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Vapor Pressure of Ethyl (5-Cyano-3,4-diphenyl-6-oxo-1,6-dihydropyridazin-1-yl)acetate by the Effusion Method

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The effusion method was used to determine the vapor pressure of ethyl (5-cyano-3,4-diphenyl-6-oxo-1,6-dihydropyridazin-1-yl)acetate (I) at 13 temperatures, in the range 123–141 °C, with a minimum of two results at each temperature. Measured vapor pressures were in the range 10^{-4}–6×10^{-4} torr and were expressed by the following equation: $\log p = 13.40 - (6891/T)$, where p is the vapor pressure in torr and T is the absolute temperature. The 95% confidence limits for the constants of the equation are respectively ±1.19 and ±486. Experimental conditions studied included effusion hole diameter and effusion time. This compound undergoes no phase change below the melting point (about 143 °C). All the results are for the crystalline phase below 143 °C. Some results by the gas saturation procedure are also included.

Introduction

The determination of vapor pressures of pure organic compounds is an important consideration, from the purely scientific standpoint and for the commercial end use. A combined knowledge of the physical properties such as vapor pressure and the biological action of a pesticide will provide a picture of any end-use hazards.

In this paper, the vapor pressures of ethyl (5-cyano-3,4-diphenyl-6-oxo-1,6-dihydropyridazin-1-yl)acetate (I) are presented in the range 123–141 °C. Figure 1 presents the structure of this compound.

Experimental Details

Apparatus and Techniques. All the apparatuses and 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 cells was from Ventron Corp., triple distilled, meeting the following specifications: gold and silver, 0.0001%; base metals, 0.0001%; nonvolatile residue, 0.0001%. It was used without further purification. Its vapor pressure was taken from the tables (*4*), by interpolation, if needed.

Effusion times ranged from 46 to 72 h, and weight decrease of the cell from 0.009 to 0.012 g. Hole diameters used were 0.54, 0.60, and 1.0 mm. The inside volume of the effusion cell was ~2.5 mL. The weight of the compound loaded into the cell was about 0.1–0.2 g (fine powder). No condensation of the compound was observed after the runs, either on the effusion hole or on the outside surface of the cell. The weight of the cell was ~54 g. The molecular species in the vapor phase are the monomers, since this compound cannot have hydrogen bonds that might form dimers, trimers, etc. No sign of reaction of the compound with the cell material (stainless steel) was observed after a run (no discoloration of the stainless steel or the compound).

Table I. Vapor Pressures of I by the Effusion Method

temp,[a] °C	10^4(vapor press.), torr	temp,[a] °C	10^4(vapor press.), torr
123.6	1	135.0	3.0
125.0	1.3	136.6	3.5
126.8	1.6	137.6	4.3
128.4	1.8	139.0	4.8
130.0	1.9	140.0	5.6
131.6	2.5	141.2	6.0
133.3	2.8		

[a] ±0.2 °C.

In the gas saturation procedure, the flow of nitrogen was varied (0.84, 2.00, and 3.9 mL min^{-1}), about the same vapor pressure always being obtained within the precision of the method.

This compound was recrystallized 3 times from boiling 96% ethanol and dried in a vacuum oven at room temperature for 3 days. The final product was a pure white powder. Anal. Calcd: C, 70.18; H, 4.77; N, 11.69. Found: C, 70.1; H, 4.9; N, 11.7. The purity by differential scanning calorimetry, run in duplicate, was 99.7, 99.8 mol %.

Results

Experimental data are presented in Table I. These data were used to obtain the following equation by a least-squares method:

$$\log p = 13.40 \pm 1.19 - (6891 \pm 486)/T \qquad (1)$$

where $\log p$ is the decimal logarithm of the vapor pressure (torr) and T is in Kelvin. Each constant is followed by its 95% confidence limit. A graph of $\log p$ vs. $1/T$ is seen in Figure 2 with the experimental values plotted. These are on a straight line, and the Clausius–Clapeyron equation is followed. It is seen that the vapor pressure of this compound is very low and changes rather slowly with the temperature.

The average molar vaporization heat is calculated from eq 1 by the formula $\Delta H = (6891)(4.59) = 31560$ cal mol^{-1} deg^{-1}.

The gas saturation procedure was also applied to this compound. However, great difficulties were experienced in this case due mainly to two reasons: (a) the constancy of temperature in the 916 Thermal Evolution Analyzer can be assured only to about ±1 °C, as compared with ±0.2 °C in the effusion procedure; (b) the sensitivity, at these low vapor pressures, is barely sufficient to differentiate vapor pressures differing by 2×10^{-4}–5×10^{-4} torr. The effusion procedure can determine these vapor pressures, but it requires careful work. The vapor pressure determined by the gas saturation procedure at 135 °C gave the following values: $n = 8$; average 2.9×10^{-4} torr; SD $= 2.2 \times 10^{-4}$ torr; relative SD = 76%. This vapor pressure agrees very well with the value by effusion, but the latter is much more precise.

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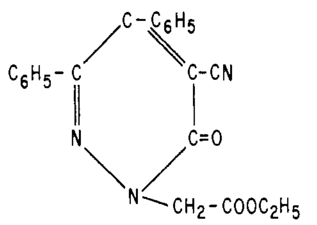

Figure 1. Structural formula of I, molecular weight 359.38.

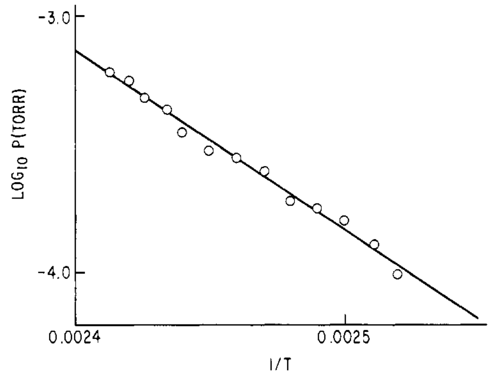

Figure 2. Graphic of log p(torr) vs. $1/T$.

Table II. Vapor Pressure of I[a]

L/R	vapor press., torr
98	5×10^{-4}
49	4.8×10^{-4}
24.5	5.1×10^{-4}

[a] L = mean free path of the molecules; R = radius of effusion hole, t = 139 °C.

Study of Some Experimental Variables

For each temperature and each effusion hole diameter, there is a minimum effusion time below which erratic results can be obtained, but above which the vapor pressure can be safely calculated.

Causes of error that may be very significant at short effusion times are as follows: (1) the sample does not reach the bath temperature; (2) the inside of the cell is not saturated with sample vapor; (3) the weighing error (±0.1 mg) becomes significant when the loss in weight of the cell is very small; (4) if the sample is not very pure, the more volatile impurities will volatilize first, making the vapor pressure too high at short effusion times. Figures 3 and 4 present the vapor pressure as a function of the effusion time, for the conditions indicated in each case. The horizontal portions represent the true vapor pressure. Similar results were reached before for other compounds (*2*).

For each temperature, there is a trend toward erratic vapor pressure with increasing hole diameter. This effect should be expected, as the theory requires that the mean free path of the molecules of the compound (L) should be much larger than the effusion hole radius (R). In most cases, this effect is small. Table II presents some results obtained for this compound. It is seen that the variation of vapor pressure, if any, is negligible. No effusion foils were available with $R > 0.5$ mm. Consequently, the minimum L/R used was 24.5.

Discussion

The relationship between the mean free path of the molecules, the radius of the effusion hole, and the requirements imposed by the theory have been discussed elsewhere (*2*). In this work, the ratio L/R was kept to a minimum of 24.5. We have shown (*2*) that even lower ratios can be used without serious errors.

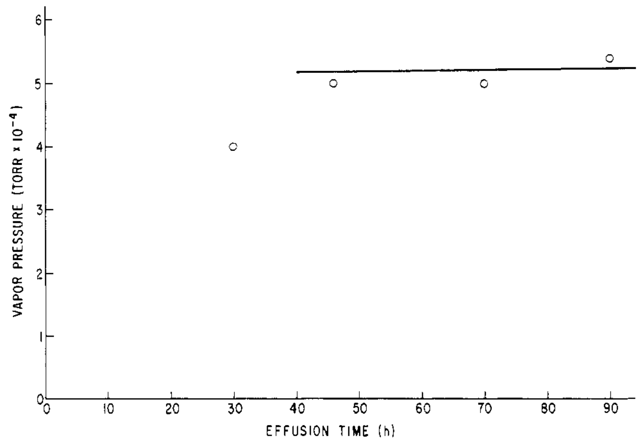

Figure 3. Vapor pressure of I, t = 139 °C, hole diameter 0.54 mm, vs. effusion time.

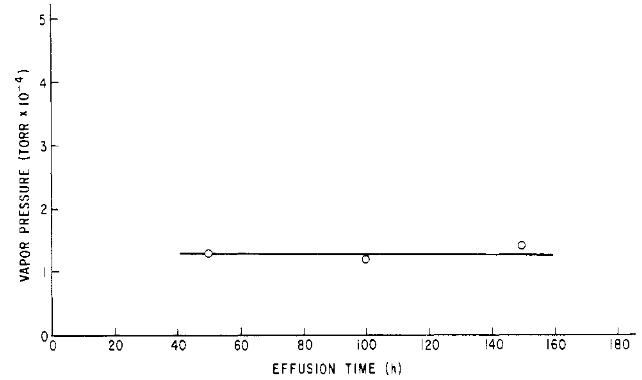

Figure 4. Vapor pressure of I, t = 125 °C, hole diameter 1.0 mm, vs. effusion time.

Conclusions

The vapor pressure of I has been measured and reported. It has been experimentally shown that (1) the Clausius–Clapeyron equation is followed, at least in the range 124–141 °C, and (2) for each temperature, a minimum effusion time is required.

Acknowledgment

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Glossary

L	mean free path of the molecules, mm
log	decimal logarithm
p	saturated vapor pressure, torr
R	radius of the effusion hole, mm
n	number of determinations
SD	standard deviation, torr
ΔH	average molar vaporization heat, cal mol^{-1} deg^{-1}

Literature Cited

(1) DePablo, R. S. *J. Chem. Eng. Data* **1976**, *21*, 141.
(2) DePablo, R. S. *J. Phys. D* **1980**, *13*, 313.
(3) Eggertsen, F. T.; Seibert, E. E.; Stross, F. H. *Anal. Chem.* **1969**, *41*, 1175.
(4) Weast, R. C., Ed. "CRC Handbook of Chemistry and Physics", 59th ed.; CRC Press: Boca Raton, FL, 1979; p D-198.

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