colors which have been attributed to complex organic molecules (Sagan, 1971). In the past it was widely held that a reducing atmosphere was necessary for the origin of life. Thus of considerable interest from the exobiological point of view is the possibility and rate at which complex organic molecules can be formed in reducing atmospheres.

There are three complementary approaches to this complex subject, none of which are capable of providing definitive answers. There is the photochemical approach with absolute reaction rate kinetics. In theory a detailed description of all important reactions, photochemical processes, transport processes and constituents should provide answers. In practice the omission of one important reaction or constituent will lead to spurious results. Given the available data base only simple hydrocarbons are amenable to this approach.

In the laboratory, attempts have been made to simulate planetary atmospheres (Sagan and Miller, 1960; Khare and Sagan, 1973; Sagan and Khare, 1982). The principal deficiency of this approach is the serious compromise of some atmospheric condition to contain the experiment within normal laboratory space, e.g., higher pressures, larger mixing

ratios. Although this approach can suggest probable constituents formed in planetary atmospheres, it does not produce rigorous results.

Attempts have also been made to use thermodynamic equilibrium at some specific temperature for a mixture of elements with solar abundance (Sagan *et al.*, 1967). There is no assurance that such an equilibrium is ever attained by the whole atmosphere on a time scale short in comparison to the age of the solar system. In limited applications to atmospheric lightning Lewis (1980a) has found very low mixing ratios for the important precursor molecule HCN on Jupiter.

The stratospheres of Jupiter, Saturn and Titan share in common the presence of aerosol layers commonly referred to as Axel dust (Axel, 1972) or Danielson dust (Danielson *et al.*, 1973). The aerosols are believed to consist of fine particles which absorb UV and visible sunlight. Since these particles are very small they are poor emitters and will heat up and collisionally transfer their energy to atmospheric molecules. These particles are widely believed to be a photochemical smog (Axel, 1972; Danielson *et al.*, 1973) and cited as evidence for complex organic chemistry (Sagan and Salpeter, 1976; Sagan and Khare, 1982). The present evidence is circumstantial and indirect; it is not a fact that chromophores and haze particles are organic molecules.

The most extensive haze layers are found on Titan (Danielson *et al.*, 1973; Smith *et al.*, 1981) as the Voyager images so vividly displayed. The extremely cold temperatures on Titan make it entirely plausible for photochemical products of CH_4 dissociation to sublime. Even simple hydrocarbons such as C_2H_2 and C_2H_6 undergo sublimation in the cold trap region (cf. *Fig. 1*). Of course C_2H_2 and C_2H_6 do not absorb in the near UV and visible portions of the spectrum. What is needed is complex molecules with conjugated bonds (e.g., polyacetylenes) and nitriles (Mizutani *et al.*, 1975). In principle this is possible on Titan although the required production rate is difficult to achieve as a consequence of the cracking efficiency of H-atom reactions (Yung *et al.*, 1983). On Jupiter and Saturn where the H-atom (and H_2) abundance is substantially larger these cracking reactions would be significantly more efficient.

Simple hydrocarbons such as C_2H_6 and C_2H_2 do not accumulate in sufficient concentrations on Jupiter and Saturn to sublime. However NH_3 and PH_3 photochemistry produces N_2H_4 and P_2H_4 which do sublime. Liquid N_2H_4 absorbs out to ~ 3500 Å and could contribute partially to the required optical properties. The photochemistry of PH_3 is not entirely understood and photochemical products containing P, N, C and H atoms have not been quantified. The number of solar photons driving inorganic chemistry is an order of magnitude larger than the solar photons producing organic chemistry (Lewis and Prinn, 1971). In summary while complex organic molecules are probably being formed in these reducing planetary atmospheres, inorganic chemistry could make a more important contribution to colors and aerosols.

CONCLUDING REMARKS

Further advances in our understanding of photochemical processes in the atmospheres of Jupiter, Saturn and Titan require a coordinated research program involving spectroscopic observations, laboratory investigations and theoretical modeling. Of high priority in the laboratory is a complete characterization of the major pathways of C_2H_2 photolysis. If metastable states and vinylidene are formed, what are their ultimate fates in H_2- and N_2-dominated atmospheres? Accurate measurements are needed for NH_2 and PH_2 reactions. Is NH_2PH_2 a viable product in Jupiter's tropopause region? What other nitrogen and phosphorus compounds are probable in the atmospheres of Jupiter and Saturn?

On Titan it is important to determine whether the apparent efficiency of H-atom cracking reactions can be circumvented to account for the suite of hydrocarbons observed by the Voyager IRIS experiment and the extensive haze layers. Titan's atmosphere, of course, shares a great similarity with the earth's atmosphere; N_2 is the dominant constituent. Both atmospheres have trace amounts of CH_4, H_2O, H_2, CO, CO_2, and other hydrocarbons. The early terrestrial atmosphere was probably mildly reducing with primarily N_2, CO_2, H_2O and H_2 (Pinto et al., 1980). A detailed understanding of the present Titan atmosphere would be beneficial to understanding the earth's primitive atmosphere and the origin of life.

ACKNOWLEDGEMENTS

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