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KINETIC ANALYSIS OF THE THERMAL DECOMPOSITION OF THE PIRIMICARB–Cu-MONTMORILLONITE COMPLEX

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ABSTRACT

The kinetics of the thermal decomposition of the pirimicarb–Cu-montmorillonite complex were studied using thermogravimetric analysis and differential thermal analysis. The curves of the complex and of free pirimicarb recorded at four different oven heating rates were used to determine the activation energy values of the thermal decomposition of both compounds. The values found for the activation energies were very similar for the two techniques used, in both cases the value for the complex being higher than that for the free compound. The results obtained indicate that the state of the pirimicarb (free or adsorbed by montmorillonite) has an effect on the thermal stability of the pesticide both in its formulations and in the soil.

INTRODUCTION

After application, pesticides are adsorbed to a greater or lesser extent by the components of the organic or inorganic colloidal fractions of the soil [1,2]. The adsorption process, which partly governs the behaviour of the pesticide in the soil, acquires greater relevance in the case of cationic or polar organic compounds and when there are swellable smectite-like laminar silicates present in the clay (this kind of mineral can adsorb the pesticide, forming adsorption complexes [3,4]). The later behaviour of the pesticide with respect to environmental factors will be different to the behaviour observed when the compound is in its free state. Moreover, pesticides are also often formulated in powder form, adsorbed mainly on smectite clays [5]. Studies on the effect of temperature on the decomposition rate of complexed pesticide are of special interest.

In the present work, we studied the kinetics of the thermal decomposition of the interlayer complex formed by the carbamate pesticide pirimicarb (2-dimethylamino-5,6-dimethylpyrimidin-4-yldimethylcarbamate) with Cu-montmorillonite. This complex, studied in an earlier work using X-ray diffraction and IR spectroscopy [6], has a $d(001)$ basal spacing of 18.55 Å and the mechanism of its formation is basically of the ion-dipole type between the Cu^{2+} cations and the oxygen atom of the C=O group.

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EXPERIMENTAL

The < 2 μm fraction of Tidinit montmorillonite [7] saturated with Cu^{2+} was used. The pirimicarb employed was from Imperial Chemical Industries, PLC (England).

The pirimicarb–Cu-montmorillonite complex was prepared by treating the silicate with a solution of 0.4 M pirimicarb in 1,2-dichloroethane for 15 days. The complex was washed with the same solvent to remove the excess pesticide and then dried at room temperature.

The thermogravimetric (Perkin–Elmer TGS-2) and differential thermal analysis (Perkin–Elmer DTA 1700) techniques were used. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of pirimicarb and of the complex were obtained with oven heating rates of 5 °C, 10 °C, 15 °C and 20 °C min^{-1} in an atmosphere of N_2 (flow rate 80 ml min^{-1}).

RESULTS AND DISCUSSION

Figure 1 shows the TG and DTA curves of pirimicarb and of the pirimicarb–Cu-montmorillonite complex obtained at an oven heating rate of 10 °C min^{-1}. The loss of weight in the range 140–300 °C corresponds to the pyrolysis of the pirimicarb; the complex shows two consecutive weight losses, probably arising from the decomposition of adsorbed pirimicarb by ion–dipole and coordination mechanisms as reported in earlier studies [8].

In the curves obtained at different heating rates (5 °C, 10 °C, 15 °C and 20 °C min^{-1}) a shift in the decomposition temperature towards higher values can be seen as the heating rate is increased. The results were used to determine the activation energies using the methods proposed by Ozawa [9] and Flynn and Wall [10]. According to these researchers, the activation energy E and the frequency factor A of the Arrhenius equation ($K = Ae^{-E/RT}$) can be determined from the slope of the straight line resulting from the logarithmic plot of the heating rate versus the reciprocal of the absolute temperature, for an identical weight loss. Figure 2 shows the plot corresponding to three weight losses and Table 1 shows the mean values of the activation energies obtained from the slopes.

If one considers, as is logical, that the initial portion of the TG curves can be fitted by a first-order reaction equation, it is then possible to calculate the relationship between the half-life, the temperature and the percentage conversion. In this study we considered low weight losses of below 10% for calculating the activation energy.

Table 1 also shows the values of the rate constants and the half-life of pirimicarb. The temperature is seen to exert a pronounced effect on the rate constant and, in turn, the magnitude of this effect depends on the activation energy. The variation in the rate constant and half-life with temperature is

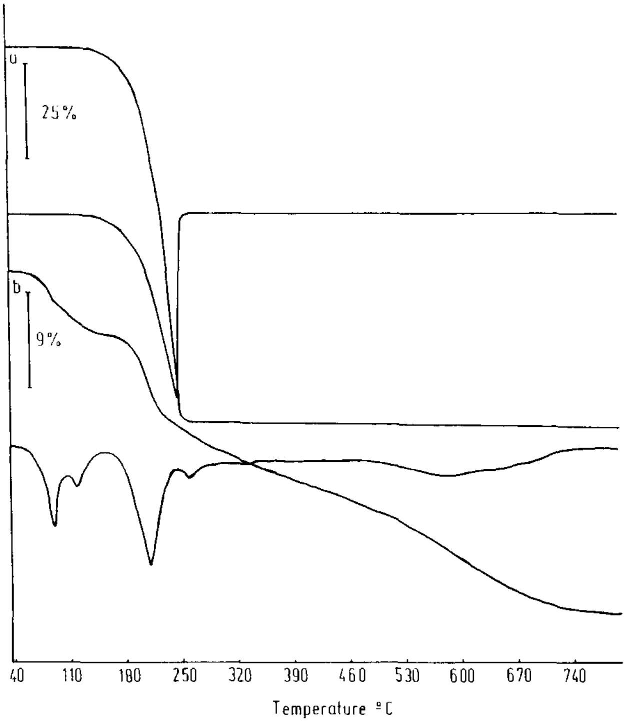

Fig. 1. TG and DTG curves of (a) pirimicarb and (b) the pirimicarb–Cu-montmorillonite complex.

seen to be greater for the complex, for which the activation energy of the decomposition process is greater.

Figure 3 shows the DTA curves of pirimicarb and of the pirimicarb–Cu-montmorillonite complex obtained at an oven heating rate of 10 °C min^{-1}. The endothermal effect in the range 170–370 °C arises from the pyrolysis of pirimicarb. In the case of the complex, it is seen as a broad peak arising

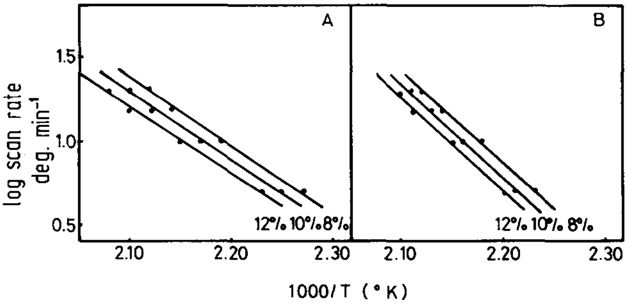

Fig. 2. Arrhenius plots corresponding to three weight losses: (A) pirimicarb and (B) the pirimicarb–Cu-montmorillonite complex.

TABLE 1

Activation energies and enthalpies of thermal decomposition of pure pirimicarb and of the pirimicarb–Cu-montmorillonite complex, and values of the rate constant K and half-life at three different temperatures

Compound	E (kcal mol^{-1})		ΔH (kcal mol^{-1})	T (°C)	K (min^{-1})	Half-life		
	TG	DTA				Days	Hours	Minutes
Pirimicarb	16.5	18.7	6.4	100	6.62×10^{-4}	–	17	27
				130	3.44×10^{-3}	–	3	21
				160	1.42×10^{-2}	–	–	48
Complex	20.2	23.8	17.4	100	1.23×10^{-4}	3	21	57
				130	1.33×10^{-3}	–	8	39
				160	1.04×10^{-2}	–	1	6

from the existence of pirimicarb adsorbed according to the aforementioned double mechanism.

DTA curves of pirimicarb and of the complex were obtained with several different heating rates (5 °C, 10 °C, 15 °C and 20 °C min^{-1}). The temperature corresponding to the maximum of the endothermal effect of the decomposition of pirimicarb decreases as the heating rate is reduced. The Kissinger equation [11,12] was used to calculate the activation energies using DTA (Table 1). These were similar to those observed with TG and confirm that the activation energy of the thermal decomposition of the complexed pesticide is greater than that of the free compound. The values of the

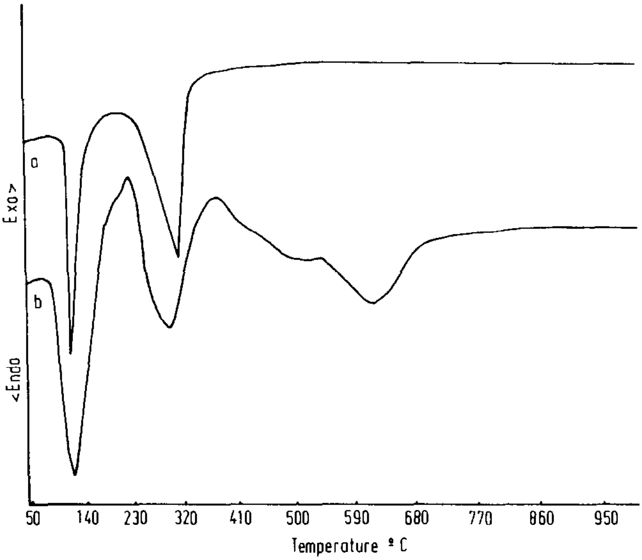

Fig. 3. DTA curves of (a) pirimicarb and (b) the pirimicarb–Cu-montmorillonite complex.

thermal decomposition enthalpies, obtained using differential scanning calorimetry, found in an earlier work [8] also vary in the same way (Table 1).

According to the results it may be concluded that the disappearance of free pirimicarb from the soil as a result of thermal decomposition (maximum temperature reached in soil is from 40 to 60 ° C), compared with the evolution of this compound with respect to other factors, may be of relevance. However, the effect of thermal decomposition on the persistence of the pesticide in the soil when it is adsorbed by montmorillonite is practically nil.

Furthermore, one must take into account the fact that this pesticide is often formulated as a wettable powder adsorbed on smectite clays, and this kind of formulation will increase the stability of the pesticide in the soil. Similarly, with a view to avoiding loss of activity due to thermal decomposition, the temperature of storage will also depend on the kind of formulation.

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