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ROLE OF THE METHYLENE AMIDOGEN (H_2CN) RADICAL IN THE ATMOSPHERES OF TITAN AND JUPITER

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ABSTRACT

The methylene amidogen (H_2CN) radical can be shown to be an important intermediate in models for the formation of HCN (via $N + CH_3$) and the recombination of H to H_2 (via H + HCN) on Titan as well as in models for the formation of HCN (via $NH_2 + C_2H_3$) in the atmosphere of Jupiter. Experiments in our laboratory in a discharge flow system with mass spectrometric detection of both reactants and products have established that the major product channel (90%) for the reaction $N + CH_3$ is that leading to $H_2CN + H$. The same result was obtained for $N + CD_3 \rightarrow D_2CN + D$. We have also measured for the first time the rate constant for the reaction $D + D_2CN \rightarrow DCN + D_2$ and find $k(298\ K) > 7 \times 10^{-11}\ cm^3 s^{-1}$. The same result was obtained for the H atom reaction. This is the final step in the reaction sequence leading to HCN on both Titan and Jupiter and to formation of H_2 from H on Titan. We have also made the first measurement of the ionization potentials for H_2CN and D_2CN. From electron impact studies we obtain I.P. = (9.6+/-1.0) ev for both radicals. An upper limit of I.P. < 11.6 ev came from observations of the H_2CN radical by photoionization mass spectrometry using an Ar resonance lamp (106.7 nm). Further photoionization experiments are planned using synchrotron radiation plus monochromator as a tunable vacuum UV light source.

INTRODUCTION

The methylene amidogen (H_2CN) radical can be shown to be an important intermediate in models for the formation of HCN in the atmospheres of Titan and Jupiter and H atom recombination on Titan. Experiments in our laboratory have demonstrated that H_2CN is formed very efficiently by reaction (1)[1a].

$$N + CH_3 \rightarrow H_2CN + H \quad (90\%) \qquad (1a)$$
$$\rightarrow HCN + 2H \qquad (1b)$$
$$\rightarrow HCN + H_2 \qquad (1c)$$

Measurements were made of k_1 as a function of temperature from 200K to 423K[1b]. Reaction (1) was found to be very rapid and thus a good but limited laboratory source of H_2CN.

Very limited kinetic information is available for this radical. Only the reactions $H_2CN + H_2CN$ and $H_2CN + NO$ have been studied[2]. Therefore using reaction (1) as a source of H_2CN, we studied the reactions $N + H_2CN$ (D_2CN) (2) and (H/D) + D_2CN (3). The technique employed was discharge flow mass spectrometry at 1 Torr total pressure. Reaction (2) was studied over the temperature range 200K to 363K, whereas reaction (3) was studied at room temperature. Measurements were also made of the ionization potential for H_2CN and D_2CN.

EXPERIMENTAL

All experiments were performed in a pyrex flow tube 60 cm long and 28 mm in diameter. The flow tube was coupled via a two stage stainless steel collision-free sampling system to a quadrupole mass spectrometer (Extranuclear Laboratory Inc.). For reaction (2), N atoms and F atoms were admitted at the back of the flow tube and CH_4 or CD_4 was added through the sliding injector. For reaction (3), D_2CN was generated at the back of the flow tube by admitting N, F, and CD_4 through the sidearms, while H or D were added through the sliding injector.

RESULTS

Rate constants for reactions (2) and (3) were measured and these reactions were found to be efficient processes for the formation of HCN and DCN[3].

$$N + H_2CN \rightarrow NH + HCN \qquad (2)$$
$$N + D_2CN \rightarrow ND + DCN$$

Reaction (2) was studied at three temperatures and the following values (in units of $10^{-11} cm^3 s^{-1}$) were obtained: (3.9+/-2.2), 200K; (4.4+/-1.4), 298K; (6.7+/-2.0), 363K. Reaction (3)

$$H + D_2CN \rightarrow HD + DCN \qquad (3)$$
$$D + D_2CN \rightarrow D_2 + DCN$$

was studied at 298K and $k_3 > 7x10^{-11}$ $cm^3 s^{-1}$. No isotope effect was observed for either reaction.

Ionization potentials were measured for H_2CN and D_2CN. The mass spectrometer was calibrated for NO and HCN. From the calibration runs it was found that I.P.(ev) = I.P.(measured) - 2.6. Figure 1 shows the uncorrected results for H_2CN and D_2CN. Applying the above correction, an ionization potential of (9.6+/-1.0) ev was obtained for H_2CN and D_2CN. Photoionization experiments were performed with an Argon lamp. H_2CN was readily detected thus suggesting I.P. < 11.6 ev. A theoretical calculation of the ionization potential of H_2CN yields the value 10.8 ev[4].

DISCUSSION AND CONCLUSION

Our results show that an important source of HCN in Titan's atmosphere is the sequence of reactions

$$N + CH_3 \rightarrow H_2CN + H \qquad (1)$$
$$H + H_2CN \rightarrow H_2 + HCN \qquad (3)$$

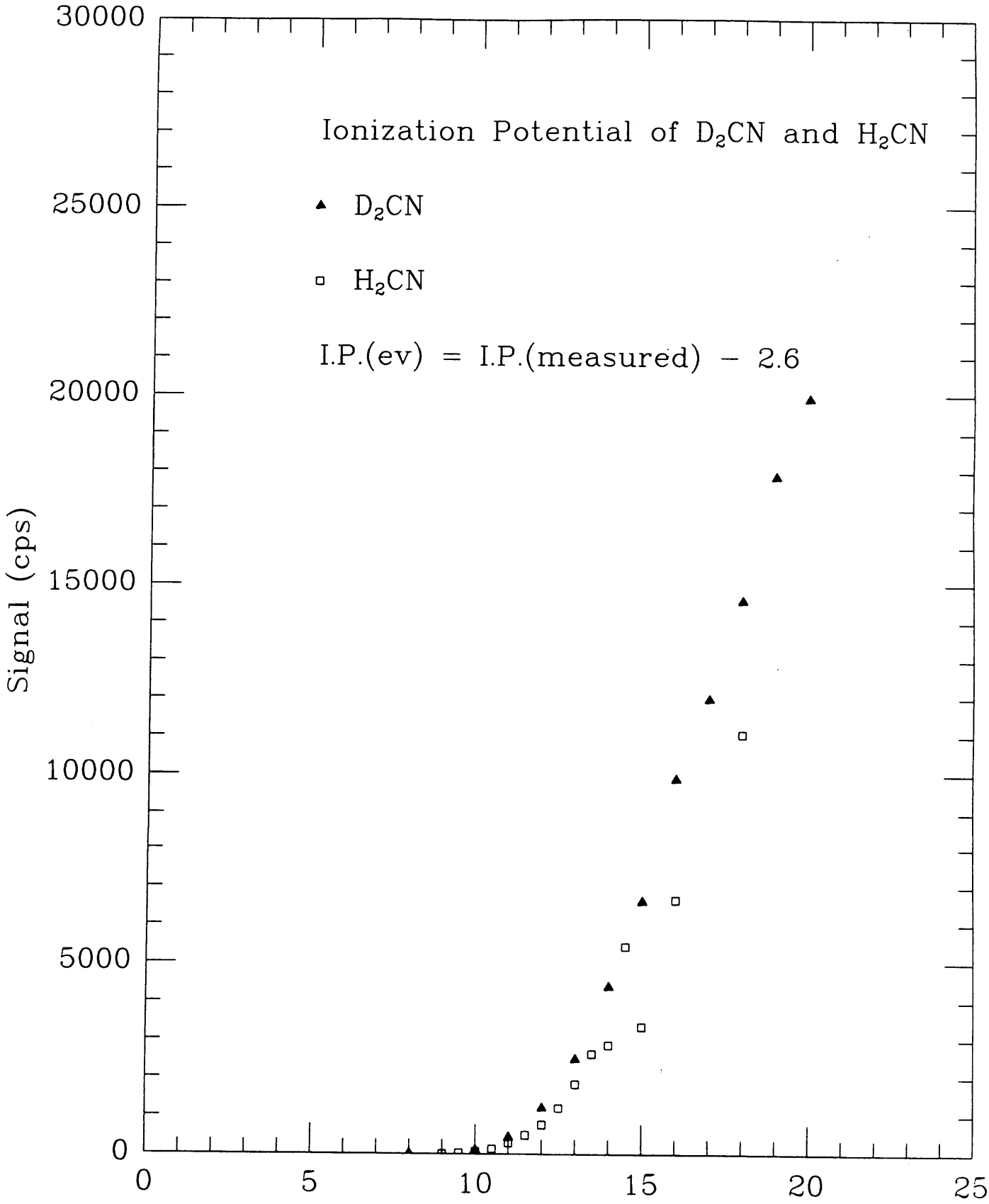

Figure 1: Electron volts (ev) uncorrected

Yung et al [5] have proposed that HCN can participate in the recombination of H on Titan by the reactions

$$H + HCN + M \rightarrow H_2CN + M \quad (4)$$

$$H + H_2CN \rightarrow HCN + H_2 \quad (3)$$

On Jupiter the coupled photochemistry of ammonia and acetylene has been proposed by Kaye and Strobel [6] to lead to the reaction

$$NH_2 + C_2H_3 \rightarrow C_2H_5N \quad (5)$$

The photolysis of the various isomers of C_2H_5N can lead to the following reactions

$$C_2H_5N \rightarrow HCN + CH_3 + H \quad (6)$$

$$\rightarrow H_2CN + CH_3 \quad (7)$$

Subsequent reaction of H_2CN with H yields HCN.

Our results provide the quantitative information needed for modelers to determine altitude profiles for H_2CN, HCN and subsequent nitrile compounds in Titan's atmosphere. These results may have important implications for modelers and instrument designers in selecting experiments to study the chemical composition of Titan's atmosphere in the upcoming Cassini mission.

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