The role of submicrometer aerosols and macromolecules in H_2 formation in the Titan haze

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Abstract

Previous studies of the photochemistry of small molecules in Titan's atmosphere found it difficult to have hydrogen atoms removed at a rate sufficient to explain the observed abundance of unsaturated hydrocarbons. One qualitative explanation of the discrepancy nominated catalytic aerosol surface chemistry as an efficient sink of hydrogen atoms, although no quantitative study of this mechanism was attempted. In this paper, we quantify how haze aerosols and macromolecules may efficiently catalyze the formation of hydrogen atoms into H_2. We describe the prompt reaction model for the formation of H_2 on aerosol surfaces and compare this with the catalytic formation of H_2 using negatively charged hydrogenated aromatic macromolecules. We conclude that the PRM is an efficient mechanism for the removal of hydrogen atoms from the atmosphere to form H_2 with a peak formation rate of ~ 70 cm^{-3} s^{-1} at 420 km. We also conclude that catalytic H_2 formation via hydrogenated anionic macromolecules is viable but much less productive (a maximum of ~ 0.1 cm^{-3} s^{-1} at 210 km) than microphysical aerosols.

1. Introduction

Observations of Titan's haze by Voyager indicate a dense layer of smog produced by ongoing charged particle photochemistry and ultraviolet (UV) radiation in Titan's stratosphere. Titan's atmospheric haze dominates its temperature, atmospheric circulation, and climate control, and photochemistry plays a key role in the structure and evolution of the haze. This means that a detailed knowledge of Titan's photochemistry provides a deeper understanding of its global properties. Sagan et al. (1993) have produced evidence that carbonaceous macromolecules (e.g., polycyclic aromatic hydrocarbons (PAHs) and aromatic nitriles) are significant components of Titan tholin analogs. When

Khare et al. (2002) analyzed the synthesis of Titan tholin analogs from a starting mixture of 10% CH_4 and N_2 in an electrical discharge experiment, they found that aromatic rings formed within a few seconds. Bauschlicher and Ricca (2000) and Ricca et al. (2001) have performed quantum chemical calculations which confirm the viability of heterocyclic formation in the Titan haze. These aromatic macromolecules may effectively provide the "missing link" in present chemical models between simple molecules and submicrometer aerosols.

Macromolecules provide a large surface area for chemistry between themselves and the gas phase and they strongly influence this chemistry directly through their charge state (Borucki et al., 1987; Lepp and Dalgarno, 1988; Bakes and Tielens, 1994, 1998; Bakes et al., 2002). These macromolecules are efficient charge exchange intermediaries, electrophiles which acquire electrons with ease and

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transfer them to gaseous ions to produce neutral species (Bakes and Tielens, 1994). They often play a central role in gas phase chemistry and, as such, may be crucial to our understanding of the structure and evolution of any atmosphere (Bakes and Tielens, 1998). One of the necessary functions in photochemical models fulfilled by Titan's stratospheric chemistry is to remove highly reactive hydrogen atoms from the atmosphere so that unsaturated molecules such as acetylene continue to exist in abundance, providing a satisfactory match to Voyager observations. Yung et al. (1984) and Courtin et al. (1991) suggested that this may be achieved by the catalytic conversion of H to H_2 on aerosol surfaces.

In this paper, we quantify the catalytic formation of H_2 on aerosols using the ingenious *prompt reaction model* (PRM) of Duley (1996) and the catalytic reaction of anionic aromatic macromolecules with hydrogen. Determining the charge on a given aerosol with altitude in the Titan stratosphere takes the first step in the formation of an accurate chemical network (Bakes et al., 2002). With the charge distribution defined, possible mechanisms for H_2 formation are investigated and compared. In Section 2, we discuss the formation of molecular hydrogen via the PRM for submicron aerosols, while in Section 3, we discuss the formation of H_2 via anionic macromolecular catalysis. In Sections 4 and 5, we summarize our results and conclusions, respectively.

2. The formation of molecular hydrogen via large aerosols: the prompt reaction model

The formation of molecular hydrogen and its subsequent escape into space play an important role in the composition, climatology, and evolution of Titan's atmosphere. Conventional models concerning the formation of H_2 on an aerosol surface (Duley and Williams 1993) involve six main steps, namely, (1) collision of an H atom with an aerosol, (2) thermal accomodation and adsorption, (3) retention on the aerosol surface until another H atom arrives and is adsorbed, (4) H atom migration to a reaction site, (5) recombination to form H_2, and (6) ejection of this newly formed H_2 molecule.

The rate and efficiency of H_2 formation depend on the gas kinetic temperature T_k and the aerosol temperature T. Formation occurs promptly upon the collision of a gas phase H atom with the aerosol surface. Since the hydrogen atom is neutral, the electrostatic attraction between the hydrogen atom and the charged aerosol is negligible, even though the aerosol may have a sizeable charge (Bakes et al., 2002). The rate-limiting steps are (2) and (3) and their efficiency is determined by aerosol temperature, binding energy for H atoms on aerosols, and the density of H atoms.

The prompt reaction model neatly circumvents these rate-limiting steps because it does not require a hydrogen atom to be adsorbed onto an aerosol surface as a precursor to molecular hydrogen formation. Instead, it assumes that

the aerosols are already impregnated with both bonded and interstitial hydrogen atoms and that incoming H atoms from the surrounding gas react immediately with the surface H without adsorption or thermal accomodation. This is certainly a reasonable assumption for the relatively high-density environment of the Titan haze, where we expect that the aerosol surface is already substantially covered with bonded H atoms. Formation of H_2 via a "prompt" reaction on a carbonaceous aerosol surface involves interstitial hydrogen atoms at low aerosol temperatures and H atoms bonded to CH, CH_2, and CH_3 groups at higher temperatures. The H_2 formation rate F_{H_2} (i.e., dn_{H_2}/dt) for the PRM is given by Duley (1996) as

$$F_{H_2} = n_H \, v_H \, n_{aerosol} \left[N_i \sigma_i + N_b \sigma_b \right] \text{ cm}^{-3} \, s^{-1}, \qquad (1)$$

where n_H is the hydrogen atom density (cm^{-3}), based on the hydrogen atom abundance profile of Lebonnois et al. (2002), using a combination of photodissociation and heterogeneous, and gas-phase catalyzed processes (see their Fig. 6a). The aerosol number density is given by $n_{aerosol}$ and N_i and N_b are the number densities of the interstitial and bonded hydrogen atoms per aerosol, respectively. The kinetic temperature for H atoms is given by T_k, which factors into v_H, the speed of an approaching hydrogen atom. This is given by $v_H = (3kT_k/m_H)^{1/2}$, where m_H is the mass of a hydrogen atom and k is Boltzmann's constant. We have found that the speed of a hydrogen atom is one order of magnitude larger than the wind speeds on Titan. Since eddy diffusion is smaller in value than the stratospheric wind-speed in the Titan haze, we may conclude that dynamical effects on the hydrogen atom velocity may be neglected.

The term σ_i is the cross section for H atom abstraction from interstitial sites, given by

$$\sigma_i = \gamma_i e^{-\frac{q_i}{kT_k}}, \qquad (2)$$

where γ_i is the interstitial geometric cross section and q_i is the interstitial H atom activation energy for abstraction. The equation for σ_b, the cross section for bonded H atom abstraction from bonded sites, is likewise given by

$$\sigma_b = \gamma_b e^{-\frac{q_b}{kT_k}}, \qquad (3)$$

where T_k is the kinetic temperature for H atoms. The aerosol temperature determines how hydrogen atoms are attached to the aerosol surface, whether this is via occupation of interstitial sites on the one hand, or bonded sites on the other. At aerosol temperatures ≥ 40 K, interstitial sites are *unoccupied* (Duley 1996). Below, we evaluate how important occupied interstitial sites are relative to bonded sites for H_2 formation via the PRM applied to Titan haze aerosols. The fraction f_i of occupied interstitial sites N_i on an aerosol surface composed of N carbon atoms is given by f_i, where

$$f_i = \frac{N_i}{N} \propto n_H \, e^{\frac{\varepsilon_i}{kT}},$$

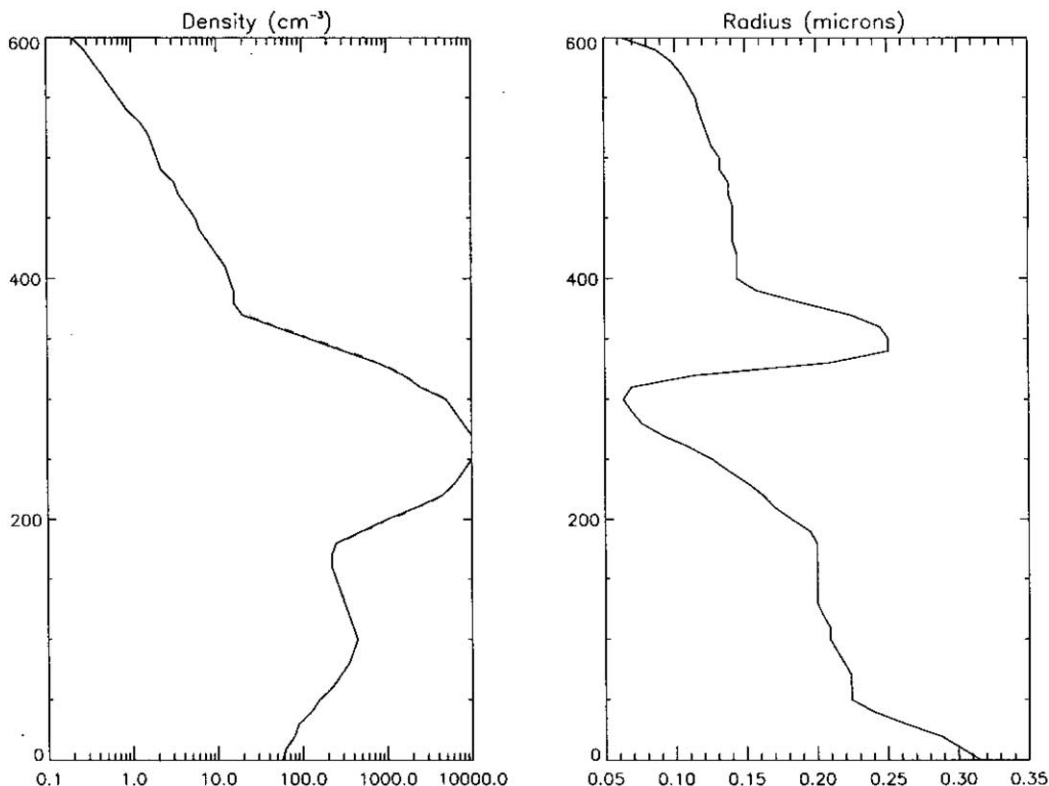where Sugai et al. (1989) give $\varepsilon_i/k \sim 1500$ K at $n_H = 100$

Fig. 1. The aerosol density and radius variation with altitude (km) used in this study, derived from the model of Barth and Toon (2002).

cm^{-3}. We take N as the surface area of a spherical graphitic aerosol divided by the cross section of a carbon atom.

Because the aerosols in the Titan haze are in thermal equilibrium with the gas phase, their temperature is much greater than the 40-K upper limit on interstitial site occupation by H atoms. This means that for the Titan H_2 formation zone, interstitial sites are negligible, and the formation rate of H_2 is therefore given as

$$F_{H_2} = n_H \, v_H \, n_{aerosol} \, N_b \, \sigma_b = n_H \, v_H \, n_{aerosol} \, f_b \, N \, \sigma_b,$$

where f_b is simply the number of bonded sites N_b on an aerosol surface composed of N carbon atoms. Under these conditions, Sugai et al. (1989) give $f_b \sim 1$ and $\gamma_b = 10^{-15}$ cm^{-2}. From the standard model of Titan's atmosphere (Lellouch 1990), we obtain T_k (200 km) = 174 K, T_k (100 km) = 145 K, and q_b/k = 1700 K (Duley, 1996). This yields σ_b (200 km) = 5.7 × 10^{20} cm^{-2} and σ_b (100 km) = 8.1 × 10^{-21} cm^{-2}. F_{H_2} can then be calculated, using Barth and Toon (2002) to obtain estimates of the aerosol density (Fig. 1).

3. The formation of molecular hydrogen via aromatic macromolecules

Molecular hydrogen may be formed via the catalytic reaction of hydrogenated macromolecular cations (Bauschlicher, 1998) or anions (Bauschlicher and Bakes, 2001). Our chemical network is shown in Fig. 2. For the Titan

haze, Bakes et al. (2002) showed that for macromolecules of size up to ~55 carbon atoms, mostly neutral and anionic species are formed, rather than singly charged cations. Cationic species appeared only at the highest altitudes (450 km or higher) and only at the 10% level, which is negligible for our purposes. For this reason, we will concentrate on the anionic macromolecules and their role in catalytic H_2 production. In future studies, we will look at what happens to hydrogen chemistry when the macromolecular size increases to around 100 component atoms. In this case, we expect the singly and multiply charged cationic fraction of macromolecules to increase (Bakes et al., 2002), although we leave an in-depth study of this effect for a later paper.

3.1. Computational methods

We have used well-established quantum chemical methods to predict the reaction energetics for the catalytic formation of H_2 via anionic macromolecules in the Titan haze. These methods are accurate and work at the quantum mechanical level of molecular chemistry. The geometries of the macromolecules were optimized and their harmonic frequencies were computed using the B3LYP hybrid functional (Becke et al., 1993; Stephens et al., 1994) in conjunction with the 4-31G or 6-31++G** basis sets (Bauschlicher and Bakes 2001). The B3LYP calculations were performed using the Gaussian 98 computer codes. For a detailed,
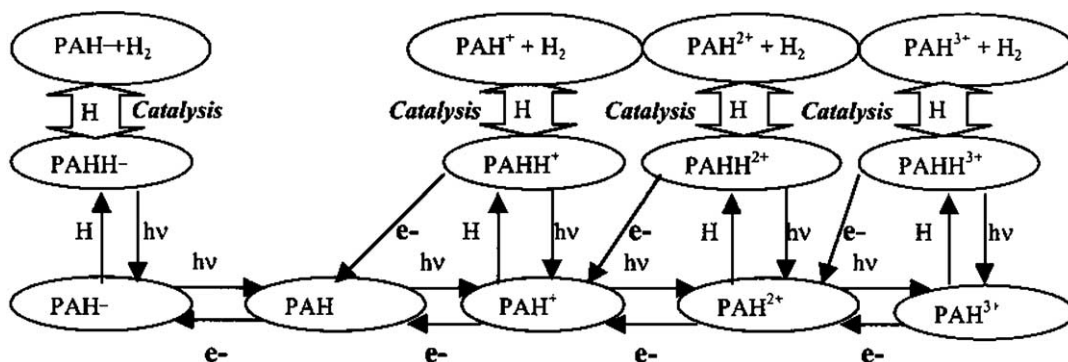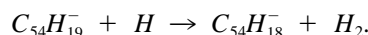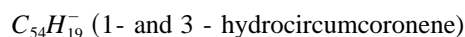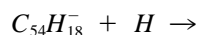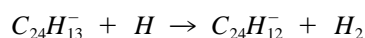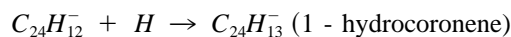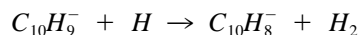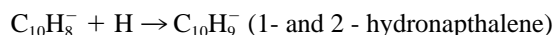
Fig. 2. The chemical network for macromolecules taken as generic PAHs. For this study, we concentrated on only the first ionization potential of our PAHs, since our macromolecules do not exceed a size of ~55 carbon atoms. This means their second ionization potential is larger than the maximum energy of secondary UV radiation incident on the haze (~8 eV, Sagan and Thompson, 1984). However, as these macromolecules increase in size to ~100 carbon atoms, second and third ionization states will emerge and the potential for the catalytic formation of H_2 via PAH cations may be considered at high altitudes (Bauschlicher, 1998).

analysis of these mechanisms and their energetics, see Bauschlicher and Bakes (2001).

3.2. Reaction pathways and energetics

Bauschlicher and Bakes (2001) have found that the anionic PAHs formed in the Titan haze can catalytically convert H to H_2 via the following reaction schemes, which are barrierless and strongly exothermic (~ 50 kcal/mole):

$$C_{10}H_8^- + H \rightarrow C_{10}H_9^- \text{ (1- and 2 - hydronapthalene)}$$

$$C_{10}H_9^- + H \rightarrow C_{10}H_8^- + H_2$$

$$C_{24}H_{12}^- + H \rightarrow C_{24}H_{13}^- \text{ (1 - hydrocoronene)}$$

$$C_{24}H_{13}^- + H \rightarrow C_{24}H_{12}^- + H_2$$

$$C_{54}H_{18}^- + H \rightarrow$$

$$C_{54}H_{19}^- \text{ (1- and 3 - hydrocircumcoronene)}$$

$$C_{54}H_{19}^- + H \rightarrow C_{54}H_{18}^- + H_2.$$

Unfortunately, our quantum-chemical calculations do not easily yield the rates of the above reactions. Such rate constant calculations require the study of a sizeable portion of the potential energy surface and are therefore computationally intensive. We are currently determining more of the potential surface for the reaction of an H atom with the 1-hydronapthalene anion in order to obtain rate constants for these mechanisms for the formation of H_2, which are relevant to a variety of astrophysical environments. Fig. 3 shows the potential energy surface for the barrierless, exothermic reaction of H with the 1-hydronapthalene anion to yield the napthalene anion plus H_2.

For hydrogenated macromolecular anions, we calculated the H_2 formation rate via

$$F_{H_2}(PAHH^-) = 2 \times 10^{-10}$$

$$\times (T_k/300)^{1/2} n_H n_{pah} f_{pahh} - cm^{-3} s^{-1},$$

where n_{pah} is the number density of macromolecules (taken from Barth and Toon, 2002) and f_{pahh-} is the fraction of macromolecules which are anionic and hydrogenated (Bakes et al., 2002, 2003). We assume the reaction proceeds at a rate given by the gas kinetic rate coefficient (Yung and DeMore, 1999). This yields the maximum possible rate for H_2 formation via PAH^- catalysis in the Titan haze.
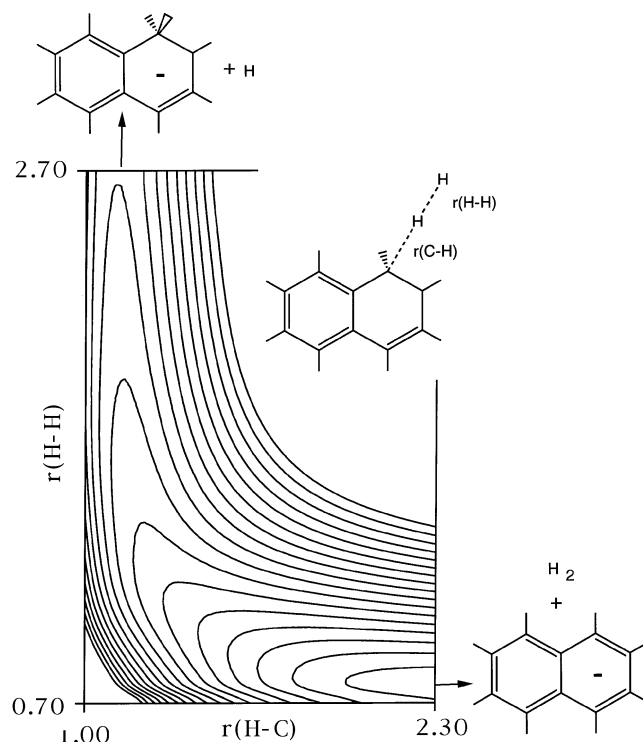

Fig. 3. The potential energy surface for the reaction of a hydrogen atom with a 1-hydronapthalene anion to yield a napthalene anion plus H_2. This catalytic reaction is barrierless and exothermic and provides an example of a potential mechanism for forming H_2 if, as Sagan et al. (1993) predicted, PAHs or PAH-like macromolecules exist in the Titan haze.
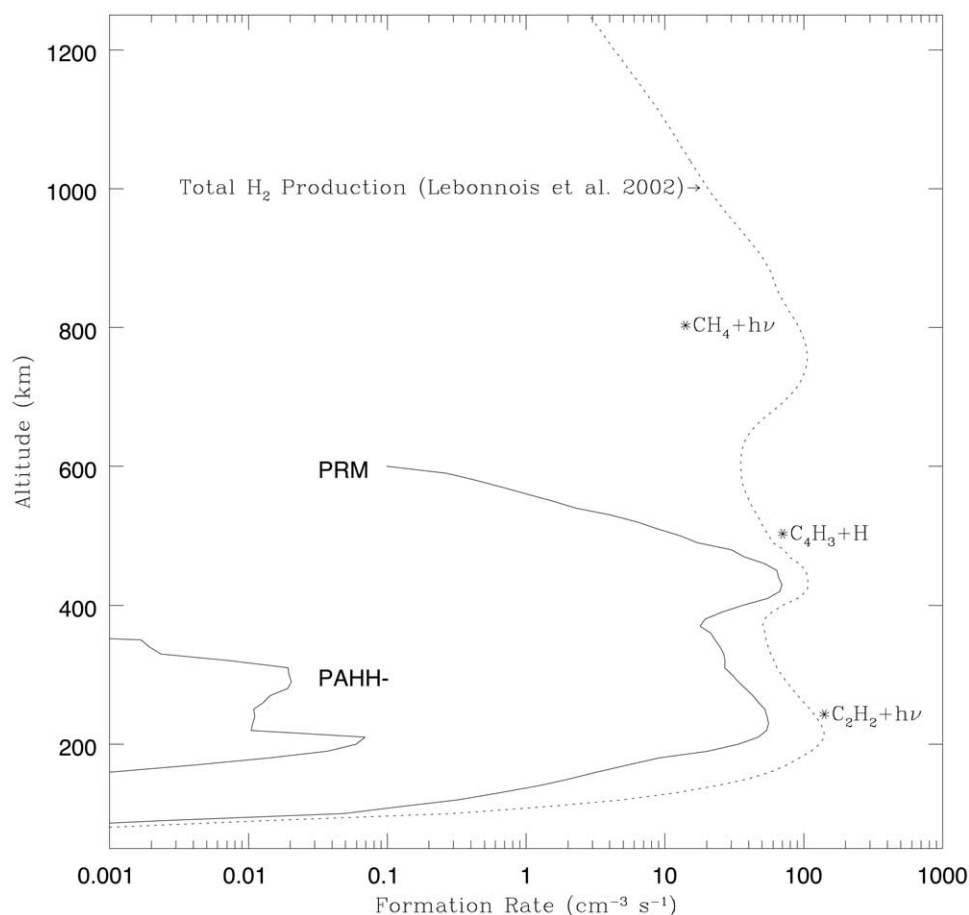
Fig. 4. The reaction rate for H_2 formation via the prompt reaction model of Duley (1996) for submicrometer aerosols and an average-sized hydrogenated PAH anion composed of 54 carbon atoms. Also shown is the total H_2 formation rate, in which the PRM was included (dotted line) in the model of Lebonnois et al. (2002). This PRM catalytic mechanism is as effective as alternative mechanisms suggested by Yung et al. (1984) for the production of H_2 at a rate sufficient to preserve the integrity of unsaturated hydrocarbons in the Titan haze. The peak values of H_2 production from the chemical mechanisms of Yung et al. (1984) are shown as asterisks.

4. Results

Fig. 4 shows the formation rate for H_2 via the prompt reaction model for Titan haze aerosols. We have used the H atom distribution and the aerosol radius and abundance from Lebonnois et al. (2002). The aerosol abundance included in Lebonnois et al. (2002) is taken from the recent model of Barth and Toon (2002). The rate of formation of H_2 is comparable to the rates listed by Yung et al. (1984, Fig. 5c) for the production of H_2 via the photolysis of small hydrocarbons such as acetylene, C_2H_2, and methane, CH_4, and via the catalytic scheme involving C_4H_3. To test the impact of the heterogenous catalytic production of H_2 via the PRM inside a photochemical model, we inserted this mechanism into the photochemical model of Lebonnois et al. (2002). These results are also shown in Fig. 4. The profile of the total production rate of H_2 is plotted, as well as the production rate from the PRM only. This confirms that the aerosol catalysis of H_2 formation provides an efficient pathway for the conversion of H to H_2 in Titan's

atmosphere and the required maintenance (Yung et al., 1984) of unsaturated chemical species in the stratosphere.

In order to compare the H_2 formation rate via the PRM with that from anionic macromolecular catalysis, we have assumed the abundance of macromolecules given by the state-of-the-art model of Barth and Toon (2002). The assumed abundance of macromolecules plays a crucial role in deducing the formation rate of H_2 via this mechanism. While this is still uncertain, we have used the best estimate currently available. By using the expected abundance of anionic hydrogenated macromolecules in the Titan haze (Bakes et al., 2002, 2003), we have computed the formation rate of H_2 molecules, shown in Fig. 4. This type of catalysis is comparably inefficient with respect to the PRM at all altitudes. This is because the formation of PAH^- dwarfs the formation of $PAHH^-$ by an order of magnitude, so that the hydrogenated anionic PAHs are of much lower abundance relative to PAH anions. Our calculations are performed with a UV radiation field representative of the daytime or summer phase of Titan's rotation. However, since the abun-

dance of anions during the daytime/summer differs from that of the nighttime/winter by a factor of only a few (Bakes et al., 2002), we do not expect the H_2 production rate during the nighttime/winter cycle to differ significantly from the results presented here.

5. Conclusions

Identifying efficient mechanisms by which reactive hydrogen atoms can be removed from the Titan haze and converted to inert H_2 has been challenging. Much excellent work has been done previously to investigate this problem (Yung et al., 1984; Courtin et al., 1991; Toublanc et al., 1995). In this paper, we have quantified potential catalytic mechanisms for the formation of H_2. We find that

- Submicrometer aerosols in the Titan haze can efficiently catalyze the formation of H_2, facilitating the removal of reactive H atoms from the atmosphere and preserving the integrity of unsaturated hydrocarbons observed in the haze.
- The formation of H_2 via the PRM applied to submicrometer aerosols produces reaction rates comparable with those of photochemical models of Titan's stratosphere.
- Hydrogenated anionic macromolecules found in the lower atmosphere of Titan can catalytically convert H atoms to H_2, but their efficiency is generally much less than the PRM at all altitudes.
- We do not expect the H_2 production rate via hydrogenated anionic macromolecules to change significantly (i.e., by no more than a factor of a few) during the day and night cycles (or summer and winter cycles) of Titan.

Finally, the results of this model have been incorporated into a state-of-the-art photochemical model of Titan's haze (Lebonnois et al., 2002) in order to quantify the effects of the PRM on Titan's hydrogen budget. Lebonnois et al. (2002) find that the PRM has a very significant effect on the H and H_2 budgets of Titan's atmosphere.

References

Bakes, E.L.O., Tielens, A.G.G.M., 1994. The photoelectric heating mechanism for very small graphitic grains and polycyclic aromatic hydrocarbons. Astrophys. J. 427, 822–838.

Bakes, E.L.O., Tielens, A.G.G.M., 1998. The effects of polycyclic aromatic hydrocar-bons on the chemistry of photodissociation regions. Astrophys. J. 499, 258–266.

Bakes, E.L.O., McKay, C.P., Bauschlicher, C., 2002. Photoelectric charging of submicron aerosols and macromolecules in the Titan haze. Icarus 157, 464–475.

Bakes, E.L.O., Tielens, A.G.G.M., Bauschlicher, C., 2003. The chemistry of charged hydrogenated PAHs and their effects on infrared emission. Astrophys. J., submitted for publication.

Barth, Erika, Toon, O.B., 2002. Microphysical modeling of ethane ice clouds in Titan's atmosphere. Icarus, in press.

Bauschlicher, Charles Jr., W., 1998. The reaction of polycyclic aromatic hydrocarbon cations with hydrogen atoms: the astrophysical implications. Astrophys. J. Lett. 509, L125–127.

Bauschlicher, C., Bakes, E.L.O., 2001. The reaction of polycyclic aromatic hydrocarbon anions with hydrogen. Chem. Phys 274, 11–14.

Bauschlicher, C.W., Ricca, A., 2001. Mechanisms for polycyclic aromatic hydrocarbon (PAH) growth. Chem. Phys. Lett. 328, 396–402.

Becke, A.D., 1993. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648–5652.

Borucki, W.J., Levin, Z., Whitten, R.C., Keesee, R.G., Capone, L.A., Summers, A.L., Toon, O.B., Dubach, J., 1987. Predictions of the electrical conductivity and charging of the aerosols in Titan's atmosphere. Icarus 72, 604–622.

Courtin, R., Wagener, R., McKay, C.P., Caldwell, J., Fricke, K.-H., Raulin, F., Bruston, P., 1991. UV spectroscopy of Titan's atmosphere, planetary organic chemistry and prebiotic synthesis. II. Interpretation of new IUE observations in the 235–335 nm range. Icarus 90, 43–56.

Duley, W.W., 1996. Formation of molecular hydrogen via the prompt reaction model. Mon. Not. R. Astron. Soc. 279, 591–594.

Duley, W.W., Williams, D.A., 1993. The formation of H_2 on interstellar dust. Mon. Not. R. Astron. Soc. 260, 37–42.

Khare, B.N., Bakes, E.L.O., Imanaka, H., McKay, C.P. Cruikshank D. Edward Arakawa, 2002. The formation of PAHs in time dependent laboratory formation of tholins. Icarus, in press.

Lebonnois, S., Toublanc, D., Hourdin, F., Rannou, P., 2001. Seasonal variations of Titan's atmospheric composition. Icarus 152, 384–406.

Lebonnois, S., Bakes, E.L.O., McKay, C.P., 2003. Atomic and molecular hydrogen budget in Titan's atmosphere. Icarus 161, 474–485.

Lellouch, E., 1990. Atmospheric models of Titan and Triton. Ann. Geophys. 8, 653–660.

Lepp, S., Dalgarno, A., 1988. Heating of interstellar gas by large molecules or small grains. Astrophys. J. 335, 769–773.

McKay, C.P., Pollack, J.B., Courtin, R., 1989. The thermal structure of Titan's atmosphere. Icarus 80, 23–53.

Ricca, A., Bauschlicher, C., Bakes, E.L.O., 2001. A computational study of the mechanisms for the incorporation of a nitrogen atom into polycyclic aromatic hydrocarbons in the Titan haze. Icarus 154, 516–521.

Sagan, C., Thompson, W.R., 1984. Production and condensation of organic gases in the atmosphere of Titan. Icarus 59, 133–161.

Sagan, C., Khare, B.N., Thompson, W.R., McDonald, G.D., M.R., Wing, Bafa, J.L. Dinh, T., Arakawa, E.T., 1993. Polycyclic aromatic hydrocarbons in the atmospheres of Titan and Jupiter. Astrophys. J. 414, 399–405.

Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J., 1994. *Ab initio* calculations of vibrational absorption and circular dichroism spectra using density functional force fields. J. Phys. Chem. 98, 11623–11627.

Sugai, H., Yoshida, S., Toyoda, H., 1989. Behavior of neutral hydrogen on substratesurfaces. Appl. Phys. Lett. 54, 1412–1422.

Toublanc, D., Parisot, J.P., Brillet, J., Gautier, D., Raulin, F., McKay, C.P., 1995. Photochemical modeling of Titan's atmosphere. Icarus 113, 2–26.

Yung Y.L., DeMore, William B., 1999. Photochemistry of Planetary Atmospheres. Oxford Univ. Press, Oxford.

Yung, Y.L., Allen, M., Pinto, J.P., 1984. Photochemistry of the atmosphere of Titan: comparison between model and observations. Astrophys. J. Suppl. 55, 465–506.