Benzene Vapor Pressures at Titan Temperatures: First Microbalance Results

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Abstract

The vapor pressure of crystalline benzene (C₆H₆) has been measured for the first time with a quartz-crystal microbalance under ultrahigh vacuum conditions from about 135 to 160 K, temperatures relevant for Titan’s atmosphere. Good agreement is found with the most recent thermodynamic analysis of higher-temperature literature results, but there is less satisfactory agreement with recently published low-temperature data obtained with a different laboratory method. An enthalpy of sublimation of 49.7 ± 0.1 kJ mol⁻¹ for benzene is reported, and a few brief comments are made concerning the connections between our new data and Titan’s atmosphere. Supporting our benzene results are new vapor-pressure measurements for crystalline H₂O ice and crystalline cyclohexane (C₆H₁₂). The latter are the first of their type and enable the two sets of recently published vapor pressures for solid benzene to be brought into close agreement.

Unified Astronomy Thesaurus concepts: Titan (2186); Astrochemistry (75); Experimental techniques (2078)

1. Introduction

Benzene (C₆H₆) is the prototypical aromatic compound, whose isolation usually is credited to Faraday and its structure to Kekulé (Faraday 1825; Kekulé 1865). This compound can be considered to be the parent of polycyclic aromatic hydrocarbons and their derivatives, which are generally accepted to be present in our solar system and other parts of our Galaxy (Allamandola et al. 1989; Tielens 2008). Some relevant benzene detections include those in meteorites, comets, the atmosphere of Titan, and the interstellar medium (Cernicharo et al. 2001; Septon 2002; Coustenis et al. 2003; Schumann et al. 2019). A search of the refereed astrochemistry literature shows that in roughly the past year alone, at least six papers have appeared with benzene in the title (Mouzay et al. 2021a, 2021b, 2021c; Dubois et al. 2021; Nna-Mvondo & Anderson 2022; Hudson & Yarnall 2022). To help understand the chemistry and physics of solid benzene in extraterrestrial environments, such as Titan’s atmosphere, here we examine one of the compound’s physical properties—its vapor pressure.

Until recently, the published vapor pressures for solid C₆H₆ consisted of measurements above about 180 K. Fray & Schmitt (2009) used literature results from 1933 to 1976 to propose an empirical equation to fit the data and that could be used to extrapolate downward to temperatures relevant to the outer solar system. Růžička et al. (2014) subsequently carried out new vapor-pressure measurements and published a critical thermodynamic analysis of the literature, resulting in an improved vapor-pressure curve with slightly lower pressures than those of Fray & Schmitt (2009) and based on a larger data set. A different approach to solid benzene’s vapor pressure was recently reported by Dubois et al. (2021), who published new measurements at 13 temperatures from 134 to 158 K for a study of Titan’s atmosphere. Their vapor pressures ranged from about 7 to 25 times higher (i.e., 600%–2400% higher) than the recommended values of Růžička et al. (2014), raising questions about the Růžička et al. (2014) work. The results of Dubois et al. (2021) and Růžička et al. (2014) are summarized in Figure 1, the points being from Dubois et al. (2021) and the dashed line from the equation of Růžička et al. (2014).

Two important motivations for our benzene work in the present paper are represented in Figure 1. First, we wanted to test the results of Růžička et al. (2014) by carrying out new laboratory measurements with a quartz-crystal microbalance (QCM). Second, we wanted to compare our measurements to the recent results of Dubois et al. (2021). We felt that the differences in the two sets of vapor pressures in Figure 1 were large enough that new work might be able to favor one set or the other. As will be seen, our new measurements are in much better agreement with the pressures recommended by Růžička et al. (2014) than with the measurements recently reported in this journal (Dubois et al. 2021).

2. Laboratory Procedures

The procedures and equipment used to determine vapor pressures of ices are described in previous publications (e.g., Hudson et al. 2017; Yarnall et al. 2020; Hudson et al. 2021), so only a summary is given here. Briefly, benzene, water, or cyclohexane vapor was condensed onto a precooled (e.g., 100 K) gold-plated substrate in an ultrahigh vacuum (UHV) chamber (P ∼ 10⁻¹⁰ Torr). The substrate was the surface of a quartz-crystal microbalance (QCM, INFICON IC6) attached to the end of an Advanced Research Systems cryostat (i.e., expander, cryocooler) with a minimum temperature of about 18 K. The resulting ice was warmed at ∼1 K min⁻¹ while the microbalance’s frequency was recorded every 2 s; an increase in frequency being observed as the ice sample was warmed and sublimed. The thickness of each ice before warming was about 1 μm as measured by laser interferometry, each sample requiring about an hour for its growth. See Hudson et al. (2017) for more on the vacuum and cryogenic systems used. A diagram of the UHV chamber is in Loeffler et al. (2016).

As in Yarnall et al. (2020), we use f₀ to designate our QCM’s frequency (in Hz) on warming with no sample present and f for
its frequency on warming with a sample. The ice’s mass per unit area ($\mu$) at each temperature was calculated from

$$\mu = \kappa \left( \frac{1}{f} - \frac{1}{f_0} \right),$$

(1)

where $\kappa = 4.417 \times 10^5$ Hz g cm$^{-2}$ (Lu & Lewis 1972). Molecular flux ($F$, molecules cm$^{-2}$ s$^{-1}$) was found from the rate of change of $\mu$ and vapor pressure was found from

$$P = F \sqrt{2\pi mkT},$$

(2)

where $m$ is the mass of a molecule of the ice. The result for each ice was a set of vapor pressures over a range of temperatures. For each such set (i.e., each ice) a conventional Clausius–Clapeyron plot of $\ln (P)$ against $1/T$ was constructed and the slope of the linear portion (correlation coefficient $>0.99$) was used to calculate an enthalpy of sublimation, $\Delta H_{subl}$. Averaging the results from several ices gave a final slope and intercept for each compound. The resulting equation then was used to calculate vapor pressures at the temperatures of interest, in the present case the temperatures being those used by previous workers (vide infra).

The manufacturer’s specifications for our quartz-crystal microbalance give a frequency resolution better than 0.1 Hz, which is sufficiently small compared to the $\sim 6$ MHz frequencies we measured that its influence on vapor pressures and enthalpies of sublimation was essentially negligible. Much more significant was the uncertainty in temperatures measured with a silicon diode at the substrate. This was estimated to be $\pm 0.5$ K or less, leading to uncertainties in vapor pressure of no more than about 1% over the 130–180 K range studied. The corresponding uncertainty in enthalpies of sublimation was less than $\pm 0.5$ kJ mol$^{-1}$.

Our use of a quartz-crystal microbalance to measure vapor pressures is neither novel nor unique, a voluminous literature being available for such work. Microbalances have been used for such varied applications as determining the vapor pressures of trinitrotoluene, fullerene, and N$_2$O (Bryson et al. 1974; Pan et al. 1992; Gershnik & Zeiri 2010). From the astrochemical community we can cite QCM usage by Sack & Baragiola (1993) on H$_2$O ice and Luna et al. (2012) to determine desorption energies. Both papers contain additional details on QCM measurements.

3. Results

3.1. Vapor Pressure of H$_2$O Ice

Before beginning our benzene work, we first measured vapor pressures for solid H$_2$O to compare the results to those in the literature. See the reviews of Feistel & Wagner (2007) and Wagner et al. (2011) for summaries of earlier vapor-pressure results. In Figure 2 we show data at 24 temperatures from Bryson et al. (1974). Superimposed on those data points is the curve of Wagner et al. (2011), which was derived from published vapor-pressure measurements and is the most recent such mathematical fit available. Our measurements with seven H$_2$O ices gave Equation (3), with pressure in torr and temperature in kelvin,

$$\ln(P) = (-6036.4) \left( \frac{1}{T} \right) + 23.3,$$

(3)

from which we calculated vapor pressures at the temperatures used by Bryson et al. (1974); see Table 1. The results are plotted in Figure 2, where excellent agreement is found between our work and the literature results. Note that below about 132 K, the vapor pressure of H$_2$O ice was too low for us to extract reliable values and above about 177 K the ice had completely sublimed, so again no vapor pressures could be measured. It might have been possible to optimize our conditions to study H$_2$O ice at lower temperatures, but complications can arise below $\sim 140$ K from amorphous H$_2$O ice, as described by Sack & Baragiola (1993). Although those same authors did not publish vapor pressures, they did report fluxes of sublimating H$_2$O molecules that agreed with those of Bryson et al. (1974), with whom we also agree, as seen in Figure 2.
Table 1  
Vapor Pressures of Crystalline H$_2$O Ice$^a$

| T/K | $P/10^{-8}$ Torr (This Work) | $P/10^{-8}$ Torr (Wagner et al. 2011) | $P/10^{-8}$ Torr (Bryson et al. 1974) |
|-----|-----------------------------|--------------------------------------|--------------------------------------|
| 131.80 | 0.020 | 0.017 | 0.063 |
| 134.50 | 0.049 | 0.042 | 0.082 |
| 136.90 | 0.017 | 0.094 | 0.266 |
| 141.00 | 0.377 | 0.343 | 0.430 |
| 141.10 | 0.388 | 0.354 | 0.470 |
| 142.90 | 0.659 | 0.609 | 0.613 |
| 144.00 | 0.005 | 0.082 | 0.008 |
| 144.90 | 1.170 | 1.100 | 2.080 |
| 146.30 | 1.730 | 1.640 | 1.770 |
| 147.50 | 2.400 | 2.300 | 2.650 |
| 148.50 | 3.150 | 3.030 | 4.700 |
| 149.34 | 3.950 | 3.820 | 3.900 |
| 151.00 | 6.110 | 5.980 | 5.500 |
| 151.10 | 6.270 | 6.140 | 8.640 |
| 153.19 | 10.70 | 10.70 | 13.30 |
| 153.50 | 11.60 | 11.50 | 11.60 |
| 159.00 | 44.20 | 45.60 | 37.30 |
| 159.20 | 46.30 | 47.90 | 41.70 |
| 159.50 | 49.70 | 51.40 | 70.40 |
| 159.58 | 50.60 | 52.40 | 72.00 |
| 159.78 | 53.00 | 55.00 | 57.80 |
| 169.20 | 421.0 | 462.0 | 500.0 |
| 174.57 | 1240 | 1400 | 1490 |
| 176.83 | 1920 | 2200 | 2330 |

Note.  
$^a$ Temperatures are those of Bryson et al. (1974). Values at other temperatures can be found by using Equation (3). Where Bryson et al. (1974) gives more than one value for a vapor pressure at a single temperature, the average of those values is listed here. Vapor pressures are given to three significant figures. Vapor pressure uncertainties in this work are about 1%. See the text.

3.2. Vapor Pressure of C$_6$H$_6$Ice

Having verified our approach using solid H$_2$O, which probably has been studied more than any other extraterrestrial ice, we turned to benzene, our title compound. Following the same procedure as before, we vapor deposited C$_6$H$_6$ onto the surface of our microbalance’s precooled substrate at 100 K; a temperature chosen to give a crystalline ice (Ishii et al. 1996). The resulting solid then was warmed while recording the corresponding QCM frequencies as a function of temperature. Using the method already described, we extracted temperature-pressure data from four ices, prepared a Clausius–Clapeyron plot in each case, and fit the data for each ice with a linear function, ln $P$ versus $1/T$. Averaging gave the following equation:

$$\ln(P) = (-5978.2) \left(\frac{1}{T}\right) + 25.6. \quad (4)$$

From Equation (4), we calculated vapor pressures at the temperatures used by Dubois et al. (2021), the results being shown in Figure 3. The dashed line on the graph is the most recent fit available for benzene data from Růžička et al. (2014), based on their recommended sublimation pressures and laboratory measurements. Table 2 summarizes results from all three sources at the same temperatures. Table 3 lists vapor pressures at 5 K intervals based on our C$_6$H$_6$ ices.

3.3. Vapor Pressure of C$_6$H$_{12}$Ice

Vapor pressures of both benzene (C$_6$H$_6$) and cyclohexane (C$_6$H$_{12}$) ices were reported by both Jackowski (1974) and Ha et al. (1976) for temperatures from about 280 to 220 K. The cyclohexane results in those papers were extrapolated from a temperature range to 150 K by Dubois et al. (2021) for calibrating their thermocouples; the extrapolation being necessary due to the lack of laboratory data in the 220 to 150 K region. Recognizing this lack of data below 220 K, and having obtained favorable results with H$_2$O and C$_6$H$_6$ ices, we also measured vapor pressures of solid cyclohexane using the equipment and procedures already described. Measurements on three ices gave Equation (5) for the 135–154 K region:

$$\ln(P) = (-5776.1) \left(\frac{1}{T}\right) + 26.3. \quad (5)$$

Figure 3. Vapor pressures of crystalline benzene in this work compared to literature results. The temperatures for the points (red squares) for the present work are the same as those used by Dubois et al. (2021).

Table 2  
Vapor Pressures of Crystalline Benzene$^a$

| T/K | $P/10^{-8}$ Torr (This Work) | $P/10^{-8}$ Torr (Růžička et al. 2014) | $P/10^{-8}$ Torr (Dubois et al. 2021) |
|-----|-----------------------------|--------------------------------------|--------------------------------------|
| 134.8 | 0.706 | 0.934 | 21.9 |
| 137.2 | 1.130 | 2.010 | 16.3 |
| 138.8 | 2.530 | 3.290 | 33.0 |
| 142.5 | 7.750 | 9.910 | 95.4 |
| 145.1 | 16.40 | 20.80 | 182 |
| 145.4 | 17.90 | 22.60 | 254 |
| 146.4 | 23.70 | 29.80 | 746 |
| 148.9 | 47.10 | 58.40 | 1390 |
| 151.4 | 91.30 | 112 | 1480 |
| 153.4 | 153.0 | 186 | 1260 |
| 154.3 | 192 | 232 | 4130 |
| 154.9 | 223 | 269 | 6120 |
| 157.6 | 432 | 514 | 6720 |

Note.  
$^a$ Temperatures are those of Dubois et al. (2021). Vapor pressures rounded to three significant figures. Values at other temperatures can be found by using Equation (4). Vapor pressure uncertainties in this work are about 1%. See the text.
Table 3: Vapor Pressures of Crystalline Benzene

| T/K  | P/10^8 Torr (This Work) |
|------|-------------------------|
| 135  | 0.754                   |
| 140  | 3.67                    |
| 145  | 16.0                    |
| 150  | 63.2                    |
| 155  | 229                     |

Note. Vapor pressures rounded to three significant figures. Values at other temperatures can be found by using Equation (4). Vapor pressure uncertainties are about 1%. See the text.

Table 4: Vapor Pressures of Crystalline Cyclohexane

| T/K  | P/10^8 Torr (This Work) |
|------|-------------------------|
| 135  | 0.194                   |
| 140  | 4.67                    |
| 145  | 128.3                   |
| 150  | 483.7                   |
| 154  | 1310.2                  |

Note. Vapor pressures rounded to three significant figures. Values at other temperatures can be found by using Equation (5). Vapor pressure uncertainties are about 1%. See the text.

Figure 4: Vapor pressures of crystalline cyclohexane. The dashed and solid lines are extrapolations from ~220 K using the equations of Ha et al. (1976) and Jackowski (1974), respectively. The five points (red squares) are from our lab measurements.

The motivation for our work was its use for understanding the properties and behavior of benzene in Titan’s atmosphere. Our main finding is that the vapor pressures for solid C6H6 are only about 6% of the values of Dubois et al. (2021). From this, multiple implications and predictions will follow. Specifically, the lower vapor pressures we report will result in higher altitudes for C6H6 condensation, a smaller condensation rate, and a smaller size for the resulting cloud particles. These expectations have already been described by Vinatier et al. (2018) and Dubois et al. (2021), to which readers are referred for details including multiple useful graphs. See also the analyses of Barth (2017).

Before suggesting reasons for the disagreement of the two more recent sets of laboratory measurements in Figure 3, we first should note some differences between the lab methods used. In our work, solid benzene was warmed to initiate sublimation and to begin data collection. All measurements were of temperature and mass loss of the ice from which a vapor pressure was found, avoiding possible complications from, for example, supersaturation of a benzene vapor (e.g., Ha et al. 1976). In contrast, in the work of Dubois et al. (2021) data collection began when solid benzene was forming by condensation of benzene vapor onto a cold surface. The constancy of band areas of the resulting solid infrared spectrum was used to determine when solid-vapor equilibrium had been reached, at which point the benzene vapor’s pressure and the solid’s temperature were recorded.

Several suggestions can be offered to explain the differences in the benzene vapor-pressure measurements seen in Figure 3. For example, it is not entirely clear if the procedure described

4. Discussion

3.4. Sublimation Energies of Ices

Having vapor pressures for three icy solids, we were able to calculate the enthalpy of sublimation (ΔHsubl) of each. The slopes of the lines represented by Equations (3)–(5) equal -ΔHsubl/R, where R is the ideal gas constant (8.31446 × 10^-3 kJ K^-1 mol^-1). From these slopes we calculated ΔHsubl = 50.2 ± 0.1 and 49.7 ± 0.1 kJ mol^-1 for H2O ice and C6H6 ice, respectively, for the temperature ranges we covered. These two
in Dubois et al. (2021) will yield equilibrium vapor pressures since any benzene subliming (e.g., 140 K) encounters room-temperature C₆H₆ vapor (e.g., 298 K). Also, sharp IR peaks at 3700–3600 cm⁻¹ in Figure 2 of Dubois et al. (2021) show that the benzene ice sample was slightly contaminated with trapped H₂O (Engdahl & Nelander 1985). Another concern is that the IR spectra for 7 of the 13 data points (i.e., those above ∼146 K) listed do not match literature spectra for crystalline benzene of the past 75 yr (e.g., Halford & Schaeffer 1946; Mair & Hornig 1949; Hollenberg & Glover 1967; Ruiterkamp et al. 2005; Hudson & Yarnall 2022). A possible solid–solid phase transition of crystalline benzene to explain dramatic spectral changes near 146 K has neither calorimetric (Oliver et al. 1948) nor crystallographic (Fortes & Capelli 2018) support.

All of the above are important considerations, but not necessarily responsible for the vapor-pressure differences in Figure 3. We believe that the main source of difference in the two sets of lab measurements of the solid benzene’s vapor pressures is the extrapolations of cyclohexane data (Jackowski 1974; Ha et al. 1976) from 220–280 K and 1–40 Torr down to 145–150 K and 10⁻⁷–10⁻³ Torr by Dubois et al. (2021), and the use of the extrapolated results for temperature calibrations. As our Figure 4 shows, the temperatures of our cyclohexane vapor pressures are about 8 K higher along the horizontal axis than those found in the extrapolations.

We have two suggestions for bringing the results of Dubois et al. (2021) into accord with our own work. First, the temperature calibrations and adjustments based on extrapolations of cyclohexane data (Jackowski 1974; Ha et al. 1976) from ∼220 K down to ∼150 K should be rejected in favor of ice temperatures recorded by the thermocouples of Dubois et al. (2021). This will raise the temperature of each of the authors’ benzene vapor-pressure measurements by ∼8 K. Second, only the authors’ six data points below 146 K should be accepted as reliable benzene ice results, a suggestion that is supported by the IR data. In fact, these are the only data points used by Dubois et al. (2021) in their study of Titan’s atmosphere. The result of these two suggestions is to shift the points of Dubois et al. (2021) in Figures 1 and 3 by about 8 K to the right, leading to considerably improved agreement between the recent lab results, as seen in Figure 5. Such an 8 K shift also means that the benzene vapor pressures reported for temperatures of ∼146 K and higher actually correspond to ∼154 K and higher. We have found that solid benzene sublimes rapidly under a vacuum at those temperatures (Yarnall & Hudson 2022), so it is not surprising that the IR spectra reported by Dubois et al. (2021) at ∼146 K and above do not match those of C₆H₆ ice.

Having determined the vapor pressures of benzene ices near 135–160 K, it is reasonable to try to connect our results to the most recent higher-temperature measurements (Růžička et al. 2014). In Figure 6, we show both low- and high-temperature vapor pressures of solid benzene. Equation (6), the Cox equation (Cox 1936), is the curve connecting the two sets of points, with $A₀ = 3.0944$, $A₁ = -3.1695 \times 10^{-4}$ K⁻¹, and $A₂ = -5.1088 \times 10^{-2}$ K⁻² determined by a least-squares fit of the data. Following Růžička et al. (2014), benzene’s triple point temperature and pressure were used for $T₀$ and $P₀$ (i.e., $T₀ = 278.674$ K, $P₀ = 55.891$ Torr):

$$\ln \frac{P}{P₀} = \left(1 - \frac{T₀}{T}\right) \exp (A₀ + A₁T + A₂T²).$$

The fit in Figure 6 for benzene is excellent, but measurements between about 160 and 230 K are still needed.

Before ending, we want to point out that this study shows the importance of having more than one research group measuring physical properties of compounds of interest to planetary scientists and others. Having measurements from more than one source, and using more than one method, allows independent comparisons and checks to be made that otherwise would be impossible, avoiding the dangers involved when only a single source of laboratory results is available.

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