

THERMODYNAMIC PROPERTIES OF HALOGENATED DIBENZO-P-DIOXINS,
DIBENZOFURANS AND PESTICIDES,

B. F. Rordorf¹, B. Nickler¹ and C.M.J. Lamaze²

1 Central Research, Physics, CIBA-GEIGY Ltd., 4002 Basle, Switzerland.

2 Laboratoire de Chimie Physique des Surfaces et des Processus aux Interfaces, Université de Nancy I, France.

ABSTRACT

Vapor pressures are important parameters for environmental fate modeling of chemicals. Vapor pressure curves were obtained for eighty pesticides using an automatized gas saturation method with on-line GC analysis. Special consideration was given to a variety of phenomena of importance to the outcome of the vapor pressure results: sample contamination by impurities or amorphous phase, solid to plastic phase transitions, crystal modifications, measurements on free acids and on labile pesticides. A vapor pressure correlation method has in the past been developed for halogenated dibenzo-p-dioxins and dibenzofurans and has been used to predict vapor pressures for twenty-nine halogenated dibenzo-p-dioxins and for fifty-five chlorinated dibenzofurans. The present pesticides were chosen to contain a number of common structure elements with these compounds measured in the past and this data should be valuable for developing vapor pressure estimation methods.

INTRODUCTION

While vapor pressure data has been collected in agrochemical handbooks and manuals over the years, such data is mostly not traceable to scientific publications. Full vapor pressure curves are required to deduce enthalpies and entropies of sublimation (evaporation). However they are rarely available for pesticides. Assessment and comparison of such data is complicated by the variety of vapor pressure methods used. Direct comparability of the experimental data is of importance when the determined thermodynamic parameters are used in correlation methods.

Vapor pressure measurements on 36 halogenated dibenzo-p-dioxins and dibenzofurans have been reported in the past (3). Additional curves have been obtained for 1,6-DCDD, 1,2,3-T₃CDD, 1,7,8-T₃CDD, 2,3,7-T₃CDD, 1,2,7,8-T₄CDD, 1,3,7,8-T₄CDD, 1,2,4,7,8-PCDD, OCDD, 2,8-DCDF, 1,3,7-T₃CDF, 2,4,7-T₃CDF, OCDF, 2,7-dichloro-9-fluorenone, 2,4,7-trichloro-9-fluorenone and 2,4,7-trichlorofluorene. Some of these new compounds are related by constant chlorine substitution patterns.

EXPERIMENTAL

Vapor pressure curves were obtained by an automatized gas saturation method with on-line GC analysis (4). Enthalpies of fusion and melting points were measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2 with a data station 3500.

RESULTS AND DISCUSSION

A few selected vapor pressure curves are displayed in Figure 1. The vapor pressure curves of octachlorodibenzo-p-dioxin and of octachlorodibenzofuran have been remeasured (4). Somewhat different values for the molar enthalpies and entropies of sublimation have been obtained from these new recordings: $h_s = 149822$ J/mol and $s_s = 311.8$ J/mol K (120 to 200°C) for OCDD (Table 1, bottom) and $h_s = 143702$ J/mol and $s_s = 308.3$ J/mol K (105 to 261°C) for OCDF (Table 1, top).

Fig. 1 Vapor pressure curves of fluorene (1), 9-fluorenone (2), 2,4,7-trichlorofluorene (3), 2,4,7-trichloro-9-fluorenone (4), 1,2,4,7,8-pentachlorodibenzo-p-dioxin (5), octachlorodibenzofuran (6) and octachlorodibenzo-p-dioxin (7). The melting point (mp) of fluorenone is indicated and the linear regressions are traced for the solid and liquid phases respectively. All of the remaining curves are for the solid compounds.

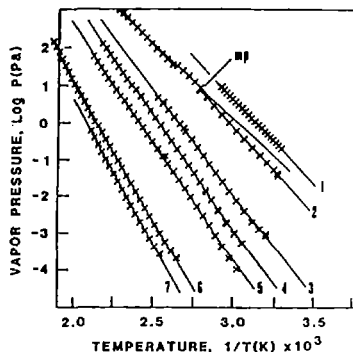
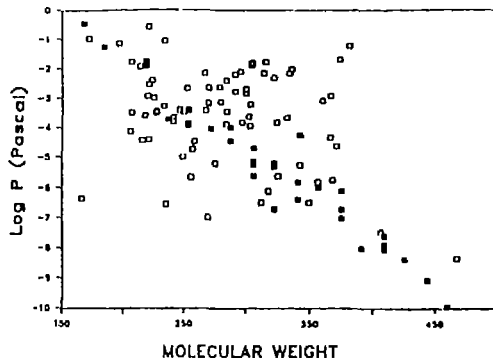


TABLE 1

| t(°C) | | | | | t(°C) | | | | |
|-------|-------|-------|-------|-------|-------|--------|--------|--------|--------|
| mPa | | | | | mPa | | | | |
| 105.6 | 0.230 | 0.224 | 0.218 | 0.213 | 185.6 | 560 | 574 | 573 | 573 |
| 110.5 | 0.377 | 0.367 | 0.362 | 0.354 | 190.7 | 846 | 840 | 852 | 851 |
| 115.5 | 0.627 | 0.623 | 0.626 | 0.618 | 195.8 | 1094 | 1100 | 1102 | 1102 |
| 120.6 | 1.09 | 1.09 | 1.09 | 1.08 | 200.9 | 1633 | 1640 | 1643 | 1643 |
| 125.5 | 1.87 | 1.88 | 1.88 | 1.87 | 205.9 | 2401 | 2414 | 2416 | 2420 |
| 130.5 | 3.19 | 3.22 | 3.20 | 3.21 | 210.9 | 3513 | 3528 | 3526 | 3539 |
| 135.5 | 5.40 | 5.43 | 5.42 | 5.42 | 215.9 | 5105 | 5130 | 5135 | 5133 |
| 140.4 | 8.98 | 8.99 | 9.04 | 9.00 | 221.0 | 7353 | 7397 | 7417 | 7403 |
| 145.4 | 14.7 | 14.7 | 14.8 | 14.8 | 226.0 | 10627 | 10752 | 10784 | 10776 |
| 150.5 | 24.0 | 24.1 | 24.1 | 24.1 | 231.0 | 15136 | 15202 | 15329 | 15269 |
| 155.5 | 38.5 | 38.6 | 38.5 | 38.5 | 236.0 | 22294 | 22572 | 22455 | 22685 |
| 160.5 | 63.4 | 64.2 | 64.2 | 63.5 | 241.1 | 31556 | 31887 | 32149 | 32006 |
| 165.6 | 97.7 | 99.2 | 101 | 101 | 246.1 | 48268 | 48287 | 48265 | 48125 |
| 170.5 | 152 | 151 | 157 | 156 | 251.1 | 71468 | 73785 | 76375 | 75799 |
| 175.6 | 236 | 241 | 246 | 234 | 256.2 | 98377 | 101697 | 105899 | 105964 |
| 180.6 | 366 | 381 | 374 | 375 | 261.2 | 129504 | 137929 | 139425 | 139924 |
| 120.1 | 0.277 | 0.283 | 0.279 | 0.280 | 165.0 | 24.7 | 25.3 | 25.4 | 25.6 |
| 124.9 | 0.444 | 0.448 | 0.449 | 0.445 | 170.0 | 40.1 | 41.1 | 40.7 | 41.2 |
| 129.9 | 0.725 | 0.740 | 0.741 | 0.743 | 175.0 | 64.2 | 64.8 | 66.8 | 66.1 |
| 134.9 | 1.23 | 1.25 | 1.26 | 1.25 | 180.0 | 99.3 | 102 | 105 | 103 |
| 139.9 | 2.06 | 2.09 | 2.09 | 2.11 | 185.0 | 155 | 159 | 160 | 160 |
| 144.8 | 3.47 | 3.52 | 3.54 | 3.55 | 189.8 | 239 | 261 | 246 | 260 |
| 149.8 | 5.72 | 5.82 | 5.85 | 5.86 | 194.7 | 366 | 386 | 400 | 379 |
| 154.7 | 9.33 | 9.51 | 9.54 | 9.59 | 199.7 | 556 | 586 | 587 | 607 |
| 159.7 | 15.2 | 15.3 | 15.3 | 15.4 | | | | | |

Recorded vapor pressures of octachlorodibenzo-p-dioxin (bottom) and octachlorodibenzofuran (top).

Fig. 2 Extrapolated vapor pressures for 25°C of the following compounds: DD, 1-MCDD, 2-MCDD, 137-T3CDD, 2378-T4CDD, 12347-PCDD, 123478-H6CDD, 1234678-H7CDD, OCDD, 36-DCDF, 1234678-H7CDF and OCDF where C stands for chlorine (further chlorinated DD's and DF's of ref. 3 are included in this Figure but not in Fig. 3). The pressures for the dibenzo-p-dioxins (DD) and dibenzofurans (DF) (filled symbols) are compared to the values for various pesticides (open symbols; see Figure 3 for a list of compounds).



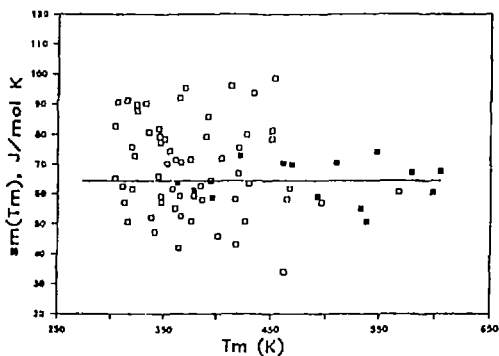
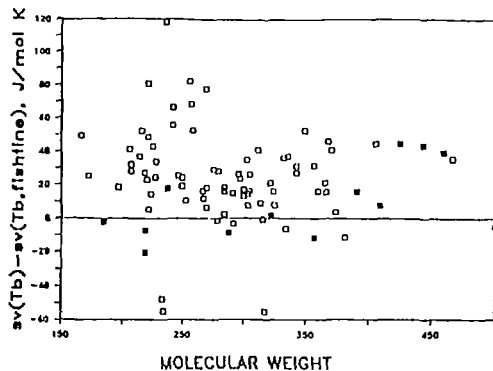
Extrapolated 25°C vapor pressure values for halogenated dibenzo-p-dioxins, dibenzofurans and pesticides are compared in Figure 2. Extrapolations involved in some of the cases a recalculation from the liquid to the solid phase curves using the experimental enthalpies of fusion from the DSC measurements. The dioxin and furan values show a clear-cut correlation with the molecular weight. In contrast to these compounds related by homology, no such correlation is observed for the pesticides.

Added confidence in the vapor pressure measurements was gained by a comparison of the enthalpies of fusion obtained from DSC and the values from the difference of slopes of the vapor pressure curves. This comparison was possible where vapor pressure measurements were accessible in both solid and liquid phases. The measurement of enthalpies of fusion (h_m) and the melting points (T_m) by DSC permitted us to test Walden's and Fishtine's rules. The calculated entropies of fusion ($s_m = h_m / T_m$) were plotted against T_m for all of the compounds (Fig 3, bottom). A correlation close to Walden's rule (64 J/mol K compared to the usually assumed value of 56.5 J/mol K) is apparent for the rigid halogenated dibenzo-p-dioxins and dibenzofurans. The entropies of fusion for the pesticides on the other hand show a great amount of scatter.

Liquid phase vapor pressure curves were directly measured for many of the pesticides. Often the liquids were not experimentally accessible. The vapor pressure curves over the liquids were then calculated from the solid phase vapor pressure curves using the enthalpies of fusion from the DSC. These curves for the liquid compounds were extrapolated up to the boiling point. The curvatures for these extrapolations were estimated by group contribution methods for the dioxins and furans (1). Fixed values of Δc_p (gas minus liquid) of -70 J/mol K were assumed for the pesticides. The extrapolations were done in an iterative procedure using the integrated Clausius-Clapeyron equation by a similar method as described in (1).

These extrapolations permitted us to test Trouton's rule and in its enhanced version Fishtine's rule. The latter rule estimates entropies of evaporation at the boiling point as $s_v(T_b) = K_f(36.61 + R \ln T_b) + R \ln p^0$ with the Fishtine constant $K_f = 1.01$, the gas constant $R = 8.314$ J/mol K and $p^0 = 101325$ Pa. Figure 3 shows the differences of the extrapolated entropies minus the estimations by the Fishtine' rule as a function of molecular weight of the compounds. A great amount of scatter is apparent for both the dioxins/furans and the pesticides. A similar picture results when plotting the entropy differences against $\ln T_b$. Some of the scatter is probably due to uncertainties of the measured enthalpies of sublimation, of evaporation and of fusion, as well as to the estimated Δc_p values used.

Fig.3 Bottom: entropies of fusion at the melting point (T_m , Waldens rule). Top: calculated minus predicted entropies of evaporation at the boiling point (T_b , Fishline rule). Filled symbols stand for dibenzo-p-dioxins and dibenzofurans (Fig. 2) and open symbols for these pesticides: aldrin, ametyne, atrazine, azamethiphos, azinphosmethyl, banvel, barban, bifenox, bromophos-methyl, captafol, chloranil, chlorbenside, chlorbufas, chlordane, chlordimeform, chlorfenethol, chlorfenvinphos, chlorfenson, chloroneb, chloropham, chlorthiamid, cyromazine, chlorthal-methyl, 2,4-D, 2,4-DB, diazinon, dichlobenil, dichlofenthion, dichlorophen, dichlone, dichlorphos, dichlorprop, dicloran, dicofol, dieldrin, dihydroheptachlor, diuron, endosulfan, endrin, fenchlorphos, fenoprop, fenthion, fluometuron, fthalid, genite, heptachlor, imazalil, isazofos, lindane, linuron, metalaxyl, methidathion, metolachlor, neburon, nitrofen, penconazole, parathion, pentachlorophen, phosalone, phosphamidon, profenofos, prometon, prometryn, propanil, propazine, propiconazole, quitozene, simazine, sulfallate, 2,4,5-T, swep, temephos, terbutryne, tetrachlorvinphos, tetradifon, tetrasul, trichloronat, triclopyr, trifluralin, triallate.



In conclusion we developed a large thermodynamic data set on environmental contaminants. This data permits us for the first time to test some of the widely used thermodynamic rules as applied to high molecular weight / low volatility compounds. These rules were mostly developed for much more volatile compounds. They have rarely been directly tested for organic substances of low volatility in the past. More high quality thermodynamic data is clearly needed on this class of compounds of high environmental impact.

REFERENCES

1. B.F. Rordorf, *Chemosphere*, **18**, 783-788 (1989).
2. B.F. Rordorf, 33rd Conference of the International Association for Great Lakes Research, May 13 to 17, 1990.
3. B. F. Rordorf, L.P. Sarna, G.R.B. Webster, S.H. Safe, L.M. Safe, D. Lenoir, K. H. Schwind and O. Hutzinger, Ninth International Symp. on Chlorinated Dioxins and Related Compounds, Toronto 1989.
4. B.F. Rordorf, *Chemosphere*, **15**, 1325-1332 (1986).