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Phase behavior of propane and *n*-pentane aerosol particles under conditions relevant to Titan

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ABSTRACT

The phase behavior of propane and *n*-pentane aerosols was studied under conditions relevant to Titan's atmosphere. Pure propane or *n*-pentane aerosols and mixed aerosols (mixed with either acetylene, carbon dioxide, or water aerosols) were generated in a bath gas cooling cell. The phase behavior of the aerosols was studied using infrared spectroscopy. Pure propane aerosols remained in a disordered phase during the timescale of the experiment, whereas *n*-pentane aerosols underwent a phase transition from an initially disordered phase into a crystalline phase. For the homogeneous crystallization of *n*-pentane aerosols in a nitrogen bath gas the surface and volume nucleation constants were found to range from 10^{12} to 10^{14} cm^{-2} s^{-1} and from 10^{11} to 10^{13} cm^{-3} s^{-1}, respectively. The presence of solid acetylene, carbon dioxide, or water aerosols did not affect the phase behavior of propane aerosols but significantly accelerated the crystallization of *n*-pentane aerosols with acetylene aerosols acting as the most efficient crystallization nuclei.

1. Introduction

The stratosphere of Saturn's largest moon, Titan, consists of about 98% nitrogen (N_2) and 1.4% methane (CH_4) gas, with the CH_4 concentration increasing to 4.9% below an altitude of 8 km (Niemann et al., 2005; Vinatier et al., 2010b). In the upper atmosphere, a rich CH_4 photochemistry leads to the formation of numerous hydrocarbons and nitriles (Vinatier et al., 2010b), which can condense to form aerosols and clouds in lower atmospheric regions. The phase behavior of simple hydrocarbons is particularly important for aerosol and cloud formation, and more generally for the conditions on Titan (Brown et al., 2010; Lang et al., 2011; Vinatier et al., 2010a; Wang et al., 2010b). The aerosol condensates, depending on their size, shape, optical properties and phase, affect the atmospheric radiation balance *via* scattering and absorbtion of light (Hartmann et al., 2011). The phase behavior of aerosol condensates also impacts cloud dynamics, including the cloud lifetime, precipitation rates and chemical processes.

We have recently initiated a series of laboratory studies to improve the microphysical understanding of the multifarious phase behavior of simple hydrocarbon aerosols with relevance to Titan's atmosphere (Firanescu et al., 2011, in preparation; Lang et al., 2011; Preston et al., 2010; Signorell and Jetzki, 2007; Sigurbjörnsson and Signorell, 2008a;Wang et al., 2009, 2010a,b). Note that with the term "aerosols" we refer exclusively to tropospheric cloud condensates, and not to the aerosols making up the haze layers at higher altitudes, which are commonly referred to as Titan aerosols. Our major focus has been on CH_4 and ethane (C_2H_6) aerosols as two of the most important cloud forming species on Titan (Ádámkovics et al., 2007; Atreya et al., 2006; Barth and Toon, 2006; Brown et al., 2010; Griffith et al., 2006; Tokano et al., 2006). Data from the Cassini mission were crucial for identifying and characterizing these clouds. Our laboratory studies on CH_4 aerosols are consistent with a layered CH_4 cloud structure on Titan, which consists of liquid CH_4–N_2 droplets below ~16 km in altitude, supercooled liquid CH_4–N_2 droplets between ~16 and 19 km, and solid CH_4 particles above ~19 km (Firanescu et al., 2011; Wang et al., 2010a). The results revealed the particular importance of N_2 for Titan's CH_4 clouds. The clouds can contain up to 30% N_2 in the condensed phase, which, for example, prolongs the lifetime of supercooled droplets. Similarly, we have found that incorporating the omnipresent CH_4 and N_2 gas can significantly stabilize supercooled C_2H_6 droplets in Titan's atmosphere (Firanescu et al., in preparation; Lang et al., 2011; Wang et al., 2010b). The formation of such ternary droplets (Firanescu et al., in preparation) depresses the freezing point of liquid droplets and stabilizes supercooled droplets against freezing. For further details and the influence of other aerosol species likely to be present on Titan, such as acetylene (C_2H_2), we refer to Wang et al. (2010b) and Lang et al. (2011).

The present paper is devoted to the study of the phase behavior of propane (C_3H_8) and *n*-pentane (n-C_5H_{12}) aerosol

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condensates under conditions that are representative of Titan's troposphere and lower stratosphere. So far, pentane (C_5H_{12}) has not been detected on Titan, neither as a gas nor in condensed form, although it is a likely product of Titan's CH_4 photochemistry. Navarro-Gonzalez et al. (2001) simulated corona discharges in laboratory experiments and identified n-C_5H_{12} and its isomers amongst other hydrocarbons, including C_2H_6 and C_3H_8, as products. This demonstrates that C_5H_{12} could exist in Titan's atmosphere and hence, at high enough concentrations, could condense to form aerosol particles. In contrast to C_5H_{12}, C_3H_8 gas has already been identified as a product of Titan's CH_4 photochemistry (Coustenis et al., 2010; Maguire et al., 1981; Nixon et al., 2009; Roe et al., 2003) with a stratospheric volume mixing ratio of $4.2 \pm 0.5 \times 10^{-7}$ (Nixon et al., 2009). So far the existence of condensed C_3H_8 has not be confirmed (Coustenis et al., 1999), but it is believed to be one of the main constituents of Titan's lakes, with an estimated mole fraction of 7–8% (Cordier et al., 2009). C_3H_8 condensation to aerosols has not been observed directly, but it is clearly expected to occur around or below an altitude of 60 km at a relatively high rate (total atmospheric pressure = 40 mbar, T = 81 K) (Coustenis et al., 1999). Since C_2H_2 is expected to form aerosol particles in the same region (Coustenis et al., 1999) mixed C_3H_8–C_2H_2 systems have to be taken into account, in particular with regard to the crystallization behavior of C_3H_8 aerosol condensates. Titan's temperature profile allows for the existence of C_3H_8 in the liquid as well as the solid phase. Although not part of the present study, we note that the chemistry of solid C_3H_8 on Titan has been the subject of several laboratory studies. This includes the irradiation of C_3H_8 ice as well as chemical reaction of C_3H_8 with radicals such as the ethynyl radical, C_2H, or the butadiynyl radical, C_4H, which are abundant in many astrophysical environments (Berteloite et al., 2010; Kaiser et al., 2010; Tran et al., 2005).

The crystallization behavior of C_3H_8 and n-C_5H_{12} aerosol condensates under conditions relevant to Titan's atmosphere is the focus of the present paper. Owing to their very different melting points, C_3H_8 (T_{fus} = 85.5 K, Thalladi and Boese, 2000; T_{trip} (C_3H_8) = 85.52 K, Pavese and Besley, 1981) and n-C_5H_{12} (T_{fus} = 143.4 K, Wei, 1999; T_{trip}(n-C_5H_{12}) = 143.48 K, Ruzicka and Majer, 1994) are interesting to compare. Crystallization seems to be fast for n-C_5H_{12} but exceptionally slow in the case of C_3H_8 (Boese et al., 1999; Snyder and Schachtschneider, 1963). Bulk C_3H_8 was found to crystallize in the space group $P2_1/n$ (Boese et al., 1999) and bulk n-C_5H_{12} in the space group *Pbcn* (Boese et al., 1999; Mathisen et al., 1967). In the present work, rapid-scan mid-infrared spectroscopy is used to monitor phase transitions in C_3H_8 and n-C_5H_{12} aerosol condensates and to determine crystallization rate constants. The influence of N_2 – the major gaseous constituent of Titan's atmosphere – and of other species, such as C_2H_2, carbon dioxide (CO_2), and water (H_2O), is reported and discussed. Section 2 briefly describes the experimental setup followed by the results for C_3H_8 and n-C_5H_{12} aerosols in Sections 3.1 and 3.2, respectively.

2. Experimental

Aerosol particles were generated in a custom-built bath gas cooling cell and characterized by IR extinction spectroscopy (Fig. 1A). Details of the experimental setup have been presented in previous publications (Firanescu et al., 2006; Lang et al., 2011; Signorell et al., 2006), so only a brief summary is provided here. The temperature, pressure and gas phase composition in the cooling cell can be controlled over a broad range, which allows us to simulate the conditions in various planetary and lunar atmospheres. The experiments described below, with N_2 as the bath gas at a total pressure of 550 mbar and at a temperature of 78 K, closely mimic the conditions in Titan's atmosphere at an altitude of ~18 km.

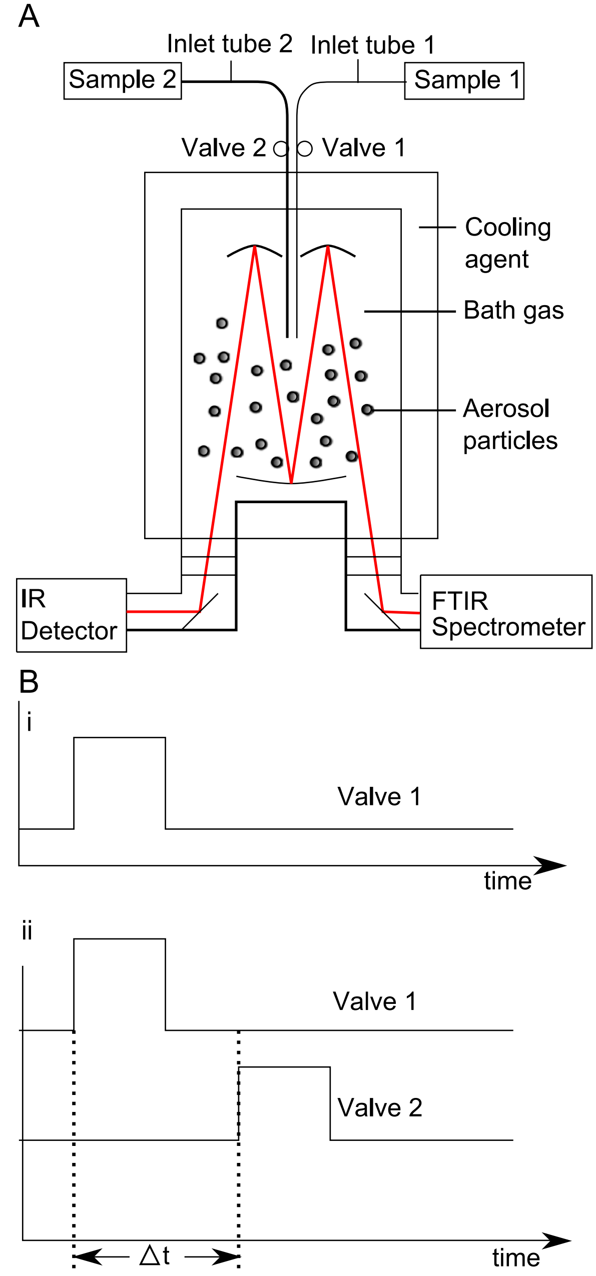

Fig. 1. (A) Sketch of the experimental setup. (B) Injection schemes for gas samples: (i) one-component and premixed injection and (ii) sequential injection with a time delay Δt between the two pulses.

Pure or multicomponent aerosol particle ensembles were generated by injecting warm (T = 293 K) sample gases (diluted in He or N_2) into a pre-cooled (T = 78 K) bath gas. Rapid cooling of the injected sample leads to supersaturation of the gas of interest and eventually to aerosol particle formation. The bath gas was either He or N_2 at pressures of 550 or 800 mbar. The backing pressure of the sample gas was typically 1.5 bar. For the mixed aerosols, the ratios of C_3H_8 or n-C_5H_{12} to CO_2, C_2H_2, or H_2O were typically 4:1, 3:1, 2:1 or 1:1. In an attempt to obtain the IR spectra of liquid C_3H_8 and n-C_5H_{12} droplets, their spectra were also recorded above the respective melting points of the bulk by adjusting the cell temperature with a heating unit.

To form pure and various mixed aerosol particles different injection methods were used. In our system, two different sample