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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\textsubscript{2}H\textsubscript{2}) on cosmic dust analogues over the temperature range encountered in Titan’s atmosphere below 600 km. The uptake coefficient, $\gamma$, 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\textsubscript{2}H\textsubscript{2} on Mg\textsubscript{2}SiO\textsubscript{4}, MgFeSiO\textsubscript{4} and Fe\textsubscript{2}SiO\textsubscript{4}, respectively, indicating that $\gamma$ is independent of Mg or Fe active sites. The uptake of C\textsubscript{2}H\textsubscript{2} was also measured on SiO\textsubscript{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 cyclo-trimerization of C\textsubscript{2}H\textsubscript{2} to C\textsubscript{6}H\textsubscript{6} was found to be $2.6 \times 10^{-5} \exp(-741/T)$ s\textsuperscript{-1}, with an uncertainty ranging from $\pm 27$ % at 115 K to $\pm 49$ % at 181 K. A chemical ablation model was used to show that the bulk of cosmic dust particles (radius 0.02 - 10 \textmu m) 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 C₆H₆ via uptake of C₂H₂ on cosmic dust, followed by cyclo-trimerization and desorption, is probably competitive with gas-phase production of C₆H₆ between 80 and 120 km.

**Keywords:** Titan Atmosphere; Cyclo-trimerization of acetylene; Benzene formation; Cosmic dust; Kuiper belt.

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 with the main haze region occurring from ~ 220 km to the surface. A detached haze layer lies in the mesopause region around 500 km. 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 (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆), benzene (C₆H₆) and hydrogen cyanide (HCN), provide feedstocks for formation of these aerosols. C₂H₂ is the second most abundant minor species after C₂H₆ and is predominantly formed by photodissociation of C₂H₄ above ~600 km. The vertical profile of C₂H₂ was determined by 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.
These models, based on kinetics measured in the laboratory, reveal that the major loss pathways for C₂H₂ are: hydrogenation to C₂H₄; formation of C₄H₂ (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 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}SiO₄ where 0 ≤ n ≤ 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\(_2\)H\(_2\)) 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\(_6\)H\(_6\). 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\(_2\)H\(_2\) molecules on cosmic dust is C\(_6\)H\(_6\). 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\(_4\)H\(_4\) metallocyclic intermediate species (Ormerod et al., 1993a; Pacchioni and Lambert, 1996).
This species can then react with another adsorbed $\text{C}_2\text{H}_2$ species to form $\text{C}_6\text{H}_6$ [Hoffmann et al., 1992; Janssens et al., 1998; Ormerod et al., 1991; Patterson and Lambert, 1988; Patterson et al., 1989] or 2 $\text{C}_2\text{H}_4$ molecules react together to form cyclo-octatetraene ($\text{C}_8\text{H}_8$) which then thermally decomposes to yield $\text{C}_6\text{H}_6$ and $\text{C}_2\text{H}_2$ [Pacchioni and Lambert, 1994; Ramirez-Cuesta et al., 1995]. Interestingly, cyclo-trimerization of $\text{C}_2\text{H}_2$ 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 $\text{C}_2\text{H}_2$ 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 $\text{C}_6\text{H}_6$ formation through cyclo-trimerization of $\text{C}_2\text{H}_2$ 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 $\text{C}_6\text{H}_6$ formation rate through $\text{C}_2\text{H}_2$ uptake on cosmic dust particles, and compared with the gas-phase $\text{C}_6\text{H}_6$ 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

$\text{C}_2\text{H}_2$ uptake experiments were performed using a dual borosilicate ($\text{SiO}_2$) flow tube system (Figure 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$_2$H$_2$/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.

Figure 1. Schematic diagram of the dual flow tube apparatus: K = K-type thermocouples; MF = mass flow controller; N = needle valve; P = pressure gauge; QMS = quadrupole mass spectrometer; R = rotary pump T = turbo pump; V = 2- or 3-way valve.
The olivine (MgFeSiO$_4$), forsterite (Mg$_2$SiO$_4$) and fayalite (Fe$_2$SiO$_4$) 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$_2$H$_2$ (BOC, > 98.5 %) in He (BOC, CP grade) with mixing ratios of $1.41 \times 10^{-4}$, $2.48 \times 10^{-4}$ and $1.41 \times 10^{-3}$ 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$_2$H$_2$, butadiene (C$_4$H$_4$), C$_6$H$_6$ and C$_8$H$_8$ were monitored. In a typical experiment, the C$_2$H$_2$/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$_2$H$_2$, 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$_2$H$_2$ in
He gas flow was switched off (initial uptake experiment) or swapped to the pure He gas flow (full C$_2$H$_2$ saturation) which was then terminated once the flow tubes had reached ~ 260 K through the controlled removal of dry ice from the cooler box. The experiments were repeated at least 3 times for each analogue under a fixed set of conditions. Between each initial uptake experiment when the same dust analogue was used, the sample inside the dust flow tube was heated using a heat gun to roughly 60 °C for a minimum of 5 minutes to ensure all the C$_2$H$_2$ molecules had desorbed (confirmed by monitoring m/z = 26 with the QMS). For the full saturation uptake experiments, a fresh dust analogue sample was used.

The QMS data was background corrected with respect to the mass signal when no gas was flowing. To take into account any drift in the C$_2$H$_2$ mass signal intensity, the data from the reference flow tube was plotted against time and a line of best fit applied. This was then used to correct the reference C$_2$H$_2$ mass signal to a value of 1×10$^5$ counts (average initial m/z = 26 signal in the reference flow tube) over the full experiment. The drift in the C$_2$H$_2$ mass signal for the initial uptake was small (< 1000 counts over ~14 minutes) whereas the drift in the longer-duration full uptake experiments followed a decay curve (~100,000 counts over 100 minutes). The drift correction factor (with respect to time) derived from the reference flow tube was applied to the data from the dust flow tube for that experiment. An additional step to reduce the effect of the mass signal drift was to run the QMS (collecting background spectra) for at least 30 minutes prior to the start of an experiment. The same background and mass signal drift correction procedures were applied to any other masses of interest in the mass spectra.
2.2. **UHV Apparatus**

The heterogeneous chemistry of C\(_2\)H\(_2\) on dust analogues was explored using an ultra-high vacuum (UHV) apparatus (Figure 2). This system has been described previously by Vondrak et al. (2006). Briefly, the ~25 L chamber is pumped by a 550 L s\(^{-1}\) turbo-molecular pump backed by a rotary pump, achieving a base pressure of typically < 3 \times 10^{-9} \text{ mbar}. The chamber is equipped with a quadrupole mass spectrometer (Hiden, HAL 3F 301 RC PIC), reflection-absorption infrared spectroscopy (RAIRS) system (Brucker, IFS 66/S), a needle valve (NUPRO, SS48K) for gas dosing and an inert ion (Ar\(^+\)) sputter source which was modified to function as a leak valve for this study. A cylindrical stainless steel sample mount (12 mm diameter and 2.5 mm thickness) was coated on one side with a thin layer of Fe\(_2\)SiO\(_4\) dust generated in a photochemical reactor (Saunders and Plane, 2011), and then mounted in the centre of the UHV chamber via tungsten (W) heating wires onto an oxygen-free high conductivity cold finger, which in turn was mounted onto an xyz\(\theta\) manipulator (Figure 2). The sample was liquid nitrogen cooled to a base temperature of ~115 K and could be heated resistively using the W wires embedded through the sample mount. The surface temperature was monitored using a K-type thermocouple positioned in a small hole on the side of the sample mount. Prior to each experiment the sample was annealed at 600 K for 30 minutes. It should be noted that although cosmic dust from the EKB is thought to be richer in Mg than Fe (Gainsforth et al., 2015; Zolensky et al., 2006), the results obtained in this study show that C\(_2\)H\(_2\) uptake and cyclo-trimerization of C\(_2\)H\(_2\) to C\(_6\)H\(_6\) is independent of Mg and Fe active sites at a mean temperature of 181 K. This was assumed to be the case at lower dust surface temperatures as well.
**Figure 2.** Schematic diagram of the upper (top left) and lower layer (top right) of the UHV apparatus, and the sample mount arrangement (bottom): QMS = quadrupole mass spectrometer (which can be situated at either layer); FTIR = Fourier transform infrared spectrometer.

C$_2$H$_2$ (BOC, > 98.5 %) was dosed onto the sample via the needle valve in the form of a collimated effusive beam slightly larger than the sample. This minimises adsorption (and therefore desorption) of dosed species onto other nearby surfaces such as the cold finger. Any species adsorbed onto the W wires would desorb immediately upon heating. The C$_2$H$_2$
dosing rate was calibrated using beam flux calibrations based on the procedure by Oakes (1994). Briefly, the beam flux, $F_{\text{beam}}$, is calculated from the exponential decay of a gas species starting from the point when the input gas flow has been terminated [Mangan et al., 2015].

The exponential decay is described by:

$$P = P_0 \exp^{-C_m t} \quad (1)$$

where $P$ is the pressure, $P_0$ is the initial pressure at the termination of the dose, $C_m$ is the pumping coefficient for that gas and $t$ is the time from the start of the decay. Equation 1 was linearised and $C_m$ and $P_0$ obtained from the gradient and intercept, respectively. From this $F_{\text{beam}}$ is given by:

$$F_{\text{beam}} = \frac{V_{\text{system}} C_m P_0}{k_B T A_{\text{beam}}} \quad (2)$$

where $V_{\text{system}}$ is the volume of the chamber, $k_B$ is the Boltzmann constant, $T$ the temperature of the gaseous species and $A_{\text{beam}}$ the cross sectional area of the molecular beam. $F_{\text{beam}}$ in this study was $(1.3 \pm 0.1) \times 10^{14}$ molecules cm$^{-2}$ s$^{-1}$.

In a typical experiment, a thin film of C$_2$H$_2$ was dosed onto the Fe$_2$SiO$_4$ sample. The sample was held at the required dosing temperature until just before the final stage of the experiment, when the sample was cooled to base temperature (115 K) before performing a temperature programmed desorption (TPD) analysis, where the sample was heated up to 600 K with a heating ramp of 0.96 ± 0.03 K s$^{-1}$. This ensured that all species physisorbed to the sample were desorbed, providing a clean substrate surface for the next experiment.
3. Results and Discussion

3.1. $C_2H_2$ Uptake Coefficient

A typical background-corrected mass spectrum for the initial uptake of $C_2H_2$ on $Mg_2SiO_4$ is displayed as a function of time in Figure 3. The plot shows a significant drop in the normalised mass spectrometer signal for $C_2H_2$ as the gas mixture is re-directed from the reference to the dust flow tube at ~325 s. The mass signal recovers almost instantaneously when the gas mixture is directed back to the reference flow tube at ~710 s. The rate of uptake of a gas to a solid surface is characterised by the probability that a collision will result in loss of a molecule from the gas phase. This is an empirical quantity termed the uptake coefficient, $\gamma$.

![Figure 3](image_url)

**Figure 3.** Typical mass spectrum of $C_2H_2$ uptake on forsterite. Star symbols indicate the times when the gas flow was directed from the reference to the dust and from the dust back to the reference flow tubes.
The first-order rate of loss, \(-d[N]/dt\), of the gaseous concentration of species \(N\) is given by:

\[
\frac{-d[N]}{dt} = k[N] \quad (3)
\]

where \(k\) is the rate coefficient for loss. If the residence time, \(\tau\), in the cooled section of the flow tube is significantly greater than the time for \(C_2H_2\) molecules to diffuse to the dust surface, then the rate of loss measured at the exit from the flow tube is controlled by uptake to the surface. This condition was achieved by varying \(\tau\) between 3 and 7 s, while the characteristic diffusion time across the tube was 0.01 s at a He pressure of 8 Torr. Thus \(k\) can be taken as the uptake rate coefficient, \(k_\gamma\), which is calculated from:

\[
k_\gamma = \frac{r^2a_s}{4V} = \frac{\ln([N]_0/[N]_\tau)}{\tau} \quad (4)
\]

where \(c\) is the molecular mean speed, \(a_s\) the surface area of the dust sample, \(V\) the volume of the cooled section of the flow tube, and \([N]_0\) and \([N]_\tau\) are the gas-phase concentrations of species \(N\) at the entrance and exit of the flow tube, respectively. In this study, \(\gamma\) was calculated by varying either \(a_s\) or \(\tau\).

One potential complication with this technique is knowledge of the fraction of the sample specific surface area which is actually involved in uptake of the gas. At one extreme, if a gas is readily taken up then it will only be the particles in the uppermost layers of the sample which will be directly involved. At the other, if \(\gamma\) is small then the gas will penetrate throughout the sample and be exposed to the full surface area. Possible values of \(a_s\) range from the geometric \((a_{(geo)}\), given by the cross sectional area of the dust inside the cooled region of the flow tube) to the surface area estimated from the Brunauer-Emmet-Teller (BET) isotherm \((a_{(BET)}\), determined from the uptake of \(N_2\) gas to the surface at cryogenic temperatures)
Thus, the lower limit for \(a_s (a_{GEO})\) gives an upper limit for \(\gamma\) and vice versa for \(a_s = a_{BET}\).

To determine the available surface area for the adsorption of \(C_2H_2\), the uptake experiments were repeated for different sample masses. The results for \(Mg_2SiO_4\) are displayed in Figure 4, which shows that \(\gamma\) remained constant (within experimental error) for the assumption that

**Figure 4.** The uptake coefficient (\(\gamma\)) as a function of \(Mg_2SiO_4\) dust surface area: upper panel, the geometric surface area (\(a_{GEO}\)); lower panel, the BET surface area (\(a_{BET}\)).
\(a_s=a(GEO)\). This indicates that the uptake of \(C_2H_2\) was confined to the particles in the uppermost layers of the dust analogue. When \(a(BET)\) was used, the value of \(\gamma\) decreased with increasing mass. Since the number of active sites for sticking should increase linearly with the available surface area, less than the full BET surface area must have been available for \(C_2H_2\) uptake in these experiments. The same behaviour was observed for Fe\(_2\)SiO\(_4\) and FeMgSiO\(_4\) (not shown). Thus, only the values of \(\gamma\) using \(a(GEO)\) as \(a_s\) for Mg\(_2\)SiO\(_4\), MgFeSiO\(_4\) and Fe\(_2\)SiO\(_4\) are displayed in Table 1 with the error taken as 1 standard deviation of the mean between repeats.

**Table 1.** \(C_2H_2\) uptake coefficients and \(C_2H_2-C_2H_2\) average distances on the cosmic dust analogues.

<table>
<thead>
<tr>
<th>Cosmic dust analogue</th>
<th>(\gamma) (181 K)</th>
<th>(C_2H_2-C_2H_2) average distance / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(_2)SiO(_4)</td>
<td>((1.6 \pm 0.4) \times 10^{-4})</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>MgFeSiO(_4)</td>
<td>((1.9 \pm 0.4) \times 10^{-4})</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>Fe(_2)SiO(_4)</td>
<td>((1.5 \pm 0.4) \times 10^{-4})</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>&lt; (5.8 \times 10^{-8})</td>
<td>-</td>
</tr>
<tr>
<td>SiC</td>
<td>&lt; (3.6 \times 10^{-7})</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1 shows that the \(\gamma\) values for Mg\(_2\)SiO\(_4\), MgFeSiO\(_4\) and Fe\(_2\)SiO\(_4\) are the same within experimental error, yielding an average \(\gamma = (1.7 \pm 0.4) \times 10^{-4}\). These results suggest that the uptake of \(C_2H_2\) is independent of Mg or Fe active sites on the analogue surface, indicating that \(C_2H_2\) uptake will occur on any un-ablated cosmic dust with an olivine (and probably pyroxene) composition. Whether the \(C_2H_2\) uptake was controlled by SiO active sites was explored by comparing the uptake of \(C_2H_2\) on the bare borosilicate (SiO\(_2\)) flow tube walls at 295 and 181 K. This yielded \(\gamma < 5.8 \times 10^{-8}\) over this temperature range.

Uptake of \(C_2H_2\) on SiC was also not measurable, with \(\gamma < 3.6 \times 10^{-7}\) (the upper limit to \(\gamma\) for SiC is larger than for SiO\(_2\) because of the difference between the geometric surface area of the
SiC analogue sample and the walls of the flow tube (14.9 and 119 cm², respectively)). Other MSP analogues that could be formed in Titan’s atmosphere include metal-organics. However, measuring uptake on these species is not possible since they tend to be unstable in air.

Additional initial C₂H₂ uptake experiments were performed on Mg₂SiO₄ by varying τ, which was achieved by varying the mass flow rate through the flow tubes at constant, but maintaining a constant pressure by using the pumping line between the second 3-way tap and the mass spectrometer orifice (Figure 1). The average results are displayed in Figure 5 with the error taken as one standard deviation for each τ data set. A line of best fit was applied to the experimental data (solid red line) which passes through the origin (within experimental error). From the gradient, a value of \( \left(1.9 \pm 0.4\right) \times 10^{-4} \) was obtained for γ, which is within experimental error of the value obtained when τ was fixed (i.e. when the value of \( \sigma_s \) was determined).

![Figure 5. C₂H₂ intensity response with respect to the residence time of C₂H₂ in the flow tube, τ, on Mg₂SiO₄.](image)
For some of the experiments on 0.5 g of Mg$_2$SiO$_4$, MgFeSiO$_4$ or Fe$_2$SiO$_4$, the uptake of C$_2$H$_2$ was continued until the C$_2$H$_2$ mass signal returned back to the pre-dust exposure level, at which point the dust analogue had become saturated. This enabled the average distance between two C$_2$H$_2$ molecules, $d_{av}$, to be calculated. Note that fresh dust analogue samples were used for these full saturation uptake experiments. The total number of C$_2$H$_2$ molecules adsorbed onto the C$_2$H$_2$-saturated dust in the flow tube, $C_{2H2surf}$, was obtained by integrating the area above the m/z = 26 trace up to the mass signal intensity observed in the reference flow tube (after background and mass signal drift correction). $d_{av}$ was then calculated using equation 5:

$$d_{av} = \frac{a_s}{\sqrt{C_{2H2surf}}}$$

(5)

where $a_s$ was set to $a_{(GEO)}$. Table 1 shows that $d_{av}$ ranges from 2 to 4 Å for the fully saturated Mg$_2$SiO$_4$, MgFeSiO$_4$ and Fe$_2$SiO$_4$ dust analogues. These $d_{av}$ distances are similar to the total length of a C$_2$H$_2$ molecule (3.3 Å), which is close enough (if energy barriers are not too large) for C$_2$H$_2$ to polymerize to form products such as C$_4$H$_4$, C$_6$H$_6$ and C$_8$H$_8$.

3.2. Heterogeneous Chemistry of C$_2$H$_2$ on Olivines

The formation of C$_2$H$_2$ oligomers on Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$ was explored by performing an extended version of the C$_2$H$_2$ uptake experiment (Figure 6). Once the dust analogue had become saturated (around 5650 s in Figure 6), the C$_2$H$_2$/He flow was switched to pure He and the dust temperature held at 181 K until the gas-phase C$_2$H$_2$ concentration had returned to the background level. The dust temperature was then raised through the controlled removal of dry ice from the cooler box. The resulting heating ramp is shown in the insert plot in Figure 6. The C$_6$H$_6$ mass trace was background corrected using the same procedure as for C$_2$H$_2$.
(Section 2), and scaled to the C$_2$H$_2$ concentration using their respective ionization cross sections.

**Figure 6.** Uptake of C$_2$H$_2$ and conversion into C$_6$H$_6$ as a function of time. Between 1000 and 5600 s, the Fe$_2$SiO$_4$ dust analogue at 181 K became saturated when exposed to a flow of C$_2$H$_2$ in He. The flow was then switched to pure He until 16500 s, when the dust temperature was increased (temperature ramp shown in the insert plot).

During the C$_2$H$_2$ uptake part of the experiment (1000 - 5650 s in Figure 6), the gas-phase C$_6$H$_6$ signal increases, clear evidence that cyclo-trimerization of C$_2$H$_2$ is occurring on the dust surface. When the gas mixture was changed over to pure He, the intensity of C$_6$H$_6$ reached a temporary plateau for ~3500 s before continuing to rise. This second increase in C$_6$H$_6$ intensity occurred before applying the heating ramp (at 16500 s), indicating that the surface was warm enough for C$_6$H$_6$ desorption to occur. The remaining C$_6$H$_6$ and C$_2$H$_2$ desorbed from the surface
when the dust temperature increased through the controlled removal of dry ice from the cooler box.

*C₆H₆* can exist in more than a dozen isomeric forms which could give rise to the observed signal at *m/z* = 78. However, there are three pieces of evidence that the *C₆H₆* species in the present study is benzene. First, Figure 7 shows a typical set of *C₂H₂* and *C₆H₆* TPD traces resulting from a *C₂H₂* uptake experiment at 115 K. Also shown in this plot is a TPD trace of benzene directly dosed onto the olivine dust in a separate experiment. Note that both *C₆H₆* desorption peaks have coincident falling edges (within experimental error), which is typical of sub-monolayer coverages desorbing from a surface containing multiple binding sites e.g. Thrower et al. (2009). It is unlikely that other *C₆H₆* isomers would have such similar temperature-dependent desorption kinetics as benzene. Second, cyclo-trimerization studies of *C₂H₂* at low temperatures on metal surfaces have identified benzene as the *C₆H₆* product through ultraviolet photoelectron spectroscopy Sesselmann et al., 1983; Tysoe et al., 1983 and high-resolution electron energy loss spectroscopy Jungwirthova and Kesmodel, 2000. Third, consideration of the reaction energetics indicates that benzene is most likely the *C₆H₆* product. All linear forms of *C₆H₆* (e.g. 2,4-hexadiyne) and fulvene are very unlikely to form at low temperatures because at least one *sp* H atom shift would be required, involving a large energy barrier. For the remaining compounds where an H atom shift is not required, we have calculated the enthalpy of formation from 3 *C₂H₂* molecules at the cbs-qb3 level of theory Frisch et al., 2009. The $\Delta H^\circ$ values are -597, -290, -271 and -117 kJ mol⁻¹ for benzene, benvalene, dewar benzene and prismane, respectively. The enormous relative stability of benzene is consistent with the experimental evidence (see above) that this is the form of *C₆H₆* produced in the present study.
Figure 7. C$_2$H$_2$ and C$_6$H$_6$ TPD traces obtained from C$_2$H$_2$ cyclo-trimerization, and C$_6$H$_6$ dosed directly onto the Fe$_2$SiO$_4$ sample, which was held at 115 K.

The intermediate species C$_4$H$_4$ was also monitored during these experiments but the mass trace (not shown) remained below the QMS detection limit indicating that this species, if formed, is a short-lived intermediate which undergoes further reaction on the surface to form the observed C$_6$H$_6$. Hence, the steady-state concentration of C$_4$H$_4$ was too low to observe by TPD under our experimental conditions, as in studies of cyclo-trimerization on palladium crystal surfaces (Abbet et al., 2001; Janssens et al., 1998). In contrast, cyclo-trimerization studies of C$_2$H$_2$ on palladium and copper surfaces have detected C$_4$H$_4$ by using techniques which directly probe the surface e.g. near-edge X-ray absorption fine structure (Ormerod et al., 2001).
al., 1993b), laser-induced thermal desorption spectroscopy (Abdelrehim et al., 1995), temperature programmed reaction (Kyriakou et al., 2005), and sum frequency generation (Öberg et al., 2012).

In order to confirm that C$_6$H$_6$ was produced from C$_2$H$_2$ cyclo-trimerization, rather than being an impurity in the C$_2$H$_2$, a set of C$_2$H$_2$ dosed time delay TPD experiments were performed using the UHV apparatus. Here, C$_2$H$_2$ was dosed onto the Fe$_2$SiO$_4$ coated sample with the sample held at 130 K for 7940 s. The time between terminating the C$_2$H$_2$ dose and starting the TPD linear heating ramp was varied in order to examine whether the amount of C$_6$H$_6$ observed changed with respect to the delay time. The C$_6$H$_6$ TPD yield was obtained by integrating the C$_6$H$_6$ TPD peak with respect to time. **Figure 8** demonstrates a clear linear trend between C$_6$H$_6$ TPD yield and the delay time, which passes through the origin (within experimental error). This confirms that the source of the C$_6$H$_6$ mass trace observed in this study was cyclo-trimerization of C$_2$H$_2$ on the dust analogue surface.
Figure 8. C₆H₆ TPD yield plotted as a function of the time delay between termination of the C₂H₂ dose (with the Fe₂SiO₄ sample held at 130 K) and start of the TPD linear heating ramp.

The first-order cyclo-trimerization rate of C₂H₂ to form ½ of a C₆H₆ molecule, \( k_{CT} \), in the dual flow tube experiments was calculated by dividing the production rate of C₆H₆ molecules per second by \( C₂H₂_{surf} \), when the dust analogue becomes saturated with C₂H₂ (before the gas mixture was switched to pure He). On Mg₂SiO₄, a mean of four separate experiments gave \( k_{CT} = (5.0 \pm 1.7) \times 10^{-7} \) s⁻¹ with a 1 standard deviation error. A single experiment was performed on Fe₂SiO₄ giving \( k_{CT} = 1.7 \times 10^{-7} \) s⁻¹ which is probably within experimental error of the result on Mg₂SiO₄. For modelling purposes (Section 4), we use an overall value for \( k_{CT} \) on olivines of \( (4.3 \pm 2.1) \times 10^{-7} \) s⁻¹.

The temperature dependence of \( k_{CT} \) was investigated using the UHV apparatus by dosing C₂H₂ onto the sample held at 115, 130 and 181 K for a fixed delay time (8040 s) before performing TPD analysis. A typical set of C₂H₂ and C₆H₆ traces are displayed in Figure 7. The desorption peak for C₂H₂ begins immediately indicating that C₂H₂ was desorbing from the Fe₂SiO₄ surface during the dose and subsequent delay time. The surface concentrations of C₂H₂ and C₆H₆ at each sample temperature were obtained from the corresponding TPD peak using the same procedure as that for the C₆H₆ TPD yield. The C₆H₆ surface concentration was divided by the delay time (i.e. the time between the end of the C₂H₂ dose and the start of the TPD) and the C₂H₂ surface concentration to give \( k_{CT} \). The results at 115, 130 and 181 K are \( (4.1 \pm 1.1) \times 10^{-8} \), \( (2.5 \pm 0.6) \times 10^{-7} \) and \( (2.0 \pm 0.5) \times 10^{-6} \) s⁻¹, respectively. Thus, \( k_{CT} \) increases with temperature, which has been seen previously in studies of C₂H₂ cyclo-trimerization on Pd.
al., 1996; Janssens et al., 1998). Note that the UHV value of $k_{CT}$ at 181 K is larger by a factor of \(~5\) than the corresponding value obtained using the dual flow tube apparatus (at the same temperature). This is because the TPD data does not account for the decrease in the C$_2$H$_2$ surface concentration due to desorption after the C$_2$H$_2$ dosing is stopped; hence the UHV method provides an upper limit for $k_{CT}$ at 181 K. However, at 115 K the desorption of C$_2$H$_2$ would be much slower, and hence the $k_{CT}$ value measured at this temperature should be correct. Combining this 115 K value with the 181 K measurement in the dual flow tube yields the Arrhenius expression $k_{CT} = 2.6 \times 10^{-5} \exp(-741/T) \text{ s}^{-1}$. Taking account of the errors in the two measured data points, the error in $k_{CT}$ varies from \(\pm27\) to \(\pm49\%\) between 115 and 181 K.

4. Implications for Titan’s Atmosphere

4.1 Modelling the cosmic dust abundance

To explore the formation of C$_6$H$_6$ in Titan’s atmosphere via the heterogeneous chemistry of C$_2$H$_2$ on un-ablated cosmic dust particles, a 1D model was constructed. The vertical profiles of temperature, eddy diffusion coefficient ($K_{zz}$), pressure and C$_2$H$_2$ number density and were taken from the Caltech/JPL 1D model of Titan’s atmosphere (Allen et al., 1981; Gladstone et al., 1996; Li et al., 2014; Yung et al., 1984; Zhang et al., 2010), and interpolated onto a 1 km resolution grid extending from 0 to 605 km. These profiles are illustrated in Figure 9.
Figure 9. Vertical profiles of (a) temperature and eddy diffusion coefficient ($K_{zz}$) and (b) pressure and $C_2H_2$ concentration in Titan’s atmosphere, taken from the Caltech/JPL 1D model [Li et al., 2014].

Data collected from the Pioneer 10 meteoroid detector and from the Student Dust Counter (SDC) on the New Horizons mission has been modelled by Poppe and Horanyi (2012) to obtain the differential number flux ($d\phi/d\log_{10}(r)$) of dust particles from the EKB entering the
Saturnian system, including Saturn’s satellites and rings. In a recent update, Poppe (2016) has now added contributions from Jupiter Family (JFC), Halley Type (HTC), and Oort Cloud (OTC) comets into the model. Figure 10 illustrates the contributions from each of these sources, and the resulting total differential flux of particles into Titan’s atmosphere. It should be noted that the Oort Cloud flux is really an upper limit, since the Pioneer 10 data can, strictly speaking, be fit with only contributions from JFC and EKB grains. While the HTC grains are included for completeness, they contribute very little to the overall flux. The modelled differential flux can be fit to the following parameterisation of particle radius $r$ (in m):

$$\frac{d\phi}{d\log_{10}(r)} / \text{particle m}^{-2} \text{s}^{-1} = 6.22 \times 10^{-34} \times r^{-[7.96 + 0.506 \log_{10}(r)]}$$

Figure 9 shows this parameterisation extrapolated from the particle size range measured (0.45 - 100 $\mu$m) down to 20 nm. The gradual fall-off in the differential flux is expected because solar radiation pressure ejects very small particles from the solar system, and the Saturnian magnetosphere may also prevent small particles reaching the moons, as has been modelled in the case of Jupiter (Colwell and Horanyi, 1996). The dust is assumed to have a density of 2500 kg m$^{-3}$ (Han et al., 2011), and was segregated into 38 size bins increasing geometrically in particle radius from 0.016 to 129 $\mu$m. The total mass of unablated cosmic dust into Titan’s atmosphere is then 0.14 tonnes per earth day, which is an order of magnitude less a previous estimate of 1.4 t d$^{-1}$ (Molina-Cuberos et al., 2001). However, this estimate was based on extrapolations of dust grain models from 1 AU, which Poppe (2016) has pointed out will over-predict the mass input by about 1 order. In any case, the differential flux illustrated in Figure 9 is essentially based on two data points (Pioneer 10 and the SDC), so is probably uncertain within an order of magnitude.
Figure 10. Differential flux of cosmic dust particles into Titan’s atmosphere, showing the total flux made up of particles from the following sources: EKB=Edgeworth Kuiper Belt; JFC=Jupiter family comets; HTC=Halley comets; OCC=Oort Cloud comets. The line labelled Fit is the parameterisation in eqn. 6.

We now examine the fraction of these dust particles that will ablate. The Chemical ABlation MODel (CABMOD) \cite{Vondrak2008} was adapted to treat meteoric ablation in Titan’s atmosphere starting at 1200 km. For a given meteoroid mass, velocity and entry angle, CABMOD predicts the ablation rate of individual meteoric elements through sputtering (i.e. through inelastic collisions with atmospheric molecules), and by evaporation of oxides and atoms once the particle melts. EKB particles were taken to have an olivinic composition, as determined by the analysis of Comet 81P/Wild 2 dust samples \cite{Gainsforth2015}. 
Zolensky et al., 2006, with an Fe:Mg ratio of ~0.6: this implies, according to the olivine phase diagram, the particles melting at 1750 K (Vondrak et al., 2008). Figure 11 is an example of CABMOD output, showing the predicted elemental injection rates for a meteoroid with an entry velocity of 18 km s\(^{-1}\) and a mass of 100 µg. The most volatile elements, Na and K, are released at ~550 km, whereas the main constituents Fe, Si and Mg are released about 70 km closer to the surface. Because of Titan’s large scale height, which is roughly 40 km at these meteoric ablation altitudes, ablation occurs over a much wider range of altitudes compared to the terrestrial planets (Molina-Cuberos et al., 2008; Vondrak et al., 2008; Whalley and Plane, 2010).

![Figure 11](image)

**Figure 11.** Ablation profiles of individual elements for a 100 µg \((r = 200 \mu m)\) meteoroid entering Titan’s atmosphere at 18 km s\(^{-1}\) and 35° to zenith.

Figure 12 shows the mass fraction of a meteoroid that ablates, plotted as a function of particle radius/mass and entry velocity. The dust entry velocity into Titan’s atmosphere ranges from...
2.6 - 29.1 km s$^{-1}$, with a mean of 18 km s$^{-1}$ \cite{Molina-Cuberos:2001}. The plot shows that particles smaller than 10 $\mu$m do not reach the melting point of 1750 K, so a very small fraction (<1%) of mass is lost by sputtering. Larger particles exhibit more severe loss through melting and evaporation, so a particle of 200 $\mu$m (~100 $\mu$g) loses up to 90% of its mass at the highest entry velocities. However, these larger particles sediment very rapidly through Titan’s atmosphere; it is only particles smaller than 10 $\mu$m that contribute significantly to the available surface area for heterogeneous chemistry (see below).

![Figure 12](image)

Figure 12. Ablated fraction of a meteoroid with a particle density of 2500 kg m$^{-3}$ as a function of mass and velocity.
The flux of dust particles of different sizes being transported vertically by eddy diffusion and sedimentation is given by:

\[ \phi_i = -K_{zz} \left( \frac{\partial N_i}{\partial z} + \left( \frac{1}{T} \frac{\partial T}{\partial z} + \frac{1}{H} \right) N_i \right) + w_i N_i \]  

(7)

where \( \phi_i \) is the vertical flux of particles in dust size bin \( i \), \( K_{zz} \) is the eddy diffusion coefficient, \( N_i \) is the dust number density, \( H \) is the atmospheric scale height, and \( w_i \) is the sedimentation velocity. \( w_i \) can be determined from a form of Stokes’ law which describes a spherical particle falling through a stationary fluid [Jacobson, 2005]:

\[ w_i = \frac{2(\rho_{dust} - \rho_{air})}{9 \mu} g r_i^2 C_{scf} \]

(8)

where \( \rho_{dust} \) and \( \rho_{air} \) are the dust and air density; \( \mu \) is the dynamic viscosity of \( N_2 \) at temperature \( T \); \( g \) is the gravitational constant (1.352 m s\(^{-2}\) for Titan); \( r_i \) is the particle radius and \( C_{scf} \) is the Cunningham slip correction factor which takes into account the non-continuum effects of drag on small particles. \( C_{scf} \) is estimated from equation 9, where \( \lambda \) is the mean free path of the air molecules, and \( A_1, A_2 \) and \( A_3 \) are dimensionless coefficients which for \( N_2 \) are equal to 1.249, 0.42 and 0.87, respectively [Kasten, 1968].

\[ C_{scf} = 1 + \frac{\lambda}{r_i} \left( A_1 + A_2 \exp \left( \frac{-A_3 r_i}{\lambda} \right) \right) \]

(9)

Because the number density of these un-ablated cosmic dust particles is relatively small, and they rapidly become coated with a monolayer of \( C_2H_2 \) (see below), coagulation should not play a major role as they descend through the atmosphere. Under steady-state conditions, the flux of particles in each size bin is then constant throughout the atmosphere to the surface. Equation 7 was solved using a time-implicit integration scheme [Shimazaki, 1985]. Figure 13 shows the resulting size distributions of particle number density \( (N) \) and volumetric...
surface area ($A_s$), as a function of height between the surface and 600 km. It is clear that most of the available surface area for heterogeneous chemistry is below 150 km, and is provided by small particles ($0.04 < r < 2 \mu m$). The highest values of $A_s$ are therefore located in the same atmospheric region as the main haze layer below $\sim 220$ km (Rages and Pollack, 1983; Smith et al., 1981).
Figure 13. A plot of the size distribution of un-ablated cosmic dust particle number
density, $N$, (top panel) and volumetric surface area, $A_s$, (bottom panel) as a function of
altitude.

4.2 Heterogeneous chemical kinetics

The kinetics of $C_2H_2$ uptake, cyclo-trimerization and $C_6H_6$ desorption were then treated by
solving the following coupled differential equations for the time that the particles spend in
each model layer during their descent to the surface:

$\frac{d[C_2H_2^{ads}]}{dt} = \frac{\gamma}{4} \varepsilon A_{t}[C_2H_2] - k_{CT}[C_2H_2^{ads}]$  \hspace{1cm} (11)

$\frac{d[C_6H_6^{ads}]}{dt} = \frac{k_{CT}[C_2H_2^{ads}]}{3} - k_d[C_6H_6^{ads}]$  \hspace{1cm} (12)

$\frac{d[C_6H_6]}{dt} = k_d[C_6H_6^{ads}]$  \hspace{1cm} (13)

where $k_d$ is the first-order rate of $C_6H_6$ desorption. Since the composition of the EKB dust
particles is assumed to be chondritic \cite{Gainsforth et al., 2015, Zolensky et al., 2006} and hence
essentially olivinic, we use here the mean measured value for $\gamma$ of $1.7 \times 10^{-4}$. Note that the
laboratory measurement was made at 181 K, and the temperature dependence of $\gamma$ could not
be measured at lower temperatures using the flow tube system. Since uptake coefficients
typically have negative temperature dependences (see discussion in \cite{Frankland et al. (2015)}),
$\gamma$ is probably higher in most of Titan’s atmosphere below 300 km \cite{Flasar et al., 2005}, and so
the rate of uptake should be a lower limit.
The uptake of C\textsubscript{2}H\textsubscript{2} was restricted to sub-monolayer coverage (i.e. < 10\textsuperscript{15} molecule cm\textsuperscript{-2}). This was achieved in the model by ensuring that as the coverage of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{6}H\textsubscript{6} approached this limit, \( \gamma \) in eqn. 11 was reduced to zero in proportion to the remaining available adsorption sites on the dust particle. Note that although the adsorption of other less volatile species in Titan’s atmosphere could reduce the available surface sites for C\textsubscript{2}H\textsubscript{2} adsorption, C\textsubscript{2}H\textsubscript{2} is the second most abundant minor species in Titan’s atmosphere with a mixing ratio which remains fairly constant between 500 and 150 km \cite{Teanby et al., 2006}, as shown in Figure 9b. Furthermore, Titan’s atmospheric temperature is too high for the most abundant species in Titan’s atmosphere (N\textsubscript{2} and CH\textsubscript{4}) to be physisorbed on the cosmic dust surface \cite{Chickos and Acree, 2002, Collings et al., 2015}.

The temperature-dependent C\textsubscript{2}H\textsubscript{2} cyclo-trimerization rate on olivine measured in this study is \( k_{CT} = 2.6 \times 10^{-5} \exp(-741/T) \) s\textsuperscript{-1}. The rate of desorption of C\textsubscript{6}H\textsubscript{6} was set equal to \( k_{d} = 9 \times 10^{12} \exp(-45 \text{ kJ mol}^{-1} / RT) \) s\textsuperscript{-1}, where first-order desorption kinetics are assumed because the coverage of C\textsubscript{6}H\textsubscript{6} on the dust surface will be sub-monolayer, as cyclo-trimerisation only occurs on surface-active sites. The pre-exponential factor is set to the vibrational frequency of a C\textsubscript{6}H\textsubscript{6} molecule against the olivine surface. We have calculated this using electronic structure theory at the B3LYP/6-311+g(2d,p) level in the Gaussian G09 program \cite{Frisch et al., 2009}. Figure 14 illustrates a C\textsubscript{6}H\textsubscript{6} molecule bound to a surface Fe atom. The arrows on the atoms are displacement vectors of the vibrational mode corresponding to desorption, which has a calculated frequency of 302 cm\textsuperscript{-1} \((=9 \times 10^{12} \text{ s}^{-1})\), a typical value for desorption kinetics \cite{Attard and Barnes, 1998}. The binding energy in the exponential term was set to 45 kJ mol\textsuperscript{-1}, which has been measured for the sublimation of C\textsubscript{6}H\textsubscript{6} \cite{Chickos and Acree, 2002}.
Figure 14. A C₆H₆ molecule adsorbed onto an Fe atom at the olivine surface (at the B3LYP/6-311+g(2d,p) level of theory). The blue arrows on the atoms are displacement vectors for the vibration at 302 cm⁻¹, which is an Fe-C₆H₆ stretch orthogonal to the surface corresponding to the desorption coordinate.

4.3 Production of C₆H₆

Figure 15 shows the modelled rate of C₆H₆ production between 600 km and the surface, resulting from C₂H₂ uptake, cyclo-trimerization, and desorption of C₆H₆. The production rate increases by a factor of 10⁷ between 600 and 90 km. There are two reasons for this: the dust surface area increases by a factor of ~10⁵ because the sedimentation rate of the particles decreases with decreasing height; and the C₂H₂ number density increases by a factor of ~1500 (Figure 9b). Above 80 km, the ratio of adsorbed C₂H₂ to C₆H₆ on the dust is > 10⁴, consistent with C₆H₆ desorption not being rate-limiting. Model sensitivity experiments show that the cyclo-trimerization step is rate-determining above 80 km, so the kinetic uncertainty in the C₆H₆ production rate between 80 and 550 km arises from the ~±50% uncertainty in kₜ (Section 3); in contrast, decreasing kₕ by a factor of 10 has a negligible effect on the C₆H₆ production rate profile. The greatest contribution to the uncertainty in the C₆H₆ production
rate arises from the order-of-magnitude uncertainty in the dust flux into Titan’s atmosphere (Poppe, 2016), and this is illustrated by the uncertainty envelope in Figure 15.

**Figure 15.** The C$_6$H$_6$ production rate from the uptake of C$_2$H$_2$ on cosmic dust, cyclo-trimerization and desorption, shown as a function of altitude. The dashed lines encapsulate the uncertainty in the dust flux into Titan’s atmosphere. The heterogeneous rate is also compared to gas-phase C$_6$H$_6$ formation rates (reaction numbers defined in the text).

Below 90 km the C$_6$H$_6$ production rate mirrors the temperature profile (Figure 9a): the temperature falls rapidly from 130 K at 90 km to 70 K at 50 km, before warming up to 94 K near the surface (Yung et al., 1984). Because $k_d$ has a significant activation energy (see above), at these cold temperature desorption of C$_6$H$_6$ becomes very slow and rate-limiting, so that
the dust particles smaller than 0.2 μm become completely coated in C₆H₆ and further uptake of C₂H₂ ceases. At this point there is the possibility that photochemistry (or possibly cosmic-ray induced chemistry) could lead to the formation of larger organic molecules such as polyaromatic hydrocarbons (PAHs) on the dust surface.

The heterogeneous C₆H₆ formation rate can be compared with direct gas-phase production, which occurs via the following seven reactions in the Caltech/JPL model:

\[
\begin{align*}
2C_3H_3 + M & \rightarrow C_6H_6 + M \quad (M = \text{third body i.e. } N_2) \\ (R1) \\
H + C_6H_5 + M & \rightarrow C_6H_6 + M \\ (R2) \\
CH_3 + C_5H_3 + M & \rightarrow C_6H_6 + M \\ (R3) \\
C_4H_5 + C_2H_2 & \rightarrow C_6H_6 + H \\ (R4) \\
C_6H_5 + H_2 & \rightarrow C_6H_6 + H \\ (R5) \\
C_6H_5 + CH_4 & \rightarrow C_6H_6 + CH_3 \\ (R6) \\
C_6H_6 (\text{linear}) + H & \rightarrow C_6H_6 + H \\ (R7)
\end{align*}
\]

The rates of these C₆H₆ formation routes calculated in the JPL model are also depicted in Figure 15, which shows that heterogeneous production may well be competitive with reactions 4 - 7 between 80 and 120 km. In fact, recent experimental work at the University of Leeds has shown that a key photochemical intermediate in this gas-phase chemistry, singlet methylene (\(^1\text{CH}_2\)), is quenched by N\(_2\) much more rapidly to the relatively unreactive \(^3\text{CH}_2\) ground state at temperatures below 150 K than extrapolations from above 250 K indicate (pers. comm. K. Douglas). This will reduce the efficiency of these gas-phase production routes and increase the relative importance of heterogeneous production.
At this point it is worth considering the possible interactions of cosmic dust and C$_2$H$_2$ with the tholin particles of which the main haze layer below 220 km is thought to be composed (Cable et al., 2012; Wilson and Atreya, 2003). The low-temperature cyclo-trimerization of C$_2$H$_2$ is catalysed by surface metal atoms (Fe, Mg in this study; Pd and Cu surfaces discussed in Section 3.2), and so is unlikely to occur on “pure” organic tholin surfaces. Presumably, coagulation between cosmic dust and tholin particles would reduce the reactive metal silicate surface available for cyclo-trimerization. However, the 1D model in this study shows that between 250 and 80 km the cosmic dust particles are completely coated with non-polar C$_2$H$_2$, and this probably reduces the likelihood of coagulation with tholins (or other cosmic dust particles).

A final point concerns the deposition of C$_6$H$_6$ to the surface. In the very cold lower troposphere the cosmic dust particles are likely to be coated with C$_6$H$_6$ (see above); the direct deposition of coated particles to the surface would then constitute a flux of about 3 molecule cm$^{-2}$ s$^{-1}$. The downward flux of gas-phase C$_6$H$_6$ can be estimated using equation 7 (with the dust sedimentation velocity $w = 0$) and the modelled mixing ratio gradient at 50 km (5.2 ppt km$^{-1}$), yielding $\sim 1 \times 10^6$ molecule cm$^{-2}$ s$^{-1}$. Even allowing for uncertainties in $K_{zz}$ and the dust flux, deposition from the gas phase should clearly dominate.

5. Summary and Conclusions

This study shows that the uptake of C$_2$H$_2$ on cosmic dust particles may be a significant source of C$_6$H$_6$ in Titan’s atmosphere. Because of the relatively small mass of the moon, dust particles enter at low speeds and encounter an atmosphere where the pressure increases gradually. Hence a much smaller fraction of the particles ablate compared with the terrestrial planets, providing a significant surface area for heterogeneous chemistry. The uptake coefficient of
C$_2$H$_2$ on olivine particles (synthesized as analogues of cosmic dust), and the temperature-dependent rate of cyclo-trimerization to form C$_6$H$_6$ were measured in a flow tube and a UHV apparatus. The uptake coefficient on a range of olivine compositions from forsterite to fayalite was $(1.7 \pm 0.4) \times 10^{-4}$. The first-order cyclo-trimerization rate was $2.6 \times 10^{-5} \exp(-741/T)$ s$^{-1}$ between 115 and 181 K, and was also independent of Mg/Fe ratio in the olivine.

The chemical ablation model CABMOD was used to show that for dust particles between 0.02 and 10 µm in radius entering Titan’s atmosphere at speeds up to the maximum of 29 km s$^{-1}$, less than 1% of mass loss occurred through sputtering. Significant mass loss did not occur because the particle temperature did not reach 1750 K when melting and evaporation would cause much more rapid ablation. A 1D model describing the sedimentation of cosmic dust between 600 km and the surface of Titan, together with C$_2$H$_2$ uptake, cyclo-trimerization and desorption of C$_2$H$_6$, shows that this heterogeneous pathway is probably competitive with the gas-phase production routes included in existing models between 80 and 120 km in Titan’s troposphere.

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