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THERMODYNAMIC PROPERTIES OF POLYCHLORINATED COMPOUNDS: THE VAPOR PRESSURES AND ENTHALPIES OF SUBLIMATION OF TEN DIBENZO-PARA-DIOXINES

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ABSTRACT

The vapor pressure curves of ten chlorinated dibenzo-p-dioxines and of ten chlorinated benzenes were measured by a gas flow method with integrated gas chromatographic analysis. At least 60 vapor pressure points distributed over 10 to 20 temperatures between 30 and 200°C were recorded for each compound. Correlations between the measured vapor pressure curves and the degree of chlorine substitution showed linear dependecies of the log (p) values on the substitution number for fixed temperatures. Corresponding correlations for the enthalpies and entropies of sublimation allowed the estimation of the vapor pressure curve of 2,3,7,8 tetrachloro-dibenzo-p-dioxin (TCDD). At 25°C a vapor pressure of $(4.5 \pm 2) \times 10^{-6}$ pascal is found for TCDD. An enthalpy of sublimation of 115 to 125 kJ/mol and an entropy of sublimation of 280 to 320 J/mol K is estimated for the linear vapor pressure curve between room temperature and 150°C.

INTRODUCTION

Vapor pressure measurements are an important source of basic thermodynamic data. The fate of pollutants in the environment to a large extent can be controlled by their vapor pressures. Inspite of this, little vapor pressure data has been reported for low boiling polychlorinated compounds. Some data exist on polychlorinated benzenes (ref.1,2) and on polychlorinated biphenyls (ref.3,4). The present data are to our knowledge the first vapor pressure reportings on polychlorinated dioxins.

METHODS AND RESULTS

All vapor pressure measurements have been done with the gas saturation method (ref.5). Partial vapor pressure measurements are possible with a fully automatic instrument which includes online gas chromatographic analysis (Fig. 1). Careful design of the gas saturation experiment is essential for reliable data. Complete inert gas saturation, minimal adsorbtion effects, normal pressure over the sample and a good control of temperature profiles must be assured. Temperature profiles in which temperatures are controlled to ± .1 K over the sample region are crucial for correct temperature measurements. The omission of a capillary between sample and adsorbent is a frequent source of errors.

Figure 2 shows transport equations for the saturation experiment (ref.5,6). Mass transport occurs by viscous flow and by diffusion (1). The pressure drop accross the capillary is negligible (2) for the used flow conditions (ref.6). The partial pressure P_{2i} over the sample is obtained from the mass flow rates of the sample $\dot{n}_2$ and the inert gas $\dot{n}_1$ (3). The mole fraction of sample vapor upstream of the capillary is given by x_{2i}. A_T is a coefficient for mass transport by diffusion (4) and a capillary is used to suppress this contribution (5).

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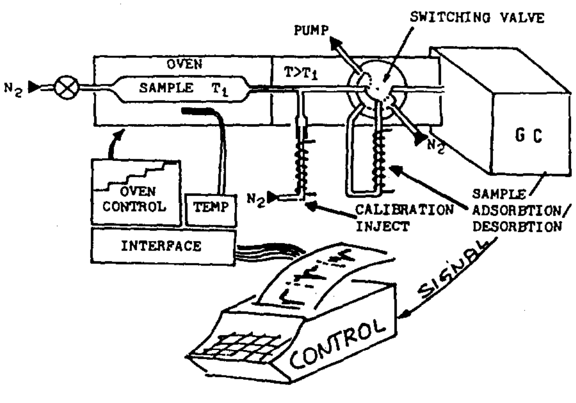
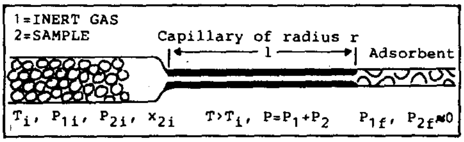


Fig. 1. Dynamic head space vapor pressure instrument. Adsorbtion (——) and flash desorbtion (•••) positions are indicated for the switching valve. The adsorbent (GC-Tenax) is used in a T-configuration. Typical inert gas (N_2) flow rates were 10^2 ml/min. Flow rates of .2 ml/min were used for vapor pressures above 10 pascal. Typical collection times were .5 to 20 min. Packed GC-columns (SE - 30, 3%) were used. Typical samples contained 1 to 5 mg of substance coated on 5g of glass beads (diameter .2mm).



TRANSPORT EQUATION FOR BINARY GAS FLOW

$$J_\nu = \dot{n}_\nu / r^2\pi = - D\ c\ dx_\nu/dz + c\ x_\nu v \qquad (1)$$

MASS FLUX OF SPECIES ν — BINARY DIFF. COEFFICIENT — TOTAL GAS CONC. (mol/cm³) — MOLE FRACTION SPECIES ν — VISCOUS PLUS DIFFUSION VELOCITY

$\dot{n}_\nu$ IS THE MASS FLOW OF SPECIES ν (mol/sec)

SOLUTIONS:

$$P_{2i} \approx x_{2i} \cdot P_f \qquad (2)$$

$$x2i = \frac{\dot{n}_2}{\dot{n}_1 + \dot{n}_2} \left(1 - \exp - \frac{\dot{n}_1 + \dot{n}_2}{A_T} \right) \qquad (3)$$

COEFFICIENT FOR MASS TRANSPORT BY DIFFUSION:

$$A_T = r^2\pi\ P\ D_T / l\ R \qquad (4)$$

RELATIVE CONTRIBUTION OF DIFF. TO MASS TRANSPORT:

$$q = \frac{\dot{n}_{2diff}}{\dot{n}_2 - \dot{n}_{2diff}} = \left(\exp (\dot{n}_1 / A_T) - 1 \right)^{-1} \qquad (5)$$

Fig. 2 Transport equations and their solution for the gas saturation experiment. The relative contribution (q) of diffusion to mass transport is suppressed by the proper choice (l = 70mm, r = .4mm) of a capillary. Contributions below 1% are predicted for flow rates above .01 ml/min. A binary diffusion coefficient D of .075 cm²/sec was assumed in this calculation (D for anthracene at 25°C).

RESULTS AND DISCUSSION

Vapor pressure reference compounds were used to test the instrument described in Figure 1. It was found from a careful review of the literature that there are only a few reference compounds available for low pressures. A critical selection of literature reportings for a given compound is often necessary (ref.6). Vapor pressures measurements on anthracene (ref.7) and on 1,4 dichlorobenzene (Table 1) with the present instrument are in good agreement with data reported in reliable literature sources (ref.1).

TABLE 1
Vapor pressures of 1,4 dichlorobenzene: (a) present data, (b) reference 1.

Temp.(C)	(a)	(b)		(a)	(b)
25	158.1 Pa	137.2 Pa	Enthalpy-subl.	65.40 *)	65.70 #)
50	1217.6 Pa	1066.2 Pa	(kJ/mol)		
75	6992.7 Pa	6172.3 Pa	Entropy-subl.	261.46*)	260.96#)
100	31774 Pa	28239 Pa	(J/mol K)		
125	119380 Pa	106741 Pa	*) linear regression,	30 to 50°C	
150	383592 Pa	344804 Pa	#) values for 11°C		

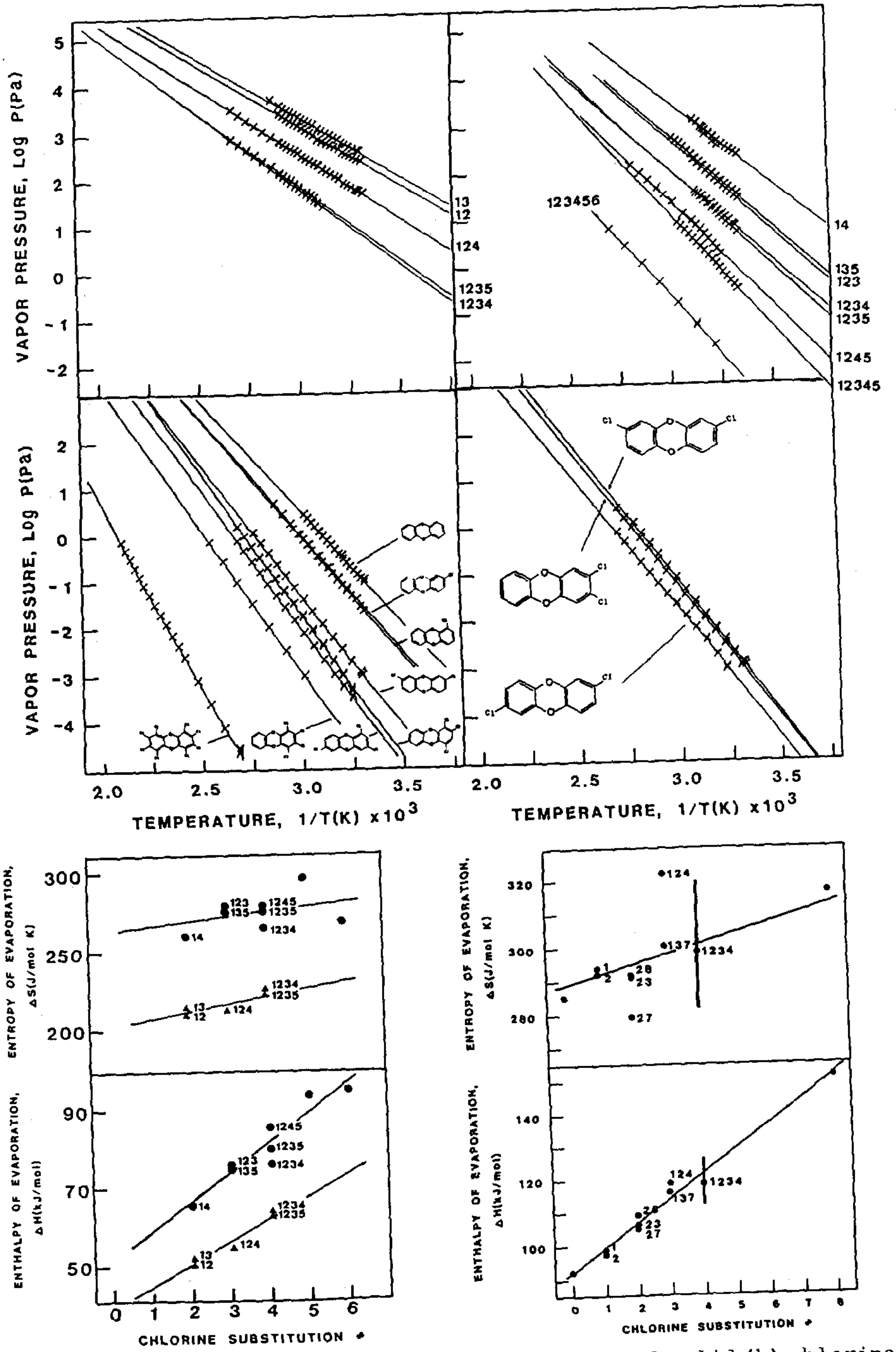


Fig. 3. Measured vapor pressures (x) of liquid (a) and solid (b) chlorinated benzenes and of ten dibenzo-p-dioxins (c,d). The vapor pressures were measured and plotted (x) five times for each temperature setting. Entropies (e) and enthalpies of sublimation of liquid (▲) and solid (●) benzenes and of dibenzo-p-dioxins (g,h) are plotted as a function of the degree of chlorine substitution. The chlorine substitution positions are indicated by numbers in the figures.

TABLE 2
Predicted vapor pressures of 2,3,7,8 tetrachlorodibenzo-p-dioxin. The vapor pressures were calculated using the estimated enthalpies (115 to 125 kJ/mol) and entropies (280 to 320 J/mol K) of sublimations for tetrachloro isomers indicated by vertical bars in figure 3 (g,h).

Temperature (C)	Vapor Pressure (Pa)
25	3.5 to 6.3 x 10^{-6}
50	1.3 to 3.1 x 10^{-4}
75	2.8 to 8.9 x 10^{-3}
100	3.9 to 15.9 x 10^{-2}
125	4.4 to 21.9 x 10^{-1}

Figure 3 shows the measured vapor pressure curves of chlorinated benzenes (a,b) and of chlorinated dioxins (c,d). The vapor pressures are strongly dependent on the degree of chlorine substitution. This data illustrates both a large dynamic range (over 10^{8}) and a high repeatability of the present method.

Standard molar enthalpies (h^{o}) and entropies (s^{o}) of evaporation were obtained by linear fits of this data (Fig.3 e-h). Vapor pressures can be calculated for given temperatures from $R \ln P(\text{pascal}) = s^{o} + h^{o}/T(K)$ with R = 8.3143 Joule/mol K.

Correlations between the measured vapor pressures and the extent of chlorine substitution showed linear dependencies of log P values on the substitution number for fixed temperatures (ref.7). Similar correlations hold between the enthalpies or the entropies of evaporation and the substitution number (Fig.3 e-h). Different correlations hold for the liquid and solid benzenes due to the enthalpies and entropies of fusion. The correlations for the dibenzo-p-dioxins allowed an estimation of enthalpies and entropies of sublimation for tetrachlorodibenzo-p-dioxins (vertical bars in Fig.3 g,h). The calculated vapor pressure curve of 2,3,7,8 tetrachlorodibenzo-p-dioxin, which is toxic to small animals, is given in table 2.

For 25°C the estimated vapor pressure of 3.5 to 6.3 x10^{-6} Pa translates into a total evaporated mass of 450 to 820 nanograms/m^{3} of TCDD if equilibrium is established. The present estimations will help to reduce the safety risks of a vapor pressure experiment on 2,3,7,8 tetrachlorodibenzo-p-dioxin.

REFERENCES

1 C. G. De Kruif, A. C. G. Van Genderen, J. C. W. G. Bink and H. A. J. Oonk, J. Chem. Thermodynamics, 13 (1981) 457-463.

2 D. R. Stull, Eng. Chem. 39 (1947) 517.

3 J. W. Westcott, C. G. Simon and T. F. Bidleman, Environ. Sci. Technol., 15 (1981) 1375-1378.

4 L. P. Burkhard, D. E. Armstrong and A. W. Andren, J. Chem. Eng. Data, 29 (1984) 248-250.

5 H. Kvande and P. G. Wahlbeck, Acta. Chem. Scand., A30 (1976) 297-302.

6 E. Marti, A. Geoffroy, B. F. Rordorf and M. Szelagiewicz, Proc. Int. Conf. Thermal Anal., 1 (1980) 305-312.

7 B. F. Rordorf, Proceedings of the 4th Int. Symp. on Chlorinated Dioxins and Related Compounds, Chemosphere (1985).