LABORATORY MEASUREMENTS AND METHANE PHOTOCHEMISTRY MODELING

P. N. Romani†

Science Systems and Applications Inc., 7375 Executive Place, Suite 300, Seabrook, MD 20706

†Author's mailing address:

Mail Code 693.2, NASA/Goddard Space Flight Center, Greenbelt, MD 20771

ABSTRACT

Methane is photolyzed by the solar UV in the stratosphere of Saturn. Subsequent photochemistry leads to the production of acetylene (C_2H_2) and diacetylene (C_4H_2). These species are produced where it is relatively warm (T $\geq$ 140K), but the tropopause temperature of Saturn ($\approx$80K) is low enough that these two species may freeze out to their respective ices. Numerical models which include both photochemistry and condensation loss make predictions about the mixing ratios of these species and haze production rates. These models are dependent upon knowing reaction pathways and their associated kinetic reaction rate constants and vapor pressures. How uncertainties in the chemistry and improvements in the vapor pressures affect model predictions for Saturn are discussed.

PHOTOCHEMISTRY

Acetylene (C_2H_2) is produced from the photolysis of methane (CH_4) in the stratosphere of Saturn by the solar UV and subsequent photochemistry. The sink for C_2H_2 is either transport downward, condensation in the lower stratosphere (to its ice), or photolysis;

$$C_2H_2 + h\nu \longrightarrow C_2H + H \quad (1)$$

$$\longrightarrow C_2 + H_2 \quad (2)$$

C_2H either recycles C_2H_2;

$$C_2H + CH_4 \longrightarrow C_2H_2 + CH_3 \quad (3)$$

$$C_2H + H_2 \longrightarrow C_2H_2 + C_2H_3 \quad (4)$$

$$C_2H + C_2H_6 \longrightarrow C_2H_2 + C_2H_5 \quad (5)$$

or makes diacetylene (C_4H_2);

$$C_2H + C_2H_2 \longrightarrow C_4H_2 + H \quad (6)$$

which condenses out in the lower stratosphere (also to its ice).

Reaction rates for (3) - (6) have been measured only at room temperature, while the temperature range in the region of interest in the stratosphere of Saturn is $80 < T < 150K$. The extrapolation of the reaction rates to lower temperatures can be done using the Arrhenius equation;

$$A \cdot \exp[- \Delta E / (R \cdot T)] \quad (7)$$

where A is the frequency factor and ΔE is the activation energy. Either A or ΔE can be calculated from theory. Then from the measured room temperature reaction rate, the other term can be deduced. Calculating ΔE from BSBL theory and then deriving A produces rate constants of (cm^3 $molecules^{-1}$ sec^{-1});[1]

$$C_2H - H_2 \quad k = 5.7 \times 10^{-11} \exp(-1762 / T) \quad (8)$$

$$C_2H - CH_4 \quad k = 6.5 \times 10^{-12} \exp(-503 / T) \quad (9)$$

$$C_2H - C_2H_6 \quad k = 1.8 \times 10^{-11} \exp(-302 / T) \quad (10)$$

(Set 1). Calculating A from BEBO theory and then deriving ΔE yields the following different rate constants;[1]

$$C_2H - H_2 \quad k = 1.9 \times 10^{-11} \exp(-1460 / T) \quad (11)$$

$$C_2H - CH_4 \quad k = 3.1 \times 10^{-12} \exp(-252 / T) \quad (12)$$

$$C_2H - C_2H_6 \quad k = 6.9 \times 10^{-12} \quad (13)$$

(Set 2). This is the same as used by Yung, Allen and Pinto in modeling Titan photochemistry.[2] Using Set 2 leads to less C_4H_2 production and more C_2H_2 recycling than using Set 1. Recently, Stephans et al. measured the reaction rates of C_2H - H_2 and C_2H - C_2H_2.[3] Their rates are 3 and 5 times the rates

reported by Laufer and Bass.[4] Note, however, that Laufer and Bass measured the appearance of products (C_2H_2 and C_4H_2) while Stephans measured the disappearance of C_2H (a reactant).

The fate of the C_2 produced in (2) is uncertain;

$$C_2 + H_2 \longrightarrow C_2H + H \qquad (14)$$

$$C_2 + CH_4 \longrightarrow C_2H + CH_3 \quad a \qquad (15a)$$

$$\longrightarrow C_2H_2 + {}^1CH_2 \quad b \qquad (15b)$$

Even though $[CH_4] \ll [H_2]$ in the stratosphere of Saturn, the reaction rate with CH_4 is fast enough to overcome the relative abundance difference. These two reactions have been measured only at room temperature and above.[5,6]

VAPOR PRESSURES

Previously, the lowest temperatures at which the vapor pressures of C_4H_2 and C_2H_2 had been measured were 190K and 98K respectively. The new vapor pressure measurements by Masterson et al., have extended this to 127K and 80K for diacetylene and acetylene respectively.[7] This has removed the need for extrapolating the C_2H_2 vapor pressure, and reduced the temperature range of extrapolation for C_4H_2 from 110K to 47K. The analysis of the this new vapor pressure data is not yet complete, however.

DISCUSSION

The C_2H_2 mixing ratio from the photochemical model is compared to its saturation mixing ratio (from the data of Masterson et al.[7]) in Figure 1. The lower boundary condition is downward transport with the maximum possible velocity. Lowering the downward transport velocity increases the C_2H_2 mixing ratio at the tropopause and thus increases the supersaturation and the likelihood of condensation. Extrapolation of the previous vapor pressure data resulted in higher vapor pressures and the model would have predicted no possible condensation. The chemical production rate of acetylene in the model is on the order of 6.5×10^8 molecules cm^{-2} sec^{-1}, or 3×10^{-14} grams cm^{-2} sec^{-1}, capable of dominating the haze production rate (Table I.). However, the

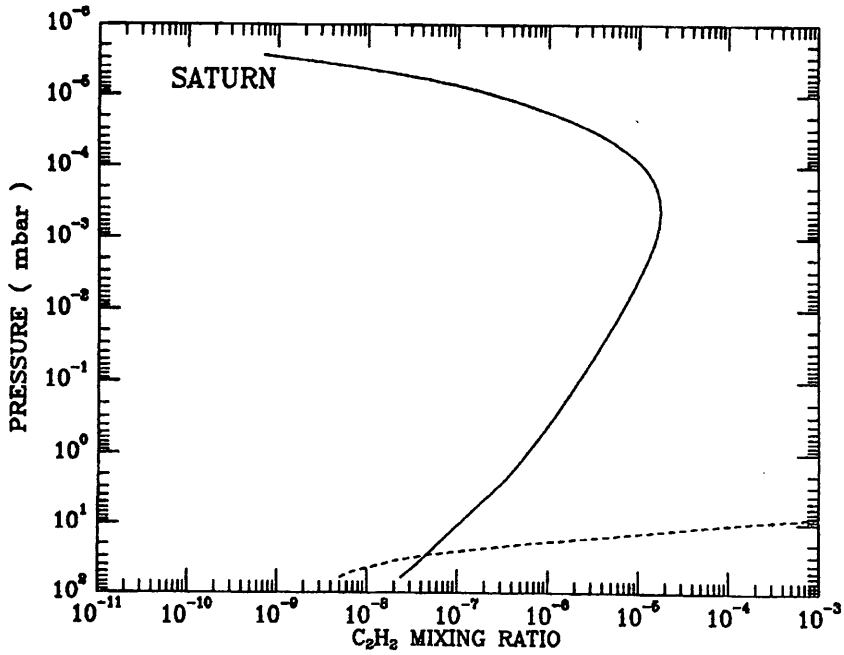

Figure 1 - Acetylene mixing ratio vs. pressure in the stratosphere of Saturn. Solid line is from the photochemical model, dashed line is maximum mixing ratio from saturation vapor pressure data of Masterson et al.[7]

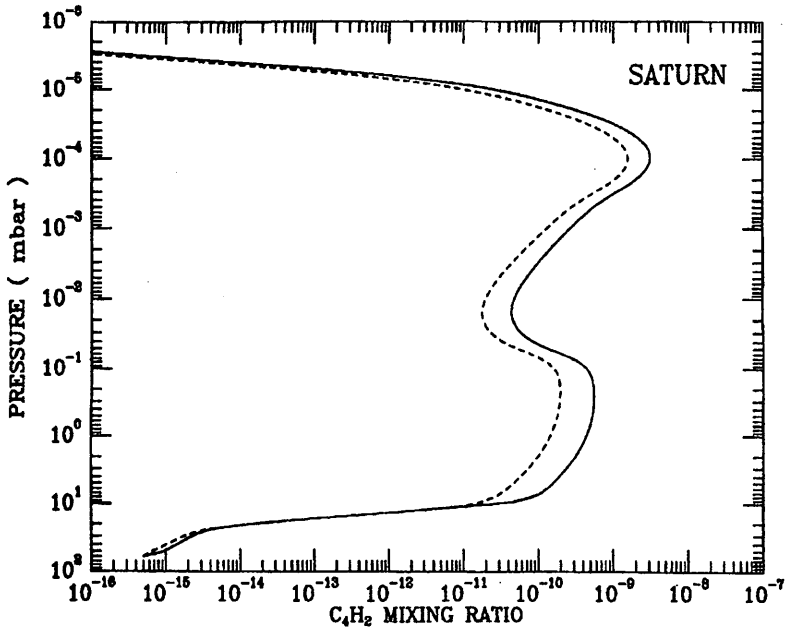

Figure 2 - Diacetylene mixing ratio vs. pressure in the stratosphere of Saturn. Solid line is for Set 1 C_2H reaction rates, dashed line Set 2 reaction rates, both assume (a) pathway for $C_2 + CH_4$. Rapid decrease in mixing ratio for pressures greater than 10 mbar is due to condensation.

TABLE I

DIACETYLENE HAZE LOCATION AND PRODUCTION RATES

CHEMISTRY	T	P	#	grams
a pathway for $C_2 + CH_4$ Set 1 C_2H reaction rates	103.0	11.0	1.3×10^{7}	1.0×10^{-15}
b pathway for $C_2 + CH_4$ Set 1 C_2H reaction rates	103.0	11.0	4.8×10^{6}	4.0×10^{-16}
a pathway for $C_2 + CH_4$ Set 2 C_2H reaction rates	100.0	12.0	1.8×10^{6}	1.5×10^{-16}
b pathway for $C_2 + CH_4$ Set 2 C_2H reaction rates	100.0	12.0	6.7×10^{5}	5.5×10^{-17}

T - Temperature in degrees Kelvin at which C_4H_2 begins to condense

P - Pressure in mbar at which C_4H_2 begins to condense

\# - Column production rate of C_4H_2 haze in molecules cm^{-2} sec^{-1}

grams - Column production rate of C_4H_2 haze in grams cm^{-2} sec^{-1}

supersaturation with the maximum downward velocity case is ≈ 4 and may not be enough to initiate condensation.

Changes in the C_4H_2 mixing ratio due to changes in the C_2H reaction rates are shown in Figure 2. Similar effects are seen with changes in the C_2 + CH_4 pathway with the (a) pathway producing the larger C_4H_2 mixing ratios. As can be seen in Table I, uncertainties in the chemistry cause more than an order of magnitude variation in the predicted C_4H_2 haze production rate.

Measurements of the C_2H and C_2 reaction rates at lower temperatures are needed to improve model predictions. Secondarily the products of the C_2 + CH_4 reaction should be identified. Improved C_2H_2 vapor pressures have shown that C_2H_2 is now a possible source of the observed stratospheric haze on Saturn. C_4H_2 is a probable source, whose importance could be better constrained with better knowledge of the chemistry and vapor pressure measurements at lower temperatures (the C_4H_2 vapor pressure is still being extrapolated over 50K).

REFERENCES

[1]R. L. Brown and A. H. Laufer, J. Phys. Chem. **85**, 3826 (1981).

[2]Y. Yung, M. Allen, and J. Pinto, Ap. J. Supp. **55**, 564 (1984).

[3]J. W. Stephans, J. L. Hall, H. Solka, W.-B. Yan, R. F. Curl, and G. P. Glass, J. Phys. Chem. **91,** 5740 (1987).

[4]A. H. Laufer and A. M. Bass, J. Phys. Chem. **83**, 310 (1979).

[5]L. Pasternack and J. R. McDonald, Chem. Physics **43**, 173 (1979).

[6]W. M. Pitts, L. Pasternack, and J. R. McDonald, Chem. Physics **68**, 417 (1982).

[7]C. Masterson, J. Allen, G. Kraus, R. Khanna, in prep. (1989).

ACKNOWLEDGEMENTS

I am deeply indebted to L. Stief, J. E. Allen, C. Masterson, and R. Khanna for assistance in understanding laboratory data. I am supported at NASA Goddard Space Flight Center, Greenbelt, Maryland, by NASA contract NAS5-30134.