

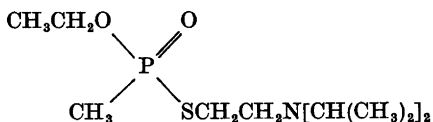
# The Vapour Pressure of *O*-Ethyl,*S*-2-(*N,N*-diisopropylamino)-ethylmethylphosphonothioate

HARALD FROSTLING\*

Research Institute of National Defence, Dept. 1, S-172 04 Sundbyberg 4, Sweden

The vapour pressure of the super toxic compound *O*-ethyl,*S*-2-(*N,N*-diisopropylamino)-ethylmethylphosphonothioate has been determined in the temperature range 7.5–42.4°C. The substance was sprayed into a specially designed rotating aerosol chamber and the analysis was carried out with the aid of a combined flame photometric–flame ionization method. The volatility of the compound at 25°C was found to be  $3.0 \pm 0.5 \text{ mg m}^{-3}$  and  $\Delta H_{\text{vap}} = 100.0 \text{ kJ mol}^{-1}$ .

The vapour pressure of the super toxic compound *O*-ethyl,*S*-2-(*N,N*-diisopropylamino)-ethylmethylphosphonothioate



with  $\text{LC}_{50} = 5 \text{ mg m}^{-3} \text{ min}^{-1}$  has earlier been determined at room temperature. The results have been expressed in the form of volatility and reported to vary between 3 and 30  $\text{mg m}^{-3}$  at 25°C.<sup>1–4</sup> Between the volatility  $V_t$  and the vapour pressure the following relation is valid:

$$V_t = m/V = Mp/RT \quad (1)$$

where  $m$  is the mass of the vapourized substance in the volume  $V$  and  $p$  is the vapour pressure at the temperature  $T$ . The variations in volatility found in earlier determinations may be due to the different measurement methods used.

The dynamic or air-flow method can be

used and the amount of condensed vapour can be detected by using a  $^{32}\text{P}$ -labelled compound and subsequent measurement with the aid of a Geiger-Müller counter.<sup>5</sup> With this method it is, however, impossible to decide if the measured value obtained originates from the actual compound or some of its  $^{32}\text{P}$ -containing decomposition products.

## METHOD

To avoid such disadvantages a special analysis method was utilized which employed a combined flame ionization–flame photometric detector (FID–FPD). With this method it is possible to achieve a reliable control process of the condition of the compound used during the measurements. An approximate calculation could be made of the ratio of the carbon response (FID) to the phosphorus response (FPD). The responses of the two different detectors are known from earlier experiments.<sup>6,7</sup> For the FID the response is almost linear to the number of C-atoms in the molecule. Divergences of the recorded values compared with the precalculated ratios and arising from decomposition of the substance could in this way be observed during the measurements.

By using a technique to disperse the substance in aerosol form into the rotating aerosol chamber, a rapid equilibrium was obtained between the individual particles and the vapour phase.<sup>8</sup> A small continuous sampling from the drum –  $1 \text{ } \frac{\circ}{\circ\circ} \text{ min}^{-1}$  of the total volume – did not influence the equilibrium.

\* Also affiliated to Institute of Analytical Chemistry, University of Stockholm, Sweden.

## EXPERIMENTAL

The *O*-Ethyl,*S*-2-(*N,N*-diisopropylamino)-ethylmethylphosphonothioate was synthesized according to the description of Fagerlind *et al.*<sup>9</sup> The small amount, 1–2 %, of one of the initial substances (2-isopropylaminoethyl chloride) present did not influence the FPD-response. Depending on the high toxicity of the compound a special routine was worked out for a safe handling of the equipment in connection with the dispersion of the compound.

The spray generator was sealed against the atmosphere and the outlet of the rotating drum was connected to the atmosphere *via* a collective filter with a capacity of 1.2 m<sup>3</sup> min<sup>-1</sup> made up of activated carbon and an aerosol filter. The sealing rings were replaced when a leakage was observed at a testing with an overpressure of  $\leq 100$  N m<sup>-2</sup>.

The sample outlet in the drum was equipped with two aerosol filter papers in series, each of them with a reported filtration efficiency of 99.99 % for particles with a MMD of 0.3  $\mu$ m.<sup>10</sup> To avoid condensation of the gaseous sample in the connection between the drum and the analysis apparatus the connection was heated to a temperature somewhat higher than that of the temperature within the drum.

The vapour pressure determinations were done in the temperature region 7.5–42.4°C. For the measurements above room temperature the heat regulation system of the drum was utilized, while measurements below this temperature were done with the whole equipment placed in an air-conditioned room. The temperature variations for the heat regulation system of the drum were  $\pm 0.2^\circ\text{C}$  and at about  $\pm 0.5^\circ\text{C}$  in the air-conditioned room. Between the three first recordings at every temperature, a new spray generation was carried out in order to be certain that a saturation equilibrium between the walls of the drum and its sample volume was established.

The decontamination of the drum and the analysis apparatus was done with a commercial detergent with a high content of sodium perborate (20 %).<sup>11</sup>

## RESULT

The FPD-responses at the different temperatures are listed in Table 1. The conversions of the FPD-responses ( $\mu\text{A}$ ) to the concentration values ( $10^{-4}$  g mol P m<sup>-3</sup>) are done with the aid of a calibration diagram. The concentrations are also expressed in mg m<sup>-3</sup>, the simple relationship that  $0.0374 \times 10^{-4}$  g mol P m<sup>-3</sup> of the compound is equivalent to 1 mg m<sup>-3</sup> being valid. No values for the ratio FPD/FID response are listed in the table for the three lowest temperatures as the FID-amplifier did not function at these temperatures. The decreasing values for the ratios at higher concentrations depend on the different character of the two detectors, *i.e.* the response is linear to the concentration for the FID and nonlinear for the FPD and decreases with the concentration. The vapour phase can be considered to be an ideal gas and the molar volume of the aerosol particles is negligible compared with that of the vapour. The concentration of the vapour phase found at the analysis can therefore be converted to vapour pressure by the aid of the familiar gas laws. The Clausius-Clapeyron equation may be integrated on the assumption that  $\Delta H_{\text{vap}}$  is constant within the temperature interval ( $\sim 35^\circ\text{C}$ ) and gives

$$\log p = -A/T + B \quad (2)$$

Table 1.

Temp (°C)	(K)	FPD-response (mean value) ( $\mu\text{A}$ )	Concentration ( $10^{-4}$ g atom P m <sup>-3</sup> )	(mg <sup>-3</sup> )	Vapour pressure (Torr)	Ratio FPD/FID ( $\times 10^2$ )
7.5	280.7	0.010	0.012	0.32	$2.1 \times 10^{-5}$	—
11.0	284.2	0.011	0.014	0.36	$2.4 \times 10^{-5}$	—
15.2	288.4	0.023	0.035	0.94	$6.4 \times 10^{-5}$	—
19.1	292.3	0.031	0.048	1.28	$8.9 \times 10^{-5}$	4.4
22.0	295.2	0.044	0.074	1.98	$13.8 \times 10^{-5}$	4.2
28.2	301.4	0.11	0.23	6.15	$43.7 \times 10^{-5}$	2.2
33.1	306.3	0.13	0.28	7.48	$54.1 \times 10^{-5}$	1.8
37.0	310.2	0.24	0.60	16.1	$118 \times 10^{-5}$	1.3
42.4	315.6	0.37	1.00	26.7	$199 \times 10^{-5}$	1.1

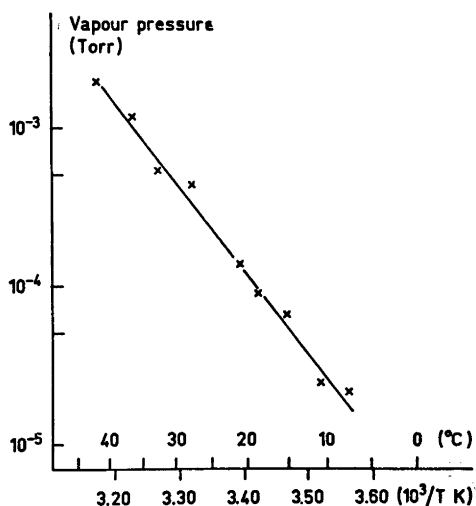


Fig. 1. The vapour pressure as a function of temperature.

$$\text{where } A = \Delta H_{\text{vap}}/2.303R \quad (3)$$

The constants in eqn. (2) were determined with the least squares method in a PDP-8 computer and were found to be  $A = 5235$ ,  $B = 13.90$  and the residual mean square = 0.0058. The relationship (3) gives  $\Delta H_{\text{vap}} = 100.0 \text{ kJ mol}^{-1}$ .

The volatility of the title compound in 25°C was  $3.0 \pm 0.5 \text{ mg m}^{-3}$ . The vapour pressure as a function of the temperature is shown in Fig. 1.

*Acknowledgement.* I thank Mr. N. Ekman and Mr. L. Pettersson for valuable laboratory assistance.

## REFERENCES

1. FOA Om, BC Warfare Agents, FOA Info, Stockholm 1969, p. 36.
2. Chemical and Bacteriological (Biological) Weapons and the Effects of their Possible Use, United Nations Publication A/7575, New York 1969, p. 90.
3. The Problem of Chemical and Biological Warfare, Sipri, Stockholm 1971, Vol. 1, p. 86.
4. Bescherming Tegen Toxische Stoffen, Chemisch Laboratorium TNO, den Haag 1973.
5. Kensington Adam, N. Physical Chemistry, Clarendon Press, Oxford 1962, p. 237.
6. Frostling, H. and Brantte, A. *J. Sci. Instrum.* 5 (1972) 251.

7. Frostling, H. *J. Sci. Instrum.* 6 (1973) 863.
8. Frostling, H. *Aerosol Sci.*, Academic 1973, Vol IV, pp. 5,411.
9. Fagerlind, L., Lindgren, I., Santesson, J., J., Stensiö, K.-E., Wallerberg, G. and Östman, B. FOA 1 report A 1541-C2(C4), 1971.
10. Ringquist, G. *VVS-Tidskrift* 4 (1965) 195.
11. Kowalska, M., Lindgren, I. and Santesson, J. FOA 1 report A 1573-C2(C5), 1973.

Received September 6, 1973.