THERMOANALYTICAL STUDIES
ON MONTMORILLONITE-PIRIMICARB COMPLEXES

M. Sánchez-Camazano and *M. J. Sánchez-Martín*

CENTRO DE EDAFOLOGÍA Y BIOLOGÍA APLICADA, C.S.I.C.
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The thermal decomposition of the interlayer complexes of homoionic samples of montmorillonite with the carbamate insecticide pirimicarb (2-dimethylamino-5, 6-dimethyl pyrimidin 4-yl-dimethyl carbamate) was studied using TG and DSC techniques. The decomposition of the organic compound was followed by IR spectroscopy and X-ray diffraction. It was observed that the thermal decomposition of pirimicarb is catalyzed by adsorption by the clay. Both the catalytic capacity of the clay and the values of the decomposition enthalpies depend on the characteristics of the interlayer cation of the montmorillonite.

The carbamate insecticide pirimicarb (2-dimethylamino-5, 6-dimethyl pyrimidin-4-yl dimethyl carbamate) forms regular interlayer complexes with homoionic samples of montmorillonite. These complexes, previously studied by X-ray diffraction and IR spectroscopy [1] have a d(001) basal spacing that ranges between 16.98 and 18.55 Å, according to the type of interlayer cation; the mechanism of interaction is mainly ion-dipole between the oxygen atom of the $C=O$ group of the organic molecule and the interlayer cations of the silicate.

In the present work thermoanalytical studies were performed on Cu, Cd, Mg, Ca and Ba montmorillonite complexes with pirimicarb using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The decomposition of the organic adsorption compound was followed by X-ray diffraction and IR spectroscopy.

The relevant literature cites studies on the thermal decomposition of complexes of montmorillonite with organic compounds [2–4] but references to montmorillonite-organic pesticide complexes are very scarce, and they are concerned with the thermal stability of complexes of montmorillonite with certain organophosphorus compounds [5], with chlordimeform [6] and with paraquat [7].

Experimental

The <2 μm fraction of Tidinit montmorillonite (Morocco) [8] saturated with Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+} and Cd^{2+} cations [9] was used. The pirimicarb was obtained from Imperial Chemical Industries (PLC) (England). It is a crystalline solid product with a melting point of 90.5°.

The montmorillonite-pirimicarb complexes were prepared by treating the silicate with a solution of pirimicarb in 1,2-dichloroethane (0.4 mole) during 15 days. The suspensions were filtered, the complexes washed with 1,2-dichloroethane to remove excess insecticide and then dried at room temperature. It should be noted that Ba montmorillonite subjected to this prolonged treatment with the solution of pirimicarb forms a complex with a basal spacing of $d(001) = 17.66$ Å; the formation of this complex had not been observed previously with shorter periods of treatment.

The TG and DSC curves of pure pirimicarb (diluted with Al_2O_3), of the complexes and of the physical mixtures of montmorillonite with pirimicarb were obtained on a Perkin–Elmer TGS–2 Thermogravimetric Analyzer and DTA 1700 High Temperature Differential Thermal Analyzer. Both instruments have automatic cooling devices (with free and controlled rates) that begin to function once the desired temperature is reached. The heating rate of the furnace was 12 deg min^{-1} and a stream of N_2 was employed at a flow rate of 45 ml min^{-1}. The X-ray diffraction diagrams were obtained with a Philips 1730 diffractometer. The IR spectra were recorded on a Beckman–Acculab–6 double beam spectrophotometer using the KBr pellet technique.

Results and discussion

Figure 1 shows the TG and DTG curves of pure pirimicarb and of the complexes of pirimicarb with montmorillonite saturated with different cations. The TG curve of the pure compound shows a weight loss corresponding to the thermal decomposition of the compound in the 130–275° temperature range, representing a 100% loss of the compound. The curves of the complexes show the weight losses due to dehydration (50–150°) and dehydroxylation (600–700°) of the clay and also two weight losses in the 160–390° and 400–550° temperature ranges. In the Cu and Cd montmorillonite complexes the weight loss in the 160–390° temperature range is greater than that taking place between 400 and 550°; in the Mg, Ca and Ba montmorillonite complexes, the opposite occurs.

In order to discover the evolution mechanism of the montmorillonite-pirimicarb complexes during the thermal treatment, an X-ray diffraction and IR spectroscopic
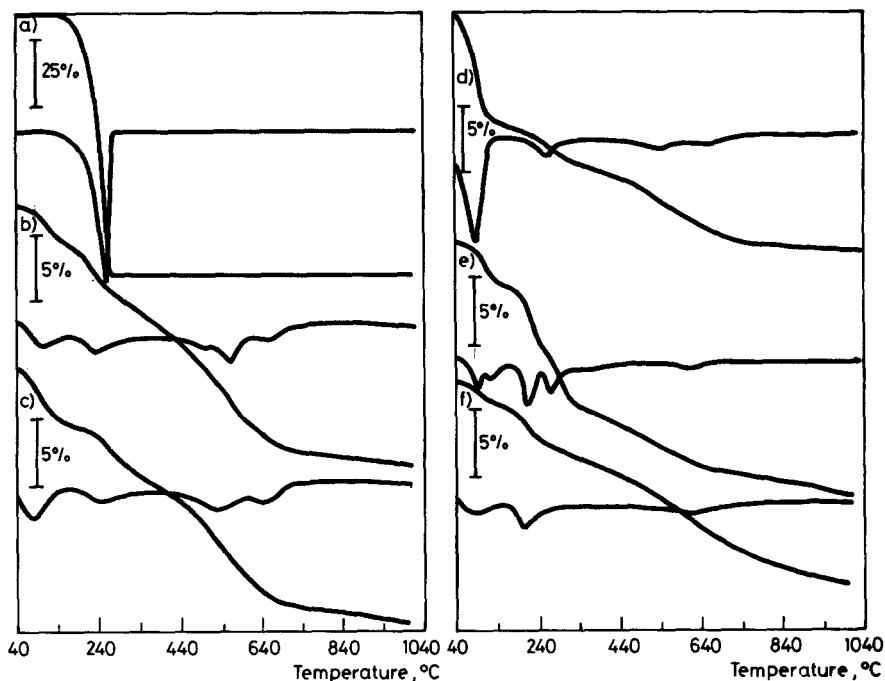
Fig. 1 TG and DTG curves of: a) Pure pirimicarb and b) to f) complexes of pirimicarb with montmorillonite saturated with cations: Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+} and Cd^{2+}

study was performed on the samples removed from the sample container of the TG furnace after each weight loss. After the weight loss in the 160–390° range the complexes yield X-ray diffraction patterns with $d(001)$ spacings of 12.27–12.62 Å, showing that a destruction of the initial complex with a high spacing has occurred (16.98–18.55 Å). After the third weight loss all the complexes give the same spacing of 11.0 Å. Figure 2 shows the X-ray diffraction patterns corresponding to the evolution of the Cu-montmorillonite-pirimicarb complex.

Figure 3 shows the IR spectra of pure pirimicarb, of the air-dried Cu-montmorillonite-pirimicarb complex and of this same complex removed from the sample container of the furnace after each of the weight losses. A study of these spectra and of those corresponding to the remaining complexes under the same conditions reveals: a) in the air-dried complexes, the presence of the main pirimicarb bands with shifts in those corresponding to the stretching vibration of the C=O (1710 cm^{-1}) and C—N (1510 cm^{-1}) groups and of those of the pyrimidine ring (1435 and 1390 cm^{-1}), as a result of the interaction of pirimicarb with the interlayer cations (1); b) after the weight loss in the 160–390° range, the
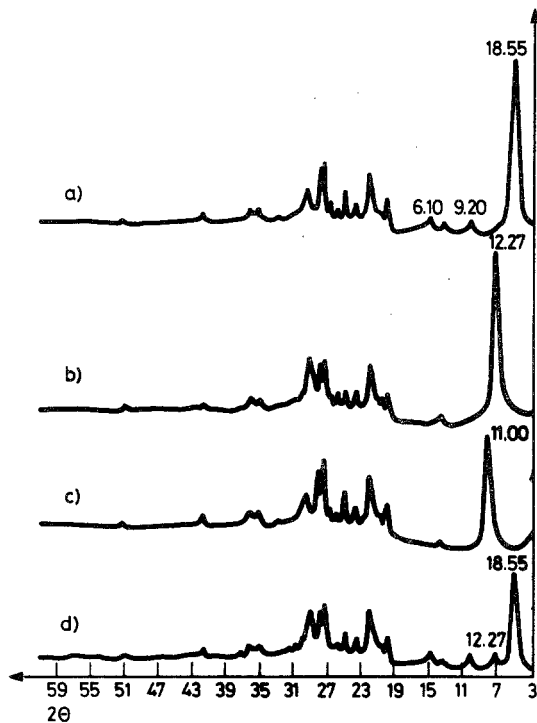
Fig. 2 XR diffraction diagrams of: a) Cu montmorillonite-pirimicarb complex, b) and c) Cu montmorillonite-pirimicarb complex removed from the sample container of the TG furnace after the weight losses in the 160–390° range and in the 400–550° range and d) Cu montmorillonite-pirimicarb mixture removed from the furnace at 190° (after the melting of the pirimicarb)

disappearance of the stretching band corresponding to the $C=O$ group of the pirimicarb and the persistence of the bands corresponding to the pyrimidine ring (1600, 1520, 1450, 1370 and 1335 cm^{-1}) and c) after the third weight loss, the disappearance of all the pirimicarb bands. These results are in concordance with those obtained using X-ray diffraction technique and furthermore show that after the second weight loss a compound is present in the interlayer space of the clay; this is a product of the decomposition of pirimicarb and does not contain the $C=O$ group though it does contain the pyrimidine ring.

The montmorillonite-pirimicarb mixtures, prepared with a proportion of pirimicarb similar to that found in the complexes, yield TG curves that are practically identical with those of the complexes. X-ray diffraction (Fig. 2d) and IR spectroscopy reveal that after the melting of the organic compound (105°) the complex is formed in the melt phase; the latter thermal decomposition process is the same as that of the corresponding complexes.
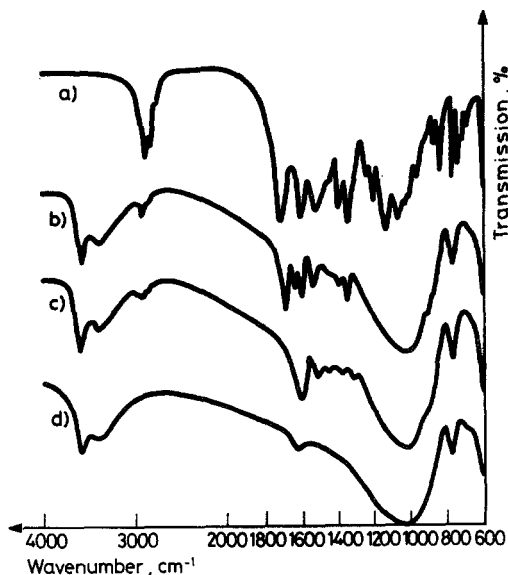
Fig. 3 IR spectra of: a) Pure pirimicarb, b) Cu montmorillonite-pirimicarb complex, c) and d) Cu montmorillonite-pirimicarb complex removed from the sample container of the TG furnace after the weight losses in the 160–390° range and in the 400–500° range

According to these findings, it may be deduced that the molecules of free, adsorbed or clay-mixed pirimicarb decompose at 160–390°, giving off volatile products. The UV spectrum of the gases collected under water at the outlet of the furnace is the same in all three cases. These volatile products are given off in the heating of pirimicarb, while in the heating of the complexes or of the mixtures, some of them must remain partially trapped by the clay. Regarding the retained compound, according to the IR spectrum of the complex after the weight loss in the 160–390° range and taking into account the general behaviour of carbamate pesticides during thermal treatment [10], this is likely to be 2-dimethylamino-5, 6-dimethyl pyrimidine-4-ol. The UV spectrum of the gases collected under water at the outlet of the furnace after the weight loss in the 400–550° range is different from that corresponding to the gases given off in the weight loss occurring in the 160–390° range. The retention of the volatile compound must occur with greater ease in the case of the montmorillonites saturated with alkaline earth cations than those saturated with transition metal cations. The high ionic potential of these transition metal cations specially when they are dehydrated, leads to a strong electrostatic attraction between the cations and the layers of montmorillonite which hinders adsorption of the organic compound in the interlayer space [11].

The nature of the interlayer cation of montmorillonite also affects the temperature at which pyrolysis of the complexes takes place. These temperatures vary according to the saturating cation in the following order $Cu = Cd < Mg < Ca < Ba$. The pyrolysis temperature of pirimicarb is higher than the pyrolysis temperature of all the complexes. Firstly, it may be seen that the pyrolysis of pirimicarb is catalyzed by adsorption. Indeed, the interaction between the $C=O$ group of the pesticide and the interlayer cations decreases the double bond nature of the $C=O$ group, which must affect the stability of the molecule adsorbed. The greater the polarizing power of the cation, or the greater its capacity to accept electron pairs, the greater is the interaction energy and hence the greater is the effect on the stability of the molecule, which will decompose at temperatures lower than in the free state. These catalytic properties of the surface of montmorillonite in the decomposition of herbicides and insecticides have been reported elsewhere [12, 13].

It should also be noted that in the Cu-montmorillonite complex the second weight loss occurs in two stages, in the temperature ranges of 160–235° and 235–390° these must correspond to pyrolysis of the complex with loss of decomposition products corresponding to ion-dipole and coordination interaction. The latter kind of interaction with electron pair donor atoms is specially favoured in the case of the Cu^{2+} cation with vacant d orbitals [11].
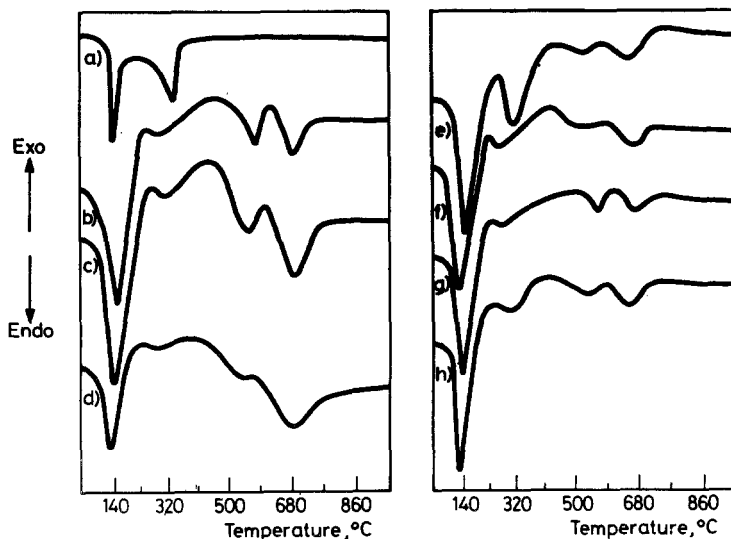

Fig. 4 DSC curves of: a) Pure pirimicarb, b) to f) complexes of pirimicarb with montmorillonite saturated with cations Mg^{2+}, Ca^{2+}, Ba^{2+}, Cu^{2+} and Cd^{2+}, g) Mg montmorillonite-pirimicarb mixture and h) Cu montmorillonite-pirimicarb mixture

Figure 4 shows the DSC curves of pure pirimicarb, of the complexes of pirimicarb with the different homoionic samples and of the mixtures of Mg and Cu montmorillonite with pirimicarb. In the curve corresponding to pure pirimicarb, two endothermic peaks can be seen; these correspond to the melting (105°) and pyrolysis of the compound (310°). Apart from the endothermic peaks corresponding to the dehydration and dehydroxylation of the clay, the curves of the complexes and of the artificial mixtures show further two endothermic peaks. The temperature ranges within which these effects take place are the same as those in which the weight losses occur in the TG curves. The peak at 160–390° must correspond to the pyrolysis of the complexes and the peak at 400–550° to the elimination of the decomposition products trapped by the clay. The relationship between the magnitude of these two endothermic effects in the different complexes is the same as that existing between the corresponding weight losses in the thermogravimetric curves.

The pyrolysis enthalpies of pure pirimicarb and of complexes of pyrimicarb with montmorillonite saturated with different cations are given in Table 1. The pyrolysis

Table 1 Pyrolysis enthalpies of pure pirimicarb and of complexes of pirimicarb with montmorillonite saturated with different cations

Sample	ΔH, cal g^{-1}
Pirimicarb	26.8
Mg	15.6
Ca	12.8
Ba	7.4
Cd	18.1
Cu	73.2

enthalpies of the complexes are the sum of the decomposition enthalpy of the adsorbed pirimicarb and the desorption enthalpy of the decomposition products. The values are lower than the decomposition enthalpy of pure pirimicarb, in accordance with the catalytic effect of adsorption in the thermal decomposition of the pesticide, and to a certain extent are related to the ionic potential of the interlayer cations. An exception is the Cu-montmorillonite complex owing to the fact that the peak (broad and flat) must correspond to the overlap of the two weight losses that are observed in the TG curves and that have been mentioned above.

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Zusammenfassung — Mittels TG und DSC Techniken wurde die thermische Zersetzung der Zwischenschichtkomplexe von homoionischen Proben von Montmorillonit mit dem Karbamatinsektizid Pirimicarb (2-Dimethylamino-5,6-dimethylpyrimidin-4-yl-dimethylkarbamat) untersucht. Die Zersetzung der organischen Verbindung wurde mittels IR-Spektroskopie und Röntgendiffraktion verfolgt. Es wurde beobachtet, daß die thermische Zersetzung von Pirimicarb durch Adsorption an dem Ton katalysiert wird. Sowohl die Katalysatorkapazität des Tones als auch die Werte für die Zersetzungsenthalpie hängen von der Art der Zwischenschichtkationen des Montmorillonites ab.

Резюме — Методом ТГ и ДСК изучено термическое разложение прослоистых комплексов гомоионных образцов монтмориллонита с карбаматпроизводным инсектицидом пиримикарб (2-диметиламино-5,6-диметилпиримидин-4-ил-диметилкарбамат). Исследование продуктов разложения было проведено с помощью ИК спектроскопии и рентгенофазового анализа. Найдено, что термическое разложение пиримикарба катализируется адсорбцией его этим минералом. Каталитическая способность минерала и значения энтальпий разложения зависят от характеристик межслоевого катиона монтмориллонита.