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Formation of hydrocarbons on Titan: Impact of rapid association reactions at low pressure

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1. Introduction

In the 1980's, Voyager revealed that complex organic molecules were present in Titan's atmosphere but the actual mechanisms leading to this rich chemistry were largely unknown. The recent Cassini results indicate that the chemistry ocurring in Titan's upper atmosphere is far more complex than anticipated. The detection of heavy positive and negative ions [13] reveals that much of the molecular growth occurs in the upper atmosphere rather than at lower altitudes [5, 12].

Photochemical models predict that three-body association reactions (A + B + M $\rightarrow$ AB + M) are the main production route for several hydrocarbons, including alkanes [2, 3]. The kinetic parameters of these reactions strongly depend on density and are therefore extremely difficult to constrain by experimental measurements as the low pressure of Titan's upper atmosphere cannot be reproduced in the laboratory. As a consequence, they have to be extrapolated outside the range of measurements, leading to high uncertainties. According to these extrapolations, three-body association reactions are only efficient in Titan's lower atmosphere. However, radiative association reactions (A + B $\rightarrow$ AB + hν) do not depend on pressure and can therefore still be efficient in the upper atmosphere. Unfortunately, they are largely uncharacterized and have consequently been neglected in photochemical models so far.

Because of their potential importance at higher altitude, association reactions can have an important contribution to our understanding of molecular growth and better constraints for them are required. In the recent years, theoretical calculations of kinetics parameters have become more and more reliable [7]. We therefore performed ab initio transition state theory based master equation calculations for several radical-radical and radical-molecule association reactions. The computed kinetics parameters were included in our photochemical model of Titan. We present here the main results and discuss their impact for the organic cycle.

2. Photochemical model

The 1-dimensional photochemical model of Titan used in this investigation is adapted from several elements described previously. The background atmosphere and eddy diffusion coefficient are based on Cassini observations [15]. We scale the neutral densities of N_2 and CH_4 measured by the Ion Neutral Mass Spectrometer (INMS) upward by a constant factor of 2.6 which is found necessary in order to have the INMS measured densities in agreement with the atmospheric density derived by the HASI and the Cassini Attitude and Articulation Control Subsystem (AACS) observations [8]. Detailed calculations for the energy deposition of photons and photoelectrons have been performed [4] and the aerosol opacity in the stratosphere has been constrained by the Huygens probe [6]. The chemical network includes hydrocarbons [9], nitrogen [14] and oxygen [1] bearing species and takes into account both neutral and ion chemistry [10, 11].

The hydrocarbon chemistry has been updated with a new set of kinetics parameters for association reactions. Ab initio TST calculations were performed for 12 reactions selected for their major role in Titan's chemistry. For the other 56 radical-radical reactions present in the model but not specifically studied, we estimate the kinetics parameters from basic chemical rules. The calculations indicate that the rate constants increase dramatically with the number of heavy atoms involved and that the pressure dependence of three-body association reactions is not as sharp as previously estimated. Moreover, radiative association is found to be fast and cannot be neglected. The existence of large rates at low density suggests that recombination at low pressure could significantly affect the chemistry of Titan's atmosphere.

3. Results

The model results show that inclusion of the new reaction rates has two primary consequences. The first, and simplest, is an increase in the density of alkanes in the upper atmosphere. This is obviously a result of the increased rate coefficients for production of these species, namely CH_3 + CH_3 $\rightarrow$ C_2H_6, CH_3 + C_2H_5 $\rightarrow$ C_3H_8 and C_2H_5 + C_2H_5 $\rightarrow$ C_4H_{10}. The second consequence is a significant change in the mole fraction of C_4H_2 in the stratosphere as well as smaller changes for C_6H_6 in the mesosphere and C_2H_2 and C_2H_4 in the stratosphere.

Considering that our model does not address possible variations of the mole fractions with latitude or local time and considering all the uncertainties in the chemical network, the profiles of most hydrocarbons are generally in good agreement with the observations. It is however difficult to say whether or not the new rate constants provide a better fit to the observations. The only exception is C_4H_2, which presents a significant improvement in the stratosphere. The calculated column integrated rates for some selected species will be summarized along with relevant observational constraints.

4. Summary and Conclusions

Our ab initio TST calculations indicate that association reactions are fast even at low pressure for adducts having as few as three heavy atoms. These drastic changes have however only moderate consequences for Titan's composition. The total production and condensation rates of hydrocarbons change only by a factor of a few. This is due to the fact that changes impact levels of the atmosphere where the density and consequently production rates are low. It would be very interesting to check the impact of these new rate constants on other environments, such as giant and extrasolar planets as well as the interstellar medium.

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References

[1] Hörst, S. M., et al.: The origin of oxygen species in Titan's atmosphere, J. Geophys. Res., Vol. 113, pp. E10006, 2008.

[2] Krasnopolsky, V. A.: A photochemical model of Titan's atmosphere and ionosphere, Icarus, Vol. 201, pp. 226-256, 2009.

[3] Lavvas, P., et al.: Coupling photochemistry with haze formation in Titan's atmosphere. Part II: Results and validation with Cassini/Huygens data, Planet. Space Sci., Vol. 56, pp. 67-99, 2008.

[4] Lavvas, P., et al.: Energy deposition and primary chemical products in Titan's upper atmosphere, Icarus, Vol. 213, pp. 233-251, 2011.

[5] Lavvas, P., et al.: The detached haze layer in Titan's mesosphere, Icarus, Vol. 201, pp. 626-633, 2009.

[6] Lavvas, P., et al.: Titan's vertical aerosol structure at the Huygens landing site: Constraints on particle size, density, charge, and refractive index, Icarus, Vol. 210, pp. 832-842, 2010.

[7] Miller, J. A., and Klippenstein, S. J.: Master equation methods in gas phase chemical kinetics, J. Phys. Chem. A, Vol. 110, pp. 10528-10544, 2006.

[8] Müller-Wodarg, I. C. F., et al.: Horizontal structures and dynamics of Titan's thermosphere, J. Geophys. Res., Vol. 113, pp. E10005, 2008.

[9] Vuitton, V., et al.: Formation and distribution of benzene on Titan, J. Geophys. Res., Vol. 113, pp. E05007, 2008.

[10] Vuitton, V., et al.: Ion chemistry and N-containing molecules in Titan's upper atmosphere, Icarus, Vol. 191, pp. 722-742, 2007.

[11] Vuitton, V., et al.: Negative ion chemistry in Titan's upper atmosphere, Planet. Space Sci., Vol. 57, pp. 1558-1572, 2009.

[12] Wahlund, J.-E., et al.: On the amount of heavy molecular ions in Titan's ionosphere, Planet. Space Sci., Vol. 57, pp. 1857-1865, 2009.

[13] Waite Jr., J. H., et al.: The process of tholin formation in Titan's upper atmosphere, Science, Vol. 316, pp. 870-875, 2007.

[14] Yelle, R. V., et al.: Formation of NH_3 and CH_2NH in Titan's upper atmosphere, Faraday Discuss., Vol. 147, pp. 31-49, 2010.

[15] Yelle, R. V., et al.: Methane escape from Titan's atmosphere, J. Geophys. Res., Vol. 113, pp. E10003, 2008.