

Vapor Density and Apparent Vapor Pressure of Lindane (γ BHC)

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Vapor density associated with solid phase lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer, or γ BHC) measured by a gas-saturation technique was 3.5, 2.9, and 2.4 times greater than predicted from published vapor pressure values at 20, 30, and 40° C, respectively. The equation $\text{Log}_{10} P = 13.544 - (5288/T)$ expresses the relationship found between apparent vapor pressure and absolute temperature. The heat of vaporization

of lindane was found to be 24.17 kcal per mole. The data indicate that the discrepancy between measured and reported vapor pressure values may be due to incomplete saturation of the sphere cavity in the effusion manometer method, especially at lower temperatures. Differences are increased when vapor pressures or vapor densities are calculated for lower temperatures by extrapolation of data obtained at higher temperatures.

Volatilization and vapor phase transport are important processes in the dissipation of pesticides. Spencer and Cliath (1969) recently reported that the vapor density of dieldrin measured by a gas saturation technique was 3 to 12 times greater than predicted from published vapor pressure values which had been determined by an effusion technique. Dickinson (1956) found that the vapor pressure of DDT measured by a gas saturation method was essentially the same as that reported by Balson (1947) using an effusion manometer. We used the gas saturation technique as described for dieldrin (Spencer and Cliath, 1969) to measure the vapor pressure of DDT and obtained values for DDT corresponding to those of Balson (1947) and Dickinson (1956). This paper reports measurement of vapor density and apparent vapor pressure of lindane, and discusses the possible reasons for differences in reported vapor pressures for lindane by the two techniques.

EXPERIMENTAL

Vapor density of lindane (γ BHC) in association with solid phase lindane (an Entomological Society of America pesticide standard obtained from City Chemical Corp., New York, 100% γ isomer of 1, 2, 3, 4, 5, 6-hexachlorocyclohexane) was determined by a gas saturation method using high-purity nitrogen as a carrier gas. The details of the apparatus and procedures have been described (Spencer and Cliath, 1969). Briefly, in the gas saturation method a current of inert gas is passed through or over the material slowly enough to insure equilibrium vapor saturation. In our studies the vapor density of lindane was determined by measuring the amount of lindane in a stream of nitrogen gas slowly moving over lindane placed in the bottom of horizontally mounted saturators or through a column of glass beads treated with lindane. The lindane was removed from the nitrogen gas stream in gas washing bottles containing hexane. The lindane content of the hexane was determined with a gas-liquid chromatograph equipped with an electron-capture detector using only the G.C. peak for γ BHC for quantification. Thus, for the data in this paper, lindane and 100% γ BHC are synonymous. Impurities do not interfere with the measurement of vapor density; nevertheless, a check for impurities in a hexane solution of the lindane sample produced only the peak for γ BHC when injected into the gas chromatograph.

In the first procedure dry nitrogen gas was passed over 1 g of lindane placed in the bottom of horizontally mounted 6 ×

43-cm glass columns either with or without water in the chamber; in the second procedure humidified nitrogen gas was passed through 6 × 43-cm glass columns filled with 1300 g of glass beads, 0.47 mm in diameter, treated with either 1 or 2 g of lindane in 25 ml of acetone. After thorough mixing, the acetone was evaporated and 2 to 5 ml of water was added with an atomizer to moisten the beads. The nitrogen gas was humidified to approximately 100% relative humidity by passing it through water traps before it entered the glass-bead saturating columns. Dry nitrogen was used with the horizontally mounted columns. Spencer *et al.* (1969) had previously reported that water or the presence of evaporating water had no effect on the vapor density of pure dieldrin, but water did increase the vapor density of dieldrin applied to soil due to competition for adsorption sites on the soil. Humidified air was used with the glass beads to prevent any possible reduction of lindane vapor density due to adsorption on the glass beads. Temperature was controlled to $\pm 0.5^\circ$ C for all measurements.

RESULTS AND DISCUSSION

The vapor density and apparent vapor pressure of lindane at various temperatures are shown in Table I. The vapor density was the same with either 1 or 2 g of lindane per 1300 g of glass beads at all temperatures. This indicates that a saturated lindane vapor was present in the glass bead columns and the data for 1 and 2 g of lindane are combined in Table I. Vapor densities obtained with lindane only in horizontally mounted columns at 30° C were also the same as those obtained with glass beads. The presence of water had no signifi-

Table I. Vapor Density and Apparent Vapor Pressure of Lindane (γ BHC) at Various Temperatures

	Temperature °C	Vapor Density Ng/l	Vapor Pressure ^a mm Hg × 10 ⁻⁵
Lindane on glass beads	20	518 ± 5 (8) ^b	3.26
	30	1971 ± 27 (8)	12.82
	40	6784 ± 36 (6)	45.6
Lindane only	30 wet ^c	1925 ± 58 (3)	12.52
	30 dry	1994 ± 21 (3)	12.96

^a Calculated from vapor density, w/v , with the equation $P = \frac{w}{v} \cdot \frac{RT}{M}$ using 291 as the molecular weight (M) of the gaseous species.

^b The 95% confidence limit or 2 × standard error of the mean calculated for each series of runs. Number of runs in each series in parentheses.

^c With 100 ml of water in the saturator covering the lindane.

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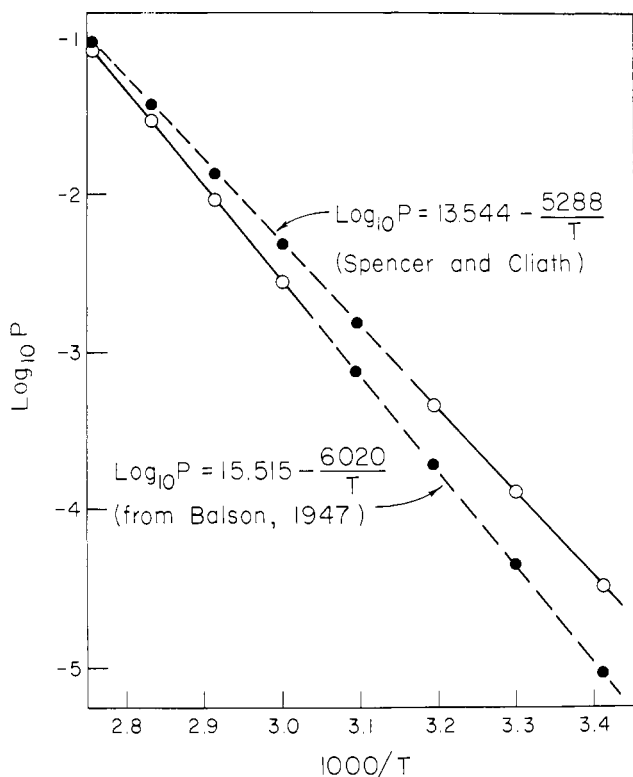


Figure 1. The relationship between temperature and apparent vapor pressure of lindane (γ BHC) by the two methods

Open circles are experimentally determined, dots are calculated

cant effect on the vapor density of lindane. The apparent vapor pressure was linearly related to temperature by the equation:

$$\text{Log}_{10} P = 13.544 - (5288/T) \quad (1)$$

The vapor densities and calculated vapor pressures are higher than reported by Balson (1947) by a factor of 3.5, 2.9, and 2.4 times at 20, 30, and 40° C, respectively. Balson measured the vapor pressure of lindane with an effusion manometer at temperatures from 60 to 90° C. For the temperature dependence of the vapor pressure he gives the formula:

$$\text{Log}_{10} P = 15.515 - (6020/T) \quad (2)$$

Estimates of vapor pressure at lower temperatures were made by extrapolation from measurements made at the higher temperatures with Equation 2.

The apparatus for measuring vapor pressure used by Balson consisted mainly of two small spheres with an orifice, fixed within a vacuum on a torsion balance. The inner walls of the spheres were covered with lindane and the number of molecules exhausting per second out of the orifice was determined from the observed twisting of the spheres as measured by the torsion balance. In this method it is assumed that the cavities inside the spheres are saturated with lindane so that the number of molecules exiting from each sphere is determined by the size of the orifice and the saturation pressure. It appears likely that the cavities within the spheres were only partially saturated with lindane, especially in the measurements carried out by Balson at low temperatures, when the

sphere orifices were relatively large. Lower degrees of vapor saturation at lower temperatures would result in greater discrepancies in vapor pressure values as the temperature decreased. One could then conclude that the temperature dependence of vapor pressure measured by Balson is too great, which would result in the vapor pressure at lower temperatures being too small.

Figure 1 is a plot of the temperature dependence of the vapor pressure from our measurements and from those of Balson over the temperature range 20° to 90° C (293.2 to 363.2° K). This indicates that the two measurements would result in identical vapor pressures for lindane at a temperature of 98.2° C. From one form of the Clausius-Clapeyron equation, the slope (m) of the line when $\text{Log}_{10} P$ is plotted vs. $1/T$ is related to heats of vaporization by the equation:

$$\Delta H_v = -2.303Rm \quad (3)$$

where ΔH_v is heat of vaporization in calories per mole when R is in calories per mole per degree. Heat of vaporization of lindane calculated with Equation 3 was 24.17 kcal per mole. The same formula using Balson's data gives a heat of vaporization of 27.5 kcal per mole. This difference in heat of vaporization results in the discrepancy in vapor pressure increasing as the temperature decreases.

Balson (1947) estimated vapor pressures of lindane at room temperature by extrapolations of measurements at higher temperatures. More complete saturation of the sphere cavities in the effusion manometer as the temperature increased would account for excessive dependence of vapor pressure on temperature, resulting in a greater discrepancy at the lower temperatures. These data indicate that the effusion apparatus should be calibrated with known standards and care should be exercised in extrapolating to temperatures outside the measuring range. Direct vapor density measurements such as these reported here probably are more directly applicable to practical problems related to vaporization of pesticides.

The fact that the vapor density of lindane is approximately three times greater than predicted from published vapor pressure values at room temperature could account for much greater than expected aerial contamination from lindane in vaporizers and in other insecticide formulations containing lindane. The finding of lindane and other supposedly non-volatile compounds in unexpected areas far from the site of application may be due to vapor phase transport in greater amounts than expected. This possibility appears to justify rechecking much of the data in the literature on vapor pressure of such compounds and further evaluating their potential volatility under conditions of field application.

LITERATURE CITED

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