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On the production of hydrocarbons in Titan's atmosphere

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Abstract. The production of $C(^1D)$ atoms and their role in the production of (C_1, C_2, C_3, C_4) hydrocarbons in Titan's atmosphere are discussed. The reaction between $C(^1D)$ atom and H_2 molecule to produce the methylidyne (CH) radical (Okabe, 1978) is suggested as a possible mechanism which provides an additional route to the production of hydrocarbons in Titan's atmosphere.

Keywords : Chemical reactions, $C(^1D)$ atoms, Titan's atmoshpere.

1. Introduction

The main constituent of Titan's atmosphere is nitrogen. Other minor constituents include HCN, HC_3N, C_2N_2, CO, CH_4 and other hydrocarbons. Except CO, data on the atmospheric constituents of Titan were obtained from UVS (ultraviolet spectrometer) and IRIS (infrared interoferometer spectrometer) on board Voyager 1 and Voyager 2, respectively in 1981 and 1983 (Young et al., 1984). Data on CO were obtained from ground-based radio observations of CO line at 115 GHz (Muhlehman et al., 1984; Marten et al., 1988). The temperature near the surface deduced from data measurements made with Voyager infrared radiometer is $\sim$95°K, somewhat warm due to green house effect produced by its atmospheric gases (Seeds, 1988; Pasachoff, 1983). This temperature is close to the triple point of methane.

Based on the above data, the vertical profiles of the nitrile compounds viz., HCN, HC_3N and C_2N_2 have been computed in Titan's atmosphere (Yung et al., 1984; Tangay et al., 1990; Hidayet et al., 1997; Lara et al., 1999). The solar photodissociation of these compounds yields the cyano (CN) radical (Bockelée-Morvan and Crovisier, 1985). The production of metastable $N(^2D)$ atoms from N_2 molecules has been discussed in detail by Lara et al. (1999) who have theoretically computed the altitude profiles of the production rate of $N(^2D)$ atoms in Titan's atmosphere which have

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maxima respectively at around 100 Km and 1000 Km altitudes. In addition, the photodissociation of the cyano (CN) radical could also yield N(^{2}D) atom (Singh et al., 1991). The reaction between CN radical and N(^{2}D) atom may produce the reactive C(^{1}D) atom (Saxena et al., 2002).

In all the photochemical models of Titan's atmosphere, proposed so far (Yung et al., 1984, Toublanc et al., 1995, Lara et al., 1996), the reactions involving C(^{1}D) atoms have not been included and the production of hydrocarbons is treated as mainly due to solar photodissociation of its atmospheric methane of primordial origin followed by reprocessing among the hydrocarbon radicals to produce other higher hydrocarbons. The other mechanisms for the production of hydrocarbons are the reactions between (i) carbon atom and H_2^+/H_3^+ ions and (ii) C^+ ion and H_2 molecule. But as most of the carbon is bound to the hydrocarbons and other molecules viz., CO and the nitrile compounds HCN, HC_3N and C_2N_2, these mechanisms may not contribute significantly in the production of hydrocarbons in Titan's atmosphere.

An attempt has been made to find yet another mechanism which could produce hydrocarbons efficiently in Titan's atmosphere. We could identify the reaction between the C(^{1}D) atom and the H_2 molecule producing CH radical (Okabe, 1978) as a mechanism which could produce the hydrocarbons in Titan's atmosphere. The purpose of the present paper is to discuss the production of C(^{1}D) atoms and to explore their role in the production of hydrocarbons in Titan's atmosphere.

1. The production of C(^{1}D) atoms

(i) From the reaction between CN radical and N(^{2}D) atom

The raction between ground state cyano (CN) radical and metastable N(^{2}D) atom to produce metastable C(^{1}D) atom (Saxena et al., 2002) viz.,

$$CN(X^2\Sigma^+) + N(^2D) \rightarrow N_2\left(^1\Sigma_g^+, v\right) + C(^1D)$$

has been explored for the production of $C(^1$D) atoms in Titan's atmosphere. As is apparent, the reaction is exothermic and obey conservation of spin. As regards activation energy, it is zero when the reactants are in their respective ground states (Warnatz et al., 1996). In the proposed reaction, the N-atom is in an excited state. The suggested reaction is, therefore, expected to be equally fast as or faster than the reaction:

$$CN(X^2\Sigma^+) + N(^4S) \rightarrow N_2(^1\Sigma_g^+) + C(^3P); k = 1.73 \times 10^{-9}T^{-0.5}$$

(Warnatz et al., 1996)

(ii) From the photodissociation of CO molecules

The solar photodissociation of CO molecules in Titan's atmosphere may yield C(^{1}D) atoms:

$$CO + h\nu(\lambda < 86.34nm) \rightarrow O(^1D) + C(^1D), k = 4.2 \times 10^{-8}\text{cm}^3\text{s}^{-1}$$

(at 1 au heliocentric distance during solar min. (Levine, 1985)).

2. Production of C_1 hydrocarbons

The reaction:

$$C + H_2 \rightarrow CH + H, k = 6.64 \times 10^{-10} \exp(-11,700/T)$$

Miller et al., 1997)

is endothermic by an amount of energy 1.009 eV, being the difference between the bond energies of H-H and C-H bonds and have an activation energy.

However, the reaction viz.,

$$C(^1D) + H_2 \rightarrow CH + H; k = 6.64 \times 10^{-10} \text{ (suggested)}$$

is exothermic by an amount of energy 0.254 eV and is fast and requires no activation energy (Okabe, 1978).

The methylidyne (CH) radical, thus obtained in Titan's atmosphere, may produce CH^+ ion either from photoionization or through charge transfer reactions:

$$CH + h\nu \rightarrow CH^+ + e$$
$$CH + X^+ \rightarrow CH^+ + X$$

where X is some molecule having an I.P. greater than that of CH (I.P. = 10.6 eV; Langoff, 1984), e.g., C, NH, NH_2, CN, HCN, N_2, etc.

The CH radical may also take part in ion-radical reaction producing CH_2^+ ion:

$$H_3^+ + CH \rightarrow CH_2^+ + H_2$$

where H_3^+ ions in Titan's atmosphere may be produced from the reactions:

$$H_2 + e \rightarrow H_2^+ + 2e \text{ (electron impact ionization)}$$
$$H_2 + h\nu \rightarrow H_2^+ + e \text{ (photoionization)}$$
$$H_2 + G.C.R. \rightarrow H_2^+ + e \text{ (galactic cosmic ray ionization)}$$
$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

The CH^+ and CH_2^+ ions thus produced may undergo ion-atom interchange reactions:

$$CH^+ + H_2 \rightarrow CH_2^+ + H$$
$$CH_2^+ + H_2 \rightarrow CH_3^+ + H$$
$$CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$$
$$CH_5^+ + H \rightarrow CH_4^+ + H_2$$

The various hydrocarbon ions may, in turn, produce hydrocarbon radicals from the dissociative electron recombination reactions:

$$\begin{aligned}
CH^+ + e &\rightarrow C + H \\
CH_2^+ + e &\rightarrow CH + H \\
CH_3^+ + e &\rightarrow CH_2 + H \\
&\rightarrow CH + H_2 \\
&\rightarrow CH_3 + h\nu \\
CH_4^+ + e &\rightarrow CH_3 + H \\
&\rightarrow CH_2 + H + H \\
CH_5^+ + e &\rightarrow CH_3 + H_2 \\
&\rightarrow CH_4 + H
\end{aligned}$$

The CH_5^+ ion produces methane (CH_4) also via the reactions:

$$\begin{aligned}
CH_5^+ + C &\rightarrow CH^+ + CH_4 \\
+CH &\rightarrow CH_2^+ + CH_4 \\
+CH_2 &\rightarrow CH_3^+ + CH_4
\end{aligned}$$

The methane consumed in photodissociation may thus be replenished partially.

3. Production of (C_2, C_3, C_4) hydrocarbons

The reactive $C(^1D)$ atoms may produce (C_2, C_3, C_4) hydrocarbons in Titan's atmosphere via the proposed reactions:

$$\begin{aligned}
C(^1D) \quad &+ \quad CH(^2\pi) \rightarrow C_2(^1\Sigma_g^+) + H(^2S) \\
&+ \quad CH_2(^3B_1) \rightarrow C_2H(^2\Sigma) + H(^2S) \\
&+ \quad CH_3(X^2A_2'') \rightarrow C_2H_2(^1\Sigma_g^+) + H(^2S) \\
&+ \quad C_2H(^2\Sigma) \rightarrow C_3(X\,^1\Sigma_g^+) + H(^2S) \\
&+ \quad C_2H_2(^1\Sigma_g^+) \rightarrow C_3H(^2\pi) + H(^2S) \\
&+ \quad C_2H_3(^2B_2) \rightarrow C_3H_2(^1A_1) + H(^2S) \\
&+ \quad C_2H_4(^1A_g) \rightarrow C_3H_3(^2B_1) + H(^2S) \\
&+ \quad C_3H(^2\pi) \rightarrow C_4(^3\Sigma_u) + H(^2S) \\
&+ \quad C_3H_2(^1A_1) \rightarrow C_4H(^2\Sigma) + H(^2S) \\
&+ \quad C_3H_3(^2B_1) \rightarrow C_4H_2(^1\Sigma_g) + H(^2S) \\
&+ \quad C_3H_4(^1A_g) \rightarrow C_4H_3(^2B_2) + H(^2S)
\end{aligned}$$

The above reactions are based on the concept that a carbon insertion-type mechanism prevails in reactions involving unsaturated hydrocarbons while a hydrogen atom is ejected (Herbst et al., 1994). The ground states of hydrocarbons involved in the first four of the above reactions are from Okabe (1978) and the rest are from N. SathyaMurthy (personal communication).

These reactions are exothermic, obey conservation of spin and are analogous to, and may be equally fast as or faster than, the same reactions with $C(^3P)$ atoms which Herbst et al. (1994) employed in the modelling of dense interstellar clouds. Reprocessing among the above hydrocarbon radicals produce other higher hydrocarbon radicals as shown below:

$$C_2H(^2\Sigma) + C_2H_2(^1\Sigma_g^+) \rightarrow C_4H_2(^1\Sigma_g) + H(^2S)$$

This mechanism also is one of addition followed by elimination of an H atom (Smith, 1997). The photodissociation of C_2 $(^1\Sigma_g^+)$ radical yields two $C(^1D)$ atoms (Singh et al., 1991):

$$C_2(^1\Sigma_g^+) + h\nu(93 - 121mm) \rightarrow C(^1D) + C(^1D), k = 1.0 \times 10^{-7}s^{-1}$$

(at 1 a.u. heliocentric distance during solar minimum)

This may, however, provide a minor source of $C(^1D)$ atoms in Titan's atmosphere.

4. Discussion

The applicability of the reaction between $N(^2D)$ atom and CN radical initially proposed as an additional source of cometary $C(^1D)$ atoms (Saxena et al, 2002) has been explored qualitatively in Titan's atmosphere which is mainly composed of nitrogen (N_2) and also has CO and nitrile compounds as its minor constituents. It is envisaged that the $C(^1D)$ atoms could be produced via this reaction and from the solar photodissociation of CO molecules. The $C(^1D)$ atoms thus produced could play an important role in the production of hydrocarbons in Titan's atmosphere.

Above Titan's tropopause at $z \simeq 45$ km (Yung et al., 1984) in the stratosphere the volume mixing ratio $\sim 6 \times 10^{-5}$ of CO molecules is higher than the mixing ratios $\sim 10^{-7} - 10^{-8}$ of the nitrile compounds HCN, HC_3N and C_2N_2 (Yung et al., 1984; Lutz et al., 1983). As such the production of $C(^1D)$ atoms from photodissociation of CO molecules could be more important than their production from the suggested mechanism in Titan's stratosphere.

The atmosphere of Titan is about 1.6 times as dense as earth's atmosphere and nitrogen (N_2) constitutes about 85% of its atmospheric constituents (Seeds, 1988; Pasachoff, 1983). The number density of $N(^2D)$ atoms at around 1000 Km altitude is expected to be significantly higher than their number density at around 100 Km altitude because of their smaller loss rate at higher altitudes. Based on observational data on HCN, HC_3N and C_2N_2 from Voyager, the derived vertical profiles show that the volume mixing ratios of these nitrile compounds are about two orders of magnititude higher at around 1000 Km altitude than near 100 Km altitude (Figure 8a, Yung et al., 1984). Therefore, the photo production rate and the number density of the CN radical from the nitrile compounds are expected to be higher at around 1000 Km altitude than near 100 Km altitude. The proposed reaction could, therefore, be an important source of $C(^1D)$ atoms around 1000 Km altitude in Titan's thermosphere.

The neutral-neutral reactions and ion-neutral reactions have already been extensively explored in Titan's atmosphere (Yung et al., 1984; Ip et al., 1990; Toublanc et al., 1995; Lara et al., 1996). However, the reactions involving $C(^1D)$ atoms have not been included in their models. In the present paper, a scheme for the production of a few Cn ($n = 1, 2, 3, 4$) hydrocarbons in Titan's atmosphere from the reactions involving $C(^1D)$ atoms is suggested. Because of extremely cold conditions in Titan's atmosphere, only those chemical reactions which require no activation energy are of relevance.

The merit of the suggested reaction viz.,

$$C(^1D) + H_2 \rightarrow CH + H(Okabe, 1978)$$

for the production of CH in Titan's atmosphere is that it requires no activation energy and is fast with a rate coefficient of 6.64×10^{-10} cm^3 s^{-1}. It thus provides an additional precursor to the production of C_1-hydrocarbons in Titan's atmosphere. For the production of (C_2, C_3, C_4)-hydrocarbons, a new set of valid reactions is proposed in the present work. This could provide an additional route to the production of C_2H_2, C_3H_4 and C_4H_2 which are amongst the hydrocarbons observed. The detailed numerical computations are deferred to a future paper.

Conclusions

1. The reaction between CN radical and $N(^2D)$ atom may produce $C(^1D)$ atoms in Titan's atmosphere which is rich in nitrogen and also has nitrile compounds HCN, HC_3N and C_2N_2 which are parents of CN.
2. The reaction between H_2 molecule and $C(^1D)$ atom to produce CH radical may provide an additional route to the production of hydrocarbons in Titan's atmosphere.

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