J. Chem. Eng. Data **1981**, *26*, 237-239

Vapor Pressure of Dimethyl Tetrachloroterephthalate

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The vapor pressures of dimethyl tetrachloroterephthalate have been determined in the range 75-160 °C. Thirty-five temperatures were used with a minimum of two results at each temperature. Measured vapor pressures were in the range 0.0007-1.478 torr and are expressed by the following equation: log p = 12.79 ± 0.18 - (5480 ± 72)/T, where log p is the decimal logarithm of the vapor pressure (torr) and T is the absolute temperature. Each constant of the above equation is followed by the 95% confidence limits. Experimental conditions studied included effusion hole diameter and effusion time. This compound has no phase change below its melting point (~160 °C). Effusion procedure and gas saturation method were used in this work. The average molar vaporization heat is calculated as ~25 kcal/mol in the interval 75-160 °C.

Introduction

The determination of vapor pressures of pure organic compounds is an important consideration not only from the purely scientific standpoint but also for their commercial end use. The application of pesticides in agriculture and their potential action in humans make it necessary to know their absolute volatilities and, hence, their vapor pressures. A combined knowledge of the vapor pressure and the biological action of a pesticide will provide a clear picture of the end-use hazards. Some countries are beginning to require the determination of vapor pressures of pesticides as a precondition for marketing. In the U.S.A., the Environmental Protection Agency is preparing proposed pesticide guidelines that include the determination of the vapor pressures and volatilization rates from water and soil. In this paper, the vapor pressures of dimethyl tetrachloroterephthalate (Dacthal) (Diamond Shamrock Corp.) are presented in the range 75-160 °C. The equation relating vapor pressure and temperature, and a discussion of some experimental conditions are also given.

Experimental Details, Apparatus, and Techniques

All of the apparatus and the techniques used in this work have already been described elsewhere (*1-3*). Further experimental details are given below.

The mercury used for the calibration of the effusion foils was from Ventron Corp., triple distilled, with the following analysis: gold and silver, 0.0001%; base metals, 0.0001%; nonvolatile residue, 0.0001%. It was used without further purification. The vapor pressure of mercury was taken directly from the tables, using linear interpolation if needed (*5*). Effusion times ranged from 2 to 240 h; the loss in weight was 0.0012-0.052 g; effusion hole diameters were ca. 0.1, 0.5, and 1.0 mm; the effusion foil thickness was ~0.03 mm; the inside volume of the cell was ~2.5 mL; the amount of sample loaded into the cell was 0.1-0.2 g (fine powder); and the overall weight of the cells was 53-55 g, weighed to ±0.1 mg. No condensation of the vapor was observed after a run either over the hole or on the outside surface of the cell. The molecular species in the vapor phase were assumed to be the monomers, since this compound cannot form hydrogen bonds that might form dimers, etc.

No sign of reaction between the cells (stainless steel) and the compound was observed, even after long effusion times (no discoloration of the steel or the compound).

Table I. Vapor Pressures of Dacthal-Effusion Method

temp (±0.1), °C	vapor press., torr	temp (±0.1), °C	vapor press., torr
80.0	0.00182	105.0	0.0195
85.0	0.00310	110.0	0.0311
90.0	0.00483	115.0	0.0493
95.0	0.00765	120.0	0.0727
100.0	0.01275	125.0	0.116

Table II. Vapor Pressure of Decthal-Gas Saturation Procedure

temp (±1), °C	vapor press., torr	temp (±1), °C	vapor press., torr
70	0.0007	126	0.105
75	0.00116	127	0.136
82	0.0022	131	0.185, 0.15
90	0.0058	135	0.219
96	0.0081	136	0.258
100	0.0109	140	0.302
104	0.017	141	0.369
110	0.027	145	0.436
111	0.035	146	0.518
112	0.040	150	0.733, 0.614
115	0.052	155	0.941
118	0.055	156	1.14
121	0.086	160	1.478

In the gas saturation procedure, the flow of nitrogen was varied (0.84, 2.00, and 3.90 mL/min) at the same vapor pressure, indicating saturation.

This compound was prepared by the procedure of Lindeman (*4*), purified by three recrystallizations from boiling acetone, dried in a vacuum oven at room temperature for 48 h, ground, and obtained as a pure white powder. Calculated chemical composition: C, 36.1%; H, 1.8%; Cl, 42.7%. Found by analysis: C, 36.2%; H, 1.8%; Cl, 42.6%. The purity was 99.6% by gas chromatography and 99.9 mol % by differential scanning calorimetry (20 °C/min). The structural formula and the molecular weight are given in Figure 1.

Results

Experimental data are presented in Tables I and II for the effusion and gas saturation method, respectively. All of the results of both tables were combined and used to obtain the following recommended logarithmic equation for the range 75-160 °C:

$$\log p(\mathrm{torr}) = (12.79 \pm 0.18) - (5480 \pm 72)/T \qquad (1)$$

where log p is the decimal logarithm of the vapor pressure (torr) and T is the temperature in Kelvin. Each constant of the equation is followed by the 95% confidence limits. The average of the absolute percentage differences between the original and the fitted data from eq 1 is 6.7%. The average molar vaporization heat as calculated from eq 1 is 25 kcal/mol in the range 75-160 °C. A graph of eq 1 with the experimental results plotted is seen in Figure 2. The points are on a straight line, and the Clausius-Clapeyron equation is obeyed.

The effusion procedure has a higher precision than the gas saturation procedure. The absolute percentage deviations between the results of Tables I and II and the fitted values from eq 1 are respectively 3.2% and 8.0%.

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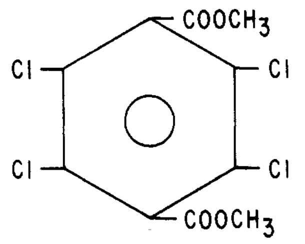

Figure 1. Structural formula of the compound. The molecular weight is 331.96.

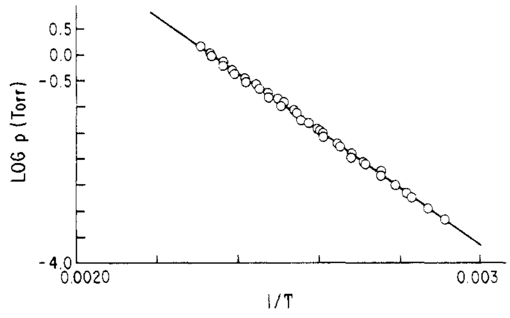

Figure 2. Graph of log (vapor pressure) vs. 1/*T*.

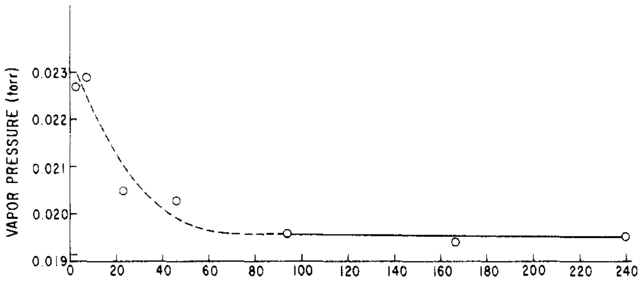

Figure 3. Variation of vapor pressure with effusion time; 105 °C; hole diameter, 0.1 mm.

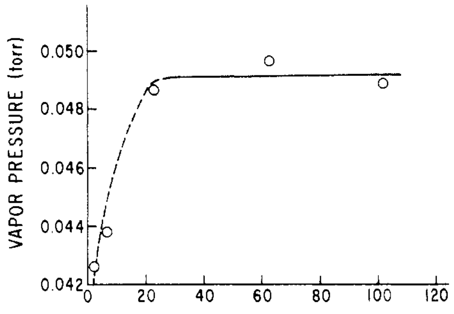

Figure 4. Variation of vapor pressure with effusion time; 115 °C; hole diameter, 0.1 mm.

Study of Some Experimental Variables

For each temperature and each effusion hole diameter, there is a minimum effusion time below which erratic results will be obtained. The causes of error, which may be severe at short effusion times, are the following: (1) the sample does not reach the bath temperature; (2) the inside of the cell is not saturated with the sample vapor; (3) the weighing error becomes significant when the total loss in weight is very small; (4) the more volatile impurities evaporate first, making the vapor pressure too high. Figures 3-6 present the apparent variation of vapor pressure with the effusion time. There is always a horizontal portion of the curve which indicates the true vapor pressure at the specified temperature. Similar findings were reported for the vapor pressure of other compounds (*2*). The broken lines in Figures 3-6 correspond to erratic pressures, due to the mentioned causes.

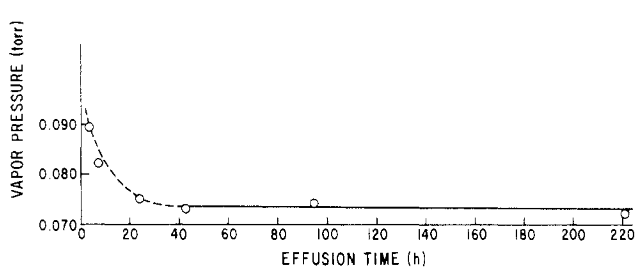

Figure 5. Variation of vapor pressure with effusion time; 120 °C; hole diameter, 0.05 mm.

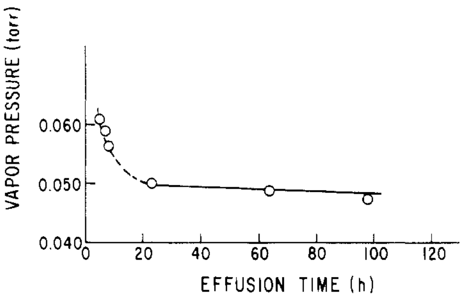

Figure 6. Variation of vapor pressure with effusion time; 115 °C; hole diameter, 0.05 mm.

Table III. Influence of *L*/*D* Ratio on the Vapor Pressure

temp, °C	*L*/*D* ratio	vapor press., torr	temp, °C	*L*/*D* ratio	vapor press., torr
80	12	0.00182	115	3	0.0489, 0.0497
80	51	0.00182	115	6	0.0489
90	4.4	0.00506, 0.0046	120	4	0.0721, 0.0733
90	26	0.0048, 0.0046		8	0.0733, 0.0741

For each temperature, there is a trend toward erratic apparent vapor pressure, with increasing hole diameter. This trend is generally small, unless too small *L*/*D* ratios are used (see Discussion). In our particular case, this effect, if any, was negligible. Table III presents some results obtained at different temperatures.

Discussion

The requirments imposed by the theory of the effusion procedure and the relationships between the mean free path of the molecules (*L*) and the diameter of the effusion hole (*D*) have been discussed elsewhere (*1*, *2*). In this work, the values *L*/*D* ranged from 2 to 82. The specific gravity of this compound is ~1.6 g/cm^3, this value being needed to calculate *L* by the equation already cited in the literature (*2*).

When one takes into account the uncertainty in the *L* calculation and the discrepancy in the value of *L*/*D* above which the theory is valid, it seems that the best policy is to study the apparent variation of the vapor pressure with *L*/*D* and take the constant value obtained as the true vapor pressure. Our reported data were obtained with different *L*/*D* values and effusion times.

The effusion cell constants were determined by the procedure already described in ref *1* by calibration with mercury. The same constants determined from the dimensions of the effusion hole and the appropriate correction factors agreed to ca. ±10%. The actual constants used in this work were those determined from the calibration with mercury. Two reasons can be cited for this preference: (1) there is still considerable uncertainty about the accuracy of the correction factors due to the thickness of the effusion foil and other parameters; (2) the cell constants determined by calibration with hexamethylbenzene, whose vapor pressures are known, coincided to ~5-10% with those determined with mercury.

Conclusions

The vapor pressure of dimethyl tetrachloroterephthalate has been measured and reported. It has been experimentally shown that (a) the Clausius-Clapeyron equation is followed, at least in the range 70-160 °C, (b) for each temperature and each hole diameter, a minimum effusion time is required, and (c) for each temperature the L/D ratio should be above a certain minimum. The effusion method seems to be more precise than the gas saturation method using the 916-TEA.

Acknowledgment

Linda Vargyas, Barbara Blackford, and Julia Black are thanked for the analysis of several samples for this work. Herbert Olson is thanked for the final preparation of the figures.

Glossary

p	saturated vapor pressure, torr
kcal	kilocalorie
T	absolute temperature, Kelvin
log	decimal logarithm
L	mean free path of the molecules of vapor inside the effusion cell, mm
D	effusion hole diameter, mm

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Received for review June 26, 1980. Accepted February 17, 1981.

Chemical Equilibria in Condensed-Ring Systems. Isomerization Equilibria of *cis*- and *trans*-Decalin

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Equilibrium constants for the isomerization of *cis*- and *trans*-decalin were measured in the liquid phase at 6.4 MPa H_2 pressure and temperatures between 545 and 621 K. The enthalpy of isomerization was found to be −2.75 ± 0.05 kcal/mol and the entropy of isomerization was found to be −0.60 ± 0.07 eu. While these values agree with previously published data, absolute values of equilibrium constants differ by approximately 10%.

Catalytic hydroconversion is an important process for the upgrading of heavy crudes, residua, and coal liquids to distillate fuels. The multiphase reactions which occur during the hydroconversion of these highly aromatic feeds are both varied and complex; however, a key reaction is the addition of hydrogen to condensed polynuclear aromatic hydrocarbons. Furthermore, at the temperatures and pressures used in some processes, there exists a very real possibility of equilibrium limitations. Unfortunately, there have been very few chemical equilibrium measurements made on polynuclear aromatic hydrocarbons, so that it is difficult to predict a priori a possible limitation.

A survey of the literature shows that most of the experimental work to date has been done in the vapor phase for compounds containing one or two aromatic rings (*1-4*). One experimental liquid-phase study was also presented (*5*). A limited amount of work has been published on three-ring systems (*4*, *5*) but to date there are no data available on four-ring compounds. Similarly, there are no data available on alkyl-substituted polynuclear aromatics and little available on heterocyclic species. Since there are significant amounts of these present in coal liquids and residua, these data are also needed.

This paper describes a new experimental equilibrium cell which has been designed to obtain liquid-phase hydrogenation equilibrium data and presents experimental results for the isomerization equilibria of *cis*- and *trans*-decalin which differ from previously published experiments.

Experimental Section

The liquid-phase experiments described in this paper were carried out in the equilibrium cell shown in Figure 1. The entire experimental layout is shown in Figure 2. The cell was constructed of 316 stainless steel with an internal volume of approximately 60 cm^3. The bolted closure design utilized a self-energizing metal O-ring (UPA Components U6420-0275-SEB) to obtain the seal. The inside surface of the cell was coated with a Solaramic coating (Solar Turbines International, S-5210-2C) approximately 0.05 mm thick. Stirring was accomplished magnetically by using a combination hot plate/stirrer (Corning PC-351) with a glass-coated magnetic stirring bar (A. H. Thomas). The cell was wrapped with electrical heating elements and insulation on the top and sides; the temperature was controlled to ±0.5 °C of setpoint with a Doric Control:80 digital controller. Pressure was maintained constant with two Mity-Mite back pressure regulators to ±0.1 MPa of setpoint and the pressure was read digitally. The equilibrium cell was designed for temperatures up to 450 °C at 10 MPa. Direct sampling of the liquid phase was accomplished through a ${}^1/_8$-in. (3.18-mm) o.d. capillary dip tube (i.d. = 0.012 in.). Outside the cell this tube was connected to a microcapillary valve (Precision Sampling 460050) and a 7-cm needle from a 1-μL syringe. The total volume of the sampling system was calculated to be less than 10 μL. However, to prevent contamination of samples, 25-50 μL of liquid was withdrawn from the cell and discarded prior to taking each sample. A small volume sample was then withdrawn directly into a capped septum bottle containing 1 mL of *n*-heptane plus internal standard (*n*-decane). Samples were analyzed by gas chromatography on an HP 5834A GC equipped with FID using a 10-ft. (3-m) column packed with 3% Dexil 300

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