

TGA investigation of the volatilisation of fipronil at elevated temperatures

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Abstract

In the present work, thermogravimetric analysis (TGA) was used to study the vaporisation behaviour of fipronil in the temperature range of 150 to 230 °C, i.e., below and above the melting point of the insecticide. The sublimation and evaporation rates were measured using isothermal thermogravimetric analysis. The vapour pressure was estimated assuming that the ideal gas law holds and that the rate of mass loss can be accounted for by the variation of the evaporation rate with liquid depth within the sample crucible and the vapour diffusion coefficient for the evaporating compound into the nitrogen gas. From this, the sublimation enthalpy was determined to be $120 \pm 4 \text{ kJ}\cdot\text{mol}^{-1}$, while the enthalpy of evaporation was $72 \pm 5 \text{ kJ mol}^{-1}$. Separate measurements using benzoic acid indicated that the vapour pressure predicted by the thermogravimetric method employed could be accurate to within about 12 %.

Keywords: Fipronil, thermogravimetric analysis, sublimation, evaporation, enthalpy, vapour pressure.

1. Introduction

Fipronil is a broad-spectrum, low-application-rate insecticide that belongs to the class of compounds known as phenylpyrazoles (Figure 1) [1-4]. This systemic neurotoxin is widely used for controlling pest organisms of animals and crops, e.g. fleas, weevils, ants, ticks, rootworms, mosquitoes, and termites [5]. Fipronil and its major metabolite, fipronil sulfone, kill insects by non-competitively binding to the γ -aminobutyric acid (GABA) receptor thereby blocking channels involved in the transmission of neural signals [6, 7]. Its distinctive mode of action presents a potent alternative for controlling insects that have developed resistance to classical insecticides such as pyrethroids, carbamates, organophosphates and organochlorines [3, 8].

Long-life insecticidal netting and mesh provides an effective method for malaria vector control [9]. Insects, e.g. malaria transmitting mosquitoes, are killed when they come into contact with the surface of the fibres where the insecticide has accumulated [10]. Mapossa *et al.* [11] investigated the incorporation of fipronil into polyethylene film produced by a direct extrusion process. During the polymer conversion processes, it was observed that fipronil crystals deposited on the die face of the extruder, suggesting that the fipronil was subliming. Pesticides in general, and fipronil in particular, pose serious health hazards when they come into skin contact or when inhaled [12]. This risk is enhanced when the toxic compound presents itself in the ambient air at the temperature where it is processed. This propensity is related to the vapour pressure of the toxic substance. Therefore, the vapour pressure should be known as it can guide the implementation of appropriate safety measures to avoid health-threatening exposure or contact.

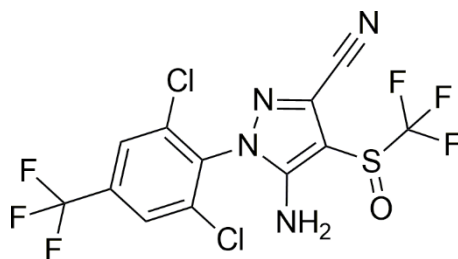


Figure 1. Structural formula of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile (fipronil).

In preliminary studies, thermogravimetric analysis (TGA) of fipronil showed very little mass loss when heated to 140 °C, indicating the absence of a hydrate or a solvate. However, when heated

beyond 150 °C, a significant mass loss was observed even below the melting range of 195 to 203 °C [14]. This could not be accounted for by the presence of volatile impurities in the substance. The purpose of this study was to investigate the propensity of fipronil to sublime at elevated temperature. This will lead to better understanding of the mass loss observed during manufacturing of fipronil-containing polymer film at temperatures between 180 and 210 °C [11]. Knowledge of the chemical and physical properties of insecticides is essential for reliable environmental fate and risk assessments and the subsequent design of effective mitigation and remediation strategies [15]. The vapour pressure is among the most important physical properties because it plays an important role in governing the gas-phase concentration of pesticides and their stability during long distance transport [16].

The TGA method is a useful tool for obtaining estimates of the vapour pressure of organic compounds. Compared to conventional methods of vapour pressure measurement, its advantages include the simplicity of the experimental set-up, short experimental times and small amounts of the compound are required for analysis [17-20]. Initial TGA-based vapour pressure studies [21, 22] based the TGA data analysis on Langmuir evaporation [23]. However, the Langmuir model is strictly valid for volatilisation into a vacuum. Therefore, it can only be used to predict the vapour pressure from TGA mass loss measurements conducted at vacuum conditions [17, 24].

TGA mass loss measurements are usually performed at finite pressures with a gas flowing past the partially filled crucible. The space above the sample is filled with the gas as well as some of the volatilising compound present. The mean free path, i.e. the average distance over which a gas molecule travels between successive collisions with other molecules is very small. At ambient conditions in air, it is only about 66 nm [25]. Furthermore, according to the kinetic theory of gases the root means square velocity is given by the equation:

$$v_{rms} = \sqrt{3RT/M} \quad (1)$$

where M is the molar mass of the molecule in g mol^{-1} . With nitrogen as the gas, this velocity is predicted to be about 23 m s^{-1} , i.e. very fast. The implication is that the evolved sample molecules are subjected to heavy pummelling by the nitrogen gas molecules as they travel upwards to escape from the open-top crucible. This means that the rate of migration of an evaporating sample molecule through the gas trapped inside the crucible is much lower than the maximum rate possible

as predicted by the Langmuir equation. Therefore, diffusion effects must be considered when attempting to estimate vapour pressures from TGA mass loss rates.

In the gravimetric method for the determination of liquid evaporation rates, the sample is held in a partially filled, cylindrical open-ended crucible. Analytical solutions, appropriate to this geometry, can be derived. They can account for the variation of the evaporation rate with liquid depth within the sample crucible and the vapour diffusion coefficient for the evaporating compound into the gas. Two different purge gas flow configurations are possible as shown in Figures 2(a) and 2(b).

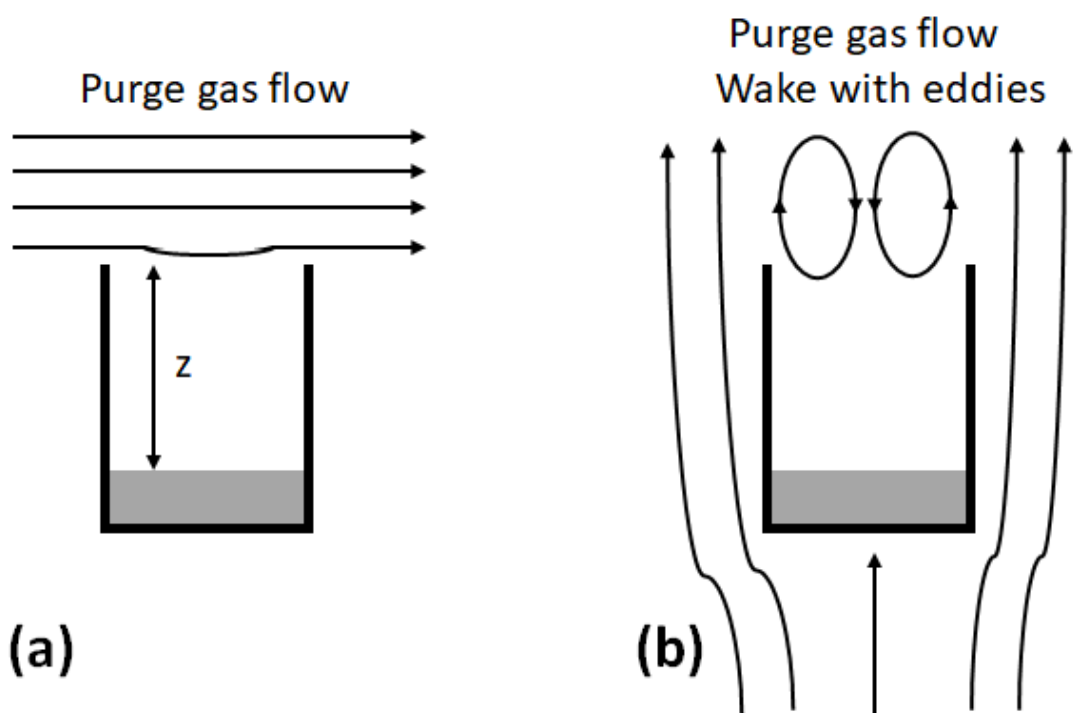


Figure 2. (a) Cross- and (b) axial purge gas flow configurations used for measuring the sublimation and evaporation rates of compounds in the TGA apparatus.

Pieterse and Focke [17] analysed the case in which the gas flows across the top of the crucible as shown in Figure 2(a). In Figure 2(b) the gas flow is in an axial upward direction past the cylindrical crucible. This latter case was first analysed by Beverley, Clint and Fletcher [18]. The streamlines defining the gas flow are also shown schematically in Figure 2. In both cases, the passing gas stream induces secondary flow patterns at the top entrance to the crucible. Depending on the flow rate, these may even take the form of vortices or eddies as shown in Figure 2(b). This means that

the gas column inside the crucible is not necessarily quiescent. Furthermore, it implies that the actual diffusion path length is not well-defined. The earlier physical models used to describe the evaporation from the open cylindrical containers did not take these effects properly into account. However, their effects can be minimised by careful control of the gas flow rate [17]. Still, Parker and Babas [20], Rong, Gregson and Parker [19] and Zghal et al. [26] did derive corrections for both the cross-flow (Figure 2(a)) and the axial flow (Figure 2(b)) configurations.

Goel et al. (2007) determined the vapour pressure-temperature relationships for fipronil, in the sub-cooled liquid state, using a gas chromatographic retention time technique. They reported data up to a temperature of 45 °C. The isothermal TGA method is ideally suited to investigate the vapour pressure for fipronil at higher temperatures. Hence, this study investigated the thermal properties of fipronil with specific focus on its sublimation and evaporation behaviour at temperatures encountered during the conversion processes used to prepare polyethylene-based mesh and film containing fipronil as the contact insecticide.

2. Materials and methods

2.1 Materials

5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile (fipronil, 96 % purity) was supplied by Avima, South Africa. Reagent grade benzoic acid (≥ 99.5 %) was purchased from Sigma Aldrich (South Africa). All the chemicals were used without further purification.

2.2 Equipment

Mass loss determinations were carried out using a TA Instruments Q600 SDT. A multipoint temperature calibration was performed using indium, zinc and gold calibration standards. Mass calibration was carried out using the manufacturer supplied mass calibration set. The measurements were carried out in dynamic nitrogen (N₂) atmosphere. The amount of sample was kept low (approximately 5 mg placed in an open 90 μ L alumina crucible) in order to minimize thermal gradients but sufficient to fully cover the bottom of the crucible. The depth of the empty

pan was measured to be 3.53 mm. When initially filled, the depth to the sample surface was 3.38 mm. This means that the maximum change in the pan depth amounted to 4.4 %.

2.3 Non-isothermal TGA and DSC measurements

A dynamic TGA temperature scan, from ambient to 300 °C, was performed on fipronil. The heating rate was 1 °C min⁻¹ with nitrogen flowing at a rate of 120 mL min⁻¹. The purpose of the run was to identify the location of the mass loss steps and the temperature where the mass loss rate reached a plateau. The DSC curve was used to identify phase transitions associated with mass loss events.

2.4 Determination of optimum flow rate

Isothermal TGA experiments were conducted at 190 °C. The furnace temperature was programmed to increase at a linear heating rate of 10 °C min⁻¹ from ambient to the target temperature and then maintained at this temperature. The N₂ gas flow rate was varied from 60 to 160 mL min⁻¹ in order to identify the optimum condition for the sublimation studies.

2.5 Determination of sublimation/evaporation rates

The sublimation or evaporation rates (dm/dt) of fipronil at a given temperature were determined using isothermal TGA in the temperature range 150 to 230 °C. A constant N₂ gas flow rate of 120 mL min⁻¹ was used during these experiments. The furnace temperature was programmed to increase at a linear heating rate of 10 °C min⁻¹ from ambient to the target temperature and then it maintained at this temperature. Mass loss rates were determined from a region where the temperature was constant, and the mass loss rate varied linearly with time.

Similar experiments were conducted using benzoic acid as a reference standard in order to validate the method employed for vapour pressure estimation by TGA. The same method and instrumental configuration used for fipronil was applied except that the isothermal sublimation rates of benzoic acid were studied over a temperature range of 40 °C to 70 °C.

2.6 Estimating the vapour pressure from TGA mass loss curves

The TGA set-up employed in this study comprised a cylindrical sample cup with an inert purge gas sweeping over the top as shown in Figure 2(a). In this set-up, the rate of evaporation is controlled by diffusion through the stagnant gas layer above the sample. According to Pieterse and Focke [17], the rate of vaporisation is given by Equation (2):

$$S_{AB} = P_A D_{AB} = \frac{zRT}{M_A A} \frac{dm_A}{dt} \quad (2)$$

where dm_A/dt is the TGA-measured mass loss rate (i.e. sublimation/evaporation rate) in g s^{-1} ; S_{AB} is the nitrogen permeability of the evaporating substance in $\text{Pa m}^2 \text{s}^{-1}$; P_A (Pa) is the sample vapour pressure at absolute temperature T (K); $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is the gas constant; D_{AB} ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient; M_A (g mol^{-1}) is the molar mass of the vaporising compound; A (m^2) is the cross-sectional surface area of the sample cup, and z (m) the depth of the gas-filled part of the sample cup. The variation in the diffusion path length (z) which is given by the effective depth to the surface of the sample, due to the volatilisation of the sample, was taken into account in the application of equation (2).

The data analysis was based on the assumptions that the vapour behaves as an ideal gas, that the enthalpy of phase change is constant and that the molar volume of the compound in the condensed state is negligible compared to that of the vapour. With these assumptions, the temperature dependence, in the range investigated, is given by the Clausius-Clapeyron vapour pressure equation:

$$\ln P_A = a - b/T \quad (3)$$

where the symbols and their units are as for Equation (2); a and b are adjustable constants with $b = \Delta H/R$, where ΔH is the enthalpy of sublimation or vaporisation in J mol^{-1} .

The diffusion coefficient for the vaporising compound was estimated using the Fuller correlation [27] using the exposition by Poling, Prausnitz and O'Connell [28]. The diffusion coefficient is given in Equation (4):

$$D_{AB} = \left[\frac{10^{-7} \sqrt{1/M_A + 1/M_B}}{P \left(\sqrt[3]{V_A} + \sqrt[3]{V_B} \right)^2} \right] T^{1.75} = CT^{1.75} \quad (4)$$

where D_{AB} is the diffusion coefficient in $\text{m}^2 \text{s}^{-1}$; T is the temperature in K; P is the pressure in atm; M_i is the molecular mass of compound i in g mol^{-1} , and V_i is the diffusion volume for compound i in $\text{cm}^3 \text{mol}^{-1}$. The values for nitrogen are $M_A = 28.02 \text{ g mol}^{-1}$ and $V_A = 18.5 \text{ cm}^3 \text{mol}^{-1}$. The values for benzoic acid were calculated to be $M_B = 122.12 \text{ g mol}^{-1}$ and $V_B = 20.1 \text{ cm}^3 \text{mol}^{-1}$ while for fipronil they were $M_B = 437.15 \text{ g mol}^{-1}$ and $V_B = 377.41 \text{ cm}^3 \text{mol}^{-1}$ respectively. The constant C lumps together the system pressure and all the invariant molecular quantities inside the square brackets of Equation (4). The atmospheric pressure, during the time periods in which measurements were conducted, was essentially 1 atm. This means that the constant C assumed the values 4.188×10^{-10} and $2.345 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \text{K}^{-1.75}$ for benzoic acid and fipronil respectively. Combining Equations (2) and (4) yields an equation that allows the estimation of the logarithm of the vapour pressure from the TGA measurements:

$$\ln P_A = \ln \left(\frac{S_{AB}}{CT^{1.75}} \right) \quad (5)$$

The values assumed by the parameters a and b , in the vapour pressure vs. temperature correlation presented by equation (3), were determined by least-squares regression. From these, the enthalpies of sublimation, or evaporation, were calculated via the expression $\Delta H_i = bR$.

3. Results and discussion

3.1 Non-isothermal TG

Figure 3 shows a dynamic temperature scan for fipronil. It shows the progressive mass loss caused by the sublimation and evaporation processes as the temperature increases. It is clear that mass loss starts above a temperature of ca. 140 °C. The TGA and DTG mass loss curves in Figure 3(a) suggest that the volatilisation of fipronil occurs in a single step resulting in nearly complete mass loss by 240 °C. The DSC trace in Figure 3(b) reveals three independent endothermic events. The first event starts from ca. 140 °C, and takes the form of a broad trough that deepens as the temperature is increased before abruptly returning to the baseline position at temperatures above 220 °C. The observed trend is consistent with the enthalpy associated with, initially, the sublimation of the solid and then the eventual evaporation of the molten fipronil occurring over a wide temperature range (ca. 140 – 235 °C). The deepening of the trough indicates accelerated volatilisation as the temperature is increased. According to Saxell et al. [14], fipronil melts in the

temperature range 195 to 203 °C. Therefore, the sharp endothermic peak, located at 201.2 °C, is attributed to the melting of the solid fipronil still present at this temperature. Note that at this temperature this amounted to only 72.8 % of the initial sample amount. In Figure 3(a), at the peak melting temperature, there is also a hint of a kink in the DTG curve. This is expected for a transition from sublimation of the solid to the evaporation of the melt [29]. The working temperature range, for the determination of the enthalpy of sublimation, was therefore selected to range from 150 to 195 °C to ensure that the data used represented the sublimation process. The small endothermic event, located around 185 °C, is attributed to enantiotropic solid-solid transition of fipronil [30]. The insecticide is known to exist in at least four different polymorphic and pseudo-polymorphic forms in patent [31, 32] and open literature [33]. A co-pending publication describes five different polymorphic forms of fipronil which were identified using single crystal X-ray diffraction (SCXRD) analysis.

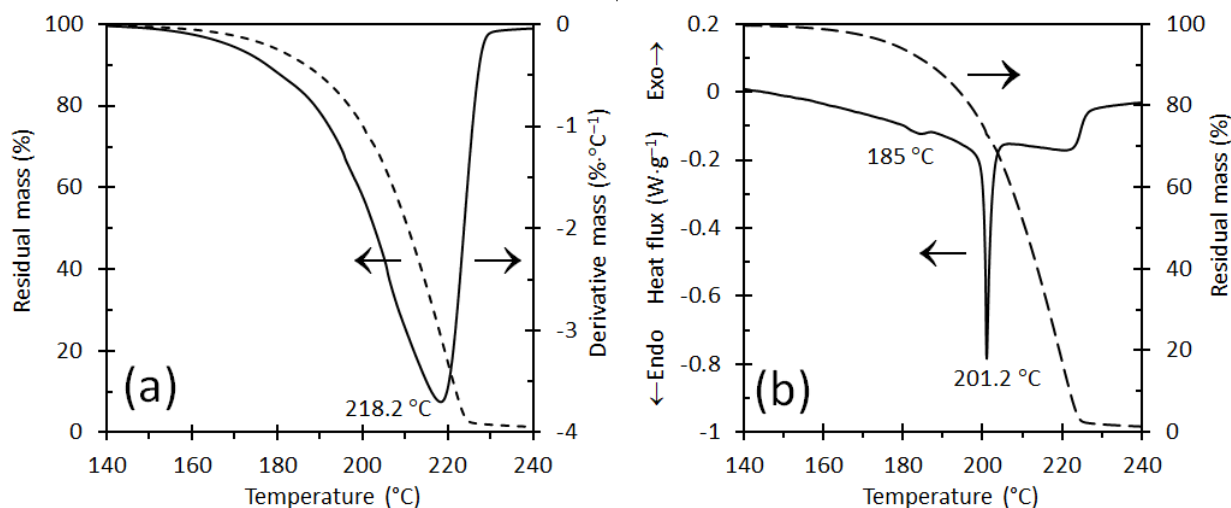


Figure 3. Thermal response curves for fipronil heated at a rate of 1 °C min⁻¹ in N₂ flowing at rate of 120 mL min⁻¹. (a) TGA and DTG curves, and (b) TGA and DSC curves.

3.2 Determination of optimum flow rate

Figure 4 shows the effect of the gas flow rate on the measured gas permeability (S_{AB}) of fipronil, calculated from equation 1. The measured values were independent of the flow rate in the range 80 to 160 mL min⁻¹. Based on this outcome, it was decided to perform all further experiments at

a flow rate of 120 mL·min⁻¹. This flow rate was also used for the TGA runs performed on benzoic acid.

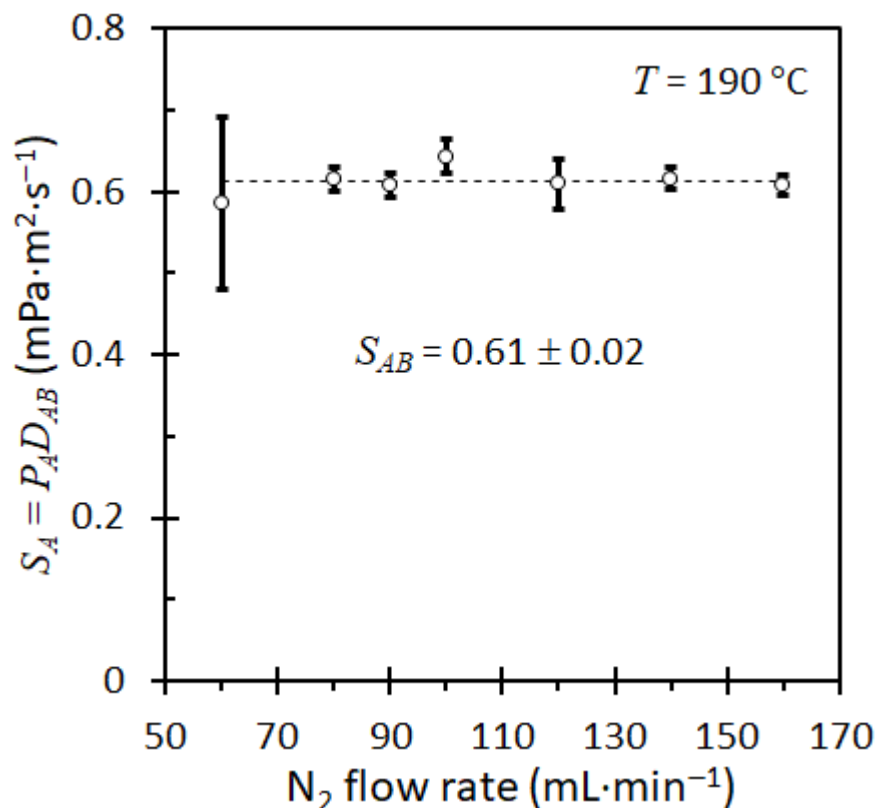


Figure 4. Variation of apparent nitrogen gas permeability of fipronil as a function of the flow rate of the carrier gas at 190 °C.

3.3 Vapour pressure estimates for benzoic acid

Benzoic acid is an established calibration standard for thermal analysis techniques [34, 35]. In order to validate the vapour pressure measurement technique employed, mass loss curves for benzoic acid were recorded in the temperature range 40 °C to 70 °C [36]. Figure 5 compares the resulting estimates for the vapour pressure of benzoic acid, calculated using Equation 5, to the reference data reported by Monte *et al.* [34]. The vapour pressure results obtained with the present TGA method are consistent with an enthalpy of sublimation of 97 ± 4 kJ mol⁻¹. This is 7 % higher than the 90.1 kJ mol⁻¹ associated with the literature data [34]. The mean absolute deviation between the present values those of Monte, Santos, Fulem, Fonseca and Sousa [34] amounts to 6 % with a maximum deviation of 12 %. This confirms previous assertions [17] regarding the accuracy of vapour pressure measurements attainable with the TGA method. The deficiencies of

the TGA method are such that it only provides rough estimates for the vapour pressure of compounds. Nevertheless, the TGA-based estimates results are sufficiently accurate for initial screening experiments, and they are useful for many practical applications.

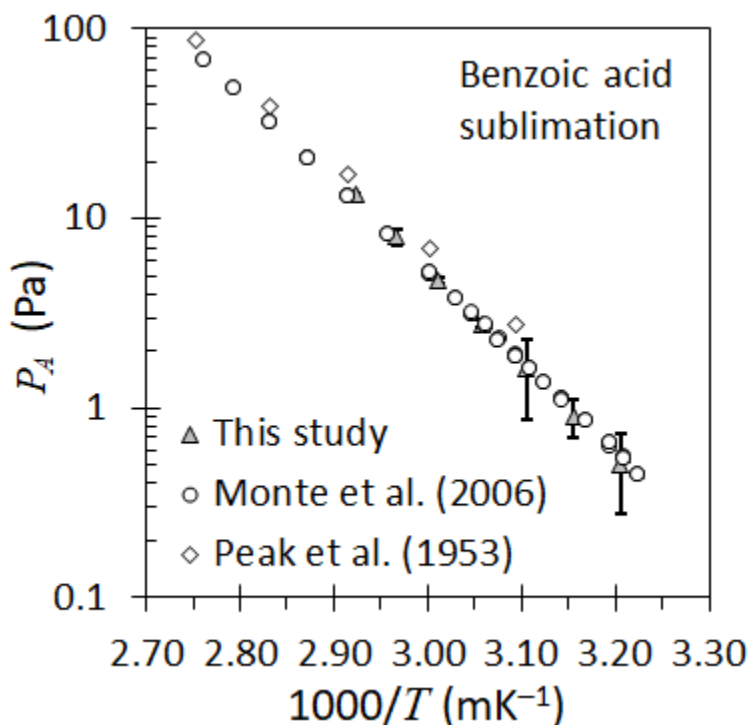


Figure 5. Present estimates for the vapour pressure of benzoic acid compared to published data [34].

3.4 Determination of sublimation/evaporation rates of fipronil

Figure 6 shows isothermal TGA mass loss curves obtained for fipronil at selected temperatures. The vaporisation measurements performed at the lower temperatures continued for up to 3.5 h. With the temperature set at 150 °C, the mass loss rate remained constant over the time period 27.5 minutes to 38.33 min for this sample. The cumulative mass loss at the end of the experiment only amounted to 0.35 mg (0.50%).

Mass loss was complete after ca. 2 h for the sample exposed to a temperature of 195 °C. However, samples heated to higher temperature did not show complete mass loss. Instead, the formation of

a thermally stable residue was evident. This means that the fipronil decomposes at elevated temperatures, forming stable, non-volatile char residues. Interestingly, the amount of stable char formed increased as the imposed isothermal temperature was increased.

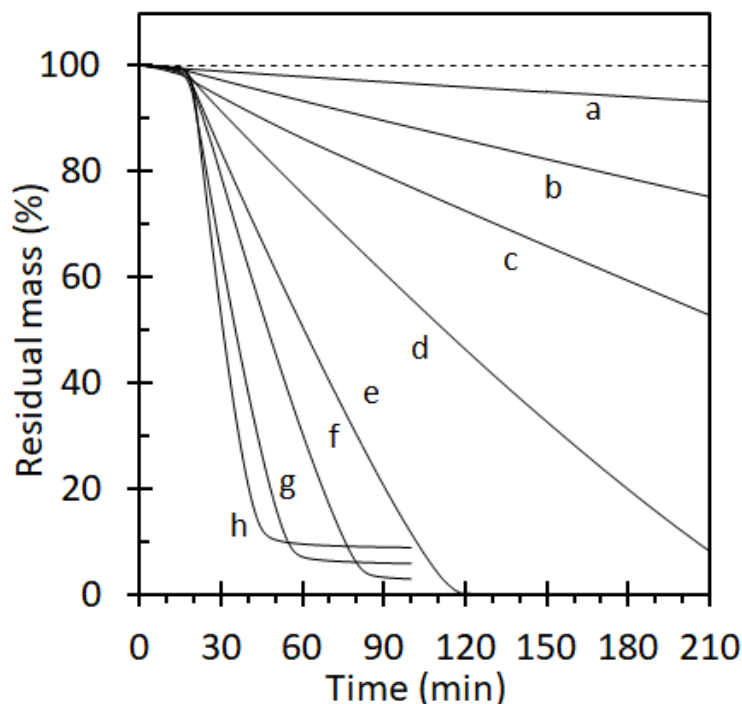


Figure 6. Time-dependent TGA mass loss curves for fipronil obtained at selected isothermal conditions. (a) 150 °C; (b) 165 °C; (c) 175 °C; (d) 185 °C; (e) 195 °C; (f) 200 °C; (g) 210 °C, and (h) 230 °C.

Once the applied isothermal temperature was reached, the sample mass initially decreased linearly with time for all the samples. However, for the samples heated to higher temperatures, deviations from the expected linear behaviour were evident at longer times. This is probably attributable to progressive decomposition of fipronil during its exposure to elevated temperatures. It is imperative to minimise potential measurement errors that might result from the effect of such decomposition reactions. In order to avoid this, and also for measurement consistency reasons, all the vapour pressure estimates were based on the mass loss rates measured in the time interval 27.5 to 30 min. In this range, the mass loss varied linearly with time for all samples with the correlation coefficients exceeding 0.9999.

3.5 Vapour pressure predictions for fipronil

Figure 7 plots the vapour pressure data for fipronil as extracted from the isothermal TGA runs. The sublimation enthalpy was determined to be $120 \pm 4 \text{ kJ mol}^{-1}$ while the enthalpy of evaporation was $72 \pm 5 \text{ kJ mol}^{-1}$. Based on Hess's Law, the difference between the enthalpies of sublimation and evaporation is the heat of fusion, which amounts to 47.5 kJ mol^{-1} . This is in reasonable agreement with the value, 44.5 kJ mol^{-1} , experimentally obtained by DSC analysis (Figure 3(b)).

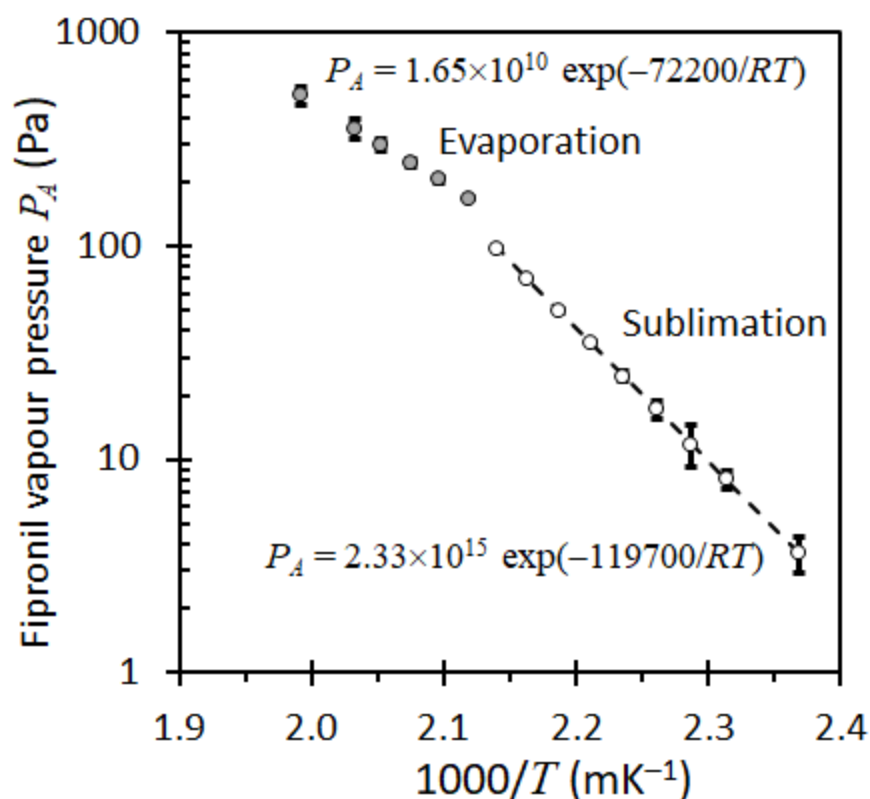


Figure 7. Fipronil vapour pressures vs. temperature predicted on the basis of TGA mass loss data.

4. Conclusions

Dynamic and isothermal TGA experiments were conducted to explore the thermal behaviour of fipronil. The insecticide featured a sharp melting endotherm at $201.2 \text{ }^\circ\text{C}$. It showed a strong tendency to sublime below this temperature. The volatilisation at elevated temperatures was accompanied by a decomposition reaction that led to the formation of a non-volatile char residue.

The sublimation and evaporation enthalpies were determined and the data indicates that fipronil will likely sublime at polymer processing temperatures above 150 °C.

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Conflicts of Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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