Vapor Pressure of Solid 1,4-Dithiane

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The vapor pressures of low-volatility chemical warfare (CW) agents, their byproducts and degradants, and simulants are important physical data that are needed for accurate vapor generation, for filter modeling and testing, and for assessing the environmental fate of the materials. This report documents the measurement of the vapor pressure of 1,4-dithiane (DTH), a byproduct associated with vesicant chemical warfare agent bis-2-chloroethyl sulfide (HD), in the range of (296.65 to 376.95) K. By combining our measurements with a study of the thermodynamic properties of the compound in the subambient range, we were able to calculate Antoine parameters that can be used to extend estimates of the vapor pressure from $T = (256.95 \text{ to } 376.95)$ K. We have calculated a value of 10.6 Pa for the vapor pressure of the compound at 298.15 K. This contrasts with the accepted value of 107 Pa.

Introduction

The compound 1,4-dithiane (DTH) (CAS R.N. 505-29-3, M.W. 120.24, structure in Figure 1) is a degradant of the vesicant chemical warfare agent bis-2-chloroethyl sulfide (HD).[1] The melting temperature of DTH is 112.3 °C, and its boiling temperature is 199.5 °C.[2] It is nearly always present in aged samples of HD and is stable in the environment. For this reason, environmental studies of sites formerly involved in the production or storage of HD must consider the presence of the compound and estimate its fate. One of the factors used to estimate the persistency of a compound in the environment is its vapor pressure. Our experimental data appear to show that the estimate of the vapor pressure of 1,4-dithiane used within the chemical warfare defense community may be overestimated by a factor of 10.

At least one reference cites a vapor pressure for 1,4-dithiane of 1.57 Torr (209.3 Pa) at 25 °C.[3] A technical report published by M. J. Small at Fort Detrick gives a vapor pressure of 0.8 Torr (106.7 Pa) at the same temperature.[4] However, we have been unable to trace the source of the original data cited as the source in ref 4, a 1978 literature review attributed to Arthur D. Little. The data point has, nevertheless, continued to be cited in a circular fashion, most recently in 2002[5] and 2007,[6] for example. The vapor pressure in refs 5 and 6 was obtained from a literature review in *Environmental Health Perspectives*,[7] which cites ref 2 and states, "Small calculated physical properties for degradation products of sulfur mustard predicted to be stable in the environment". In fact, although Small provided an equation in Appendix C of the report that can be used to estimate vapor pressures of compounds, a careful reading of the text as a whole leaves some ambiguity as to whether this was the method that he used to calculate the vapor pressure listed for 1,4-dithiane. Table 4 of that report, a listing of several physical properties of sulfur mustard and its degradants, merely refers to the Arthur D. Little report and includes a footnote applicable to the datum for 1,4-dithiane stating, "See reference for saturated vapor pressure data at other temperatures". The explanatory note appears to imply that Small merely extracted the data point from the literature review that he cited. Without access to the Arthur D. Little report, we were unable to determine how the data were originally derived, i.e., whether they were based upon experimental observations within the ambient temperature range or extrapolated from data at higher temperatures.

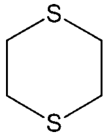

Figure 1. Structure of 1,4-dithiane (DTH).

Small provided several equations that have come to be used in estimating the persistence of chemical warfare agents and related contaminants in the environment. Among these, volatility potential (VP)[8] was calculated thus:

$$\mathrm{VP} = \frac{P_0}{C_{\mathrm{sol}}(K_{\mathrm{oc}})} \tag{1}$$

where P_0 is the vapor pressure of the contaminant; C_{sol} is the aqueous solubility; and K_{oc} is the partition coefficient between the soil organic carbon and water. The volatility potential is, therefore, directly proportional to the vapor pressure, underscoring the importance of having reliable data.

Experimental Section

1,4-Dithiane was obtained from Sigma-Aldrich Chemical Co. (Milwaukee, WI, cat. no. D217700) at a stated purity of ≥ 97 %. Analysis by GC-MS returned a purity of 99.9 %, while NMR analysis (^{13}C and ^{1}H, referenced to an internal standard) showed the purity to be (96.9 ± 4.1) %.

We used an ASTM vapor saturation method[9] to determine the vapor pressure of DTH at 296.65 K. This method has been used by other scientists at the Edgewood Chemical Biological Center to determine the vapor pressure of a variety of chemical warfare agent related compounds,[10−12] including solid bis(2-

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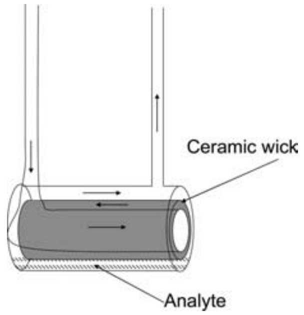

Figure 2. Schematic of the saturator cell, used to generate continuous vapor streams of compounds for determining vapor pressure. The arrows indicate the direction of flow of the nitrogen carrier gas.

chloroethyl) sulfide (HD).[13] We have measured the vapor pressures of a variety of compounds, including benzene, diethyl disulfide, and 2-chloroethyl ethyl sulfide, at temperatures as low as 261.15 K and as high as 296.15 K, yielding deviations of < 1 % from the literature values.[14] A stream of nitrogen carrier gas is passed through the saturator cell (Glassblowers.com, Turnsersville, NJ) suspended in a Julabo (Allentown, PA) F25 constant temperature bath. The carrier gas makes three passes across the surface of the conical ceramic wicking mechanism (Figure 2), establishing a saturated equilibrium between the vapor and condensed phases of the compound. If the moles of the target analyte and carrier gas are known, the partial pressure of the analyte can be calculated using the ASTM method from ref 9 using eq 2

$$P = P_{\text{sat}} \frac{n_{\text{analyte}}}{n_{\text{carrier}} + n_{\text{analyte}}} \tag{2}$$

where P is the pure compound saturation pressure at the pressure of the saturator cell; P_{sat} is the pressure in the saturator cell; n_{analyte} is the number of moles of the analyte; and n_{carrier} is the number of moles of carrier gas.

The number of moles of the compound (n_{analyte}) for eq 2 was obtained from the mass loss of the compound, which we determined by weighing the saturator cell at the beginning and end of the experiment on a Sartorius (Goettingen, Germany) BP211D analytical balance having a reproducibility of ≤ 0.1 mg and linearity of ≤ 0.2 mg. Before weighing the saturator cell, the accuracy of the balance was checked with a standard weight set at points above and below the mass of the saturator cell, indicating a performance better than the manufacturer's specifications. Following the individual experiments, the saturator cell was dried with a lint-free paper towel and equilibrated to room temperature for at least two hours. Prior to placing the saturator cell in the weighing chamber, we passed it across a deionizing bar (Haug, Mississauga, ON, model EN-C). We then recorded at least four readings and calculated the mean. The number of moles of nitrogen (n_{carrier}) was obtained using the ideal gas law from the carrier rate and time, which was controlled by Brooks Instrument (Hatfield, PA) model 5850S mass flow controllers and recorded in Labview (National Instruments, Austin, TX). The linearity of the S series mass flow controllers is adjusted using a second-order polynomial, resulting in uncertainties of approximately 1 % or better of rate at flow ≥ 25 % of full scale. The pressure (P_{sat}) was recorded continuously in Labview with an Omega Engineering (Stamford, CT) DPI 740 digital barometer. The bath temperature was controlled to within ± 0.05 K and recorded in Labview. The temperature of the bath was verified with a NIST traceable liquid-in-glass thermometer with divisions of 0.1 K and an accuracy of ± 0.02 K. The uncertainties of all mass, temperature, flow, and pressure instruments used in the laboratory were checked periodically. The vapor was sampled periodically with a Dynatherm (CDS Analytical, Oxford, PA) thermal desorption system and analyzed by an Agilent (Santa Clara, CA) 6850 gas chromatograph equipped with a flame ionization detector to determine its purity.

The vapor pressure was measured in the range of (352.25 to 376.95) K using a TA Instruments (New Castle, DE) 910 differential scanning calorimeter (DSC) with a 2200 controller in accordance with an ASTM method.[15] The measurement consists of heating a small specimen of the test material in the DSC cell through the boiling temperature at a controlled rate while the pressure (vacuum) on the cell is held constant. At the boiling temperature, the vaporized specimen escapes from the sample pan through a small orifice ("pinhole") in the lid. The energy associated with the transition from liquid to vapor is recorded as a sharp boiling peak (endotherm), and the boiling temperature is taken at the intersection of tangents to the curve at the onset of boiling. The experimental pressure, measured with a mercury manometer, is the pressure in the cell as the specimen boils. This process is repeated with new specimens at different pressures to obtain points to be fitted to the vapor pressure curve. The DSC used in this study was calibrated in accordance with ASTM Practice E 967: observed onset temperatures for water and indium were well within the method uncertainty of ± 1 K for the endotherm onset temperatures.

In 2003, we investigated use of pinholes larger than those specified in the ASTM method to extend the useful range of the technique to pressures below the 5 kPa recommended limit.[16] With larger pinholes at lower pressures, boiling endotherms remained sharp and appeared, at least qualitatively, to resolve the problem with peak broadening typically observed at low pressures. In follow-on quantitative studies using octanol, the results were still in reasonable agreement with the literature,[17] with deviations of less than 2 K from the expected values down to about 1 kPa. However even with the larger pinholes, the method accuracy degraded below 1 kPa.

Results and Discussion

We introduced the 1,4-dithiane into the saturator cell by first dissolving the compound in dichloromethane (Sigma-Aldrich, ≥ 99.5 %), pipetting the solution in the cell, and then purging off the solvent with dry nitrogen. We then monitored the output of the saturator cell periodically with a Bruker Optics (Billerica, MA) IFS-66V infrared spectrometer equipped with a multipass gas cell set to 8.02 m until no detectable solvent remained in the vapor.

Saturator cell data were then obtained with gas flow rates of (500, 1078, and 2500) $\text{cm}^3 \cdot \text{min}^{-1}$ (referenced to 294.26 K, 101.325 kPa). The computed saturation vapor pressures obtained for the three trials were 9.18 Pa, 9.18 Pa, and 8.8 Pa, respectively. We would generally be skeptical of mass loss data for carrier rates greater than a few hundred cm^3 per minute and would have expected a greater loss of efficiency in the saturator cell system than we observed. The compound tended to fill the open volume between the wick and the glass wall with needle-shaped crystals of DTH. We believe this increased the effective surface area of the compound in the saturator cell and resulted in the relatively small drop in the efficiency of the cell at 2.5 L per minute.

Eight experimental points obtained through differential scanning calorimetry were included in the data used to

Table 1. Vapor Pressure Data for 1,4-Dithiane from Three Different Experimental Methods, the Values from the "Best Fit" of the Data Using the Calculated Antoine Equation, $\ln P/\mathrm{Pa} = A - B/(C + T/\mathrm{K})$, where $A = 31.4197$, $B = 8677.471$, and $C = 0.437$, and the Deviation of the Measured Values for the Pressure at Each Point from the Calculated Values[a]

	P/Pa		
T/K	exptl	calcd	$100(P_{\mathrm{exptl}} - P_{\mathrm{calcd}})/P_{\mathrm{calcd}}$
256.95	0.10	0.1009	−0.89
262.32	0.20	0.2009	−0.45
265.56	0.30	0.3004	−0.13
267.91	0.40	0.3997	0.075
269.76	0.50	0.4988	0.24
271.29	0.60	0.5976	0.40
272.6	0.70	0.6966	0.49
273.75	0.80	0.7959	0.51
274.77	0.90	0.8950	0.56
275.68	1.00	0.9930	0.70
296.65	9.18	9.127	0.58
355.75	1067	1162	−8.18
359.45	1333	1492	−10.66
362.35	1893	1810	4.59
367.35	2653	2505	5.91
370.65	3246	3090	5.05
374.05	3826	3820	0.16
374.25	3906	3868	0.98
376.95	4626	4565	1.34

[a] In the range of T = (256.95 to 275.68) K, the values shown for P_{exptl} are fitted values from ref 18.

calculate the Antoine coefficients. Two DSC values measured at pressures below 1 kPa were not included in the fit due to the increased uncertainty in this range. The measurements of vapor pressure encompassed the range of 355.75 K (1067 Pa) to 376.95 K (4626 Pa).

In 1983, de Wit et al. determined the vapor pressures and enthalpies of sublimation of 28 organic compounds containing nitrogen, oxygen, and sulfur obtained using a combined torsion−effusion and mass−loss effusion method.[18] The measurement runs consisted of 5 data points at 25 different temperatures. The authors provided a table giving fitted vapor pressure data for ten points at intervals of 0.1 Pa, encompassing 256.95 K (0.1 Pa) to 275.68 K (1 Pa) for 1,4-dithiane. These data, as well as our experimental data points, are listed in Table 1.

The data points (8 from DSC, 1 saturator cell, and 10 effusion) were pooled, and MatLab (The Mathworks, Inc., Natick, MA) was then used to do the least-squares fit of the Antoine equation[19]

$$\ln P/\mathrm{Pa} = A - \frac{B}{T/\mathrm{K} + C} \qquad (3)$$

Figure 3 shows that the coefficients derived from the combined data appear to give a good fit. The effusion points are fitted values rather than the experimental measurements (which may no longer be readily available according to our correspondence with one of the authors of that study), and we acknowledge that this method therefore lacks statistical rigor. Nevertheless, we believe that it provides a better prediction of the vapor pressure of the compound across the 120 K range than using either set of data by itself. We compared the deviations in the experimental values of the vapor pressure from the calculated values if either set of data is used by itself to do the fit. Using only the data from our laboratory and calculating a three-parameter fit (eq 3) yields a deviation of 5.38 % at 256.95 K and 1.33 % at 376.95 K. Using the least-squares fit from de Wit et al., which is linear with respect to the natural logarithm of the vapor pressure (a reasonable approach over the range of their study), gives a deviation of 4.58 % at 376.95 K.

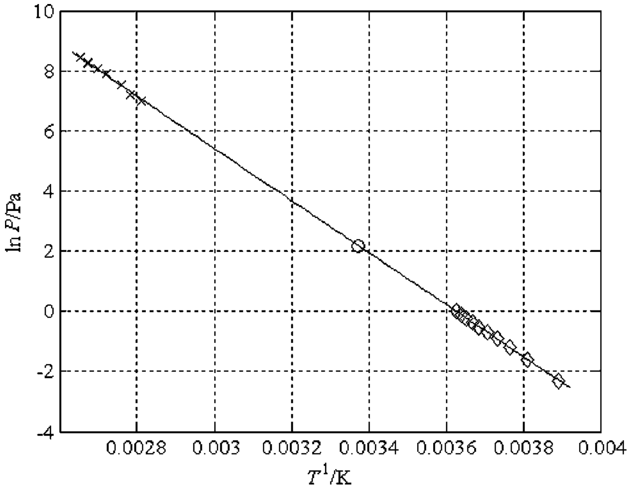

Figure 3. Vapor pressure data for 1,4-dithiane from three different experimental methods and the "best fit" of the data points from the calculated Antoine equation, $\ln P = A - B/(C + T)$, where $A = 31.4197$, $B = 8677.47$, and $c = 0.437$: ×, DSC; ○, saturator cell; ◊, de Wit et al.

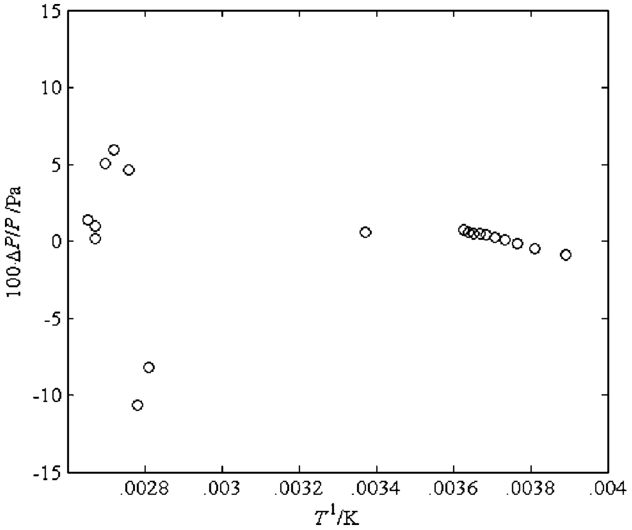

Figure 4. Fractional deviations $\Delta P = P_{\mathrm{exptl}} - P_{\mathrm{calcd}}$ of the experimental vapor pressures P_{exptl} of 1,4-dithiane from the calculated values P_{calcd}. The calculated values were obtained from a least-squares fit of eq 3. In the range of T = (256.95 to 275.68) K, the values shown for P_{exptl} are fitted values from ref 18.

The experimental temperature and vapor pressure values used to calculate the Antoine coefficients, as well as the calculated values and fractional deviations, are listed in Table 1. Figure 4 presents the fractional deviations of the experimental measurements of the vapor pressure as a function of the inverse of the absolute temperature. The vapor pressure of 1,4-dithiane at 298.15 K calculated from the coefficients in Table 1 is 10.6 Pa, more than an order of magnitude lower than the estimate in ref 4, 5, and 6.

The value for the enthalpy of sublimation ($\Delta_{\mathrm{s}}^{\mathrm{g}}H_{\mathrm{m}}$) of 1,4-dithiane in ref 18 is 72.4 $\mathrm{kJ \cdot mol^{-1}}$ (mean value from torsion effusion: 73.0 $\mathrm{kJ \cdot mol^{-1}}$ and mass effusion data: 71.8 $\mathrm{kJ \cdot mol^{-1}}$). The value calculated from the combined data is 71.9 $\mathrm{kJ \cdot mol^{-1}}$ at 296.65 K, which compares favorably with ref 18.

The expanded uncertainty in the vapor pressure obtained through the saturator cell data encompasses: (1) the uncertainty in n_{analyte}, whose fractional value may be estimated as 0.2/23.4 mg, or 0.0085, since the value is obtained by mass difference; (2) the fractional uncertainty of n_{carrier}, which is dominated by the mass flow rate, is estimated at 0.01; (3) P_{sat}, the pressure in the saturator cell, which is measured with a digital barometer having an uncertainty of 0.01; (4) the purity of the 1,4-dithiane, to which we assign an uncertainty of 0.02 (because the data indicated that the impurities were volatile, we did not include them in the Raoult equation of the partial pressure); and (5) the uncertainty in the temperature of the bath. Although we can verify the temperature of the bath to an uncertainty of 0.02 °C, the precision of the electronic control is 0.05 °C. Because the vapor pressure varies logarithmically as a function of T^{-1}, determining the effect of U_T is a bit more complex than for the other factors, although it can be estimated by calculating the difference in the vapor pressure from the computed Antoine coefficients by a change of 0.05 K in the temperature at 296.65 K: $0.09/9.18 \approx 0.01$. Thus, the fractional expanded uncertainty of the saturator cell measurement of the vapor pressure was estimated at 0.028, from the following equation[20]

$$U_P = (U_{n_{\mathrm{analyte}}} + U_{n_{\mathrm{carrier}}} + U_{P_{\mathrm{sat}}} + U_{\mathrm{pur}} + U_T)^{1/2} \qquad (4)$$

The uncertainty in the vapor pressure data obtained by DSC is dominated by the uncertainty in the boiling onset: ± 2 K. Within the range of our tests, the uncertainty in the measured values of the vapor pressure can thus be estimated with the Antoine coefficients by calculating the difference in vapor pressure that would result from a 2 K change in temperature, which ranges from approximately ± 14.5 % of the measured vapor pressure at 356 K to ± 6 % at 377 K. The variability in the measured data points vis-à-vis the fitted data is, therefore, within the expected uncertainty. The greater error in the DSC data at low pressure can be tolerated given the combination of this data set with the others to generate the Antoine curve.

Conclusions

Combining experimental observations of the vapor pressure of solid 1,4-dithiane from three different experimental methods has enabled us to calculate Antoine parameters that extend the useful range for the estimated vapor pressure from (256.95 to 376.95) K. The estimated vapor pressure of the compound at 298.15 K is (10.6 ± 0.2) Pa. This is an order of magnitude lower than the commonly cited value of 107 Pa, indicating that the environmental persistence of 1,4-dithiane is likely to be longer than previous estimates. The estimated value for the enthalphy of fusion is 71.9 kJ·mol^{-1}, consistent with the data from de Wit et al.

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