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Uptake of acetylene on cosmic dust and production of benzene in Titan's atmosphere

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ABSTRACT

A low-temperature flow tube and ultra-high vacuum apparatus were used to explore the uptake and heterogeneous chemistry of acetylene (C_2H_2) on cosmic dust analogues over the temperature range encountered in Titan's atmosphere below 600 km. The uptake coefficient, γ, was measured at 181 K to be $(1.6 \pm 0.4) \times 10^{-4}$, $(1.9 \pm 0.4) \times 10^{-4}$ and $(1.5 \pm 0.4) \times 10^{-4}$ for the uptake of C_2H_2 on Mg_2SiO_4, $MgFeSiO_4$ and Fe_2SiO_4, respectively, indicating that γ is independent of Mg or Fe active sites. The uptake of C_2H_2 was also measured on SiO_2 and SiC as analogues for meteoric smoke particles in Titan's atmosphere, but was found to be below the detection limit ($\gamma < 6 \times 10^{-8}$ and $< 4 \times 10^{-7}$, respectively). The rate of cyclotrimerization of C_2H_2 to C_6H_6 was found to be 2.6×10^{-5} exp(-741/T) s^{-1}, with an uncertainty ranging from ± 27 % at 115 K to ± 49 % at 181 K. A 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 (< 1% mass loss through sputtering), thereby providing a significant surface for heterogeneous chemistry. A 1D model of dust sedimentation shows that the production of C_6H_6 *via* uptake of C_2H_2 on cosmic dust, followed by cyclo-trimerization and desorption, is probably competitive with gas-phase production of C_6H_6 between 80 and 120 km.

1. Introduction

Titan, the largest Moon of Saturn, is the only Moon in the Solar System to have a significant atmosphere. In the lower atmosphere, a thick haze is observed (Rages and Pollack, 1983; Smith et al., 1981) with the main haze region occurring from ~220 km to the surface. A detached haze layer lies in the mesopause region around 500 km (Liang et al., 2007; Porco et al., 2005; Shemansky et al., 2005). The processes which drive formation of these haze layers are still unclear but are considered to be linked to the formation of organic aerosols (tholins). Simple organic species, such as acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), benzene (C_6H_6) and hydrogen cyanide (HCN), provide feedstocks for formation of these aerosols (Flasar et al., 2005; Shemansky et al., 2005; Waite et al., 2005).

C_2H_2 is the second most abundant minor species after C_2H_6 (Vinatier et al., 2010) and is predominantly formed by photodissociation of C_2H_4 above ~600 km (Krasnopolsky, 2014). The vertical profile of C_2H_2 was determined by Teanby et al. (2006), who obtained a mixing ratio of 4×10^{-6} between 230 and 500 km.

Photochemical models of Titan's atmosphere have been constructed based on observational data and extrapolating the rate coefficients of pertinent chemical reactions to low temperatures (Coustenis et al., 2010; Dobrijevic et al., 2014; Hebrard et al., 2007; Hebrard et al., 2013; Krasnopolsky, 2010; Krasnopolsky, 2012; Krasnopolsky, 2014; Lara et al., 2014; Lavvas et al., 2008a; Lavvas et al., 2008b; Magee et al., 2009; Wilson and Atreya, 2003; Wilson and Atreya, 2004; Wilson et al., 2003). These models, based on kinetics measured in the laboratory, reveal that the major loss pathways for C_2H_2 are: hydrogenation to C_2H_4; formation of C_4H_2 (which can go on to form more complex hydrocarbons); and condensation out of the gas phase near ~80 km (Vinatier et al., 2010). However, none of these models have considered adsorption and heterogeneous chemistry on cosmic dust or meteoric smoke particles (MSPs); the latter form from the recondensation of metallic vapours produced by meteoric ablation (Saunders and Plane, 2011).

Contributions to the flux of cosmic dust entering Titan's atmosphere are thought to originate from several sources including Edgeworth-Kuiper Belt (EKB) objects and various cometary

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families (e.g., Jupiter family and Halley type comets) (Landgraf et al., 2002; Poppe, 2016; Poppe and Horanyi, 2012). Dust from EKB objects forms through either mutual collisions or interstellar dust bombardment (Stern, 1996; Yamamoto and Mukai, 1998), while cometary grains originate from sublimation and/or sporadic outbursts (e.g., Sekanina (1996); Kelley et al. (2013)). 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 (Han et al., 2011; Poppe and Horanyi, 2012). Investigations of cometary dust (e.g. Zolensky et al. (2006) and Gainsforth et al. (2015)) assume the cosmic dust to have the composition of carbonaceous chondrites which, in this study, are represented by olivines ($Mg_{2-2n}Fe_{2n}SiO_4$ where $0 \leq n \leq 1$).

Only a small fraction of the cosmic dust entering Titan's atmosphere will actually ablate (see Section 4.1). Ablation occurs between 450–700 km, giving rise to layers of metal atoms such as Na, Fe, Mg and Si (English et al., 1996; Ip, 1990; Molina-Cuberos et al., 2008). These atoms may react with various unsaturated hydrocarbons (by addition rather than abstraction), and the metal-containing organics and nitrogen-organics then condense to form MSPs. In contrast, in the Earth's mesosphere reactions with O_3 and O_2 should lead to the formation of metal oxide and silicate MSPs (Plane et al., 2015). Both MSPs and un-ablated cosmic dust particles have the potential to interact with gas-phase species and tholins as they fall through Titan's atmosphere.

Laboratory studies have formed tholins in a N_2/CH_4 gas mixture by electron discharge and photochemistry (Cable et al., 2012; Coll et al., 2013). A range of nitrogen-rich organics and hydrocarbons are present in the tholin-like material, suggesting that co-polymerization or incorporation of small precursors (such as C_2H_2) is occurring. As the formation mechanism of tholins in Titan's atmosphere is unclear, uptake of small precursors onto MSPs and cosmic dust particles could seed the formation and the growth of tholins. If this is the case, heterogeneous chemistry on MSPs and cosmic dust particles could be a possible source for more complex organic species such as C_6H_6. This in turn could lead to further reactions resulting in the formation of poly-aromatic hydrocarbons (PAHs). Thus, greater understanding of the uptake of small precursor species and their surface chemistry on cosmic dust and MSPs is required.

One potential heterogeneous product formed from adsorbed C_2H_2 molecules on cosmic dust is C_6H_6. This conversion mechanism (known as cyclo-trimerization) has mostly been explored on pure and mixed Pd catalysts (e.g. Jungwirthova and Kesmodel (2000) and Ramirez-Cuesta et al. (1995)). In this case, cyclo-trimerization seems to occur through the rapid formation of the C_4H_4 metallocyclic intermediate species (Ormerod et al., 1993; Pacchioni and Lambert, 1994; Ramirez-Cuesta et al., 1995). This species can then react with another adsorbed C_2H_2 species to form C_6H_6 (Hoffmann et al., 1992; Janssens et al., 1998; Ormerod et al., 1991; Patterson and Lambert, 1988; Patterson et al., 1989) or 2 C_4H_4 molecules react together to form cyclo-octatetraene (C_8H_8) which then thermally decomposes to yield C_6H_6 and C_2H_2 (Pacchioni and Lambert, 1994; Ramirez-Cuesta et al., 1995). Interestingly, cyclo-trimerization of C_2H_2 does not occur on MgO (Abbet et al., 2001), which is a substrate perhaps more relevant to cosmic dust analogues.

In this study, the uptake of C_2H_2 is explored on a range of cosmic dust and MSP analogues. The apparatus and experimental procedures are outlined in Section 2, and the results are discussed in Section 3. The observation of C_6H_6 formation through cyclo-trimerization of C_2H_2 on the cosmic dust analogues is also described in Section 3. Section 4 discusses the atmospheric implications for Titan's atmosphere: the estimated available surface area of sedimenting cosmic dust particles is used in a 1-D atmospheric model to compute the heterogeneous C_6H_6 formation rate through C_2H_2 uptake on cosmic dust particles, and compared with the gas-phase C_6H_6 formation rates simulated by the Caltech/JPL 1D model of Titan (Allen et al., 1981; Gladstone et al., 1996; Li et al., 2014; Yung et al., 1984; Zhang et al., 2010).

2. Experimental procedure

2.1. Dual flow tube apparatus

C_2H_2 uptake experiments were performed using a dual borosilicate (SiO_2) flow tube system (Fig. 1). One flow tube contained the cosmic dust/MSP analogue sample and the other acted as a reference tube. Both tubes have an inner diameter of 1.0 cm and a length of 50 cm. The middle sections of both tubes pass through a box containing dry ice (38 cm in length). The flow tubes were connected together by a stainless steel and glass gas-handling line fitted with 3-way taps. A C_2H_2/He gas mixture and a pure He gas were admitted to only one flow tube at any one time, with the gas flows controlled by a calibrated mass flow controller (MKS Instruments, 20 sccm) and a needle valve, respectively. The pressure was measured with a gauge (MKS Baratron, 0–10 Torr) downstream of the mass flow controller. The temperatures inside both flow tubes were monitored using a K-type thermocouple. The exit downstream of the dual flow tubes was coupled through a 0.35 mm diameter orifice to a double-differentially pumped chamber equipped with a quadrupole mass spectrometer (QMS) (VG Scientific, SXP Elite). A second pumping line between the second 3-way tap and the orifice enabled the residence time of the gaseous species in the flow tube to be varied independently of the total pressure.

The olivine ($MgFeSiO_4$), forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4) cosmic dust analogues were prepared by a sol-gel process: stoichiometric amounts of magnesium chloride (Aldrich), ferrous (II) ammonium sulfate (Sigma-Aldrich) and sodium orthosilicate (Alfa Aesar) were mixed at room temperature and then stirred for 7 days to allow the reactions to go to completion (Frankland et al., 2015). Metal salt by-products were removed by repeated dialysis using a soxhlet apparatus with the particles held in water permeable tubing (Snakeskin 7000 MWCO). The products were then stored in a desiccator. Silicon carbide (SiC) particles (Sigma-Aldrich, 200–450 mesh) were used as an MSP analogue. For the uptake experiments, a sample mass (typically 0.5 g) was evenly distributed inside the dust flow tube before degassing by pumping overnight. Gas mixtures of C_2H_2 (BOC, > 98.5 %) in He (BOC, CP grade) with mixing ratios of 1.41×10^{-4}, 2.48×10^{-4} and 1.41×10^{-2} were prepared using standard manometric techniques.

Experiments were performed at 181 ± 2 K. Once the temperature inside both flow tubes had stabilised, the background levels (i.e. without a gas flow) of C_2H_2, butadiene (C_4H_4), C_6H_6 and C_8H_8 were monitored. In a typical experiment, the C_2H_2/He gas mixture (flow rate of 4.5 sccm) was passed through the reference flow tube until the mass traces were stable. The gas mixture was then re-directed through the dust flow tube. For the initial uptake experiments, the gas mixture was flowed over the dust until the mass signal stabilised before swapping back to the reference flow tube. For the uptake experiments which required the dust analogue to become fully saturated with C_2H_2, the gas flow was temporarily re-directed through the reference flow tube roughly every 50 scans in order to facilitate background correction. Once the end point had been reached (in either type of experiment), the C_2H_2 in He gas flow was switched off (initial uptake experiment) or swapped to the pure He gas flow (full C_2H_2 saturation) which was then terminated once the flow tubes had reached ~ 260 K through the