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The Vapor Pressure of Lindane (γ-1,2,3,4,5,6-Hexachlorocyclohexane)—A Comparison of Knudsen Effusion Measurements with Data from Other Techniques

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The vapor pressure of pesticides is an important parameter for predicting the distribution of these substances in the environment. Using the Knudsen effusion technique and highly purified samples of lindane (γ-1,2,3,4,5,6-hexachlorocyclohexane), a thorough reinvestigation of its vapor pressure has been undertaken. The results obtained are compared with previously published values, some of which show considerable scatter, especially at temperatures of natural field conditions. We consider our data to be sufficiently accurate to be used as reference values, e.g. for calibrating other less direct techniques of vapor pressure measurement. On account of our measurements in the range (292 to 326) K we recommend for lindane the vapor pressure equation $\ln p/\mathrm{Pa} = (34.53 \pm 0.21) - (11754 \pm 72)(T/\mathrm{K})^{-1}$.

Introduction

The vapor pressure of pesticides, in addition to their water solubility and the octanol/water partition coefficient, is an important physico-chemical parameter for estimation of their distribution in the environment (Klein et al., 1981). During the last decade, theoretical models have increasingly been used to gain further knowledge concerning the risk assessment of environmental chemicals (Rohleder et al., 1986; Jury et al., 1983/84). The results of these calculations can only be as reliable as the input parameters themselves. For that purpose, precisely measured physicochemical data of pesticides are needed to predict their fate in the environment. However, the measurement of the vapor pressure of pesticides, which are typically low volatile substances (for about three-fourths of the pesticides licensed in Germany, the vapor pressure is in the range (10^{-4} to 10^{-2}) Pa or even less), seems to be a problem, as the values cited in the literature frequently show 2−3 orders of magnitude difference among various authors. Of the different experimental methods to measure low vapor pressures the following are the most important: gas saturation method (Thomson and Douslin, 1971), Knudsen effusion method (Thomson and Douslin, 1971; Cordes and Cammenga, 1969), and vapor pressure balance (Sewekow, 1984).

The gas saturation technique has commonly been recommended by agencies like OECD and EPA since the experimental device is rather simple and technical substances can supposedly be measured without purification. To assess the different methods, the vapor pressure of lindane was measured and compared with values reported in the literature: Balson (1947) for the Knudsen effusion technique; Spencer and Cliath (1970) and Thomson and Douslin (1971) for the gas saturation technique; Eichler (1983) for the vapor pressure balance; Bidleman (1984), Hinckley et al. (1990), and Kim (1985) for the determination of vapor pressures from gas chromatographic retention data.

Lindane was chosen because its vapor pressure has been well measured and the vapor pressure at room temperature falls in the above-mentioned range.

Experimental Section

Apparatus. The integral mass loss type of the effusion method was used in vapor pressure determination. A more detailed description of the apparatus and procedure may be found in Cordes and Cammenga (1969). Cylindrical effusion cells of cross sectional area A made from Pyrex glass were used. At an inner height $h = 2.13r_c$ (r_c inner radius) above the sample surface the cells were closed by a molybdenum foil of thickness (0.000130 ± 0.00002) cm in the center of which was the circular effusion orifice of area a. The vapor effused was trapped on a silvered condenser cooled by liquid nitrogen. A high vacuum of less than 10^{-4} Pa residual gas pressure was established by two two-stage mercury diffusion pumps in series backed by a mechanical pump. The temperature was controlled to ±0.01 K and measured to an absolute accuracy of ±0.03 K with a mercury thermometer and a NiCr/Ni thermocouple, both calibrated against ITS-90. The Clausing factors W of the orifices ranged from 0.9605 to 0.9947; A could be varied between 0.923 and 5.027 cm^2 and a between 0.8343×10^{-3} and 49.81×10^{-3} cm^2. The orifice area a was determined by planimetry of orifice microphotographs and from direct measurements of the diameter by a traveling microscope, giving identical results to within ±0.1%. Mass loss was determined to 0.003 mg on a calibrated microbalance and corrected for buoyancy. As previously reported, the overall generally absolute accuracy of vapor pressure determination with the apparatus used was ±0.9%.

Measurements. From the kinetic theory of gases, the pressure inside the cell, p', is given by

$$p' = -\frac{1}{Wa}\left(\frac{\partial m}{\partial t}\right)_T\left(\frac{2\pi RT}{M}\right)^{0.5} \tag{1}$$

p' is close to the saturation vapor pressure p, and the relation between p' and p is

$$p = \left(1 + \frac{1}{\alpha\gamma}\,\frac{Wa}{A}\right)p' \tag{2}$$

where α is the evaporation coefficient, γ is the surface roughness, $-(\partial m/\partial t)_T$ is the rate of mass loss by effusion, R is the universal gas constant, T is the absolute temperature, and M is the molar mass. The other symbols have already been defined.

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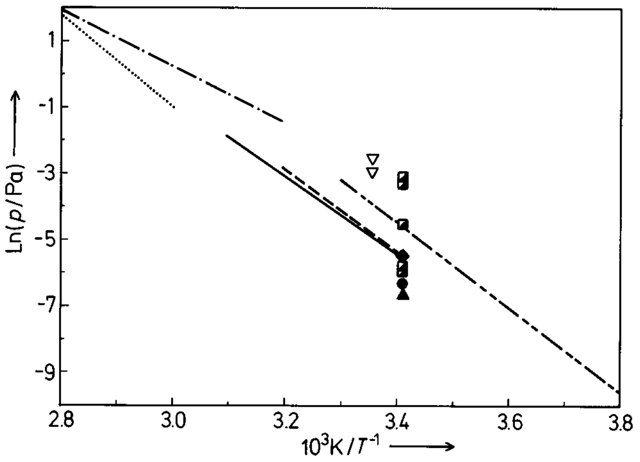

Figure 1. Plot of the vapor pressure of lindane measured by different investigators: (—•—) Hinckley et al., 1990; (···) Balson, 1947; (—) this work; (- - -) Spencer and Cliath, 1970; (— - - —) Wania et al., 1994; (▽) Bidleman, 1984; (◪) Kim, 1985; (◆) Atkins, 1971; (●) Eichler, 1983; (▲) Gückel, 1982.

Table 1. Specification of Lindane during Purification

specification of lindane	purity by DSC/mol %	R_f (value by TLC)	T_m/K (onset temp)
technical	99.78	0.38/0.42	385.13
after 1 sublimation	99.97	0.35/0.42	385.69
after 2 sublimations	99.96	0.35	385.81
after 3 sublimations	99.98	0.35	385.85

Table 2. Lindane Vapor Pressures Determined in This Work (Mean Values from Multiple Measurements)

T/K	$p/10^{-3}$ Pa
292.78	3.74
298.10	7.37
301.57	11.6
306.73	22.5
310.97	38.1
311.01	39.6
316.47	71.8
321.21	12.3
326.22	21.7

The effusion method is limited in usefulness because of its high sensitivity to impurities, especially to those which are less volatile than the substance under study. In order to obtain reproducible vapor pressures by the effusion method, it is especially important to thoroughly purify the substance. Impure samples cause a decrease in the measured vapor pressure with time as the concentrations of the less volatile substances at the evaporating surface increase (Wania et al., 1994). Commercial lindane has a purity of about 99.8%. The impurities are probably the α-isomer and β-isomer of 1,2,3,4,5,6-hexachlorocyclohexane. The vapor pressure of the α-isomer is higher by a factor of approximately 10 as compared to lindane whereas the β-isomer has a vapor pressure of about 3 orders of magnitude lower than lindane (Balson, 1947). Thin-layer chromatography (TLC) analysis of the commercial lindane showed two products with slightly different R_f values. The impurity had disappeared after the second sublimation. A third sublimation did not further change the parameters compared to the second one. In addition to TLC, the purity and melting point of lindane were measured by differential scanning calorimetry (DSC). Table 1 shows the specification of the lindane used during the purification process.

The vapor pressure measurements were carried out with lindane which had been sublimated twice and thereafter crystallized from pure ethanol to improve the texture of the sample. Different effusion measurements were required to determine the equilibrium vapor pressure. Repeated measurements of the pressure p' on a particular sample were made to test the reproducibility of the measurements and the purity of the sample. Only samples purified as described above yielded results which were independent of the number of measurements taken. Measurements with commercial lindane showed lower vapor pressures which, on repetition with the same sample under otherwise identical conditions, resulted in a further decrease with the duration of the measurements. This was probably due to impurities of lower volatility accumulating at the sample surface.

The determination of the evaporation coefficient and the surface roughness of the sample (or rather the product of both, $\alpha\gamma$) was achieved by using Knudsen cells of different effective orifice areas Wa and cross sectional areas A for measurements at a selected temperature, in our case 311.0 K. The results from 13 measurements obtained were plotted according to the eq 3 (Cordes and Cammenga, 1969),

$$p' = p - \frac{1}{\alpha\gamma}\frac{Wap'}{A} \tag{3}$$

and by a least squares fit we obtained $\alpha\gamma = 0.32 \pm 0.04$ from the slope. The saturation vapor pressure at the temperature chosen is given by the intercept. With particular Knudsen cells (with definite geometries Wa/A) measurements of p' were then performed at several temperatures in the range (292 to 326) K. The saturation vapor pressure was then calculated by eq 2 using the value determined for $\alpha\gamma$ (see Table 2).

Results and Discussion

The results for the vapor pressure are given in Table 3 including the corresponding values determined by Balson (1947) (effusion method), Spencer and Cliath (1970), and Wania (1994) and a single value by Atkins (1971) for 293 K (gas saturation technique). Only a single value determined by the vapor pressure balance method is reported by Eichler (1983). Figure 1 shows the different vapor pressure curves. Single vapor pressure values determined by other methods are also given. Gückel et al. (1982) calculated the vapor pressure of lindane from the mass loss of a plate coated with an active ingredient in a gas stream. Bidleman (1984), Hinckley et al. (1990), and Kim (1985) used gas chromatography for the determination of vapor pressure, a method which is governed by the principle that substances with different vapor pressures show different

Table 3: Vapor Pressure Curves of Lindane and Enthalpies of Sublimation—Results by Different Measuring Methods

	$\ln p/\text{Pa} = A - B(T/\text{K})^{-1}$				
ref	A	B	ΔT/K	$p_{(293.15\text{K})}/10^{-3}$ Pa	$\Delta_{\text{sub}}H$/kJ mol^{-1}
this work	34.53 ± 0.21	11754 ± 72	293 to 323	3.83 ± 0.14	97.7 ± 0.6
Atkins (1971)			293	4.13	
Balson (1947)	40.615	13862	333 to 363	1.27	115.3
Eichler (1983)			293	1.9	
Gückel et al. (1982)			293	1.34	
Hinckley et al. (1990)	25.67	8474	313 to 358	39.5	70.5
Spencer and Cliath (1970)	36.079	12176	293 to 313	4.27	101.2
Wania et al. (1994)	39.12 ± 0.23	12816 ± 104	243 to 303	9.85 ± 0.89	106.6 ± 0.9

retention times on nonpolar columns. Using a reference compound with a well-known vapor pressure curve, the vapor pressure of an unknown substance can be determined (for details see Hamilton (1980)). The numerous values shown in Figure 1 were obtained by varying the specification of the nonpolar columns and the reference compounds.

Comparison of vapor pressures determined by GC and by other techniques cannot be made directly because of a fundamental difference. The effusion and gas saturation methods yield the *solid phase* vapor pressure p_s, whereas the GC method yields the *liquid phase* vapor pressure p_l. To compare data determined by the GC method with those by other techniques, it is necessary to convert the liquid phase vapor pressure to the solid phase vapor pressure using the entropy of fusion $\Delta_{fus} S$ by

$$\ln \frac{p_l}{p_s} = \frac{\Delta_{fus} S}{R} \frac{(T_m - T)}{T} \tag{4}$$

Even after this conversion the vapor pressure values determined by GC show large scatter and are higher than most results determined by the other methods.

Balson (1947) took measurements with freely suspended effusion cells at rather high temperatures. A long extrapolation to low temperatures may not be valid and for ambient temperature leads to a vapor pressure falling low; see Table 3. In contrast to Balson highly accurate vapor pressure values can only be achieved by using effusion cells with a specific, predetermined geometry. Furthermore, deviations in the measurements might occur by an inhomogeneous temperature distribution in the sample, leading to lower vapor pressure values. To ensure satisfactory heat conduction between the crystals of the sample, it should be slightly compressed by a piston before starting the experiment.

If vapor pressures are determined by a vapor pressure balance (Eichler, 1983), this may lead to low vapor pressures, e.g. caused by incomplete adsorption on the target hanging from the balance.

The vapor pressures obtained in this work agree well with the results reported by Spencer and Cliath (1970) and by Atkins (1971). Wania (1994) used commercial lindane. The enthalpy of sublimation $\Delta_{sub}H$ is close to that reported by Spencer and Cliath (1970) and in this work, but the vapor pressures are considerably higher. This may be caused by the presence of a more volatile impurity such as the α-isomer of hexachlorocyclohexane.

Conclusion

Our investigations show that the measurement of reproducible and reliable vapor pressures of slightly volatile environmental chemicals is difficult. The results are dependent on both the method and the investigator. Similar conclusions were made by Klein et al. (1981) who compared vapor pressure measurements from different laboratories. It is necessary that one group of researchers tests all three available methods with several substances to elucidate the difficulties of the methods and the sources of errors. Up to now the Knudsen effusion technique has been regarded as rather complicated and time-consuming. The purification of the substances is the most important step prior to measuring the equilibrium vapor pressure with all cited techniques. With respect to the experimental device and the measurement itself, the Knudsen effusion method seems to be comparable in accuracy with the gas saturation technique and the vapor balance.

In the past few years vapor pressure measurements by gas chromatography have been discussed rather often (Bidleman, 1984; Hinckley et al., 1990; Kim, 1985) because standard equipment can be used. The main problem is the selection of a reference substance with a well-known vapor pressure curve. Literature vapor pressures of low-volatility substances often disagree by a factor of 2−3 or more. Therefore accurate vapor pressure values are required to be used as reference data for calibrating this less direct technique of vapor pressure measurement.

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