Dimerization of Methanimine and its charged species in the Atmosphere of Titan and interstellar/cometary ice analogs

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Titan, the massive moon of Saturn

Titan facts
- **Surface pressure: 1.6 bar**
- **Surface temperature: 94 K**
- **Main constituents of the atmosphere: N_2 (97%), CH_4(2%), H_2, C_2H_6, C_2H_2, C_2H_4, HCN, HCCCN, C_2N_2, … & the orange haze**

The atmosphere of Titan is believed to be somewhat reminiscent of the primeval atmosphere of Earth

Theoretical Calculations

Electronic structure

- **Density Functional (DFT) calculations using the B3LYP hybrid functional**
- **Basis sets: triple zeta + polarization + diffuse functions**
- **Geometry optimizations and localization of transition states at DFT level**
- **IRC calculations**
- **CCSD(T) calculations at all the optimized B3LYP geometries**
- **Thermochemical calculations for selected processes: CBS-Q and W1**

Kinetics calculations

Reaction rate coefficients:

- **Capture method**
- **Rice-Ramsperger-Kassel-Marcus (RRKM)**

$$E = A - \frac{C_4}{r^4}$$

Energy evaluated for various points along the distance coordinate of the two reactants

$$k(E) = \frac{N(E)}{h\rho(E)}$$

The microcanocical rate constant.

- **N(E) is obtained integrating the density of states up to energy E, and the rigid rotor/harmonic oscillator model is assumed.**
- **Master equation is solved for the particular energies.**

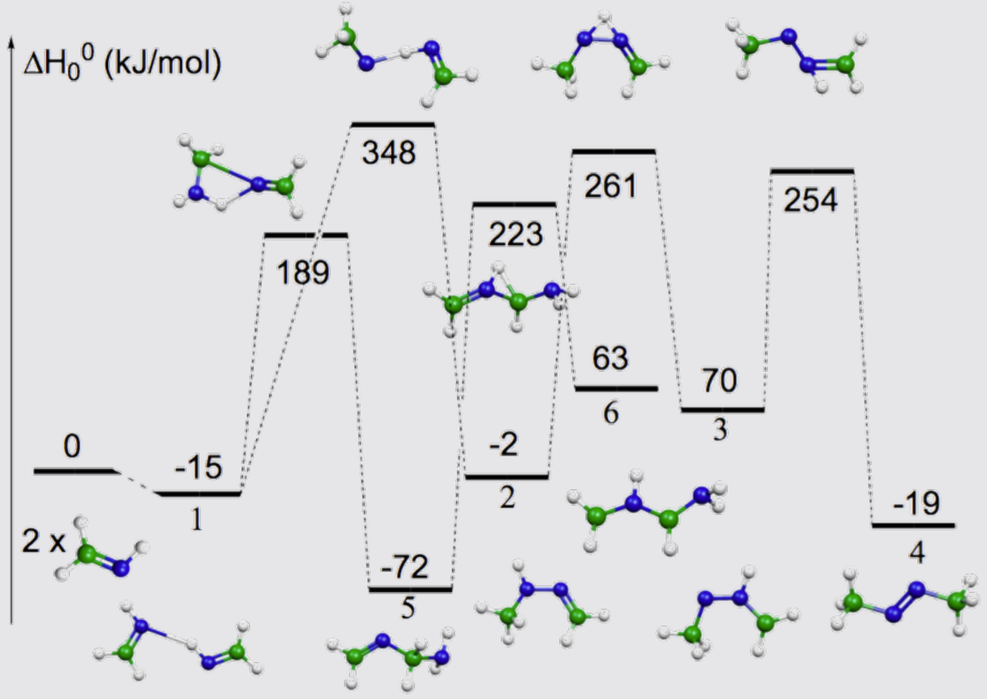
Lavvas et al. (Planet. Space Sci, 2008) have used in their models some of the CH_2NH formation routes and found a quantity of CH_2NH larger than that inferred by Vuitton et al. from the analysis of the INMS data onboard Cassini.

To explain this discrepancy, Lavvas et al. (Planet. Space Sci, 2008) have suggested that, similarly to formaldehyde, CH_2NH can polymerize under the conditions of the atmosphere of Titan. Because of the lack of data on CH_2NH polymerization process, those of formaldehyde have been used.

If the polymerization of CH_2NH is confirmed to be extensive, CH_2NH could be one of the basic building block of the nitrogen-rich organic aerosols of Titan.

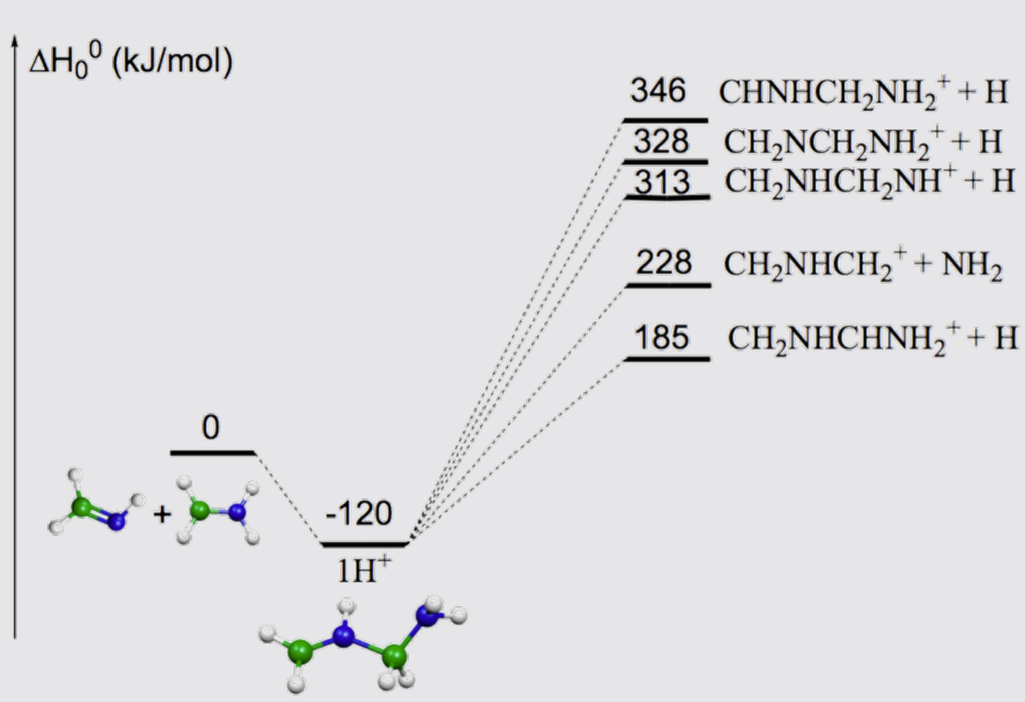
Because of the lack of data, we have decided to characterize the dimerization of CH_2NH by electronic structure calculations to assess the feasibility of this process under the conditions of Titan.

Dimerization of methanimine



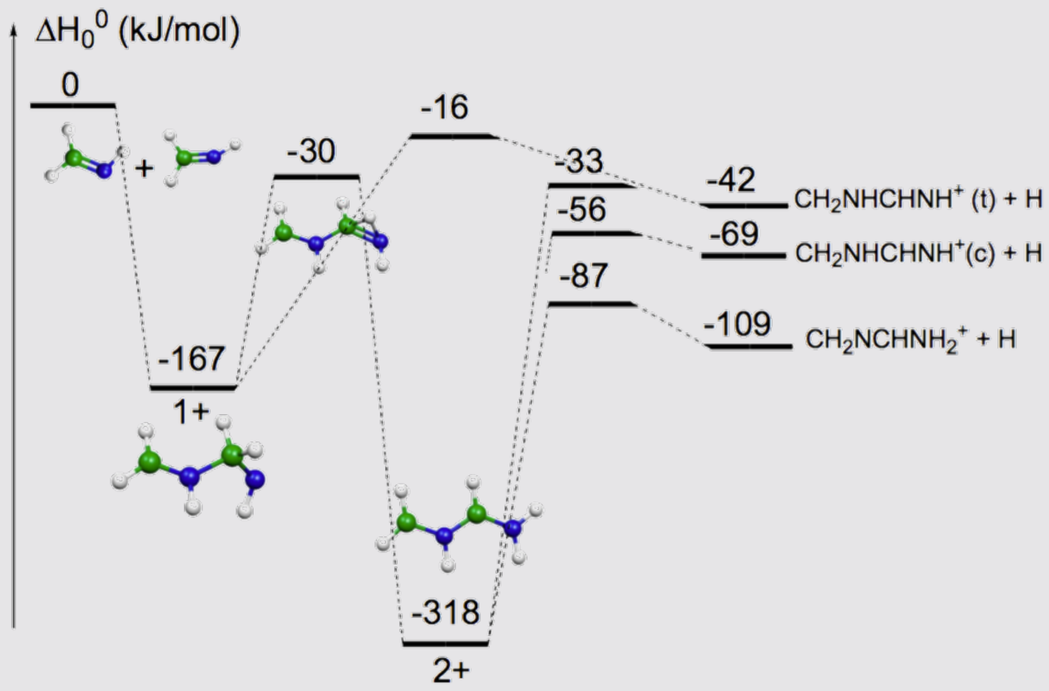
Schematic representation of the potential energy surface for the dimerization of methanimine.

Methanimine with protonated methanimine

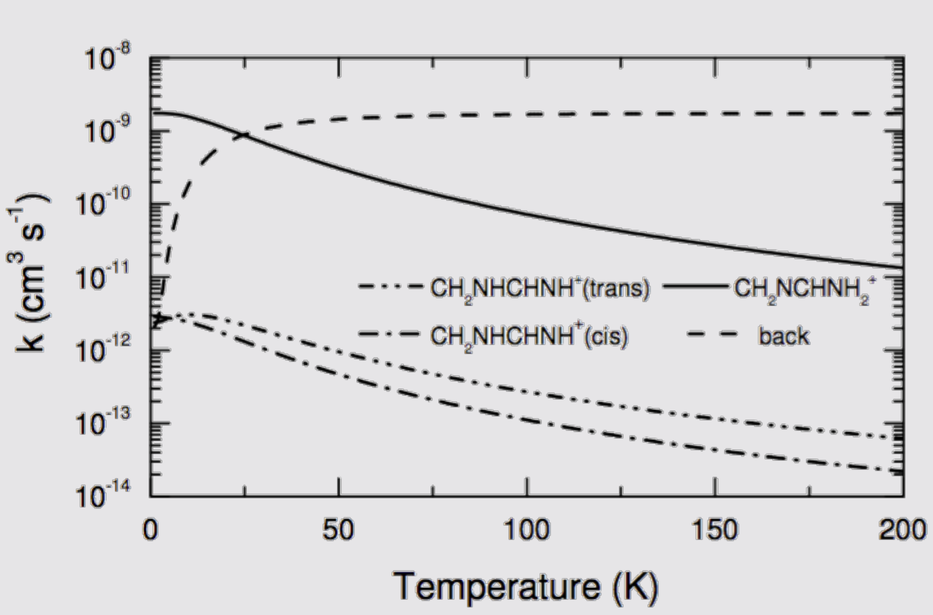


Schematic representation of the potential energy surface for the reaction between CH_2NH and $CH_2NH_2^+$.

Methanimine with ionized methanimine



Schematic representation of the potential energy surface for the reaction between CH_2NH and CH_2NH^+.



Rate constants as a function of temperature: back dissociation (dashed line), $CH_2NCHNH_2^+$ (solid line), $CH_2NHCHNH^+$ (trans) (double dot line), and $CH_2NHCHNH^+$ (cis) (dash-dot line).

For simplicity only the CCSD(T) energies (KJ/mol) are shown in the schematic representations.

Conclusions

1) **Numerous elementary reactions in the upper atmosphere of Titan lead to the formation of methanimine, an important prebiotic molecule**
2) **Polymerization of methanimine in the gas phase at low temperatures may be initiated by the presence of an ionised molecule.**
3) **In the low temperatures (Titan) and in absence of external energy sources, only reactions involving protonated/ionized forms are possible.**
4) **The amount in the upper atmosphere of Titan of ionised methanimine is small , but not negligible**