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Benzene formation in Titan's lower atmosphere

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Abstract

The production of benzene (C_6H_6) in Titan's atmosphere is a crucial step to tholin and haze formation. Two pathways which are important below 400 km are considered here. First is the gas-phase route via methylene (CH_2) radical chemistry. We show in a new laboratory study that the more reactive excited singlet state of CH_2, produced by CH_4 photolysis in Titan's atmosphere, is quenched increasingly efficiently at lower temperatures to the less reactive ground state CH_2, rather than reacting with species such as H_2 and CH_4. This has important consequences for the production of ethane and the propargyl (C_3H_3) radical, an important C_6H_6 precursor. The second route to C_6H_6 is the cyclo-trimerization of acetylene (C_2H_2) on cosmic dust analogue particles. The combination of a laboratory study of the heterogeneous chemical kinetics, combined with a new astronomical model of the cosmic dust input to Titan's atmosphere, shows that the production of C_6H_6 *via* uptake of C_2H_2 on the dust, followed by cyclo-trimerization and desorption, is competitive with gas-phase production of C_6H_6 between 80 and 120 km.

1. Introduction

The photolysis of methane by UV photons is the primary source of hydrocarbon radicals in the atmospheres of Titan and the giant planets. The photolysis channels are thought to be:

$$CH_4 + h\nu \rightarrow CH_3 + H \quad (R1a)$$

$$\rightarrow {}^1CH_2 + H_2 \quad (R1b)$$

$$\rightarrow {}^3CH_2 + 2H \quad (R1c)$$

$$\rightarrow CH + H_2 + H \quad (R1d)$$

Methylene, CH_2, is an important product and can be produced in either the triplet groundstate ($^3CH_2$) or the first excited singlet state ($^1CH_2$). Although the energy gap between the ground and first excited states is small (37.7 kJ mol^{-1}), the chemistry of the two species are quite different. $^1CH_2$ rapidly inserts into bonds followed by dissociation of the chemically activated intermediate, e.g.:

$$^1CH_2 + C_2H_2 \rightarrow C_3H_4^* \rightarrow C_3H_3 + H \quad (R2)$$

The formation of the propargyl radical, C_3H_3, has been proposed as an important radical route to C_6H_6 formation on Titan [1]:

$$C_3H_3 + C_3H_3 \rightarrow C_6H_6 \quad (R3)$$

with benzene being the first step in the formation of the layer of tholin aerosols at 300-400 km which surround Titan [2]. In contrast, $^3CH_2$ is relatively unreactive with closed shell molecules and its major loss processes are reactions with radical species such as H and CH_3, yielding (after several steps) C_2H_2. Both methylene species are therefore important in different aspects of Titan's complex photochemistry. For the reactions of $^1CH_2$ there is a parallel relaxation process in which collisions with C_2H_2, CH_4, H_2, and other molecular species lead to ground state $^3CH_2$. It is therefore important to quantify the competition between reaction and relaxation of $^1CH_2$ over the temperature range relevant to Titan's stratosphere.

Another route to C_6H_6 formation is via heterogeneous chemistry involving the cyclo-trimerization of acetylene:

$$3\ C_2H_2 \rightarrow C_6H_6 \quad (R4)$$

on cosmic dust or meteoric smoke particles (MSPs), which form through the recondensation of metallic vapours produced by meteoric ablation [3]. Contributions to the flux of cosmic dust entering Titan's atmosphere originate from several sources including Edgeworth-Kuiper Belt (EKB) objects and various cometary families (e.g., Jupiter family and Halley type comets) [4]. Data collected from the Pioneer 10 meteoroid detector and from the Student Dust Counter (SDC) on the New Horizons mission has been used to constrain the overall mass production rate from the EKB and the differential mass production distribution into the Saturnian system, including Saturn's satellites and planetary rings [5].

2. Experimental Results

The kinetics of the reactions of $^1CH_2$ with He, N_2, O_2, H_2 and CH_4 were measured over the temperature range 43 – 160 K by pulsed laser photolysis, monitoring $^1CH_2$ removal by laser induced fluorescence. Low temperatures were obtained with either a pulsed Laval expansion (43 – 134 K) or a low temperature, slow flow reaction cell (160 K). The rate coefficients for the reactions with N_2, O_2, H_2 and CH_4 all showed a strong negative temperature dependence. For the reactions of $^1CH_2$ with H_2 and CH_4, the branching ratio for quenching to $^3CH_2$ increases significantly between 160 and 73 K.

A low-temperature flow tube and ultra-high vacuum apparatus were used to explore the uptake and heterogeneous chemistry of C_2H_2 on cosmic dust analogues. The uptake coefficient of C_2H_2 on a variety of olivinic particles is $(1.5 – 1.9) \times 10^{-4}$ at 181 K, and the rate of cyclo-trimerization to C_6H_6 is $2.6 \times 10^{-5} \exp(-741/T)$ s^{-1}.

3. Atmospheric implications

The Leeds Chemical Ablation Model was used to show that the bulk of cosmic dust particles (radius 0.02 - 10 μm) entering Titan's atmosphere do not ablate because of the slow entry velocity (< 29 km s^{-1}) and large atmospheric scale height. Particles smaller than 10 μm sediment very slowly in the troposphere, thereby providing a significant surface for heterogeneous chemistry below 150 km. A 1D atmospheric model of dust sedimentation, C_2H_2 uptake, cyclo-trimerization and desorption of C_6H_6 shows that the peak production of C_6H_6 occurs between 80 and 120 km [6].

The implications of the measured rate coefficients and branching ratios for $^1CH_2$ were examined in a 1D transport model of Titan's atmosphere from Caltech/JPL [7], with chemistry from Moses et al. [8]. The most striking difference with the results from the present study is seen in the profile of C_2H_6, where concentrations decrease by 44% between 1550 and 800 km because of reduced CH_3 production. In contrast, the profiles for the unsaturated hydrocarbons C_2H_2 and C_2H_4 both show significant increases of 15 % and 30 %, respectively, at 50 km, moving both profiles into better agreement with the Composite Infrared Spectrometer (CIRS) limb and nadir observations. Despite this, observed concentrations of C_2H_2 below 250 km are still twice the modelled concentrations, while C_2H_4 observations are almost an order of magnitude higher. Below 500 km, an increase in C_6H_6 by up to 30% is observed, largely as a result of the increased C_2H_2.

4. Summary and Conclusions

The influence of cosmic dust on the atmospheric chemistry of Titan has been examined for the first time. The production of C_6H_6 from the cyclo-trimerization of C_2H_2 on cosmic dust analogues is shown to be efficient and competitive with gas-phase chemistry. The CH_2 radical plays a crucial role in Titan's photochemistry; this study explored the kinetics and quenching of the reactive singlet state with a range of abundant molecules such as CH_4. These reactions have unexpected temperature dependences, with significant effects on C_2H_6, C_2H_2 and C_6H_6, demonstrating the importance of carrying out laboratory measurements over the temperature range appropriate to Titan's atmosphere.

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References

[1] Wilson, E. H., Atreya, S. K.: Chemical sources of haze formation in Titan's atmosphere. Planet Space Sci., 51, 1017-1033, 2003.

[2] Lorenz, R. D.: Titan: Interior, surface, atmosphere, and space environment. Meteorit Planet Sci, 49, 1139-1140, 2014.

[3] Saunders, R. W., Plane, J. M. C.: A photo-chemical method for the production of olivine nanoparticles as cosmic dust analogues. Icarus, 212, 373-382, 2011.

[4] Poppe, A. R.: An improved model for interplanetary dust fluxes in the outer Solar System. Icarus, 264, 369-386, 2016.

[5] Poppe, A. R., Horanyi, M.: On the Edgeworth-Kuiper Belt dust flux to Saturn. Geophys Res Lett, 39, art. no.: L15104, 2012.

[6] Frankland, V. L. *et al.*: Uptake of acetylene on cosmic dust and production of benzene in Titan's atmosphere. Icarus, 278, 88-99, 2016.

[7] Li, C. *et al.*: A non-monotonic eddy diffusivity profile of Titan's atmosphere revealed by Cassini observations. Planet Space Sci., 104, 48-58, 2014.

[8] Moses, J. I. *et al.*: Photochemistry and diffusion in Jupiter's stratosphere: Constraints from ISO observations and comparisons with other giant planets. J. Geophys. Res.-Planets, 110, 2005.