Formation and distribution of benzene on Titan

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[1] We present a study of the formation and distribution of benzene (C6H6) on Titan. Analysis of the Cassini Mass Spectrometer (INMS) measurements of benzene densities on 12 Titan passes shows that the benzene signal exhibits an unusual time dependence, peaking ~20 s after closest approach, rather than at closest approach. We show that this behavior can be explained by recombination of phenyl radicals (C6H5) with H atoms on the walls of the instrument and that the measured signal is a combination of (1) C6H6 from the atmosphere and (2) C6H6 formed within the instrument. In parallel, we investigate Titan benzene chemistry with a set of photochemical models. A model for the ionosphere predicts that the globally averaged production rate of benzene by ion-molecule reactions is ~107 cm−2 s−1, of the same order of magnitude as the production rate by neutral reactions of ~4 × 106 cm−2 s−1. We show that benzene is quickly photolyzed in the thermosphere, and that C6H5 radicals, the main photodissociation products, are ~3 times as abundant as benzene. This result is consistent with the phenyl/benzene ratio required to match the INMS observations. Loss of benzene occurs primarily through reaction of phenyl with other radicals, leading to the formation of complex aromatic species. These species, along with benzene, diffuse downward, eventually condensing near the tropopause. We find a total production rate of solid aromatics of ~10−15 g cm−2 s−1, corresponding to an accumulated surface layer of ~3 m.


1. Introduction

[2] One of the more surprising results from the Cassini mission is the existence of remarkably complex molecules in the upper atmosphere of Titan [Vuitton et al., 2006a; Waite et al., 2007]. Although the existence of a robust chemistry on Titan was established by results from the Voyager mission [Hunten et al., 1984], subsequent investigations tended to focus on the chemistry of the stratosphere rather than the thermosphere and ionosphere. For example, the seminal study by Yung et al. [1984], which served as a model for all subsequent photochemical models, considered the ionosphere as only a source of N atoms. The synthesis of complex molecules in the Yung et al. [1984] and subsequent models occurs primarily (sequentially) in the stratosphere. Some later work attempted to include coupling between the chemistry of the ionosphere and neutral atmosphere, but only in a simplified way and without the benefit of strong observational constraints [Banaszkiewicz et al., 2000; Wilson and Atreya, 2004].

[3] It came as a surprise then, if not a shock, that Titan’s upper thermosphere and ionosphere contained some very heavy molecules [Vuitton et al., 2006a; Waite et al., 2007]. The general rule in planetary atmospheres is that lighter species become more abundant at high altitudes because of diffusive separation and photo- and electron-dissociation processes, which operate primarily in the upper atmosphere. Titan goes against this trend with ions as heavy as several hundred amu [Coates et al., 2007] and neutrals up to 91 amu [Vuitton et al., 2007]. It is likely that even heavier neutrals are present but are beyond the mass range of Cassini instruments.

[4] The most abundant heavy molecule in Titan’s thermosphere is the aromatic ring benzene (C6H6) [Waite et al., 2005]. The first evidence for the presence of benzene in the atmosphere of Titan was found with the Infrared Space Observatory (ISO). A column density of 2.4 × 1015 cm2 between 0.2 and 20 mbar and a mole fraction of 6.1 × 10−10 at 110 km averaged over all latitudes was retrieved [Coustenis et al., 2003]. The Composite InfraRed Spectrometer (CIRS) onboard Cassini recently provided a firm detection of benzene in Titan’s atmosphere and discovered strong benzene latitude variations in the stratosphere, with an increase of about an order of magnitude from south to north, reaching a maximum abundance of about 3.5 × 10−9 around 70°N [Coustenis et al., 2007]. Limb scans reveal that the mixing ratio profile is mainly constant with altitude from 168 to 307 km at 80°N [Vinatier et al., 2007]. These mid-IR observations are not sensitive to the high altitude benzene discovered by the INMS. Solid benzene has been tentatively identified on the surface by the Gas Chromatograph Mass Spectrometer (GCMS) [Niemann et al., 2005]. Upon the impact of the Huygens probe, the GCMS inlet line heater
warmed the Titan surface, leading to the evaporation of liquid/solid materials and rendering their detection possible. The Visual Infrared Mapping Spectrometer (VIMS) onboard Cassini also reported a tentative detection of solid benzene on the surface [R. N. Clark, manuscript in preparation, 2008]. These observations suggest that a substantial quantity of benzene is either produced by heterogeneous chemistry on the surface or through gas-phase chemistry in the atmosphere followed by condensation.

[5] The abundance of benzene detected by the Ion Neutral Mass Spectrometer (INMS) on the Cassini spacecraft [Waite et al., 2007] is far greater than found in the stratosphere and far greater than predicted by pre-Cassini models of the composition of the upper atmosphere. The data from the closed ionization source indicate a mole fraction of a few ppt at an altitude of 1000 km, whereas photochemical models predicted a mole fraction of a few ppb. This suggests that the source of benzene is in the upper atmosphere.

[6] In order to investigate the complex chemistry in Titan’s thermosphere and ionosphere further and understand its larger role in chemical cycles on Titan we present here an in-depth study of the formation and distribution of benzene on Titan. In section 2 we describe the INMS observations and data reduction in more detail than presented previously. In section 3, we analyze the response of the INMS to a gas mixture containing benzene, phenyl (C₆H₅), methyl (CH₃), and H. We explain the signal at m/z = 77 and 78 by a combination of atmospheric C₆H₅ and recombination of C₆H₅ radicals with H atoms on the walls of the closed source and the signal at m/z = 92 with the recombination of C₆H₅ with CH₃ radicals. We demonstrate that the benzene and phenyl densities required to fit the data are consistent with the results of the photochemical models discussed in section 4. The models show that benzene is efficiently produced by ion chemistry in the upper atmosphere. However, benzene is quickly photolyzed and phenyl radicals, the main photodissociation products, are ~3 times as abundant as benzene in the upper atmosphere. Loss of benzene occurs primarily through reaction of phenyl with other radicals, producing more complex aromatic species. Section 5 discusses these results and section 6 presents some concluding thoughts.

2. Observations and Data Reduction

2.1. Identification of C₆H₆ and C₇H₈

[7] Benzene has been observed in all of Cassini’s low-altitude passes through Titan’s atmosphere [Waite et al., 2007]. Here we consider only measurements obtained with the Closed Source Neutral (CSN) channel of the INMS. This operational mode utilizes an enhancement chamber in front of the mass spectrometer that concentrates atmospheric molecules resulting in higher sensitivity for inert molecules that do not react with chamber walls [Waite et al., 2005]. Observations in the Open Source Neutral mode have lower sensitivity and have not resulted in detection of benzene.

[8] CSN spectra obtained at low altitudes show a clear signal in the m/z = 73–79 region that we interpret as evidence for C₆H₆. Figures 1a–1b show spectra from the inbound and outbound legs of T16. The spectra represent averages over the 960–980 km region. Also shown are models for the benzene spectrum based on the INMS calibration [J. Cui, manuscript in preparation, 2008]. The fit is excellent, confirming the identification of benzene. The high quality of the match between models and observations implies that C₆H₆ is likely benzene rather than any of the other (numerous) isomers. Figures 2a–2f show the benzene cracking pattern from the INMS calibration and the cracking patterns from the NIST database for benzene (Figure 2b) and several other isomers of C₆H₆ (Figures 2c–2f). The NIST data for benzene is quite similar to the INMS calibration data but both differ markedly from the cracking patterns for other isomers. In particular the signal at m/z = 60–62 is strong in most isomers, but weaker in benzene and in the INMS observations of Titan. This, along with the fact that it is the most stable isomer, strongly suggests that the signal is due to benzene.

[9] The count rates at m/z = 78 in the outbound measurements are complicated by a time shift discussed below; however, the inbound data are organized quite well as a function of altitude. Figures 3a–3b show the density at m/z = 78 for T16 and T23. Here, and in the following analysis, we concentrate on data from T16 because this pass penetrated the deepest into Titan’s atmosphere and the benzene signal is strongest. Also shown are simple diffusive equilibrium models for a species of mass 78 amu assuming a constant temperature determined from analysis of the N₂ density distribution [Miuller-Wodarg et al., 2008]. These simple models provide an excellent fit to the data implying that the measured signal is due to an atmospheric species with a mass close to 78 amu. The benzene density distribution should only reflect the scale height for a mass of 78 amu if benzene is close to diffusive equilibrium. Analysis of INMS argon measurements indicates that the homopause on Titan is near 800 km [Yelle et al., 2008] and that molecular diffusion should dominate over eddy mixing at the altitudes under consideration here. For the benzene distribution to be in diffusive equilibrium however, also requires that diffusion be faster than chemical production or loss processes. We will return to this in section 5.

[10] Aside from the benzene peaks at m/z = 62–63 and 73–79, there are no clear signatures at m/z > 60 for the inbound T16 spectrum shown in Figure 1a. However, the outbound T16 spectrum, shown in Figure 1b, has sizable peaks at m/z = 64–66 and m/z = 91–92. The first feature around m/z = 65 belongs to an unaccounted species. The signal around m/z = 91 is not much higher than the signal at the surrounding m/z but is statistically significant because of the much smaller associated error bars. The molecular weight suggests the chemical formula is C₇H₈ and the feature is well fit by an INMS calibration spectrum for toluene. We therefore consider this to be detection of toluene in the INMS closed source chamber. Structurally toluene is a benzene ring with a methyl radical substituted for an H atom, so given the detection of benzene, the presence of toluene is not surprising. In addition to the presence of the toluene signature, the outbound data has a much stronger benzene signature than the inbound data.

[11] Results from spectral analysis for the inbound data from INMS measurements to date are summarized in Table 1 along with geometrical data for each encounter. We do not include results from T17 or T20 because little neutral data...
were obtained. Included in Table 1 are the derived mole fractions for the lowest altitudes sampled \((z_1)\) and the predicted abundance at a constant pressure level of \(p_0 = 1.45 \times 10^{-5} \text{Pa}\), which corresponds to an altitude of 1000 km at a latitude of 60°N. The latter values are calculated by fitting the altitude variation of the mole fraction for each pass to an exponential to predict the value at the altitude \((z_0)\) corresponding to \(p_0\). The mapping from altitude to pressure is based on the empirical model described by Müller-Wodarg et al. [2008].

[12] The derived mole fractions are roughly consistent with the preliminary results presented by Waite et al. [2007]. For reasons to be explained shortly, we believe that the derived densities do not represent the abundance of benzene in Titan’s upper atmosphere, but rather a combination of the benzene and phenyl abundance that we will refer to as \(C_6H_x\). To derive estimates of the benzene and phenyl mole fractions, it is necessary to examine the time behavior of the signals in more detail.

2.2. Time Variation of Signal

[13] Neutral species in Titan’s upper atmosphere decrease rapidly with altitude and the temporal response of the INMS is extremely fast (tens of microseconds), implying that the measured signal should increase with time up to closest approach (C/A) and decrease thereafter. For example, Figure 4a shows that measurements of ethane \((C_2H_6)\) at \(m/z = 30\) during T16 have a maximum at C/A and are fairly symmetric about this time. The time dependence of the benzene and toluene signals, shown in Figures 4b–4d, is quite different. The signals peak \(~20\) s after C/A, rather than at C/A. Using the data shown in Figures 4b–4d, we calculate a time shift relative to C/A for \(m/z = 78, 77, \) and 92 of \(27.0 \pm 0.7, 22.5 \pm 1.9, \) and \(22.2 \pm 6.6\) s. The three time shifts are consistent within the uncertainties and the average shift is quite large.

[14] In principle, an asymmetry about C/A could be caused by large horizontal variations in the atmosphere. We consider this unlikely for two reasons. First, there is no evidence that the time shift varies from pass to pass, as would be expected if it were due to horizontal variations. This is shown in Figures 5a–5c where data from three Titan passes are plotted versus time from C/A. Despite the gaps in the measurements near C/A for T18 and T21 (due to other INMS observations being conducted at these times) the time behavior of all three encounters appear similar. The geometry of the 3 encounters is quite different however. T21, for example, has a C/A at 43.3° latitude and the sub-spacecraft latitude increases monotonically with time during the encounter [Müller-Wodarg et al., 2008] while for T16 the maximum latitude of 85.5° is reached near C/A, as summarized in Table 1. Second, horizontal variations would have to be extremely large to cause the observed asymmetry. The data in Figures 5a–5c show that the INMS count rate in channel 78 is relatively constant from 0 to 50 s after C/A. The altitude changes by 12 km during that time (for T16), corresponding to a density decrease by a factor of 2, assuming that benzene has a diffusive equilibrium distribution. A constant signal implies that the horizontal variation in density must be of the same order over a latitudinal distance of 0.4°. This large a horizontal variation is unlikely and is inconsistent with the observed horizontal variations presented in Table 1. Thus we conclude that the anomalous time behavior of the signals is due to an internal process in the instrument rather than a property of the atmosphere.

[15] The low densities in Titan’s upper atmosphere permit the development of relatively large densities of radicals. The photochemical calculations to be discussed in section 4 show that \(C_6H_3\) is, in fact, more abundant than \(C_6H_6\). This is a consequence of the extremely large \(C_6H_6\) photolysis rate. Therefore we argue that the benzene and toluene are produced partly by radical recombination on the walls of the...
INMS. This hypothesis is tested with a surface chemistry model in the next section.

3. Surface Chemistry Model

[16] The time delays in the C_6H_6 and C_7H_8 signals discussed in the previous section and the large abundance of H, CH_3, and C_6H_5 radicals discussed in section 4 suggest that these species are created by recombination of radicals adsorbed on the chamber walls. This hypothesis explains the time delay observed for these species because surface-diffusion limited reactions may require a significant amount of time. It explains the presence of both C_6H_6 and C_7H_8 because these are the products produced by reaction of the main radicals in the upper atmosphere. Methane should also be produced by reaction of CH_3 and H on the surface, but at a negligible rate near C/A because the density of atmospheric CH_4 is much greater than that of CH_3. The wall reaction hypothesis helps to reconcile the photochemical models with the measured C_6H_6 signal because, as discussed in the previous section, the phenyl abundance in the upper atmosphere is predicted to be larger than the benzene abundance. The INMS is really measuring the sum of benzene and phenyl and so the required production rate of benzene is significantly reduced compared with what is required if it were to be assumed that the signal were due to benzene alone.

[17] Recombination of radicals on chamber walls is a common phenomenon in spaceflight mass spectrometers and has on occasion been used to good advantage. For example, Kasprzak et al. [1980] determined the density of N in the Venian upper atmosphere through analysis of the NO signal in the Pioneer Venus mass spectrometer under the assumption that NO was produced by desorption of NO, created by recombination of adsorbed N and O on the walls of the instrument. Other aspects of adsorption/desorption effects on spacecraft mass spectrometers are discussed in the work of Hedin et al. [1973]. Here we construct our own model for this process in order to interpret the INMS measurements in terms of atmospheric densities and the time constant for surface chemistry within the instrument.

[18] For simplicity of discussion we first consider formation of benzene. The time constants describing gas flow inside the instrument, equilibration of the walls and gas within the instrument, and the ionization and detection systems are all very small and we assume that the only significant time constant is for the rate of radical recombination on the walls of the closed-source enhancement chamber. In this case, the benzene density in the closed-source chamber is determined by the instantaneous balance between outflow from the entrance aperture to the chamber and the combination of the flow of benzene into the chamber from Titan atmosphere and desorption of benzene from the chamber walls. The desorption rate of benzene is assumed to be proportional to the triple product of phenyl surface density, H surface density, and the inverse of an empirical time constant. This time constant is determined by rate of diffusion over the surface of the chamber and the intrinsic reaction rate for adsorbed phenyl and H. To solve for the density of the adsorbed species in the chamber we
Figure 3. The variation of density with altitude for C₆H₆ (m/z = 78) and N₂ (m/z = 28, 14) measured by INMS. The solid lines indicate isothermal models to the altitude profile. (a) T16. Both C₆H₆ and N₂ are well fit by a temperature of 138 K. (b) T23. Both C₆H₆ and N₂ are well fit by a temperature of 154 K.

Table 1. Geometrical Parameters at C/A (Latitude, Longitude and Solar Zenith Angle) and C₆H₆ Mole Fractions for 12 Titan Passes

<table>
<thead>
<tr>
<th>Pass</th>
<th>Latitude, deg</th>
<th>Longitude, deg</th>
<th>SZA, deg</th>
<th>z₁, km</th>
<th>X₁</th>
<th>z₀, km</th>
<th>X₀</th>
</tr>
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<tbody>
<tr>
<td>T5</td>
<td>75.3</td>
<td>98.9</td>
<td>128.9</td>
<td>1038.6</td>
<td>2.2 × 10⁻⁷</td>
<td>987.4</td>
<td>1.4 × 10⁻⁶</td>
</tr>
<tr>
<td>T6</td>
<td>87.7</td>
<td>152.3</td>
<td>108.4</td>
<td>953.2</td>
<td>4.0 × 10⁻⁸</td>
<td>968.8</td>
<td>2.2 × 10⁻⁶</td>
</tr>
<tr>
<td>T18</td>
<td>76.6</td>
<td>12.6</td>
<td>92.9</td>
<td>972.3</td>
<td>3.8 × 10⁻⁸</td>
<td>988.6</td>
<td>2.7 × 10⁻⁶</td>
</tr>
<tr>
<td>T19</td>
<td>66.4</td>
<td>4.8</td>
<td>83.9</td>
<td>1021.4</td>
<td>9.6 × 10⁻⁷</td>
<td>994.8</td>
<td>2.4 × 10⁻⁶</td>
</tr>
<tr>
<td>T21</td>
<td>46.4</td>
<td>99.2</td>
<td>127.0</td>
<td>1020.8</td>
<td>8.9 × 10⁻⁷</td>
<td>1004.4</td>
<td>1.5 × 10⁻⁶</td>
</tr>
<tr>
<td>T23</td>
<td>33.9</td>
<td>1.0</td>
<td>54.8</td>
<td>1019.8</td>
<td>4.5 × 10⁻⁸</td>
<td>1006.0</td>
<td>6.7 × 10⁻⁶</td>
</tr>
<tr>
<td>T25</td>
<td>27.6</td>
<td>17.4</td>
<td>164.2</td>
<td>1004.7</td>
<td>1.0 × 10⁻⁷</td>
<td>1006.3</td>
<td>9.9 × 10⁻⁷</td>
</tr>
<tr>
<td>T26</td>
<td>25.7</td>
<td>1.8</td>
<td>155.4</td>
<td>991.9</td>
<td>3.5 × 10⁻⁸</td>
<td>1006.3</td>
<td>2.8 × 10⁻⁶</td>
</tr>
<tr>
<td>T27</td>
<td>39.0</td>
<td>0.4</td>
<td>146.3</td>
<td>1025.7</td>
<td>2.6 × 10⁻⁷</td>
<td>1005.9</td>
<td>4.7 × 10⁻⁶</td>
</tr>
<tr>
<td>T28</td>
<td>46.8</td>
<td>1.3</td>
<td>141.1</td>
<td>994.8</td>
<td>5.4 × 10⁻⁸</td>
<td>1004.3</td>
<td>4.5 × 10⁻⁶</td>
</tr>
<tr>
<td>T29</td>
<td>54.7</td>
<td>2.8</td>
<td>135.1</td>
<td>985.3</td>
<td>5.5 × 10⁻⁸</td>
<td>1001.4</td>
<td>3.9 × 10⁻⁶</td>
</tr>
<tr>
<td>T30</td>
<td>62.3</td>
<td>5.7</td>
<td>128.6</td>
<td>974.1</td>
<td>7.0 × 10⁻⁸</td>
<td>997.2</td>
<td>4.2 × 10⁻⁶</td>
</tr>
</tbody>
</table>

*X₁ is the derived mole fraction for the lowest altitude sampled (z₁) and X₀ is the predicted abundance at a constant pressure level of p₀ = 1.45 × 10⁻⁵ Pa, which corresponds to an altitude z₀ of 1000 km at a latitude of 60°N. X₁ and X₀ represent a combination of the benzene and phenyl mole fractions (see section 3), they are not the real benzene atmospheric mole fraction. Uncertainties mostly come from calibration and are estimated to be about 20%.
first consider the surface density on the chamber walls:

$$A_w M_i = N^o_i(t) U_w A_e - \sum_{t_j} \frac{1}{t_j} \frac{M_i}{M_i} \frac{M_j}{M_j}$$  \(1\)

where \(M_i\) is the surface density of the adsorbed radical on the walls of the closed-source chamber, the dot over \(M_i\) indicates a time derivative, \(t_j\) is the time constant describing the surface reactions of radical \(i\) with radical \(j\), \(U_w\) is the space craft velocity, \(A_e\) is the area of the aperture of the closed-source chamber, and \(A_w\) is the surface area of the closed source chamber. The quantity \(N^o_i(t)\) is the ambient atmospheric density of the \(i^{th}\) radical. The time dependence is explicit to emphasize that the system is driven by the passage of the spacecraft through different altitudes on Titan with varying atmospheric densities. The reaction of species \(i\) and \(j\) produces a surface density \(M_{ij}\) of the product species (for example, \(C_6H_3^+ + H \rightarrow C_6H_6\)). We also assume that the gas phase distribution of the product species in the chamber is in steady state with the walls; thus the rate at which gas is desorbed from the walls is equal to the outflow rate from the closed-source aperture:

$$N^o_i \frac{U_w A_e}{4} = \sum_{t_j} \frac{1}{t_j} \frac{M_i}{M_i} \frac{M_j}{M_j} \left(1 + \frac{M_i}{C_{14} i} \right)$$  \(2\)

where \(U_w\) is the thermal velocity at the wall temperature and \(N^o_i\) is the gas density in the chamber, i.e., the density measured by the INMS detection system.

[19] Solution of this set of equations gives us a model for the correlation of \(N^o_i\) with \(N^o_i(t)\). The H and CH\(_3\) densities used in the wall chemistry model come from our photo-chemical model, described in the next section. The C\(_6\)H\(_5\) and C\(_6\)H\(_6\) densities are adjusted to fit the data, but the H and CH\(_3\) are held fixed at the values predicted by photochemistry. Our knowledge of surface chemistry for the radicals considered here is too uncertain to permit determination of the chemical time constants from first principles, so we treat them as empirical parameters determined through fits of the model to the T16 data. The results of such a calculation for production of C\(_6\)H\(_6\), are shown in Figure 6. A chemical time constant of 15 s for H + C\(_6\)H\(_5\) provides the best fit to the data.

[20] Adequate fits to the data also require a direct gaseous source of C\(_6\)H\(_6\), shown as the dashed line in Figure 6. The required density from this source is 2.5 \(\times\) 10\(^{-6}\) cm\(^{-3}\), corresponding to a mole fraction of 1.3 \(\times\) 10\(^{-6}\) at an altitude of 950 km. Recently Vuitton et al. [2007] analyzed the INMS ion data for T5 and determined a mixing ratio of a few ppm for C\(_6\)H\(_6\) on Titan’s night side, in excellent agreement with the value of 1.3 \(\times\) 10\(^{-6}\) found

Figure 4. Time dependence of the signal from -200 to 200 s around closest approach for T16. (a) m/z = 30 (ethane). (b) m/z = 78 (benzene). (c) m/z = 77 (benzene). (d) m/z = 92 (toluene).
here. Also, we estimate that the density of benzene in Titan’s atmosphere is roughly one third that of phenyl, consistent with the photochemical calculations presented in the next section.

[21] The approach described here cannot be used for passes other than T16 because the spacecraft did not penetrate deep enough into Titan’s atmosphere and the signal-to-noise ratio (SNR) of the benzene signal is too low. As a consequence, we cannot explicitly retrieve the benzene density for passes other than T16. Additionally, the signal-to-noise ratio (SNR) of the toluene signal is too low for us to meaningfully constrain the chemical time constant for \( C_6H_5 + CH_3 \). We therefore adopt the time constant that we determined for \( H + C_6H_5 \). The fit is adequate but the low SNR of the measurements prevents any further conclusions for this species.

4. Chemical Models

[22] The benzene mole fractions derived in the previous section are many orders of magnitude larger than that derived for the stratosphere. Coustenis et al. [2007] report a value varying with latitude from \( 1.0 \times 10^{-10} \) to \( 3.5 \times 10^{-9} \) at approximately 110 km. This increase of mole fraction with altitude indicates that benzene is formed in the upper atmosphere. The flux, \( \Phi \), of a minor constituent is related to the mole fraction, \( X \), through

\[
\Phi = -(K + D)N_a \frac{dX}{dr} - D N_a X \left( \frac{1}{H_d} - \frac{1}{H_i} \right)
\]

where, \( D \) is the molecular diffusion coefficient, \( K \) is the eddy diffusion coefficient, \( N_a \) is the atmospheric number density, \( H_d \) is the pressure scale height of the background atmosphere and \( H_i \) is the diffusive equilibrium scale height of the minor species. Though we have insufficient data to accurately compute \( dX/dr \), the separate measurements in the thermosphere and stratosphere indicate that \( dX/dr > 0 \) and therefore \( \Phi < 0 \) and benzene is flowing downward from above. The fact that the abundance of benzene in the thermosphere is larger than in the stratosphere indicates that benzene is synthesized in the thermosphere.

[23] Lavvas et al. [2008a, 2008b] developed a one-dimensional radiative-convective/photochemical/microphysical model in order to interpret the composition measurements recently obtained by Cassini. As in previous studies, they find the primary benzene production channel to be the three-body reaction:

\[
C_3H_3 + C_3H_3 + M \rightarrow C_6H_6 + M \quad (k_{10}).
\]

[24] The model can almost reproduce the benzene stratospheric mole fraction but it fails to predict the large mole fractions in the thermosphere. The predictions are more than two orders of magnitude less than the observed abundance in the thermosphere reported here. In fact, three-body reactions are extremely inefficient at the low densities in Titan’s thermosphere and it seems clear that a chemical scheme that utilizes two-body reactions is required to explain the thermospheric abundance. This raises the question of how benzene is produced in the thermosphere.

[25] We can gain some insight into benzene production by examining the required time constants. The benzene density distribution should only reflect the scale height for a mass of 78 amu if benzene is close to diffusive equilibrium. The time constant characterizing diffusion can be estimated through \( t_D = H^2/D \), where \( H \) is the benzene scale height and \( D \) is the molecular diffusion coefficient. At 1000 km the benzene diffusion coefficient is \( D = 3.1 \times 10^9 \text{ cm}^2 \text{ s}^{-1} \) and the measured scale height is \( H = 21 \text{ km} \), implying a

**Figure 6.** Time dependence model fit for benzene (m/z = 78). Data points represent the density in the closed source obtained during T16 from –200 to 400 s around closest approach. The dotted line corresponds to the recombination of radicals on the walls of the closed source. The dashed line represents the direct gaseous source. The solid line is the sum of the dotted and dashed lines and represents the best fit of the databased on the surface chemistry model.
then the required reaction rate is roughly 
abundance as benzene, then 5 reactions are needed and the 
required reaction rate is roughly \( k \sim S/\nu N(\text{CH}_4) t_D \sim 5 \times 10^{-10} \text{ cm}^3 \text{s}^{-1} \). If we assume that benzene is synthesized in three reactions involving molecules that contain 2 and 3 carbon atoms present at the ppm level in the atmosphere then the required reaction rate is \( k \sim 2 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \). These reaction rates are consistent with ion-neutral reaction rates but not neutral-neutral reaction rates, which are much slower. This indicates that the benzene in the ionosphere is likely synthesized by ion chemistry. The likely precursor is protonated benzene, i.e., \( \text{C}_6\text{H}_7^+ \), a significant ion in Titan’s ionosphere [Vuitton et al., 2007]. Chemical models are discussed in the next subsection, where we argue that protonated and neutral benzene are closely related.

4.1. Ion Chemistry

4.1.1. Description

[26] We use an ion chemistry model based on the 0D model presented by Vuitton et al. [2006a, 2007]. The model is extended to 1D in order to allow retrieval of integrated vertical production rates. We use daytime conditions because the solar EUV energy flux is about 10 times the energy flux deposited by magnetospheric electrons [Cravens et al., 2005; Galand et al., 2006] and as a consequence complex species are more efficiently produced on the dayside. The model represents daytime conditions with a local solar zenith angle of 45°, as appropriate for T17. We concentrate on this pass because it is the only one that occurred in sunlight. Unfortunately, the neutral data for T17 were compromised and we cannot directly compare benzene and \( \text{C}_6\text{H}_7 \) densities.

[27] The background atmosphere is derived from an empirical model based on the INMS data for the thermosphere [Müller-Wodarg et al., 2008], CIRS results for the stratosphere [Vinatier et al., 2007], and Huygens results for the troposphere [Fulchignoni et al., 2005; Niemann et al., 2005], as described in the work of Yelle et al. [2008]. Profiles of \( \text{N}_2 \) and \( \text{CH}_4 \) densities and the atmospheric temperature profile are presented on Figure 7. The densities and temperature are representative of the spacecraft location at C/A for T17.

To calculate the relative production rates of \( \text{N}_2 \) (\( x = 1,2 \)) and \( \text{CH}_4 \) (\( y = 0–4 \)), we use the photoionization cross sections of Samson et al. [1987] and Stolte et al. [1998] for \( \text{N}_2 \), and of Lee and Chiang [1983] and Samson et al. [1989] for \( \text{CH}_4 \). The solar flux is based on the solar EUV flux model for Aeronomic Calculations (EUVAC), scaled to the location of Titan [Richards et al., 1994a, 1994b]. We can be fairly confident that ionization by energetic magnetospheric electrons and ions is small compared with solar ionization [Cravens et al., 2005; Galand et al., 2006] and is therefore neglected. We assume chemical equilibrium for the ion species. This is a good assumption on the dayside and at the altitudes that primarily concern us here.

[28] The chemical network includes \( \sim 150 \) ions containing up to 9 heavy atoms (carbon and nitrogen), \( \sim 40 \) neutrals and \( \sim 1250 \) ion-molecule reactions. The densities of heavier neutrals are fixed in the model at values either measured by INMS in the neutral mode or determined from the observed ion densities [Vuitton et al., 2007]. Reaction rate constants and products are mostly retrieved from existing compilations of experimental data [Anicich, 1993; Anicich and McEwan, 1997; McEwan and Anicich, 2007]. Titan’s ionospheric chemistry is driven by proton exchange reactions where ionization flows from neutrals having small proton affinities (PA) to neutrals having larger PA [Fox and Yelle, 1997; Vuitton et al., 2006a]. We assume that \( \text{CH}_2^+, \text{C}_2\text{H}_3^+\text{ and HCNH}^+ \) readily exchange a proton with neutrals having a higher proton affinity. When the reaction has not been studied, we assume the rate constant to be equal to the collision rate and calculate Langevin rates at 300 K. Use of Langevin rates for a temperature of 150 K lead only to minor changes in the modeled ion densities. Ion-electron recombination rates are retrieved from the literature. When the electron temperature dependence has not been determined, we assume the rate constant to be proportional to \( T_e^{-0.7} \) and when no data are available, we estimate the recombination rate to be equal to \( 7 \times 10^{-5} \times (300/T_e)^{0.7} \text{ cm}^3 \text{s}^{-1} \). Thermal electron temperature, as measured by the Cassini Radio Plasma Wave Spectrometer (RPWS) during the T17 encounter, are shown on Figure 7 [J.-E. Wahlund, personal communication, 2007].

[29] According to our chemical model \( \text{C}_6\text{H}_6 \) is produced primarily from the sequence of reactions presented on Figure 8 and listed in Table 2. For most reactions, the structure of the ions produced is not known because experimental data are usually based on mass spectrometry. The form of \( \text{C}_6\text{H}_5\text{H}^+ \) and \( \text{C}_6\text{H}_7\text{H}^+ \), whether cyclic or not, likely determines if electron recombination produces benzene or another \( \text{C}_6\text{H}_6 \) isomer. The reaction \( \text{C}_6\text{H}_5\text{H}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_6\text{H}_5\text{H}^+ + \text{H} \) \(( \nu (K') \) produces 2 isomers, one cyclic and one linear. The ground state isomer c-C\(_6\)H\(_5\)H\(^+\) is reactive but l-C\(_6\)H\(_5\)H\(^+\) is not [Scott et al., 1997]. Generally, when there is radiative stabilization, ring closure occurs and the cyclic form dominates [McEwan et al., 1999]. Accordingly, we assume that \( \text{C}_6\text{H}_5\text{H}^+ \) and \( \text{C}_6\text{H}_7\text{H}^+ \) are cyclic and we use rate constants corresponding to c-C\(_6\)H\(_5\)H\(^+\) and c-C\(_6\)H\(_7\)H\(^+\), if available.
The electron recombination rate of c-C$_6$H$_7^+$ has been measured for electron temperatures of 300 to 800 K but products are not known [McLain et al., 2004]. We assume that benzene and H are the only products. This is a key assumption in our model and laboratory measurements are desperately needed. It is also possible that products other than benzene would be quickly converted by subsequent reactions to benzene. Other recombination of heavy ions may also lead to benzene production, or to molecules that get converted to benzene, but these possibilities are not considered here.

### 4.1.2. Results

[31] The calculated altitude profiles for some key ions in benzene production are compared to the measured densities from T17 inbound in Figures 9a–9b. For the lighter species (Figure 9a), the model results are in good agreement with the observations, suggesting that solar UV deposition and primary ion chemistry are well described by the model. For

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**Figure 8.** Flowchart of the principal ion chemistry reactions for benzene formation.

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**Table 2. Principal Ion Reactions for Benzene Formation**

<table>
<thead>
<tr>
<th>R#</th>
<th>Reaction</th>
<th>Rate Constant*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>k'</td>
<td>CH$_4^+$ + CH$_4$ → C$_2$H$_4^+$ + H$_2$</td>
<td>9.1 × 10$^{-10}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>CH$_4^+$ + CH$_4$ → C$_3$H$_5^+$ + H$_2$</td>
<td>1.1 × 10$^{-9}$</td>
<td>[Anicich et al., 2003]</td>
</tr>
<tr>
<td>k'</td>
<td>CH$_4^+$ + CH$_3^+$ + CH$_3$</td>
<td>1.1 × 10$^{-9}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>CH$_4^+$ + HCN → HCNH$^+$ + CH$_4$</td>
<td>4.1 × 10$^{-9}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ → C$_2$H$_7^+$ + H</td>
<td>1.9 × 10$^{-10}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ → C$_2$H$_7^+$ + H$_2$</td>
<td>1.2 × 10$^{-10}$</td>
<td>[Kim et al., 1977]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + C$_2$H$_2$ → C$_2$H$_6^+$ + C$_2$H$_4$</td>
<td>1.0 × 10$^{-9}$</td>
<td>estimate</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_6^+$ + C$_2$H$_6$ → C$_2$H$_8^+$ + C$_2$H$_4$</td>
<td>1.1 × 10$^{-9}$</td>
<td>estimate</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + HCN → HCNH$^+$ + C$_2$H$_4$</td>
<td>2.7 × 10$^{-9}$</td>
<td>[Mackay et al., 1980]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + C$_2$H$_2$ → C$_2$H$_7^+$ + H</td>
<td>7.2 × 10$^{-10}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + C$_2$H$_2$ + hv</td>
<td>2.2 × 10$^{-10}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + C$_2$H$_2$ + H$_2$</td>
<td>1.2 × 10$^{-10}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_4^+$ + C$_2$H$_2$ + C$_2$H$_2$</td>
<td>1.3 × 10$^{-9}$</td>
<td>[Deakyne et al., 1987; Lifshitz and Weiss, 1980]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ → C$_2$H$_7^+$ + H$_2$</td>
<td>7.3 × 10$^{-11}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ + hv</td>
<td>6.0 × 10$^{-11}$</td>
<td>[McEwan et al., 1999]</td>
</tr>
<tr>
<td>k'</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ + C$_2$H$_2$</td>
<td>1.0 × 10$^{-10}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>N$^+$ + CH$_4$ → CH$_2^+$ + NH</td>
<td>5.8 × 10$^{-10}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>N$^+$ + CH$_4$ → CH$_3^+$ + N</td>
<td>5.8 × 10$^{-11}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>N$^+$ + H$_2$ → HCN$^+$ + H</td>
<td>4.1 × 10$^{-10}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>N$_2^+$ + H$_2$ → N$_2$ + H$_2$</td>
<td>2.0 × 10$^{-9}$</td>
<td>[Anicich, 1993]</td>
</tr>
<tr>
<td>k'</td>
<td>N$_2^+$ + CH$_4$ → CH$_3^+$ + N$_2$ + H$_2$</td>
<td>1.0 × 10$^{-10}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>N$_2^+$ + CH$_4$ → CH$_3^+$ + N$_2$ + H</td>
<td>1.0 × 10$^{-10}$</td>
<td>[Anicich et al., 2006]</td>
</tr>
<tr>
<td>k'</td>
<td>HCNH$^+$ + C$_2$H$_2$ → C$_2$H$_3^+$ + HCN</td>
<td>1.8 × 10$^{-9}$</td>
<td>[Petrie et al., 1991]</td>
</tr>
<tr>
<td>k'</td>
<td>HCNH$^+$ + C$_2$H$_2$ → C$_2$H$_3^+$ + HCN</td>
<td>1.1 × 10$^{-9}$</td>
<td>estimate</td>
</tr>
<tr>
<td>α</td>
<td>C$_2$H$_7^+$ + e$^-$ → C$_2$H$_6$ + H</td>
<td>2.4 × 10$^{-6}$</td>
<td>(300/Te)$^{1.3}$</td>
</tr>
</tbody>
</table>

*Rate constant in cm$^3$ s$^{-1}$.**
the heavier species (Figure 9b), the model reproduces the data down to ∼1100 km but at lower altitude, the model predictions systematically overestimate the observed ion densities. The modeled ion density peak decreases in altitude with the ion mass because of the smaller scale height of the heavier neutrals. However, the observed ion density peak is located around 1100 km for all the species, independently of their mass. Observational effects might cause this unexpected behavior. Because the width of the velocity distribution of heavy ions is narrower than the width of the velocity distribution of lighter ions, any mistuning of the lenses of the mass spectrometer caused by strong winds, etc. would be reflected as an underestimation of the higher masses density.

![Diagram of observed vertical profiles of some key ions during T17 inbound. The solid lines represent the predictions of the ion chemistry model.](image)

**Figure 9.** Observed vertical profiles of some key ions during T17 inbound. The solid lines represent the predictions of the ion chemistry model. (a) m/z = 14, 15, 16, 17, 28, 29. (b) m/z = 50, 51, 53, 77, 79. The C₄H₄⁺ curve has been scaled by a factor of 10.

Some chemistry is possibly missing in our model but it is not clear if this could explain the discrepancy observed at low altitude. The Electron Spectrometer (ELS), one of Cassini Plasma Spectrometer (CAPS) instruments, detected negative ions below ∼1150 km in all Titan flybys [Coates et al., 2007]. Even if the negative ion density were a substantial fraction of the electron density, positive-negative ion recombination would not substantially reduce the positive ion density, because recombination with negative ions is about 10 times slower than recombination with electrons. Also, if the chemistry is complex enough to lead to the formation of nanometer size aerosols, as suggested by the detection of high molecular mass (>10,000 amu) negative ions during T16 [Coates et al., 2007; Waite et al., 2007], ion reactions on the surface of aerosols could act as a sink for ions. Generally, addition reactions of heavier ions are faster than addition reactions of lighter ions because of their higher number of vibrational modes required to redistribute the energy liberated by the reaction. Better observational constrain on both negative ions and heavier molecular mass positive ions are required before these species can be taken into account in the model.

Our model cannot reproduce the observed ion density at m/z = 50. As explained in the work of Vuitton et al. [2007], this mass is attributed to C₆H₇ but ion-molecule reactions do not efficiently produce C₄H₂. Here we improve the previous model by including direct photoionization of C₄H₂. We use the C₄H₂ mole fraction inferred from the C₆H₇ density, the photoionization cross sections of Cool et al. [2005] and the solar flux described previously. This process forms a significant amount of C₄H₂⁺ but the modeled density profile still falls short by about one order of magnitude. As represented on Figure 8 and discussed in the next paragraph, C₆H₇ is an important intermediate in C₆H₇⁺ formation and in order to estimate the benzene production rate it is crucial that the model accurately predicts the C₆H₇⁺ density. Fragmentation of heavier ions could possibly produce C₄H₂⁺ ions but without further experimental constraints, it is not possible to include such reactions in the model. As a consequence, we scale the C₆H₂⁺ production rate by a factor of 10 in order to get a forced agreement between observed and calculated C₄H₂⁺ densities, as showed on Figure 9b.

On the night-side, Vuitton et al. [2007] showed that because the ionization rate by magnetospheric electrons is small, C₆H₇⁺ is mostly produced by proton exchange reactions between the major ions and C₆H₆, and lost by electron recombination to form back C₆H₆. As a consequence, C₆H₇⁺ is constantly recycled and ion chemistry does not contribute to a net production of C₆H₆. However, on the dayside, N₂ and CH₄ are rapidly photoionized and C₆H₇⁺ is efficiently produced by ion chemistry reactions. Figure 9b shows the altitude profile for C₆H₇⁺ ions on T17 inbound. The lower peak in the C₆H₇⁺ density is from

\[ C₆H₆⁺ + C₂H₄ \rightarrow C₆H₇⁺ + C₂H₂ \quad (k'_{16}), \]

and

\[ C₆H₇⁺ + H₂ \rightarrow C₆H₈⁺ + hν \quad (k'_{15}), \]
4.2. Neutral Chemistry

4.2.1. Description

[36] To investigate this further we have constructed a neutral photochemical/diffusion model for the distribution of benzene. The model includes eddy and molecular diffusion, photolysis, and chemistry. Our photolysis rates are based on a solar spectrum obtained with the EUV flux model for Aeronomic Calculations (EUVAC), scaled to the location of Titan [Richards et al., 1994a, 1994b]. We adopt a solar zenith angle of 60° and divide the rates by a factor of 2, to represent a global average. The temperature and total density are representative of the equatorial region, as determined in the empirical model of Müller-Wodarg et al. [2008]. The N₂ and CH₄ densities are presented on Figure 10 and the temperature profile is shown in the work of Yelle et al. [2008]. Molecular diffusion coefficients are taken from measurements presented in the literature if possible [Mason and Marrero, 1970] or calculated from molecular force constants using the standard approach [Hirschfelder et al., 1964] if no measurements are available. We found no measurements for the diffusion coefficient of benzene in N₂. We calculate that the diffusion coefficient has a value of $D_N = 2.3 \times 10^{-19} \text{cm}^2 \text{s}^{-1}$ at a temperature of 150 K. The eddy mixing profile is constrained by INMS measurements of the ⁴⁰Ar distribution in the upper atmosphere and by CIRS measurements of the C₂H₆ distribution in the stratosphere [Yelle et al., 2008] and is presented on Figure 10. The 1D chemical-diffusion model does not include ions or ion chemistry. We specify an ion-molecule production rate for benzene consistent with that inferred from our ion-molecule reaction model. The production rate is specified as a Chapman production profile with a peak at 830 km of 1.3 cm⁻³ s⁻¹ and a scale height of 75 km. The column-integrated production rate is $7 \times 10^6 \text{cm}^2 \text{s}^{-1}$ which is on the same order as the rate of $1.3 \times 10^7 \text{cm}^2 \text{s}^{-1}$ predicted by the ion chemistry model.

[37] The neutral chemical network is based on the reaction list presented in the work of Vuitton et al. [2006b]. It consists of 40 hydrocarbon species, ~130 neutral-neutral reactions and ~40 photoreactions. Chemical reactions and photolysis of C₆H₆ (benzene), C₇H₈ (toluene), C₈H₁₀ (ethylenylbenzene) and their associated radicals is described explicitly. Oxygen and nitrogen bearing species are not abundant enough to significantly affect the hydrocarbon densities and in order to avoid a significant increase of the chemical network complexity, we do not consider the nitrogen or oxygen chemistry in this study. Molecules with more than 6 carbon atoms are assumed to ultimately form soot and are no longer involved in the chemistry. Because we expect benzene rings to be conserved, complex species produced by reaction of C₆H₅ or other aromatic radicals are included in a sub-category of soot called “rings”. “Aromatics” refers to C₆H₆, C₇H₈, C₈H₁₀ and “rings”, “solid aromatics” refers to condensed C₆H₆, C₇H₈, C₈H₁₀, and “rings”. Reactions relevant to benzene production and destruction are listed in Table 3.

[38] Besides the ionospheric source, we include production through neutral chemistry and extend the chemical network considered in previous models. There have been three recent studies of the kinetics of the propargyl (C₃H₃) self-reaction at 295 K, reporting rate coefficients of ~$4 \times 10^{-11} \text{cm}^3 \text{s}^{-1}$ [Atkinson and Hudgens, 1999; DeSain and Taatjes, 2003; Fahr and Nayak, 2000]. These new results seem to supersede the threefold higher value obtained by Morter et al. [1994]. This rate coefficient is independent of total pressure and buffer choice (Ar, He, N₂) over the pressure range 3–133 mbar, indicating that the
reaction is at the high-pressure limit in the experimental conditions. The rate coefficient exhibits a slight temperature dependence from 373 to 1000 K [Giri et al., 2003; Shafir et al., 2003] but no measurement is available below room temperature. As a consequence, we used a temperature independent rate coefficient in our model. The reaction rate has never been measured in the low-pressure range. We assume that it is equal to 10 times the recombination rate of methyl (CH₃) radicals because of the higher number of channels available to redistribute the excess energy. We base our estimate on the CH₃ recombination rate of Wang et al. [2003], which was obtained from a combination of theoretical and experimental investigations down to 200 K.

[39] The C₆H₆ produced in the reaction of propargyl radicals is not necessarily in the form of benzene. Fahr and Nayak [2000] analyzed products for propargyl recombination at T = 298 K and P = 67 mbar. They detected two linear C₆H₆ (1,5-hexadiyne and 1,2-hexadiyne-5yne) with yields of 60 and 25%, respectively and a third unidentified isomer. Howe and Fahr [2003] performed product studies at a pressure range of 27 mbar to 933 mbar and at a temperature range of 295–623 K. The same two linear and three new cyclic C₆H₆ isomers (dimethylene-cyclobutene, fulvene and benzene) were identified. Benzene was a major product particularly at low pressure (~25%). The authors suggest that extrapolation of the product yield to low pressures (<15 mbar) gives a yield of about 40%, irrespective of the temperature. This is in qualitative agreement with the theoretical results of Miller and Klippenstein [2003].

In the absence of any data concerning the isomerization or reactivity of the different C₆H₆ isomers, we assume that cyclization quickly occurs and that the only C₆H₆ product is benzene.

[40] Reactions of the C₅H₃, C₆H₃, C₇H₃, C₈H₅ and C₉H₅ radicals with C₃H₂ have been considered as a potential source of C₆H₆ [Lebonnois, 2005; Wilson et al., 2003]. However, a large energy barrier makes them unimportant at low temperatures [Moses et al., 2005; Vuitton et al., 2006b] and we do not consider these reactions in our model. Instead, we include in the chemical network the reaction between C₃H and 1,3-butadiene (C₄H₄). The reaction is fast (k = 3 × 10⁻¹⁰ cm³ s⁻¹) and 1,3-butadiene is efficiently produced in the recombination of C₃H₂ radicals [Fahr et al., 1991; Nizamov and Leone, 2004]. The products have not been determined but it is usually believed that the reaction of C₃H with unsaturated molecules proceeds via attack of a π-orbital followed by rapid loss of an H atom by the energized complex initially formed. It follows that the product of reaction k₄ is most probably C₆H₆.

[41] The most important chemical loss process for benzene is photolysis, which extends as far as 270 nm [Pantos et al., 1978]. To estimate the photolysis rate, we use the cross section published by Koch and Otto [1972] and Pantos et al. [1978]. However, the photolysis of benzene is complicated, and the products are not completely characterized. Deactivation of the excited electronic states formed by absorption of ultraviolet photons lead to a transient highly excited state of the ground electronic state (C₆H₆*). This state has a lifetime of up to 2 ms and subsequently fragments into the photodissociation products [Tsai et al., 2000]. C₆H₆* can also be deactivated by collisions with N₂ [Nakashima and Yoshihara, 1982]. As a consequence, C₆H₆* can be collisionally stabilized if the background atmospheric pressure is high enough, whereas dissociation occurs if collisions are rare. Our model
explicitly calculates the \( \text{C}_6\text{H}_6^* \) density. The lifetime of 2 ms and the de-excitation coefficient \( \text{k}_3^* \) imply that dissociation occurs above 350 km and stabilization below. \( \text{C}_6\text{H}_6^* \) could also react with other molecules \( \text{k}_3^* \) or absorb a photon \( \text{J}^* \), leading to different products from single-photon absorption. We assume a reaction rate constant \( \text{k}_5^* \) of \( 5.5 \times 10^{-13} \) cm\(^3\) s\(^{-1}\) and a dissociation coefficient \( \text{J}^* \) equal to that of to benzene. Estimations of the efficiency of these processes at 900 and 200 km are summarized in Table 4.

[42] The main contribution to the photolysis rate comes from the peak in the absorption cross section near 220 nm, which is also the region used in the laboratory studies of dissociation pathways. In the near ultraviolet, we assume photodissociation products to be exclusively \( \text{C}_6\text{H}_5 \) and \( \text{H} \), thus validating the choice of eddy diffusion coefficient. The \( \text{C}_6\text{H}_5 \) profile is in extremely good agreement with the observations as well. The \( \text{C}_6\text{H}_5 \) profile is a factor of 2–3 too high, but that is still a fairly good agreement considering the numerous uncertainties in the \( \text{C}_6\text{H}_6^* \) formation and loss processes \([\text{Vuitton et al.}, \ 2006b]\).

[43] The fate of the \( \text{C}_6\text{H}_5 \) produced by benzene photolysis is to reform benzene through

\[
\text{C}_6\text{H}_5 + \text{H} + \text{M} \rightarrow \text{C}_6\text{H}_6 + \text{M} \quad \text{(k}_1^*\text{)}.
\]

or to produce toluene through

\[
\text{C}_6\text{H}_5 + \text{CH}_3 + \text{M} \rightarrow \text{C}_7\text{H}_8 + \text{M} \quad \text{(k}_2^*\text{)}.
\]

[44] There is little kinetic data on the reaction of \( \text{C}_6\text{H}_5 \) with other species. Since \( \text{C}_6\text{H}_5 \) is a rather low energy radical (\( \Delta H_F = 339 \) kJ/mol), we consider it unlikely that it could react with stable species in the atmosphere, and hypothesize that the main losses are through radical-radical reactions such as

\[
\text{C}_6\text{H}_5 + \text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_8\text{H}_8 + \text{M} \quad \text{(k}_{8a}^*\text{)}.
\]

or

\[
\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_9\text{H}_{10} + \text{M} \quad \text{(k}_{9a}^*\text{)}.
\]

[45] We assume that the rate for these reactions is \( 1.2 \times 10^{-10} \) cm\(^3\) s\(^{-1}\), based on analogy with

\[
\text{C}_2\text{H}_5 + \text{C}_3\text{H}_3 + \text{M} \rightarrow \text{C}_4\text{H}_6 + \text{M}.
\]

### 4.2.2. Results

[46] In Figure 11a, the vertical profiles of the principal neutrals are displayed for a simulation using the solar flux, chemical network and eddy diffusion coefficient stated previously. The \( ^{40}\text{Ar} \) profile is compared to the INMS \([\text{Yelle et al.}, \ 2008]\) and GCMS \([\text{Niemann et al.}, \ 2005]\) results in the upper and lower atmosphere, respectively. The \( \text{C}_2\text{H}_2, \text{C}_6\text{H}_6, \text{C}_2\text{H}_4, \text{C}_4\text{H}_2 \) profiles are compared to the CIRS measurements at 15°S \([\text{Vinatier et al.}, \ 2007]\). The model matches closely both the measured \( ^{40}\text{Ar} \) and \( \text{C}_6\text{H}_6 \) mole fractions, thus validating the choice of eddy diffusion coefficient. The \( \text{C}_2\text{H}_2 \) profile is in extremely good agreement with the observations as well. The \( \text{C}_2\text{H}_2 \) profile is a factor of 2–3 too high, but that is still a fairly good agreement considering the numerous uncertainties in the \( \text{C}_6\text{H}_6^* \) formation and loss processes \([\text{Vuitton et al.}, \ 2006b]\).

[47] The vertical profiles of the aromatic species are displayed in Figure 11b. Averages of the INMS \( \text{C}_6\text{H}_6 \) mole fractions over the 12 passes presented in Table 1 as well as the \( \text{C}_6\text{H}_6 \) mole fraction retrieved by CIRS at 15°S \([\text{Coustenis et al.}, \ 2007]\) are plotted for comparison. Figure 11c shows the vertical profiles of the principal radicals and Figure 12 the rates of the reactions that have a significant impact on the benzene mole fraction. The calculated profiles reproduce the main characteristics of the measurements. Near 900 km, electron recombination of \( \text{C}_6\text{H}_6^* \) forms \( \text{C}_6\text{H}_6 \), which is rapidly depleted by photolysis \( (\text{J}_1^*) \) to produce \( \text{C}_6\text{H}_5 \). The \( \text{C}_6\text{H}_6^* \) density in the model at 1000 km is \( 2.0 \times 10^5 \) cm\(^{-3}\), corresponding to a mole fraction of \( 1.4 \times 10^{-6} \), as displayed in Figure 11c. This is 2.5 times the benzene density at the same altitude. The INMS observations reveal a mole fraction of \( \text{C}_6\text{H}_6 \) of \( \sim 2 \times 10^{-6} \) at 1000 km in good agreement with the model results. Other abundant radicals at \( \sim 1000 \) km include hydrogen \( (\text{H}) \) and methyl \( (\text{CH}_3) \) radicals. They are produced mainly through methane photolysis above 700 km.

[48] As shown in Figure 12, photolysis is the main loss for benzene around 900 km. \( \text{C}_6\text{H}_5 \), the main photodissociation product, diffuses downward and is converted to heavier aromatics in the 350–800 km region \( (\text{k}_2^*, \text{k}_{8a}, \text{k}_{9a}) \). This process is responsible for the rapid decrease in benzene mole fraction below 900 km shown in Figure 11b. As the pressure increases, stabilization of the transient benzene becomes more important and it becomes comparable to its dissociation lifetime \( (\text{k}_1^*/\text{k}_2^* \sim 1) \) at a density of

![](image.png)

**Table 4.** Formation and Loss Processes of Hot Benzene \( \text{C}_6\text{H}_6^* \)

<table>
<thead>
<tr>
<th>R#</th>
<th>Reaction</th>
<th>Rate Constant* (cm(^3) s(^{-1}))</th>
<th>Lifetime (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J(_1^*)</td>
<td>( \text{C}_6\text{H}_6^* + \text{h} \nu \rightarrow \text{C}_6\text{H}_6^* )</td>
<td>( 2 \times 10^7 )</td>
<td>900 km 300 km</td>
</tr>
<tr>
<td>k(_1^*)</td>
<td>( \text{C}_6\text{H}_6^* \rightarrow \text{C}_6\text{H}_5 + \text{H} )</td>
<td>( &gt;5.0 \times 10^2 )</td>
<td>900 km 300 km</td>
</tr>
<tr>
<td>J(_*)</td>
<td>( \text{C}_6\text{H}_6^* + \text{h} \nu \rightarrow ) products</td>
<td>–</td>
<td>900 km 300 km</td>
</tr>
<tr>
<td>k(_3^*)</td>
<td>( \text{C}_6\text{H}_6^* + \text{N}_2 \rightarrow \text{C}_6\text{H}_5 )</td>
<td>( 5.5 \times 10^{-13} )</td>
<td>900 km 300 km</td>
</tr>
<tr>
<td>k(_5^*)</td>
<td>( \text{C}_6\text{H}_6^* + \text{C}_2\text{H}_2 \rightarrow ) products</td>
<td>( &lt;5.5 \times 10^{-10} )</td>
<td>900 km 300 km</td>
</tr>
</tbody>
</table>

*Plain: bimolecular rate constant (cm\(^3\) s\(^{-1}\)) /Bold: unimolecular rate constant (s\(^{-1}\)).

\( \Delta H_F = 339 \) kJ/mol, we consider it unlikely that it could react with stable species in the atmosphere, and hypothesize that the main losses are through radical-radical reactions such as

\[
\text{C}_6\text{H}_5 + \text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_8\text{H}_8 + \text{M} \quad \text{(k}_{8a}^*\text{)}.
\]

or

\[
\text{C}_6\text{H}_5 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_9\text{H}_{10} + \text{M} \quad \text{(k}_{9a}^*\text{)}.
\]
Thus in the lower atmosphere, stabilization of the transient state is the dominant process. Moreover, at 350 km, the recombination of H and C₆H₅ (k₁) becomes equal to the photolysis rate and destruction of C₆H₆ by photolysis stops. Below 300 km, C₆H₆ is created by recombination of C₂H₃ and C₄H₃ (k₆a), and C₃H₃ (k₁₀), producing the low altitude peak in C₆H₆ density observed by CIRS. The mole fraction in the lower stratosphere is 30 ppb, as shown in Figure 11b, which is consistent with that inferred from the mid-IR spectroscopy.

Reactions k₆a and k₁₀ contribute to most of the benzene formation via neutral chemistry, with a total integrated production rate of 4 x 10⁶ cm⁻² s⁻¹. Vuitton et al. [2007] suggested that the reaction between C₂H and C₄H₆ (k₅) could produce a significant amount of benzene. Because the C₄H₆ density is quite low, it appears that the column-integrated value is only 1 x 10⁴ cm⁻² s⁻¹, 200 times less than the other channels. The integrated benzene production rate from the electron recombination of C₆H₇⁺ is 3 times larger than the total production rate from neutral chemistry. Because of the general agreement with the observations, we believe that the model results strongly

Figure 11. Modeled neutral vertical profiles and comparison with observations. (a) Principal neutrals. ⁴⁰Ar: the stratospheric measurement was obtained by GCMS [Niemann et al., 2005] and thermospheric measurements by INMS [Yelle et al., 2008]. C₂H₂, C₂H₆ and C₄H₂: CIRS measurements at 15°S [Vinatier et al., 2007]. (b) Aromatic species. The observed C₆H₆ mole fraction in the stratosphere was retrieved by CIRS at 15°S [Coustenis et al., 2007]. Data points represent averages over 12 Titan passes of the C₆H₆ density measured by INMS and presented in Table 1. Error bars include statistic uncertainties but not calibration uncertainties. “Aromatics” refers to heavy aromatic species that are not tracked in the model. (c) Principal radicals.

Figure 12. Modeled reaction rates for some key reactions. Labels refer to the reactions listed in Tables 2, 3 and 4.

10¹⁵ cm⁻³ (~350 km). Thus in the lower atmosphere, stabilization of the transient state is the dominant process. Moreover, at 350 km, the recombination of H and C₆H₅ (k₁) becomes equal to the photolysis rate and destruction of C₆H₆ by photolysis stops. Below 300 km, C₆H₆ is created by recombination of C₂H₃ and C₄H₃ (k₆a), and C₃H₃ (k₁₀), producing the low altitude peak in C₆H₆ density observed by CIRS. The mole fraction in the lower stratosphere is ~30 ppb, as shown in Figure 11b, which is consistent with that inferred from the mid-IR spectroscopy.

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support the hypothesis that benzene is created by ion chemistry.

5. Discussion

[50] The results from the ion and neutral chemistry models presented in the previous sections show that the ionospheric production rate of C6H6 is of the right order to explain the INMS observations. These are 1D globally averaged models and do not address possible variations of C6H6 with latitude or local time. The strong dependence of both production and loss mechanisms on solar insulation suggests that horizontal variations could be large, whereas the results shown in Table 1 reveal that the measured variations are mild. Three-dimensional simulations that couple dynamics and chemistry are required to fully investigate horizontal variations but we can gain some insight from the timescales for chemical and transport processes.

[51] Three timescales are of interest, those for chemical processes, horizontal transport, and vertical diffusion. The chemical and diffusion time constants from our model are plotted in Figure 13. The calculated photolysis rate indicates that the chemical time constant in the upper thermosphere is 105 s. The diffusion time constant at 1300 km is two orders of magnitude shorter than the time constant for photolysis; it implies that diurnal variations are possible but should not be too extreme. The data shown in Table 1 are consistent with this. The observed variation is a factor of several. C6H6 is not absent on the nightside, though the one measurement on the dayside (T23) implies a larger than average mole fraction. Since benzene is mostly formed on the dayside, our nightside results imply that it is transported to the night side with no large loss.

[53] The situation is more complicated than simple diurnal variability however. The dynamics of Titan’s upper atmosphere appear to be quite vigorous [Müller-Wodarg et al., 2008] with strong meridional as well as vertical winds. The meridional winds will affect the latitudinal distribution of C6H6 and the vertical winds may alter both latitudinal and local time distributions, depending on the precise circulation pattern. Strong zonal winds will smooth diurnal variations. Longitude variations are also possible if some component of the circulation pattern is longitude dependent. Further observations and interpretation with 3-D simulation of dynamics and chemistry is needed to investigate these questions. At the present time, we can only say that the similarity in chemical, diffusive, and diurnal time constants is grossly consistent with the observed mild variations in abundance.

[54] Wilson et al. [2003] performed a study dedicated to the mechanisms for the formation of benzene in the atmosphere of Titan. They considered ion-neutral reactions and found that electron recombination of C6H7+ controls the benzene production in the upper atmosphere. However, the production rate at 1000 km is only 10−22 cm−3 s−1, one order of magnitude less than the production rate calculated here. As a consequence, the model fails to reproduce the observed benzene abundance in the thermosphere [Wilson and Atreya, 2003]. It is difficult to track down the discrepancy between their model and ours but the fact that the major production reaction in the ionosphere (k10) is missing in their model is probably one of the reasons. Only 13 out of the 22 reactions identified here as important for benzene formation (Table 2, Figure 8) are present in their reaction list.

[55] Lebonnois [2005] performed a comparative study of benzene production in Titan and Jupiter atmosphere. His model does not consider ion chemistry and the primary mechanism responsible for benzene formation is the recombination of C3H3 radicals (reaction k10 in Table 3). In the nominal simulation, the mole fraction of benzene reaches ~10−6 at 1000 km, a factor of ~200 higher than obtained here with neutral chemistry alone. For reaction k10, Lebonnois [2005] adopts a value of 1.2 × 10−10 cm3 s−1 for k∞ [Morton et al., 1994] and 4.4 × 10−23 cm6 s−2 for k0 at 150 K (10 times the rate for CH3 + CH3 retrieved by McPherson et al. [1983]). These rate constants are 3 and 80 times higher than the rate constants used here. As in our model, benzene is efficiently photodissociated into C6H5 radicals but in the model of Lebonnois [2005], the most probable fate of C6H5 is to form back benzene by reaction with H atoms (reaction AR7 in his Table 1). As a consequence, there is no efficient chemical loss for C6H5 and benzene accumulates in the atmosphere. As discussed in section 4.2, even if these reactions have yet to be studied, it is very likely that C6H5 does react with radicals other than H and that benzene is ultimately lost to heavier species. It follows that the high benzene abundance found by Lebonnois [2005] probably results from the inadequacy of the reaction list.

[56] On Earth, benzene is a major component in flames, where it appears to be associated with the formation of PAHs and soot [Frenklach, 2002]. Various mechanisms
involving either neutral [Wang and Frenklach, 1994] or ion chemistry [Calcope and Keil, 1990] have been proposed to explain the formation of benzene and PAHs in combustion processes. Building on these studies, Lebonnois [2005] and Wilson and Atreya [2003] suggested that PAHs were a major component of Titan’s haze. However, they extrapolate kinetic data obtained at high temperature and neglect the fact that the neutral reactions involved have an activation barrier that cannot be overcome at cold temperature. As a consequence, the neutral reactions leading to PAHs in combustion processes will be inefficient on Titan. Instead, we suggest that reactions of aromatic radicals with simpler radicals (CH3, C2H2, C2H4, etc.) along with self-reactions of aromatic radicals (C6H6 + C6H6) produce heavier aromatics that eventually condense and form haze that settles to the surface. We calculate a total production rate of solid aromatics of ~10^{-15} g cm^{-2} s^{-1}. 2/3 of this mass flux is traceable to benzene produced by ion chemistry. When this process is not taken into consideration, the aromatic production rate decreases by a factor of ~3, as shown in Figure 11b. Experimental studies on the reactivity of C6H5, C3H7 (benzyl) and other aromatic radicals are required to better constrain formation processes. Also, as shown in Table 4, reaction of hot benzene (k1e) is possible at lower altitudes and some reactions could lead to the formation of more complex aromatics. Finally, considering the high density and variety of ions detected in the upper atmosphere, it is also likely that there may be other pathways in ion-neutral chemistry that could lead to aromatics.

Solid benzene has been tentatively identified on Titan’s surface [Niemann et al., 2005; R.N. Clark, manuscript in preparation, 2008]. We calculate a benzene condensation rate of ~1 x 10^6 cm^{-2} s^{-1}, about 1/10 of the benzene production rate. Condensation at such a rate over the age of the solar system corresponds to an average layer of only ~20 cm of solid benzene on the surface of Titan at present. This condensate will be mixed with other more abundant deposits (for example, the acetylene layer is predicted to be 125 times thicker), rendering its detection by remote sensing more challenging. However, solid benzene could also be formed on the surface by heterogeneous chemistry if enough energy is available.

Measurements by the CAPS Electron Spectrometer imply the existence of Titan’s upper atmosphere of various negative ions ranging from ~15 to ~10,000 amu [Coates et al., 2007]. No formation processes or attribution for these ions have been proposed to date. Dissociative attachment following low energy (~9 eV) electron impact on benzene produces C6H5 [Fenzlaff and Illenberger, 1984], which has a fairly high electron affinity (1.1 eV) [Gunion et al., 1992]. More generally, dissociative electron attachment of the type:

PAH + e^- (<= 15 eV) -> PAH^* + H

is an efficient process with cross sections ranging from 10^{-17} to 10^{-14} cm^2 [Tobita et al., 1992]. As a consequence, C6H5 as well as PAH^* - are potential candidates for the negative ions observed by ELS. Complex negative ion chemistry models are necessary to further investigate this possibility.

Benzene has been observed in other astronomical objects as well. It is present in the atmosphere of Jupiter [Kim et al., 1985], Saturn [Bézard et al., 2001] and in the proto-planetary nebula CRL 618 [Cernicharo et al., 2001]. Several photochemical models have tried to reproduce the quantities of benzene observed on Jupiter and Saturn. At low-latitude, recombination of propargyl (C3H3) radicals is found to be responsible for most of the C6H6 production. In both planets, this reaction leads to abundance profiles that are ~50% weaker than needed to reproduce the benzene observations [Moses et al., 2000, 2005]. Under Jupiter high-latitude conditions where precipitation of energetic electrons is important, benzene is produced, as on Titan, through successive ion-neutral reactions followed by electron recombination of C6H5 [Wong et al., 2003]. Since the benzene abundance in Jupiter’s auroral regions is much higher than at low latitudes, this might indicate a possible role of meridional transport [Lebonnois, 2005]. Also, the models should use the two following reactions that have not been included so far:

C2H + C6H6 -> C6H6 + H, (k4)

and

C2H3 + C4H3 -> C6H6, (k6a).

Benzene has also been formed in laboratory simulations of Titan’s chemistry. Imanaka and Smith [2007] investigated the formation of complex species from a N2/CH4 gas mixture as a function of irradiation wavelengths from 50 nm to 150 nm. The formation of benzene is observed at wavelengths less than 80 nm, which corresponds to the photoionization threshold of N2. This result is qualitatively consistent with the benzene formation pathways presented on Figure 8. Above 80 nm, only methane can be ionized and the formation of benzene requires the presence of species such as hydrogen cyanide (HCN) and diacetylene (C4H2). These are quite complex molecules that are only present at low concentration in the laboratory gas mixture, if present at all (see Figure 4 in the work of Imanaka and Smith [2007]). However, if N2 is present, the formation of benzene only requires the presence of more simple species such as acetylene (C2H2) and ethylene (C2H4), which are readily available in the gas mixture. Modeling of the laboratory experiment would be useful in order to test this explanation in a more quantitative way.

6. Conclusions

The results from analysis of the C6H6 time profiles combined with photochemical models of the atmosphere are:

(1) The time dependence of the m/z = 77, 78 and 92 signals implies that benzene and toluene are mostly formed in the INMS chamber through H + C6H5 radicals and CH3 + C6H5 recombination on the walls.

(2) The amplitude of the m/z = 77 and 78 signals during T16 can be matched by a benzene mole fraction at 950 km of 1.3 x 10^{-6}.

(3) The globally integrated production rate of benzene in the ionosphere, is ~10^7 cm^{-2} s^{-1}, of the same order of magnitude as the neutral production rate of ~4 x 10^6 cm^{-2} s^{-1}. This production rate is sufficient to produce
benzene densities in Titan’s upper atmosphere of the same order as that measured by INMS.

[65] The total production rate of aromatics following benzene photolysis is about 10% of the total benzene condensation rate, and the total benzene condensation rate is about 10% of this value. If this total deposition rate has been maintained over the age of the solar system (4.5 × 10^9 years), an average layer of 3 m of solid aromatic material has been deposited on the surface of Titan. However, according to the model of the history of Titan’s interior from Tobie et al. [2006], CH_4 outgassing may have been episodic and consequently, the total organic production rate may be lower. This material might be at the origin of the particulates composing the dunes covering some of Titan’s surface [Lorenz et al., 2006].

[66] We want to emphasize that there is a need for identification of the products of C_6H_5^+ + e^− (α_1) as well as for formation pathways for C_6H_2^+. Rates and products for the ion-neutral reactions estimated in Table 2 have to be determined. Low temperature rates for C_6H_2^+ + C_6H_7 (k_10) as well as low pressure and temperature rates for the other radical reactions estimated in Table 3 are also required.

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References


Kim, J. K., et al. (1977), Product distributions and rate constants for the reactions of CH_2+, CH_3+, C_2H_5+, C_2H_4+, and C_2H_6+ ions with CH_3, C_2H_5, C_3H_7, and C_4H_9, J. Chem. Phys., 66, 1798–1805.


Puntos, E., et al. (1978), The extinction coefficient of benzene vapor in the region 4.6 to 36 eV, J. Mol. Spectrosc., 72, 36–43.


Stolte, W. C., et al. (1998), Dissociative photoionization cross sections of N2 and O2 from 100 to 800 eV, At. Data Nucl. Data Tables, 69, 171–179.


