

The role of organic haze in Titan's atmospheric chemistry II. Effect of heterogeneous reaction to the hydrogen budget and chemical composition of the atmosphere

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Abstract

One of the key components controlling the chemical composition and climatology of Titan's atmosphere is the removal of reactive atomic hydrogen from the atmosphere. A proposed process of the removal of atomic hydrogen is the heterogeneous reaction with organic aerosol. In this study, we investigate the effect of heterogeneous reactions in Titan's atmospheric chemistry using new measurements of the heterogeneous reaction rate [Sekine, Y., Imanaka, H., Matsui, T., Khare, B.N., Bakes, E.L.O., McKay, C.P., Sugita, S., 2008. *Icarus* 194, 186–200] in a one-dimensional photochemical model. Our results indicate that 60–75% of the atomic hydrogen in the stratosphere and mesosphere are consumed by the heterogeneous reactions. This result implies that the heterogeneous reactions on the aerosol surface may predominantly remove atomic hydrogen in Titan's stratosphere and mesosphere. The results of our calculation also indicate that a low concentration of atomic hydrogen enhances the concentrations of unsaturated complex organics, such as C₄H₂ and phenyl radical, by more than two orders in magnitude around 400 km in altitude. Such an increase in unsaturated species may induce efficient haze production in Titan's mesosphere and upper stratosphere. These results imply a positive feedback mechanism in haze production in Titan's atmosphere. The increase in haze production would affect the chemical composition of the atmosphere, which might induce further haze production. Such a positive feedback could tend to dampen the loss and supply cycles of CH₄ due to an episodic CH₄ release into Titan's atmosphere.

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1. Introduction

The presence of organic haze layers in Titan's atmosphere has been revealed by the Voyager and Cassini spacecrafts (Smith et al., 1981; Porco et al., 2005). The main haze layer

is at 100–300 km in altitude, and several detached haze layers are present above the main layer up to several hundreds kilometers. Titan's thick haze has been suggested to be one of the most important factors controlling the composition, climatology, and evolution of the atmosphere (e.g., McKay et al., 1989, 1991, 1999; Lorenz et al., 1999). Despite such importance, it is not fully understood what detailed mechanisms control the haze production in Titan's atmosphere.

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According to previous studies of Titan's atmospheric chemistry, the production of haze might be influenced by the hydrogen chemistry on Titan, especially the fate of highly reactive atomic hydrogen formed by photochemical reactions in the stratosphere and mesosphere (Bakes et al., 2003; Lebonnois et al., 2003; Imanaka, 2004). The haze is considered to be produced by polymerization of unsaturated gas species in Titan's atmosphere, such as polycyclic aromatic compounds, aliphatic polymers, and nitriles (Sagan et al., 1993; Clarke and Ferris, 1997; Coll et al., 1999; Ricca et al., 2001; Lebonnois et al., 2002; Khare et al., 2002; Wilson and Atreya, 2003; Imanaka et al., 2004). If the concentration of atomic hydrogen is large, these unsaturated gas species might react with atomic hydrogen to form saturated gas species, and the production efficiency of organic haze would be reduced. Thus, the efficient removal of atomic hydrogen is an essential process to maintain the current hazy atmosphere on Titan.

Yung et al. (1984) suggested two possible pathways to remove atomic hydrogen efficiently from Titan's atmosphere through conversion to inert molecular hydrogen. One is H₂ recombination catalytic schemes involving gaseous C₄H₂ and C₂H₂. Yung et al. (1984) suggested that almost all of the atomic hydrogen produced below 600 km is effectively scavenged by these recombination processes. However, subsequent studies (Toublanc et al., 1995; Lebonnois et al., 2003) found that the catalytic schemes had little influence on the atmospheric abundance of C₂ and C₃ hydrocarbons in their photochemical models. Thus, it is still uncertain whether the C₄H₂ and C₂H₂ catalytic schemes are responsible for the removal of atomic hydrogen in Titan's mesosphere and stratosphere.

Another proposed pathway to convert atomic to molecular hydrogen is heterogeneous reaction on the surface of organic aerosols (Yung et al., 1984; Courtin et al., 1991; Bakes et al., 2003; Lebonnois et al., 2003). In this heterogeneous reaction, H atom in gas phase may react with another H contained in aerosol to form H₂ molecule (Bakes et al., 2003). Using the Prompt Reaction Model (PRM), developed by Duley (1996), Lebonnois et al. (2003) indicated that this H recombination process had a major influence on the atomic hydrogen distribution at 200–500 km in altitude. Consequently, this hydrogen budget strongly affects the concentration of several higher hydrocarbons, such as C₄H₂ and C₆H₆, around the mesosphere and stratosphere. However, the PRM has a large uncertainty in the H₂ recombination rate in Titan's atmosphere, because the PRM is based on the laboratory data of hydrogenated amorphous carbon (Sugai et al., 1989) conducted at room temperature—substantially different from the low temperature conditions in Titan's atmosphere.

Recently, Sekine et al. conducted laboratory experiments to measure the reaction probabilities of heterogeneous reactions of atomic deuterium with Titan aerosol analog, termed Titan tholin, at the surface temperature of tholin ranging from 160 to 310 K (Sekine et al., 2008) (Paper I). According to Sekine et al. (2008), the heterogeneous reactions are mainly composed of (1) hydrogenation (addition of D atom into Titan tholin) and (2) HD recombination (abstraction of H from Titan tholin to form HD molecule). The reaction probability of HD recombina-

tion obtained in Sekine et al. (2008) are about 10 times larger than that predicted by the PRM under the conditions of Titan's stratosphere and mesosphere (i.e., $T = 160\text{--}180$ K). This experimental result implies that the heterogeneous reactions may become an important H removal process in Titan's mesosphere and stratosphere. However, it is unclear how the reaction probabilities obtained by the recent laboratory experiments can influence the fate of atomic hydrogen and chemical composition of Titan's mesosphere and stratosphere.

In this study, we conduct a sensitivity study in order to assess the role of the heterogeneous reactions in Titan's atmospheric chemistry by incorporating the reaction probabilities obtained in Sekine et al. (2008) into a one-dimensional photochemical model. Our goal is to evaluate the effects of the heterogeneous reactions on the hydrogen budget and chemical composition of Titan's atmosphere. We determine the dominant process for the removal of H atoms in Titan's stratosphere and mesosphere. Then, we investigate the effect of the heterogeneous reactions on the chemical composition of the atmosphere. In Section 2, we describe our photochemical model. The calculation results of this model are summarized in Section 3. In Section 4, we discuss some consequences of these results on the production of haze.

2. Description of the model

2.1. Photochemical model

The one-dimensional photochemical model used in this study is similar to the one used in Lebonnois (2005), which has been updated from Toublanc et al. (1995) and Lebonnois et al. (2003). The results obtained by the 1-D photochemical model are global, annual average of profile of chemical species in Titan's atmosphere, and therefore may best represent equatorial conditions. Our reference set of chemical reactions were shown in Lebonnois et al. (2001) and Lebonnois (2005). We briefly describe this model here, and more details may be found in Supplementary online material and the previously published papers (Toublanc et al., 1995; Lebonnois and Toublanc, 1999; Lebonnois et al., 2001, 2003; Lebonnois, 2005).

In order to test the sensitivity to the heterogeneous reactions, we fix the vertical eddy diffusion coefficient to be the same as that used in the gas-phase photochemical model of Lebonnois (2005). Thus, the calculated results for the abundances of chemical compounds may no longer show good agreement with the observations when incorporating the heterogeneous reactions in the model. However, this disagreement is not problematic since the goal of this study is to estimate the effect of the heterogeneous reactions in the hydrogen budget and chemical composition of Titan's atmosphere. It must be kept in mind that many aspects of the photochemical models are sources of uncertainties on the modeled abundances, and it is the case for this model also (Hebrard et al., 2007). However, we assume that this does not affect significantly the goal of the present study.

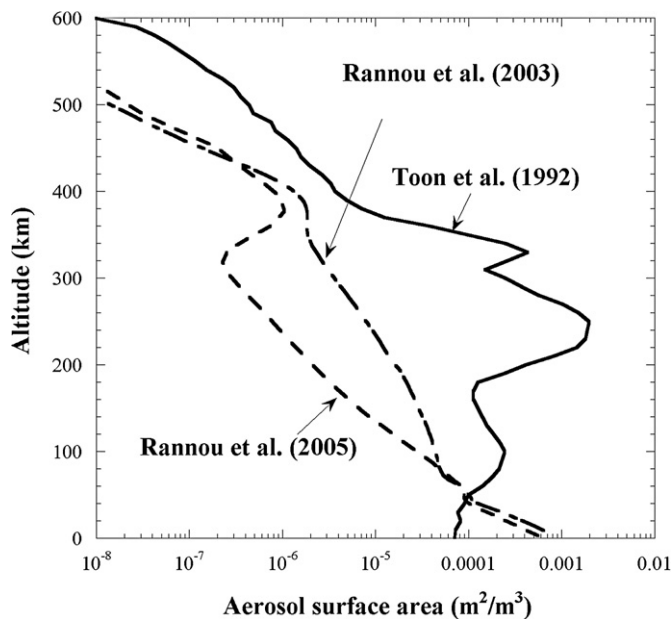


Fig. 1. Vertical profiles of aerosol surface area per atmospheric volume (m^2/m^3) provided by Toon et al. (1992), Rannou et al. (2003), and Rannou et al. (2005). For Rannou et al. (2005), we use the aerosol profile at the equator.

2.2. Heterogeneous reactions

It is noted that we assume a static aerosol distribution in the calculations. This means that the distribution and number density of aerosol does not change during the calculations, even if the production of “soot” (hydrocarbon compounds with more than 5 heavy atoms (C, N) except C_6H_5 (phenyl radical), C_6H_6 (benzene), and C_4N_2) in the atmosphere is increased by the incorporation of heterogeneous reactions into the model.

Since the reaction probabilities of the heterogeneous reactions obtained in Sekine et al. (2008) are normalized by the surface area of the tholin formed in the experiment, the H removal rates through the heterogeneous reactions in Titan’s atmosphere are given by the product of between these reaction probabilities and the surface area of Titan’s aerosol proposed in the microphysical models. We use three aerosol distributions proposed by previous microphysical models (Toon et al., 1992; Rannou et al., 2003, 2005). Fig. 1 shows the comparison of the aerosol surface area per atmospheric volume (m^2/m^3) given by the models as a function of altitude. In Sections 3.1 and 3.2, we investigate the effects of heterogeneous reaction on the atmospheric composition and hydrogen budget of Titan’s atmosphere using the aerosol distribution given by Toon et al. (1992). In Section 3.3, we compare the results using aerosol distribution by Toon et al. (1992) with those by Rannou et al. (2003) and Rannou et al. (2005) in order to investigate the sensitivity to aerosol distribution.

Table 1 summarizes the reaction probabilities of heterogeneous reactions used in this study. We use Eq. (6) in Sekine et al. (2008),

$$\eta_{\text{hydro}} = 2.08 \times \exp(-1000/T),$$

Table 1
Reaction probabilities of the hydrogenation and H_2 recombination used in this study

	Hydrogenation	H_2 recombination
Case 1	$2.08 \times \exp(-1000/T)$	$0.0019 \times \exp(-300/T)$
Case 2	$0.0019 \times \exp(-300/T)$	$0.0019 \times \exp(-300/T)$
Case 3	$0.25 \times \exp(-1700/T)$	$0.25 \times \exp(-1700/T)$
Case 4	0	0

Note. Case 1: the surface of aerosol is not saturated with hydrogen.

Case 2: the surface of aerosol is fully saturated with hydrogen.

Case 3: the prompt reaction model (PRM) in Bakes et al. (2003) and Lebonnois et al. (2003).

Case 4: gas-phase reaction only.

for the reaction probability of hydrogenation η_{hydro} and use Eq. (10) in Sekine et al. (2008),

$$\eta_{\text{abst}} = 0.0019 \times \exp(-300/T),$$

for the reaction probability of H_2 recombination η_{abst} , respectively. Since hydrogenation proceeds more efficiently than H_2 recombination (abstraction of H), the surface of the aerosols may be gradually saturated with hydrogen during their fall through the atmosphere. According to Sekine et al. (2008), this hydrogenation stops when the hydrogenated layer at the top surface of aerosol reaches to the penetration depth of H atom (i.e., $\sim 1\text{--}2$ nm). When the surface is not saturated with hydrogen, the hydrogenation proceeds at the reaction rate given by Eq. (6) in Sekine et al. (2008). If the surface is fully hydrogenated with hydrogen, the reaction rate of hydrogenation is limited by that of H_2 recombination, and therefore the hydrogenation proceeds at the rate of H_2 recombination (Eq. (10) in Sekine et al., 2008).

Since it is unclear when and where the surface of an aerosol becomes saturated with hydrogen in the actual Titan’s atmosphere, we chose 4 variations for the reaction probabilities of heterogeneous reactions. In case 1, we assume that the surface of an aerosol is not fully saturated with hydrogen in the atmosphere. Thus, both the hydrogenation and H_2 recombination proceed at the reaction probabilities given by Eqs. (6) and (10) in Sekine et al. (2008), respectively. In case 2, we assume that the surface of an aerosol is fully saturated with hydrogen. In this case, the both reactions proceed at the reaction probability given by Eq. (10). In the actual Titan’s atmosphere, the situation is considered to be intermediate between these two extreme cases. In order to compare with the previous theoretical models, we also introduce the H_2 recombination rate given by the PRM (Bakes et al., 2003; Lebonnois et al., 2003) (case 3). In case 4, we conduct the calculations without the heterogeneous process (gas-phase reactions only) to understand the effect of the heterogeneous reactions on the chemical composition of the atmosphere.

3. Results and discussion

3.1. Chemical composition of the atmosphere

3.1.1. Atomic hydrogen

Fig. 2 shows the altitude profile of H atoms mole fractions for cases 1 to 4. The major consequence of the heterogeneous

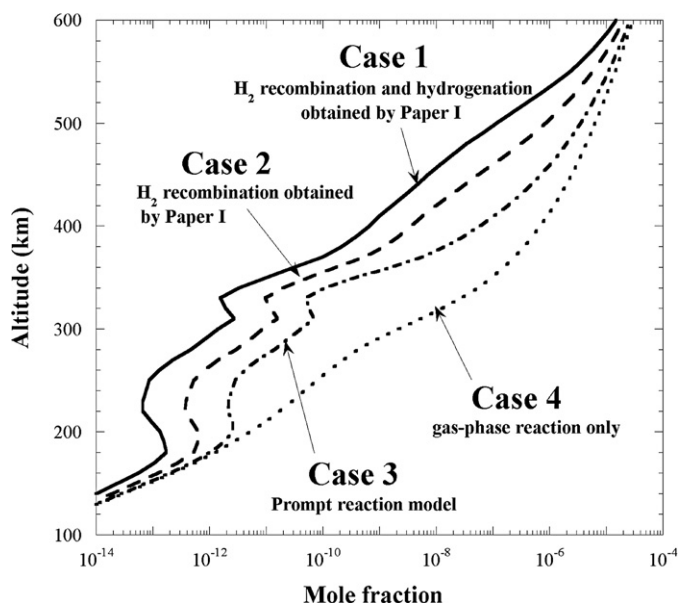


Fig. 2. Vertical profile of atomic hydrogen mole fraction: case 1 (solid line) is obtained when the aerosol surface is not saturated with hydrogen, case 2 (broken line) is obtained when the surface is fully saturated with hydrogen, case 3 (dash-dot line) is obtained when we use the prompt reaction model (PRM) by Bakes et al. (2003) and Lebonnois et al. (2003), and case 4 (dotted line) is obtained without the heterogeneous reactions.

reactions is the reduction of H atoms abundance in the region of 200–500 km in altitude. In this region, it is noted that the H mole fractions for cases 1 and 2 (with the heterogeneous reactions) are remarkably reduced (nearly 10^{-1} – 10^{-4}) compared to case 4 (without the heterogeneous reactions). This low concentration of H atom affects the abundances of several hydrocarbons and nitriles (see below in this section). This figure also indicates that the concentration of H atom is higher in case 3 (the PRM) than in cases 1 and 2 by factors of 10 to 50 in the region of 200–500 km. This is because the PRM underestimates the H_2 recombination rate via the heterogeneous reactions in the temperature range of 160–180 K.

3.1.2. Aliphatic hydrocarbons

Fig. 3 shows the mole fraction profiles of C_2 hydrocarbons in the atmosphere. This result indicates that the atmospheric abundances of C_2 species are not sensitive to the presence or absence of the heterogeneous reactions. This result is consistent with that of Lebonnois et al. (2003). This may be because the loss of these C_2 species is not mainly controlled by the reactions with atomic hydrogen, but by photodissociation.

However, for C_3 species, the mole fraction profiles are influenced by a factor of 1.5 to 5 in the region of 100–500 km in altitude as shown in Fig. 4a. The mole fractions of hydrogen-rich C_3 hydrocarbons, such as C_3H_6 and C_3H_8 , are reduced when taking into account the heterogeneous reactions, while the profile of unsaturated hydrocarbon, such as CH_3CCH , is increased. Fig. 4b also shows that the mole fraction of C_3H_2 radical is increased about 10 – 10^3 times around 200–500 km by the heterogeneous reactions. This remarkable variation in the concentrations of C_3 hydrocarbons, dependent in both sign and magnitude on the C/H ratio, is due to the effect of the hetero-

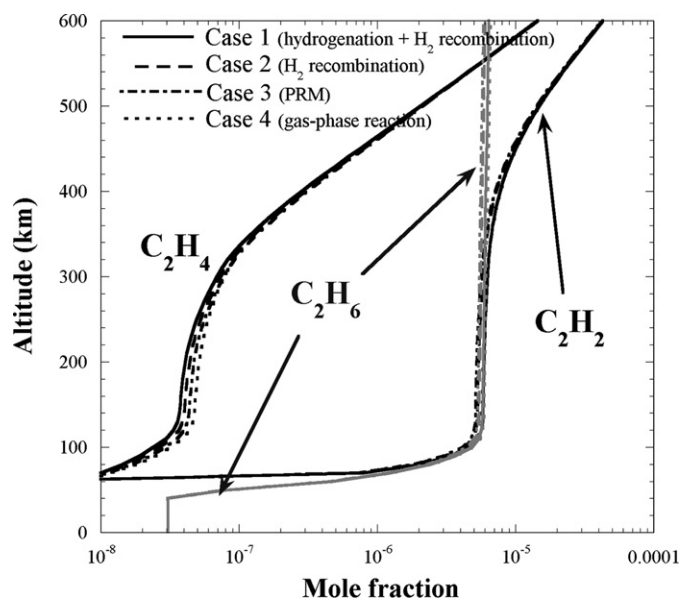


Fig. 3. Vertical profiles of C_2 hydrocarbons (C_2H_2 (black lines), C_2H_4 (black lines) and C_2H_6 (gray lines)) with (cases 1, 2, and 3 are the same as Fig. 2) and without heterogeneous reactions (case 4 is the same as Fig. 2).

geneous reactions, which remove atomic hydrogen efficiently. One of the main pathways to produce hydrogen-rich C_3 hydrocarbons is the reaction of hydrogen-poor C_3 hydrocarbons and radicals with atomic hydrogen. Thus, lower concentrations of H induced by heterogeneous reactions reduces the production of hydrogen-rich C_3 hydrocarbons, such as C_3H_6 , and increases the production of hydrogen-poor C_3 hydrocarbons and radicals, such as CH_3CCH and C_3H_2 .

For C_4 species, the influence of heterogeneous reactions on the mole fraction profiles becomes much larger than those of C_3 hydrocarbons (Fig. 5). The vertical profiles of C_4 hydrocarbons are presented in Fig. 5a. The mole fraction of C_4H_2 around 400 km in altitude is drastically increased (by a factor of 10^2 to 10^3) when taking into account heterogeneous reactions. This result is explained as follows: The heterogeneous reactions enhance the concentrations of hydrogen-poor C_3 radicals, such as C_3H_2 , in the atmosphere (Fig. 4b). Under the condition of lower H concentration, these radicals are consumed by the reaction with C_2H_2 forming C_4H_2 (see Table S1 in Supplementary online material). These reactions maintain the high concentration of C_4H_2 in the atmosphere. On the other hand, the profiles of hydrogen-rich C_4 species, such as C_4H_{10} , are reduced by a factor of 3–5 in this region. Furthermore, the increase in the mole fraction of C_4H_2 induces the increase in the concentrations of hydrogen-poor C_4 radicals, such as C_4H_3 and C_4H , in the atmosphere, since these radicals are formed by the photochemical reactions of C_4H_2 . Fig. 5b shows the mole fraction of C_4H_3 radical in the atmosphere. The concentration of C_4H_3 is increased more than 10^2 times around 400 km by the heterogeneous reactions.

Comparison of the results of C_2 , C_3 , and C_4 species suggests that the higher-molecular-weight hydrocarbons are more sensitive to the introduction of the heterogeneous reactions than lower ones. Photolysis of C_4H_2 results in the productions of

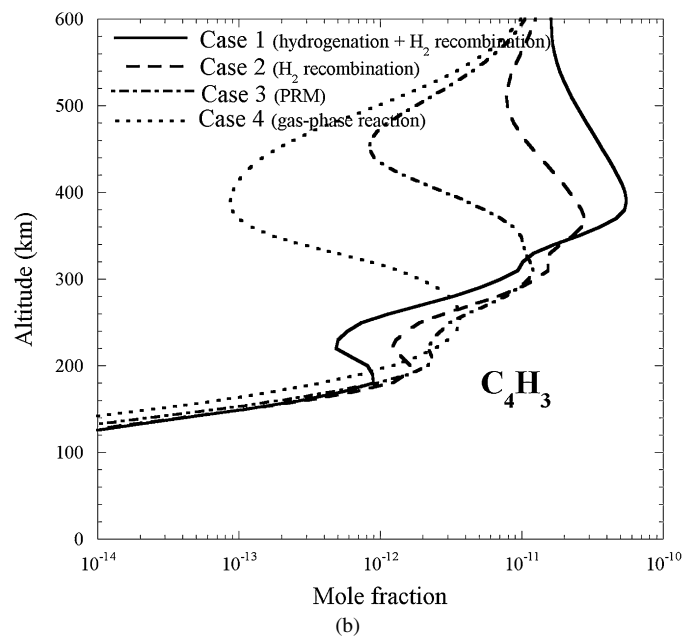
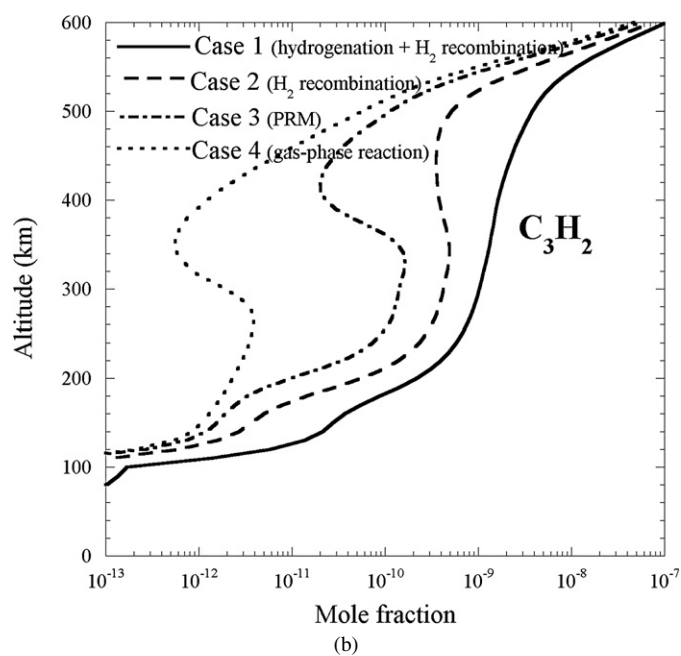
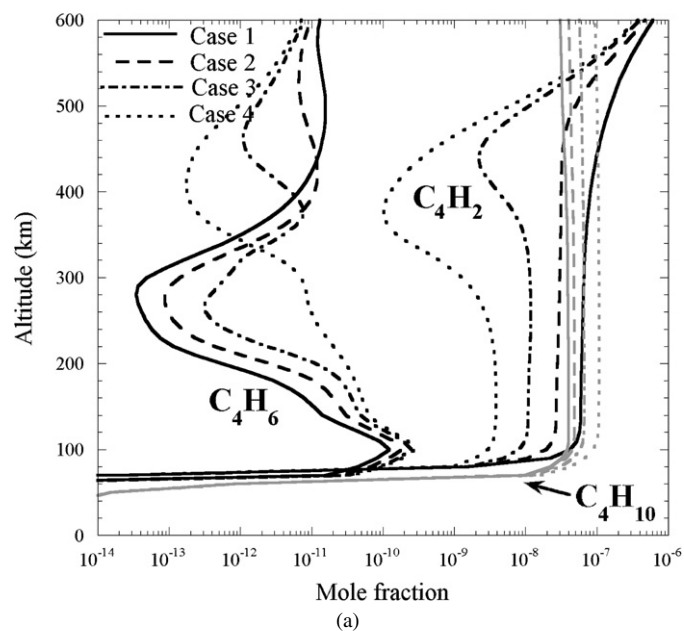
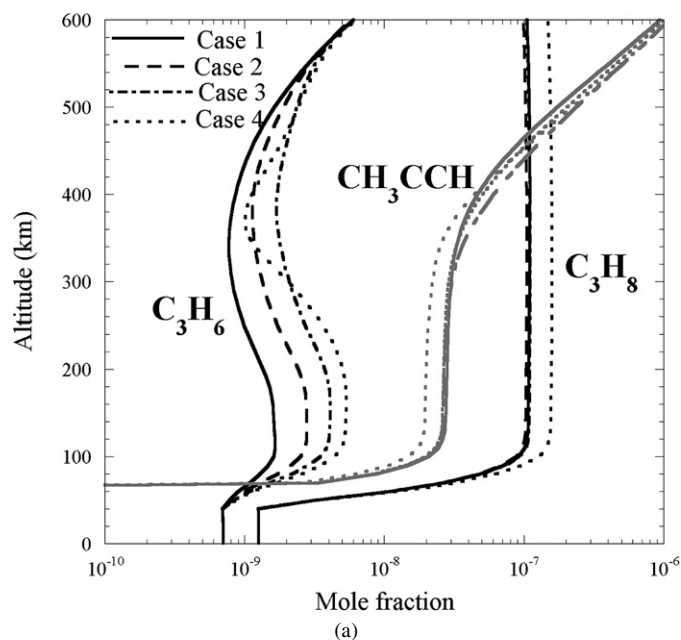


Fig. 4. Vertical profiles of C_3 hydrocarbons (a) CH_3CCH (gray lines), C_3H_6 (black lines), and C_3H_8 (black lines) molecules and (b) C_3H_2 (black lines) radical ($HC\equiv C-C(\cdot)H$) with (cases 1, 2, and 3 are the same as Fig. 2) and without heterogeneous reactions (case 4 is the same as Fig. 2).

Fig. 5. Vertical profiles of C_4 hydrocarbons (a) C_4H_2 (black lines), C_4H_6 (black lines) and C_4H_{10} (gray lines) and (b) C_4H_3 (black lines) radical with (cases 1, 2, and 3 are the same as Fig. 2) and without heterogeneous reactions (case 4 is the same as Fig. 2).

C_4H radicals and metastable excited state $C_4H_2^*$ (Glicker and Okabe, 1987). Both C_4H and $C_4H_2^*$ easily react with C_2H_2 to form C_6H_2 (Yung et al., 1984; Zwier and Allen, 1996) (see Table S1 in Supplementary online material). Larger polyynes ($C_{2n+2}H_2$), such as C_8H_2 , could be also produced by insert reactions of C_2H and C_4H into C_6H_2 and C_4H_2 . The C_4H_3 radical is also proposed as a source of aliphatic hydrocarbon polymers (Lebonnois et al., 2002). The enhancement of C_4H_2 yields higher C_4H_3 abundances (Fig. 5b), and therefore production of these polymers should also increase. In this study, we do not compute chemical compounds with more than five heavy

atoms (C, N) (except benzene, phenyl radical, and C_4N_2). However, the high concentration of C_4H_2 suggests that the presence of heterogeneous reactions remarkably promotes the production of aliphatic polymers in Titan's mesosphere and stratosphere.

3.1.3. Nitriles

Fig. 6 shows the mole fraction profiles of nitriles (HCN , HC_3N , and C_2N_2). This figure shows that the concentrations of HCN and C_2N_2 are reduced by introducing the heterogeneous reactions. One explanation for the reduction of HCN and C_2N_2 is that these nitriles are converted into complex nitrogen-containing molecules. High concentration of C_4H_2 in-

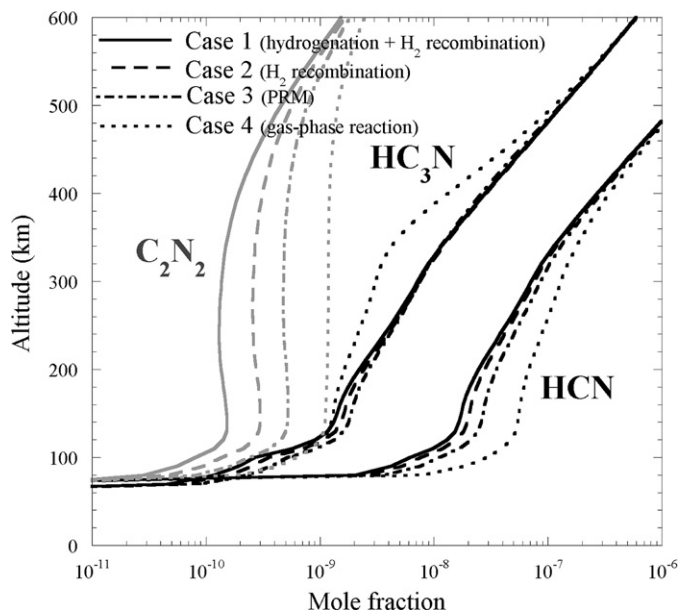


Fig. 6. Vertical profiles of nitriles (HCN (black lines), HC_3N (black lines), and C_2N_2 (gray lines)) with (cases 1, 2, and 3 are the same as Fig. 2) and without heterogeneous reactions (case 4 is the same as Fig. 2).

duces high concentrations of C_4H and C_4H_3 radicals by photochemical reactions. These radicals easily react with nitriles to form soot in our calculation scheme. Another possible explanation is that the recombination of CN and H to HCN is inhibited under low H atom concentration. The concentration of HCN is maintained mainly by the balance between photodissociation of HCN ($\text{HCN} \rightarrow \text{CN} + \text{H}$) and the recombination of CN and H ($\text{CN} + \text{H} \rightarrow \text{HCN}$). When H atoms are efficiently removed by the heterogeneous reactions, CN concentration becomes high in the atmosphere. More of CN may also form other nitriles, such as HC_3N , by the reactions with CH_4 and C_2H_2 , and therefore less return to HCN. Since HC_3N is mainly produced by the reaction of CN with C_2H_2 , the high concentration of CN maintained by the heterogeneous reactions increases HC_3N concentration around 200–400 km in altitude (Fig. 6). In Fig. 6, there is almost no difference in HC_3N concentrations between cases 1, 2 and 3. This may be because, even in case 3, the H removal rate becomes high enough to prevent the efficient recombination of HCN. In this case, the CN concentration reaches to a constant value determined by the rate of HCN photolysis, and therefore the HC_3N concentration becomes close in cases 1, 2, and 3. Lower C_2N_2 concentration in the atmosphere also may be induced by lower HCN concentration because C_2N_2 is mainly produced by the reaction of HCN with CN in our calculation scheme.

3.1.4. Aromatic hydrocarbons

The mole fraction profiles of C_6H_5 (phenyl radical) and C_6H_6 (benzene) are shown in Fig. 7. The abundance of benzene decreases by approximately one order of magnitude around 200 km in altitude, while that of phenyl radical increases (more than 10^2) around 400 km when taking into account the heterogeneous reactions. This result may be explained as follows: In Titan's stratosphere and mesosphere, benzene is photodisso-

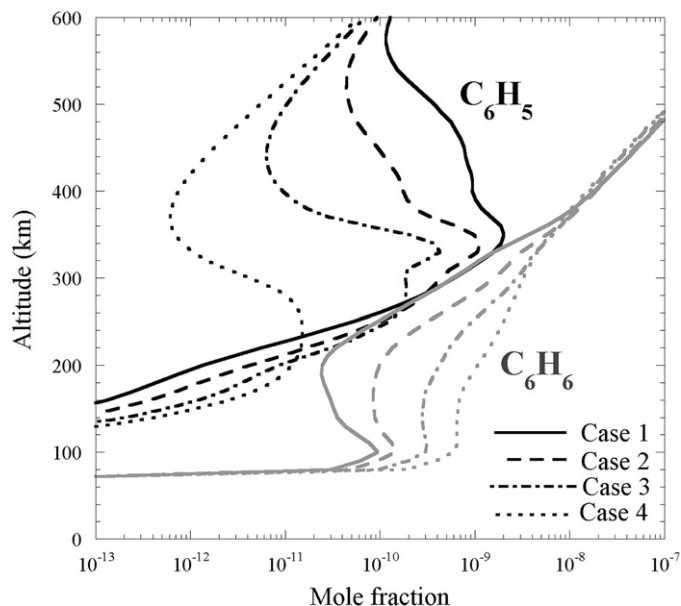


Fig. 7. Vertical profiles of aromatic hydrocarbons (C_6H_6 (benzene; gray lines) and C_6H_5 (phenyl; black lines)) with (cases 1, 2, and 3 are the same as Fig. 2) and without heterogeneous reactions (case 4 is the same as Fig. 2).

ciated and forms phenyl and hydrogen ($\text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 + \text{H}$) (Suto et al., 1992). In our reaction scheme, the phenyl radical is consumed by two reactions (Lebonnois, 2005 and Table S1 in Supplementary online material). One is the recombination to benzene by the reaction with H ($\text{C}_6\text{H}_5 + \text{H} \rightarrow \text{C}_6\text{H}_6$), and the other is the reaction with C_2H_2 to form polycyclic aromatic hydrocarbons (PAHs) ($\text{C}_6\text{H}_5 + \text{C}_2\text{H}_2 \rightarrow \text{PAHs}$ (soot)). Under the low H atom concentration induced by the heterogeneous reactions, the efficiency of recycling back to benzene may be decreased.

The phenyl radical is considered to be an important precursor for the syntheses of PAHs and nitrogen-containing polycyclic aromatic compounds (N-PACs) in Titan's atmosphere (Bauschlicher and Ricca, 2001; Ricca et al., 2001; Lebonnois et al., 2002; Wilson and Atreya, 2003). According to quantum chemical calculations, the propagation of PAHs formation is promoted through the attachment of C_2H_2 onto the phenyl radical (Bauschlicher and Ricca, 2001). The reactions of the phenyl radical with HCN and HC_3N also promote the formation of N-PACs (Ricca et al., 2001). We do not treat the formation of PAHs and N-PACs in this study. However, the high concentration of phenyl radical implies the efficient formation of PAHs and N-PACs around 300–500 km in altitude when considering heterogeneous reactions.

3.2. Hydrogen budget of Titan's atmosphere

3.2.1. Atomic hydrogen loss

The altitude profiles of the loss rate of H atom and production rate of H_2 molecule in the atmosphere are shown in Fig. 8. Figs. 8a and 8b indicate that about 70% of H atoms are consumed by the heterogeneous reactions throughout 100–600 km in altitude. When taking into account the heterogeneous reactions, the upper mesosphere (around 500–600 km

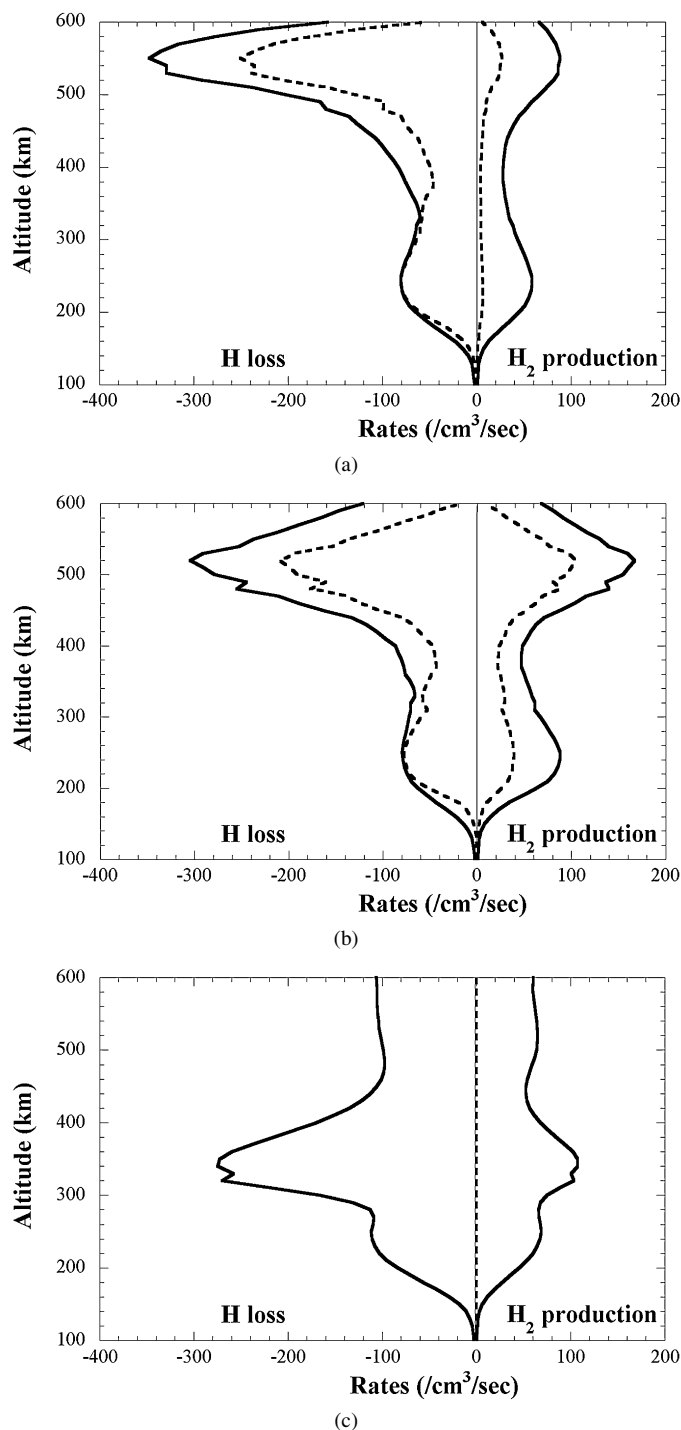


Fig. 8. Vertical profiles of the total H_2 production rate and H loss rate, (a) when the surface of aerosol is not saturated with hydrogen (case 1), (b) when the surface is completely saturated with hydrogen (case 2), and (c) when the heterogeneous reactions are not taken into account (case 4). The vertical profiles of the production and loss rates by the heterogeneous reactions are also plotted in broken lines.

in altitude) becomes the region where the H atom removal occurs most efficiently. This is because the H atoms formed in the thermosphere (>600 km) are transported downward to the mesosphere by diffusion, where the H removal takes place efficiently, and react with aerosols (Lebonnois et al., 2003). When

the heterogeneous reactions are not taken into account (Fig. 8c), the H atoms are removed from the atmosphere only through both the catalytic schemes of C_2H_2 and C_4H_2 and the reactions with unsaturated gas species to form saturated ones. In this case, the loss of H may take place most efficiently at lower altitude (~ 300 – 400 km) than the results of cases 1 and 2 because the catalytic schemes of C_2H_2 and C_4H_2 proceed via three-body reaction, which proceeds efficiently at higher atmospheric pressures. Comparing the results with and without the heterogeneous reactions, the heterogeneous reactions appear as the predominant process to remove H atoms in the stratosphere and mesosphere rather than the catalytic schemes of C_2H_2 and C_4H_2 , which have been used as a major H removal process in previous photochemical models (Yung et al., 1984; Lara et al., 1996; Wilson and Atreya, 2004).

3.2.2. Molecular hydrogen production

The profile and magnitude of the H_2 production rate are influenced not only by the presence or absence of the heterogeneous reactions but also by whether or not the surface of aerosol is saturated with hydrogen (Fig. 8). When the surface of aerosols is not saturated with hydrogen (Fig. 8a; case 1), then hydrogenation is the main reaction on the surface of aerosols. In case 1, the total H_2 production in the mesosphere and stratosphere is reduced by approximately 28% from the result without the heterogeneous reactions (Fig. 8c; case 4), because the H atoms are efficiently included into the aerosols. When the aerosol surfaces are saturated with hydrogen (Fig. 8b; case 2), the rate of the hydrogenation is limited by the H_2 recombination. In this case, the aerosols act only as a heterogeneous catalyst for the H_2 recombination. Therefore, the presence of aerosols accelerates the formation of H_2 in the stratosphere and mesosphere. The total H_2 production in the mesosphere and stratosphere is increased by about 25% from the result without the heterogeneous reactions.

Although the production rate of H_2 in the stratosphere and mesosphere is influenced by the introduction of the heterogeneous reactions, both the mole fraction of H_2 and the H_2 escape flux at the top of atmosphere are not influenced significantly by introducing the heterogeneous reactions. This is because H_2 is also formed in the thermosphere by photochemical reactions for CH_4 and C_2H_4 , such as $\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}_2$. The H_2 produced in the thermosphere contributes to approximately 70% to the total H_2 production in Titan's atmosphere in our model, reducing the impact of the change in H_2 production in the stratosphere and mesosphere on the total upward H_2 flux at the top of the atmosphere and on the overall H_2 abundance (which is of the order of 0.17% in the stratosphere). The escape flux for H_2 is 9.6×10^9 , 1.11×10^{10} , and $1.04 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ (referred to the surface) for cases 1, 2, and 4 respectively, which is in good agreement with the recent INMS/Cassini results, reporting an escape flux of $1.2 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ (Yelle et al., 2006). The H_2 abundance at 1300 km obtained by our model is about 30% higher than that of observational data (Yelle et al., 2006), since we only take into account Jeans escape, while Yelle et al. (2006) show that Jeans escape alone is not enough to have consistent H_2 escape flux.

3.3. Aerosol distribution

In the above sections, we assume that aerosol particles are spherical with radius of the order of 0.1 μm and use the aerosol distribution by Toon et al. (1992) (Fig. 1). However, some microphysical and radiative-transfer models of Titan's atmosphere have proposed different aerosol distributions in which aerosol particles are fractal aggregates of small monomers (e.g., Cabane et al., 1993; Rannou et al., 1993, 1999, 2003, 2005). Since the H removal rate by the heterogeneous reactions in Titan's atmosphere is proportional to the surface area of the aerosols, the shape and distribution of the aerosol particles may be important factors to determine the impact of the heterogeneous reactions. In this section, we briefly discuss the effect of the aerosol distribution to the chemical composition of Titan's stratosphere and mesosphere.

Here, we introduce two other aerosol distributions proposed by recent microphysical models incorporating fractal aggregates (Rannou et al., 2003, 2005). In the first one (Rannou et al., 2003), one-dimensional microphysical model is used to calculate the aggregation of monomers ($r_m = 0.066 \mu\text{m}$) and aerosol distribution in the atmosphere. In the other one (Rannou et al., 2005), the aerosol distribution and aggregation are calculated by a two-dimensional version of general circulation model (GCM) of Titan's atmosphere coupled with microphysical model. Both these models are successful at explaining the observed atmospheric features, such as Titan's geometric albedo. The vertical profiles of aerosol surface area provided by the models have been already shown in Fig. 1. Around 150–300 km in altitude, the surface areas of Rannou et al. (2003) and Rannou et al. (2005) are much smaller (1–3 orders of magnitude) than that of Toon et al. (1992). Around 400 km, however, those of Rannou et al. (2003, 2005) are only 3–5 times smaller than that of Toon et al. (1992).

Fig. 9 shows the mole fractions of C_4H_2 and C_6H_5 (phenyl radicals) using the reaction probabilities of the heterogeneous reactions for case 2 in Table 1. Around 100–200 km in altitude, the introduction of the heterogeneous reactions does not affect the mole fractions of C_4H_2 and C_6H_5 very much when using the aerosol distributions of Rannou et al. (2003, 2005). Around 300–450 km in altitude, however, these mole fractions are significantly increased by the introduction of the heterogeneous reactions with the aerosol distributions of Rannou et al. (2003, 2005), although the impact of the heterogeneous reaction is smaller than that using Toon et al. (1992). Fig. 10 shows the H atom loss and H_2 production profiles when using the aerosol distribution of Rannou et al. (2003, 2005). This figure indicates that the heterogeneous reactions are the dominant removal process of H atom around 350–450 km in altitude, while it is not below 200 km. Around 400 km, 60–75% of atomic hydrogen are consumed through the heterogeneous reactions.

These results suggest that, even using the aerosol distributions of Rannou et al. (2003, 2005), the heterogeneous reactions efficiently remove H atoms around 400 km and, therefore, enhance the abundance of complex unsaturated gas species around this altitude. In addition, these results may provide the lower limit of aerosol surface area to remove H atom efficiently by the

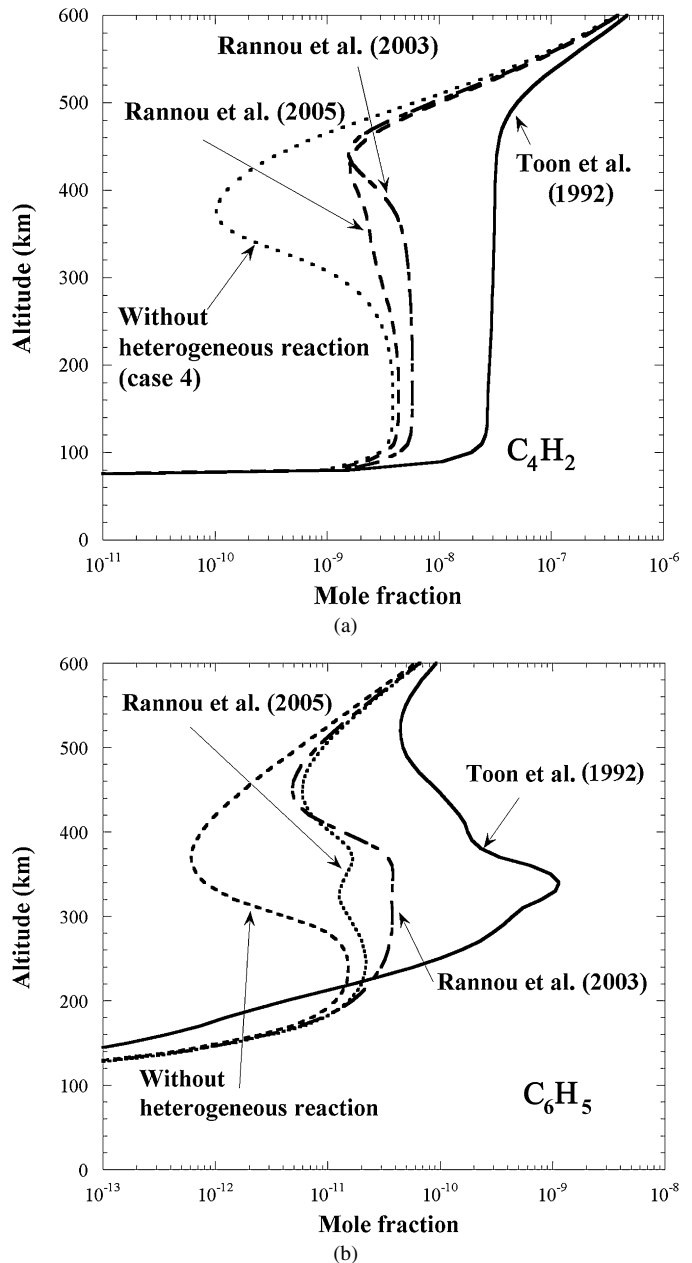


Fig. 9. Vertical profiles of (a) C_4H_2 and (b) C_6H_5 (phenyl radical) when using the surface area of aerosol by Toon et al. (1992), by Rannou et al. (2003), by Rannou et al. (2005), and without the heterogeneous reactions. The results are obtained with the reaction probabilities of the heterogeneous reactions for case 2 in Table 1.

heterogeneous reactions in the atmosphere. As described above, the aerosol surface areas of Rannou et al. (2003, 2005) around 150–300 km are 10^{-1} – 10^{-3} of that of Toon et al. (1992). Our results of the chemical composition (Fig. 9) and H loss rate (Fig. 10) around 100–200 km imply that, if the aerosol surface area in Titan's atmosphere is much smaller (i.e., 10^{-1} or less) than that of Toon et al. (1992), the heterogeneous reaction may not be an important sink for H atoms in the atmosphere. When the Cassini and Huygens observations will provide more detailed data on the shape and distribution of Titan's aerosol, the lower limit for the heterogeneous reactions may be useful

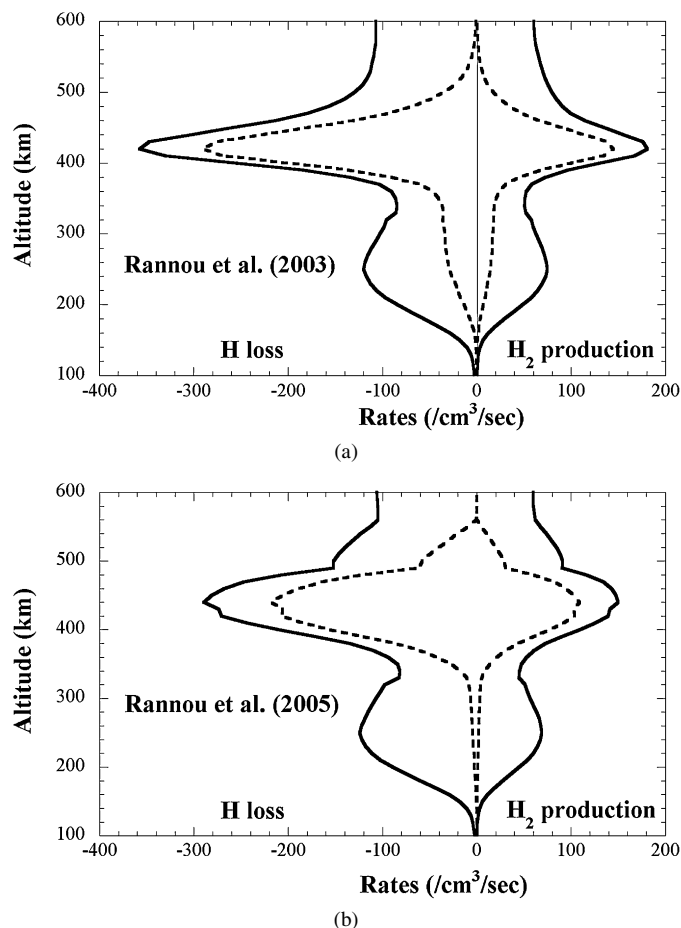


Fig. 10. Vertical profiles of the total H_2 production rate and H loss rate, (a) using the profile of aerosol surface area by Rannou et al. (2003), and (b) using that by Rannou et al. (2005). The results are obtained with the reaction probabilities of the heterogeneous reactions for case 2 in Table 1.

to consider the role of Titan's aerosol in the atmospheric chemistry.

4. Applications of the model

4.1. Haze production

Our results imply that the interactions between haze and atmosphere via hydrogen play a key role in maintaining the active organic synthesis in the present atmosphere of Titan. Fig. 11 shows a schematic diagram of the fate of atomic hydrogen in Titan's atmosphere when taking into account the effects of the heterogeneous reactions. According to our calculations, about 60–75% of the reactive atomic hydrogens are removed through the heterogeneous reactions around 400 km in altitude. In case 1, about 10% of the H atoms reacting with aerosols are converted into H_2 molecules (H_2 recombination). The H_2 molecules eventually escape from Titan's atmosphere because of Titan's low gravity. The other H atoms are captured into the aerosols (hydrogenation) and eventually deposit on the surface of Titan together with the aerosols.

The efficient removal of H atom by the haze reduces the conversion of unsaturated species into saturated ones and results

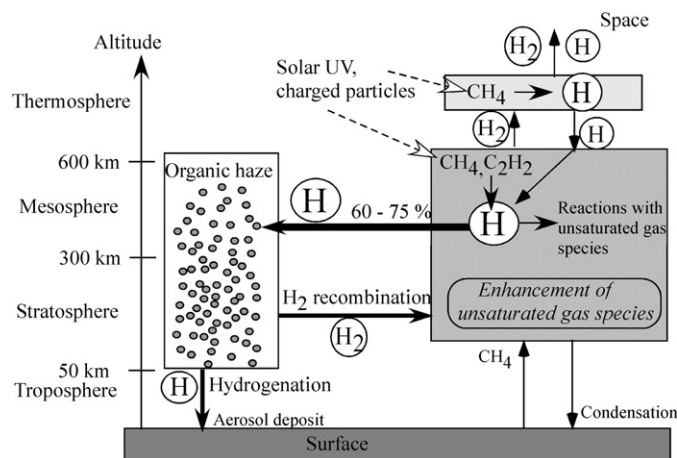


Fig. 11. Schematic diagram of the fate of atomic hydrogen in the atmosphere of Titan. The organic haze may act as a catalyst not only to remove reactive atomic hydrogen efficiently but also to enhance the concentrations of higher-molecular-weight unsaturated gas species in the stratosphere and mesosphere of Titan.

in a significantly enhancement of higher-molecular-weight unsaturated gas species. Our results show that the mole fractions of C_4H_2 and phenyl radical (C_6H_5) are enhanced more than 10^2 around 400 km by introducing the heterogeneous reactions (Figs. 5a and 7). This altitude corresponds to the aerosol formation region proposed by some microphysical models (e.g., Rannou et al., 1993, 1995, 2002). As described in Section 3.1, C_4H_2 and phenyl radical are considered to be converted into further larger aliphatic or aromatic polymers, although we do not treat these reactions in the reaction scheme. According to the previous laboratory and theoretical studies, those molecules are considered to be major building blocks of Titan's aerosol (e.g., Sagan et al., 1993; Khare et al., 2002; Lebonnois et al., 2002; Wilson and Atreya, 2003; Imanaka et al., 2004).

These enrichments of unsaturated molecules by the heterogeneous reactions might suggest that there is a positive feedback mechanism in the production of haze. If the production efficiency of haze is enhanced in the atmosphere, more of surface area of haze particles may induce efficient heterogeneous reactions. The lower H atom concentration induced by the efficient heterogeneous reactions would increase the concentration of unsaturated gas species in the upper atmosphere. The resulting increase in the precursor molecules of haze might lead to further production of haze in the upper atmosphere.

We speculate a possible effect of the positive feedback mechanism on the evolution and stability of Titan's atmosphere. The positive feedback implies that the production efficiency of haze in Titan's atmosphere may be very sensitive to the sudden CH_4 supply into the atmosphere and to the variation of energy fluxes of solar UV and charged particles into the atmosphere. For instance, according to the observations by Cassini/Huygens spacecraft (e.g., Waite et al., 2005; Niemann et al., 2005), one of the possible explanations for the present state of Titan is that current atmospheric CH_4 is replenished episodically from the interior by cryovolcanic activities (Loveday et al., 2001; Tobie et al., 2006). When CH_4 gas is released into the atmosphere episodically, the higher mole fraction of CH_4 might be expected to warm the surface through an enhanced green-

house effect. However the higher CH₄ would produce haze in the upper atmosphere. The increase in the haze production in the upper atmosphere would be a trigger for the positive feedback in the atmosphere. This means that an episodic release of CH₄ might accelerate haze production in the upper atmosphere resulting in thicker haze layer. The thicker haze layer in turn causes lowering surface temperature due to antigreenhouse effect of the haze (McKay et al., 1991). Thus, the positive feedback could be a driving force to make dense haze layers during an episodic CH₄ release which would dampen the temperature variations resulting from the CH₄ injection. Since we use a static aerosol distribution in our model, it is uncertain how the positive feedback mechanism works in Titan's atmosphere. The photochemical model in which the haze production is coupled with the atmospheric composition is a key to assess the role of the positive feedback mechanism in the evolution of Titan's atmosphere.

4.2. Cassini–Huygens mission

Our calculation result indicates that the C₄H₂ mole fraction around 400 km in altitude is very sensitive to the presence of heterogeneous reactions (Figs. 5a and 9). Thus, the observational data of C₄H₂ mole fraction in Titan's mesosphere may provide key information about the heterogeneous reactions in Titan's atmosphere. In a recent paper by Vinatier et al. (2007), the vertical profile of C₄H₂ at two latitudes in the stratosphere and mesosphere retrieved from Cassini CIRS spectra was shown in their Fig. 15. According to Vinatier et al. (2007), the C₄H₂ concentrations in 300–500 km in altitude at near the equator range around $\sim 10^{-8}$ in mixing ratio. On the other hand, Fig. 9 of this study shows that the C₄H₂ concentration in these altitudes is 10^{-9} – 10^{-10} without heterogeneous reactions, but it becomes $\sim 10^{-8}$ when considering heterogeneous reactions with the aerosol distributions by Rannou et al. (2003, 2005). This agreement implies that the heterogeneous reaction may play a key role for maintaining the concentration of C₄H₂ in Titan's atmosphere.

5. Summary

By introducing the reaction probabilities of the heterogeneous reactions obtained in Sekine et al. (2008) into a one-dimensional photochemical model, we evaluate the role of organic haze in the hydrogen budget and chemical composition of Titan's atmosphere. At the present time, a precise numerical simulation is difficult because the details of size and surface area of the aerosols are not clear. The processes of haze formation are not understood yet, so it is also difficult to estimate how the distribution of aerosol changes when the chemical composition of atmosphere changes. Despite such uncertainties in the model, our study allows us to draw the following conclusions:

- (1) The heterogeneous reactions play a key role in the removal of H atoms throughout the mesosphere and stratosphere of Titan, rather than the catalytic schemes of C₄H₂ and C₂H₂

which had been suggested as a main process in this removal in previous models. According to our calculation, about 60–75% of atomic hydrogens are consumed by the heterogeneous reactions in the mesosphere of Titan.

- (2) The H mole fraction in the stratosphere and mesosphere is reduced due to these heterogeneous reactions, and as a consequence the abundances of unsaturated higher-molecular-weight organics are significantly enhanced. For instance, introducing the heterogeneous reactions increases mole fractions of C₄H₂ and phenyl radical by more than two orders in magnitude around 400 km in altitude. These results imply that the heterogeneous reactions increase the production of aliphatic and aromatic polymers in Titan's atmosphere, therefore participating in the haze production cycle since those molecules are thought to be the source of organic aerosols.
- (3) These heterogeneous reactions suggest a positive feedback mechanism between haze production and atmospheric composition. If the haze production increases, atomic hydrogen in the stratosphere and mesosphere is removed more efficiently. This would yield enhancement of unsaturated organics in the atmosphere, and therefore further haze production. This effect might dampen cycles of haze production and temperature profiles associated with episodic CH₄ release.

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Supplementary material

The online version of this article contains additional supplementary material.

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