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The evaporation behaviour of the pesticide Triallate on the basis of its thermodynamic parameters[1]

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Abstract

Vapour pressure is an important parameter for predicting the distribution of a substance in the environment. Therefore, the vapour pressure of the herbicide Triallate was determined using the Knudsen effusion technique. At least two polymorphic phases of Triallate were identified employing thermooptical and calorimetric methods.

Keywords: Polymorphism; Vapour pressure; Volatilization

1. Introduction

Volatilization is an important process that controls the dispersal of many pesticides into the general environment as well as their effective lifetimes in the target area. Vaporization losses of 80 to 90% were found in some cases within a few days after application [1].

According to the kinetic theory of gases, vapour pressure determines the maximum evaporation rate. Therefore, vapour pressure is the most important parameter to estimate the potential volatility of a substance.

The crystal structure of a substance affects its thermodynamic properties like the melting point, the sublimation enthalpy and, thereby, the vapour pressure. Therefore, different polymorphic forms may influence the volatility of pesticides following their application.

Different authors report on vaporization losses of various pesticides higher than their respective maximum evaporation rates [1]. The measurement of the vapour pressures of pesticides, which are typically low volatile substances, seems to be a problem, as the values cited in the literature show, in case of several substances, 2–3 orders of magnitude difference between various authors [2]. Polymorphism of the invented substances might be an explanation of this inconsistency [3]. In the present paper, this hypothesis is exemplified with the herbicide Triallate by identifying two polymorphic phases.

2. Experimental

2.1. Materials

Triallate (*N*,*N*-diisopropyl-2,3,3-trichlorallyl-thiolcarbamate) is a pre-emergent herbicide used to control annual grasses and broad-leaved weeds in wheat,

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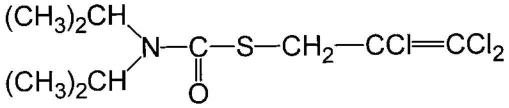

Fig. 1. Structural formula of Triallate (*N*,*N*-diisopropyl-2,3,3-trichlorallyl-thiolcarbamate).

barley, rye and sugar beet. The structural formula is given in Fig. 1. Commercial Triallate has a purity of 99.8%. Due to the high sensivity to impurities of the effusion method, all measurements were carried out with Triallate which had been twice sublimated. The purity of the highly purified substance was $\geq$99.96% as determined by DSC.

2.2. Methods

2.2.1. Vapour-pressure measurements

The integral mass loss type of effusion method was used in vapour-pressure determination. A more detailed description of the apparatus and procedure may be found in [4]. The substance under investigation was placed in cylindrical cells of cross-sectional area A made from Duran glass. For effusion measurements, the cells had an interchangable cap, which carried the circular effusion orifice of area a in the centre of a thin molybdenum foil, and which was connected to the cell body by a short, thorougly polished ground glass joint. The distance from sample surface to the foil carrying effusion hole is made equal to the cell inner diameter, as stipulated by theory. By using various combinations of orifices of effective area Wa and cells of area A the ratio Wa/A could be varied from 5.0×10^{-4} to 5.4×10^{-2}. Here, W is the calculated penetration probability of the orifice (Clausing factor) and in our cases is always close to unity but, nevertheless, taken into account.

The cells containing the sample were carefully weighed on a microbalance and positioned in an apparatus with the cell orifice opposite to a silvered condensor. The whole system was kept at constant temperature by two consecutive thermostats. To start a measurement, the air was quickly pumped out and a high vacuum maintained for a period of 3–18 h, while the vapour effusing from the hole was quantitatively collected on the condensor continuously refilled with liquid nitrogen. After the experiment, the cell was weighed again. From the kinetic theory of gases, the pressure inside the cell, p', is given by:

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

here, p' is close to the saturation vapour 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 the surface roughness, $(\Delta m/\Delta t)_T$ the rate of mass loss by effusion, R the universal gas constant, T the absolute temperature and M the molar mass.

To obtain the saturation vapour pressure p from p', it is necessary to carry out a series of measurements at constant temperature with various combinations of cells and orifices. Then $-1/\alpha\gamma$ can be calculated from the measured quantities:

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

The applicability of the effusion method is limited by its high sensitivity to impurities, especially to those which are less volatile than the substance under study. In order to obtain reproducible vapour pressures by the effusion method, it is of primary importance to thoroughly purify the substance. Impure samples cause a decrease in the measured vapour pressure with time as the less volatile substances accumulate at the evaporating surface.

2.2.2. Investigation of polymorphism

The DSC-measurements were carried out in a TA 500 calorimeter (Heraeus). Between 4 and 7 mg of Triallate were weighed into the aluminum capsules of the calorimeter. Heating and cooling rates of ±1 and ±0.5 K/min, respectively, were applied.

Both phases were prepared using the same sealed aluminium capsules using liquid nitrogen and a cryostat filled with ethanol, respectively, as cooling media for solidifying the melt of Triallate.

Polarisation microscopy was used as another method for the distinction of the two different polymorphic phases. The investigations were made with the Orthoplan (Leitz) microscope coupled with the calorimeter Mettler FP 800/FP 84. The advantage of the combination of these two methods is that the melting point of the samples can be detected after the microscopic investigation, thereby verifying that the right modification had been inspected. Molten Triallate was solidified in small glass crucibles according to the above-mentioned procedure for preparing the samples.

3. Results and discussion

The results for the vapour pressure are given in Fig. 2. On the basis of our measurements, we recommend for the (32°C)-phase of Triallate the vapour pressure equation $\ln p/\mathrm{Pa}=(41.4\pm0.3)-(13448\pm67)$ (T/K). The vapour pressure at 25°C amounts to $(2.46\pm0.18)\times10^{-2}$ Pa, and the sublimation enthalpy is $\Delta H_{\mathrm{fus}}=111.8\pm0.6$ kJ/mol.

During the calorimetric investigations, repeated cooling and heating cycles were run in the DSC. Following a second heating of Triallate (solidified melt) a second modification with a lower melting point of 25°C was detected as shown in Fig. 3.

The minimum temperature to which the melt was cooled is the decisive parameter governing the formation of the two modifications in the calorimeter. Down to −80°C, only the "usual" (32°C)-phase is formed. Cooling down to −30°C leads to mixtures of the two phases. Their ratio depends on the cooling and heating rate, respectively. More of the (32°C)-phase is formed with the slower rate (0.5 K/min).

The preparation of milligram masses was possible, if the following conditions were met:

- (32°C)-phase: typical: freezing the melt in liquid nitrogen.
- (25°C)-phase: cooling the melt for 2 min at −20°C.

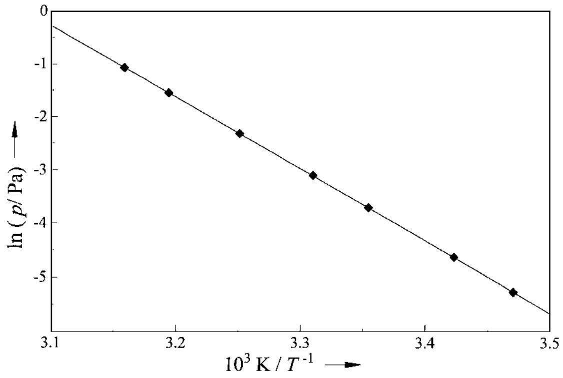

Fig. 2. Plot of the vapour pressure of Triallate.

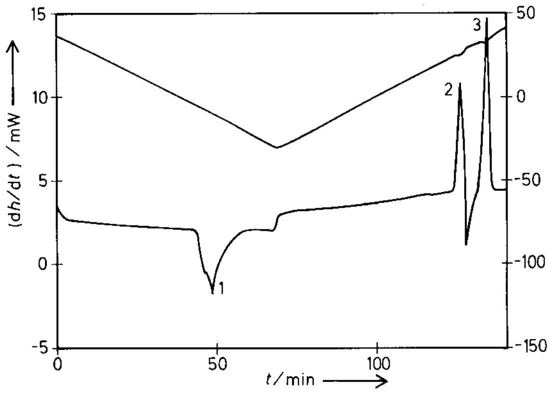

Fig. 3. DSC-curve of a cooling and heating cycle of Triallate (heating/cooling rate – 1 K/min); 1 – freezing peak; 2 – melting peak of (25°C)-phase; and 3 – melting peak of (32°C)-phase.

Efforts for preparation of the (25°C)-phase in larger masses failed. The use of bigger vessels than the small capsules of the calorimeters requires that the solidified melt has to be scratched out of them. All these attempts yielded the (32°C)-phase. A possible explanation is that the mechanical strain induces a solid–solid phase transition. To verify this assumption the (25°C)-phase was prepared in the aluminium capsules again. Afterwards, they were broken open (which causes a mechanical strain) and the Triallate was filled into new capsules. The resulting DSC curves showed a melting peak at 32°C only.

A series of samples of the (25°C)-phase was prepared and DSC-measurements were carried out weekly over a period of three months. All DSC-curves showed a melting peak of 25°C. This proves that the (25°C)-phase is stable at room temperature (below 25°C).

Pictures obtained by polarisation microscopy (magnification 120 times) are shown in Figs. 4 and 5. It can be seen that the two phases have two clearly different morphologies.

The (25°C)-phase is stable at room temperature over many months, thus the main problem of measuring its vapour pressure is to prepare the properly filled effusion cells. We observed a solid/solid-phase transition induced by mechanical strain. Therefore, in future

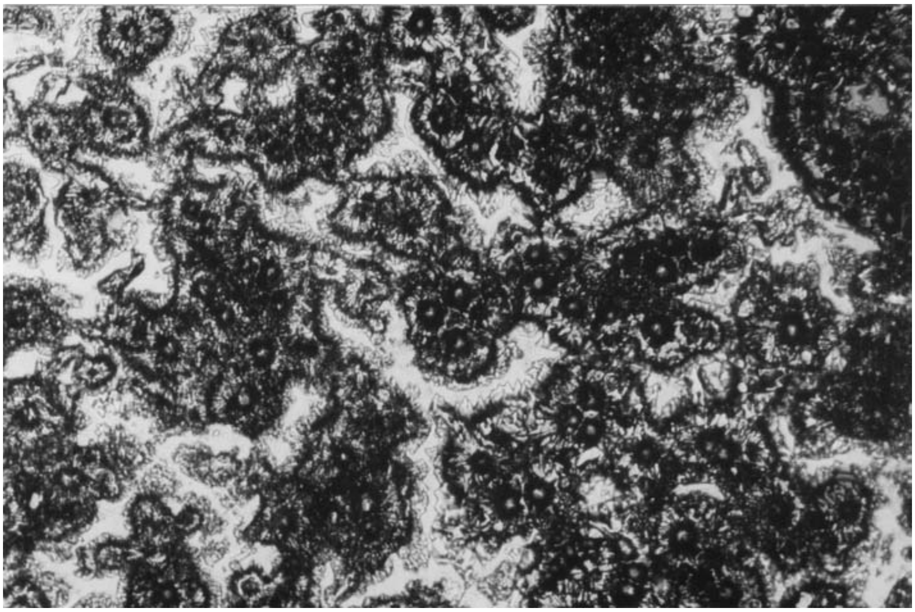

Fig. 4. The (32°C)-phase (donut shaped structure).

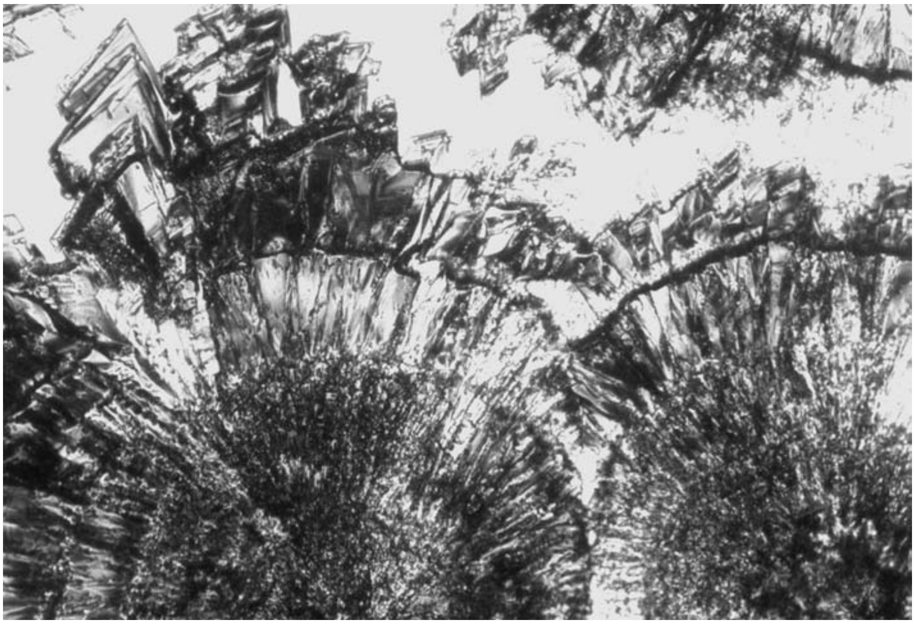

Fig. 5. The (25°C)-phase (rhombic-shaped structure).

investigations the new modification will be deposited on a porous carrier (e.g. glass filters) from its solution or melt.

Then it should be possible to investigate the influence of polymorphism on the evaporation behaviour of Triallate directly by twin measurements in our vapour pressure apparatus. The phase stability can be verified by measuring the porous carrier in the DSC without consequent mechanical strain.

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