Journal of Thermal Analysis, Vol. 44 (1995) 313-327

THERMAL ANALYSIS OF MONTMORILLONITE–AMINOTRIAZOLE INTERACTIONS

E. Morillo[*], *J. L. Pérez-Rodríguez*[**], *C. Real*[**] *and P. J. Sánchez-Soto*[**]

[*]Instituto de Recursos Naturales y Agrobiología de Sevilla, C.S.I.C., Apdo. 1052, 41080 Sevilla, Spain
[**]Instituto de Ciencia de Materiales de Sevilla, Centre Mixto C.S.I.C. Universidad de Sevilla, Apdo 1115, 41080 Sevilla, Spain

(Received 19 March, 1994)

Abstract

In the present investigation, DTA and TG techniques were used to study the thermal behaviour of montmorillonite treated with solutions of the pesticide aminotriazole (*AMT*), in nitrogen flow. These techniques have been complemented by mass spectrometry of the evolved gases (EGA-MS).

AMT is adsorbed in the interlamellar space of montmorillonite as a cation. Results obtained in this study show that this provokes a shift of the dehydroxylation peak of montmorillonite to lower temperatures than those of the untreated clay. Montmorillonite protects the adsorbed *AMT*, delaying its first decomposition step, and catalyses *AMT* final decomposition at lower temperatures.

The DTA curve of montmorillonite–*AMT* mechanical mixture differs from the sum of those of the clay mineral and the pesticide heated individually. Montmorillonite dehydroxylation occurs at lower temperature, indicating a complex formation between *AMT* and the mineral during the heating process. However the DTA of the mixture is different from that of the complex previously studied, indicating that in the complex obtained by heating the physical mixture *AMT* is adsorbed as neutral molecule or as a product of its decomposition.

Keywords: complexes, DTA-TG, EGA-MS, montmorillonite, montmorillonite-aminotriazole complex, organo-clay complex

Introduction

Differential thermal and thermogravimetric analysis have been widely used in the study of complexes of clay minerals with organic compounds [1–4]. However its application for the study of pesticide adsorption by clay minerals is relatively infrequent [5, 6].

Studies of interactions between clay minerals and organic pesticides are important in relation to environmental pollution, a knowledge of the stability of

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

pesticide-clay complexes being of special interest. Thermal methods have a particularly important place in these environmental studies [7]. Thermal methods have also been accepted as a suitable way to characterize pesticide-clay mineral complexes and properties, to establish whether adsorption complexes were formed or the clay and pesticide were present merely as mechanical mixtures, to study the type of association and the strength of bonding forces between organic pesticides and silicate layers, and to know the effect of the clay surface on the stability or degradation mechanism of the organic pesticide adsorbed.

DTA combined with mass spectrometry of the evolved gases and vapours has provided useful information on the thermal degradation of organic materials on clay minerals. These combined techniques were previously used to study the adsorption of *n*-butylamine by zeolites [8, 9] and by sepiolite and palygorskite [10].

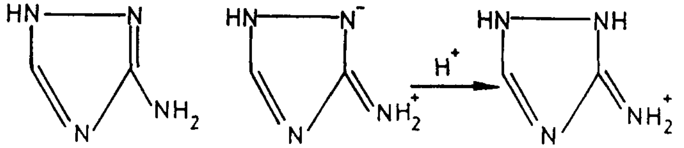
Most of the thermal analysis work on clay-organic associations has been carried out on montmorillonite [4]. This clay mineral is present in many agricultural soils. Aminotriazole is a widely applied basic pesticide. It is strongly adsorbed on montmorillonite in the ionic form, and weakly adsorbed in the neutral form [11].

In the present investigation DTA and TG techniques were used to analyse the thermal behaviour of montmorillonite treated with the pesticide aminotriazole (*AMT*). These experiments have been carried out in a nitrogen atmosphere and complemented by a mass spectrometry study of the evolved gases in order to get a better interpretation of the DTA peaks.

Experimental

The clay used was montmorillonite from Crock County, Wyoming (SWy-1), supplied by Source Clay Minerals Repository (Clay Minerals Society). The sample was used as received.

The pesticide aminotriazole (3-amino-1,2,4-triazole) was supplied by Riedel-de-Haën, with purity of 98%. This chemical is a basic compound that is able to protonate in aqueous solutions depending on the *pH*, since the *pK* is 4.14. It occurs in two desmotropic forms (I and II); 3-amino-1,2,4-triazole is in the form (I) and its salts in the imino form (III), as show in the folloing scheme:



(I) (II) (III)

Aqueous solutions of the pesticide (50 mmol/l) with *pH* similar to its *pK* were used, in order to obtain a part of the pesticide as the aminotriazolium cation (III). Aminotriazole–montmorillonite complex was prepared by treatment of the clay with the pesticide solution. The suspension was continuously shaken and the solution was changed every day during two weeks. At the end, the suspension was centrifuged, the solid washed with distilled water and left to evaporate to dryness at room temperature.

Total C, N and H content in the pesticide and in the complex were measured using a Perkin Elmer CNH elemental analyser 240-C. Total N in the complex was also determined using the Kjeldahl method.

Aminotriazole–montmorillonite mechanical mixtures used in the experiments were prepared in the same ratio clay/pesticide as in the complex.

Thermogravimetric (TG) and differential thermal analysis (DTA) experiments were simultaneously carried out on a Setaram high-temperature apparatus (Model 92, 16–18) under a flow of nitrogen (16 cm^3/min). Samples of 30 mg were covered by calcined alumina, which was also used as the reference material, vacuum outgassed for 30 minutes, and after this, flowing nitrogen (160 cm^3/min) was held for 30 minutes. A heating rate of 10 $deg{\cdot}min^{-1}$ up to 1000°C was used in all runs. Cooling rate was 90 $deg{\cdot}min^{-1}$ under nitrogen flow until room temperature. DTA-TG runs were also performed in air to know the real dehydratation weight losses.

On the other hand, in order to elucidate the nature of the gases produced during the thermal decomposition of samples, evolved gas analysis (EGA) was performed by attaching the sample tube to a Leybold-Heraeus quadrupole Q100 mass spectrometer. This system permits the simultaneous recording, as a function of temperature, of four previously selected *m/z* peaks. A heating rate of 10 $deg{\cdot}min^{-1}$ was used and all the experiments were recorded in vacuum.

Firstly, a scanning of the possible gases evolved was carried out every 50°C in order to know which were the most interesting *m/z* peaks to study. As results, evolution of gases with the following mass peaks *m/z* was carried out: 16 (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 and 42. No quantitative calibration of the system for the different masses was carried out and consequently the EGA curves should be considered only from a qualitative point of view.

Mass spectrometry experiments using solid samples were performed using a Kratos MS80 mass spectrometer operating in electron impact mode. The range scanned and recorded was $m/z=25$–300.

Results and discussion

Thermal analysis of montmorillonite

The DTA curve in nitrogen flow of untreated montmorillonite (Fig. 1) displays a large low-temperature endothermic peak with maximum at 114°C, due

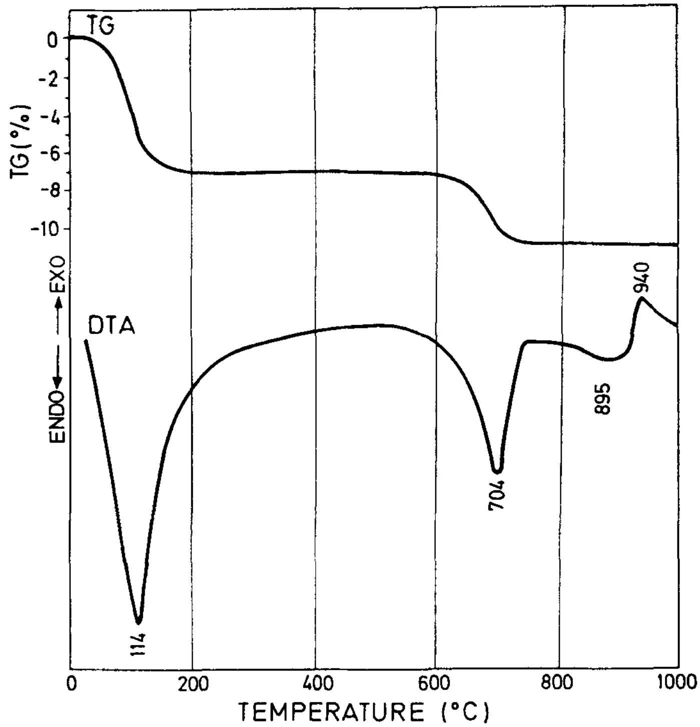


Fig. 1 DTA and TG (%) curves of Wyoming montmorillonite

to loss of adsorbed water, largely interlayer; an endothermic peak at about 704°C, due to dehydroxylation of the mineral; and a small *s*-shaped endothermic–exothermic peak system with maxima at 895 and 940°C, due to structural changes [10, 11]. The endothermic peaks at 114 and 704°C are accompanied by weight loss of 7.2 and 3.9%, respectively (total weight loss is 11.1%).

Thermal analysis of AMT

Figure 2 shows DTA and TG curves corresponding to the organic pesticide *AMT*. A very sharp and intense endothermic effect at about 160°C is observed. It is not accompanied by weight loss since it corresponds to the *AMT* melting point.

A first weight loss of 50.5% of the initial weight of sample is observed between 220 and 340°C, although it is significant that this weight loss increases when heating rate decreases, reaching 61.1% when the heating rate is 2 deg·min^{-1}. This weight loss is associated with several thermal effects on the DTA curve (Fig. 2). There is a moderate endothermic effect at 270°C, which is more easily observed in the DTA curves performed at lower heating rate

(Fig. 3). Very close to this effect there is a very sharp exothermic effect with maximum at 318°C. The final temperature of the first weight loss coincides exactly with the final temperature of the later exothermic effect. Elemental analysis of the products obtained before and after the exothermic peak has been carried out and they have also been studied by solid mass spectrometry and the evolution of evolved gases, to get an idea about the processes that could originate this first weight loss. The mass spectrometry analysis of *AMT* previously heated at 340°C (Fig. 4) indicates that a mixture of compounds is obtained after the first weight loss, with the principal component being a compound of molecular weight 126.

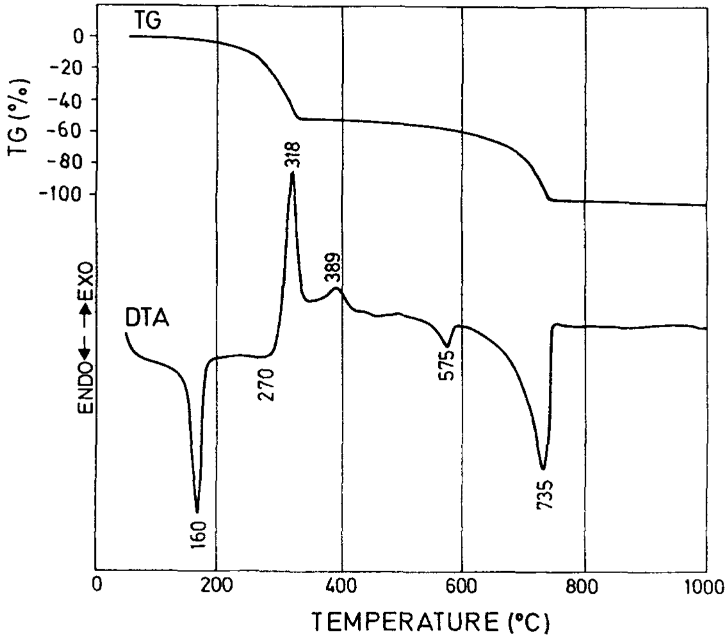


Fig. 2 DTA and TG (%) curves of pure *AMT*

The exothermic peak at 318°C is not due to oxidation of the organic compound, since the experiments have been carried out in N_2 atmosphere; it could comes from an exothermic reaction forming a more stable compound from other precursors. The exothermic peak could correspond to the formation of the compound molecular weight 126. It is assumed that the formation of this compound needs a previous decomposition of pure *AMT* in some other products which react between them to form it. Such decomposition needs energy, so it would explain the presence of the endothermic effect observed at 270°C. A part of the decomposition products are gaseous and their releasing gives as result the weight loss observed from 220°C (Fig. 2).

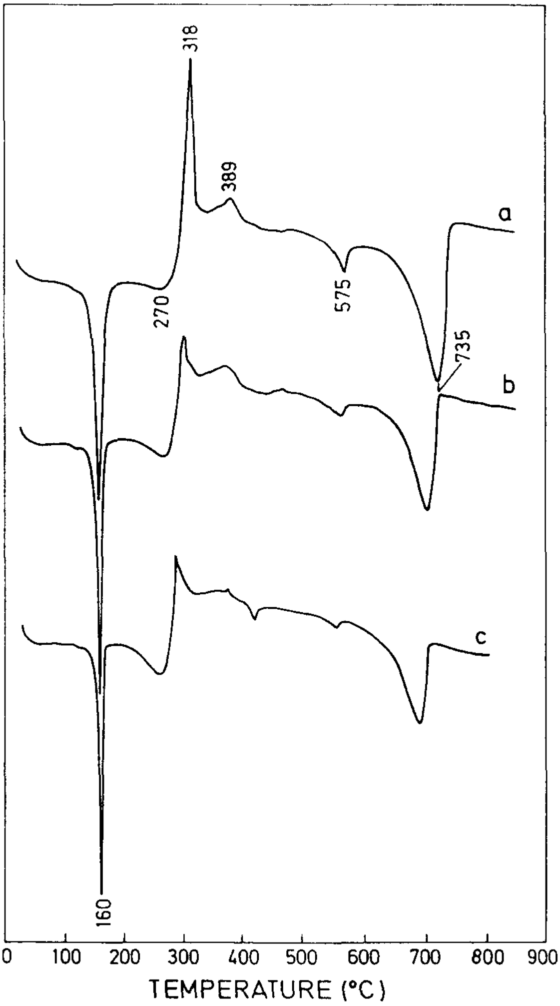


Fig. 3 DTA curves of pure *AMT* heated at 10(a), 5(b) and 2(c) deg·min^{-1}

The analysis of evolved gases (Fig. 5) shows the N_2, HCN and NH_3 liberation in this temperature range, and it can be also observed the release of a gaseous compound of molecular weight 41.

From 340°C very little weight loss is observed until reaching 600°C. At this temperature the total decomposition of the organic product takes place. The evolution of a great amount of gases such as N_2, HCN, H_2O and NH_3 is observed in the EGA curves (Fig. 5). This total decomposition is accompanied by an endothermic effect with maximum at 736°C and after this point, the decomposition finishes. The weight loss obtained during the *AMT* heating process is about 96%.

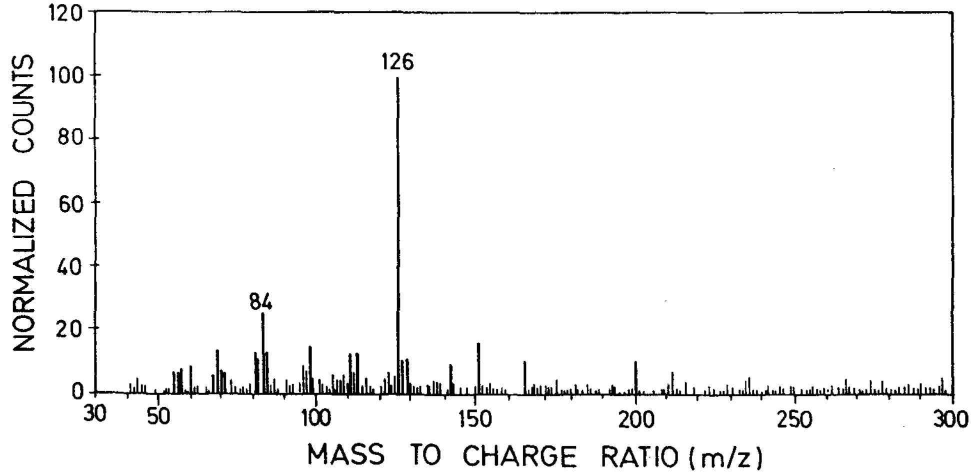


Fig. 4 Mass spectrogram for species present after heating *AMT* at 340°C

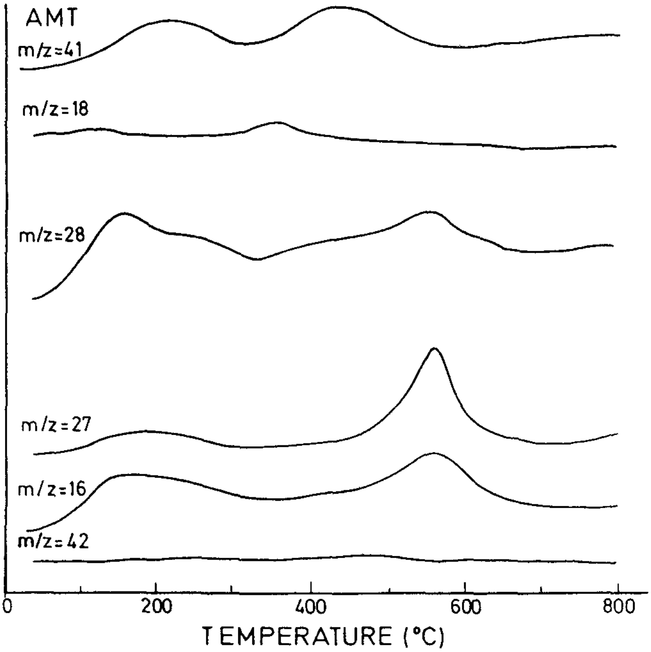


Fig. 5 Gas evolution curves obtained by thermal analysis of pure *AMT*. Mass peaks $m/z=16$ (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 (×10) and 42 (×10)

Thermal analysis of montmorillonite–AMT complex

The DTA curve of montmorillonite-*AMT* complex is shown in Fig. 6. Three clear zones can be observed: The first is from room temperature to ~ 300°C, where the dehydration endothermic effect of montmorillonite is detected. The peak temperature is 126°C, slightly higher than in pure montmorillonite (Fig. 1). This is not the normal behaviour of clay–organic complexes, because the presence of organic compounds makes the clay hydrophobic [4]. This provokes a shift of the dehydration peak towards lower temperatures. However, in our case the shift to higher temperatures may be due to a hindered liberation of interlamellar water, produced by the presence of *AMT*. There are sites where water molecules are more external and others where they are more lightly bound, leading to a wider dehydration effect, with the maximum shifted to higher temperature than in pure montmorillonite.

There is another reason for impediment water release: interlamellar water could be participating in the bonding between montmorillonite and *AMT*. Treatments of the clay with *AMT* have been carried out using pesticide solutions at

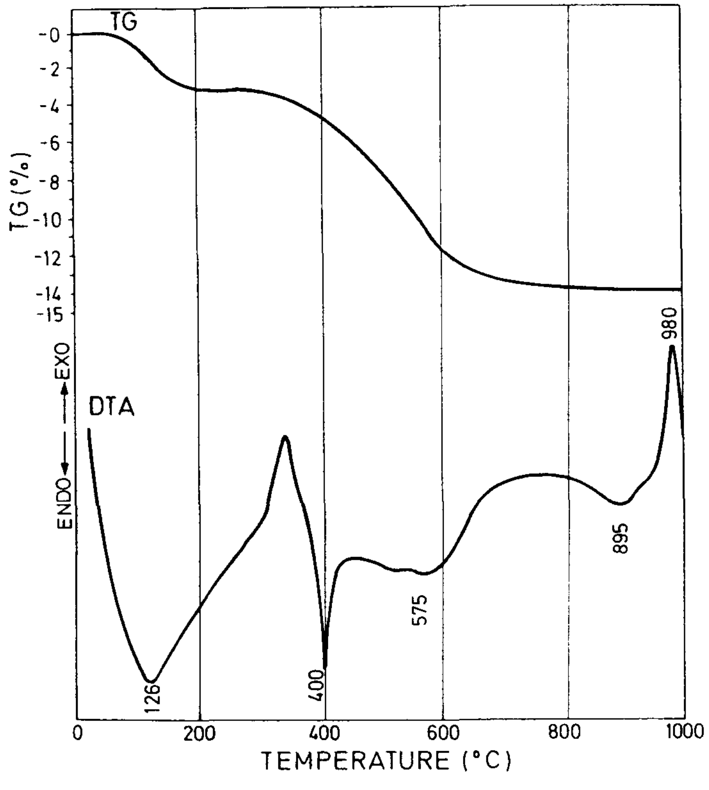


Fig. 6 DTA and TG (%) curves of montmorillonite–*AMT* complex

pH 4, to obtained part of the *AMT* in cationic form. In this form, complex formation can be through cationic interchange between cationic *AMT* and the interlamellar inorganic cations. However, under such conditions there are also *AMT* neutral molecules in solution, and, as was demonstrated in a previous paper [11], they could remain around interlamellar inorganic cations as polarized molecules, coordinated to them through water bridges.

The weight loss from dehydration of montmorillonite–*AMT* complex is about 3%, instead of the 7.2% observed for pure montmorillonite. This indicates that a great part of the clay hydration water has been substituted by *AMT*.

The second region of the DTA curve of the complex begins at approximately 340°C, and is the zone where thermic reactions of the organic material take place. According to the literature, this region presents, in inert atmosphere, wide weak and not well defined endothermic peaks, which are assigned to pyrolysis and liberation of the organic material, the clay surface and the exchangeable cations probably exerting a catalytic action [1, 14].

The DTA curve of montmorillonite–*AMT* complex shows a very narrow, sharp endothermic peak about 400°C, besides the wide effect normally found in this zone. As stated above, pure *AMT* shows a very sharp endothermic peak at 160°C corresponding to its melting point (Fig. 2), but no effect of this kind is observed in the DTA curve of the complex. In the case of montmorillonite–*AMT* complex, the pesticide is adsorbed in the interlamellar space mainly as aminotriazolium cation(III), so its physical properties and molecular structure have changed in such a way that it is not forming a separate phase that can be melted at the same temperature as pure *AMT*. Moreover, the organic compound adsorbed on montmorillonite gives it a protective coating effect, which is another reason why the adsorbed pesticide does not melt until 400°C. Similar behaviour was observed by Heller-Kallai *et al.* [2] in the DTA curves of pyrophyllite- and talc-stearic acid associations (although it is a different kind of adsorption). It was therefore inferred that the acid is adsorbed, and does not form a separate phase that can be melted.

The DTA curve of montmorillonite–*AMT* complex seems to indicate that two phenomena could be taking place almost simultaneously: the melting of the adsorbed organic compound and its pyrolysis and release of gases from decomposition products.

Gas evolution curves seem to corroborate this hypothesis (Fig. 7). NH_3, HCN and N_2 curves show an important release of these gases about 400°C. After this temperature, a decrease in the gas evolution curves is observed, and the release goes on but in smaller amount. At the same time, it is observed the release of a high proportion of a gaseous compound of molecular weight 41 and another of molecular weight 42, but in much lower proportion (Fig. 7).

The TG curve of the complex (Fig. 6) shows a weight loss starting at 340°C, when the endothermic effects of pyrolysis and fusion begin. This weight loss goes on after 400°C and at about 500°C the slope of this curve changes, due to the release of water from montmorillonite dehydroxylation and gases from or-

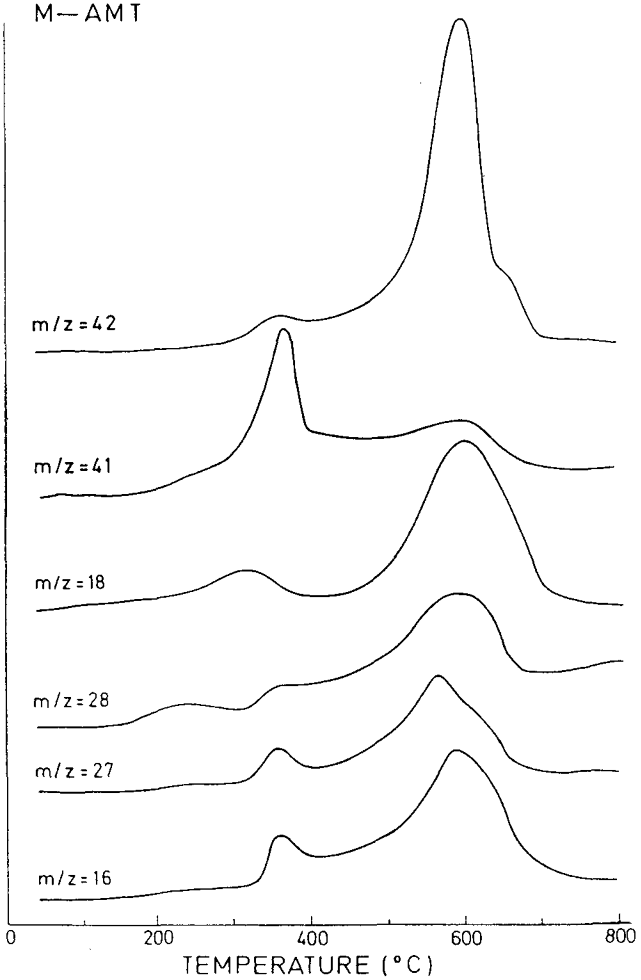


Fig. 7 Gas evolution curves obtained by thermal analysis of montmorillonite-*AMT* complex (*M-AMT*). Mass peaks $m/z = 16$ (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 (×10) and 42 (×10)

ganic compound decomposition. The dehydroxylation takes place at 575°C, a lower temperature than in pure montmorillonite (704°C). This behaviour has been observed frequently for organo-clay complexes [4, 10, 15, 16], but the reason is at the present unknown. This is further evidence of the organo-clay complex formation.

In some cases, pyrolysis of the organic matter is not completed in the temperature range of the second region and is traced in the third region by giving rise to peaks which overlap the dehydroxylation peak of the clay mineral. This also happens in montmorillonite-*AMT* complex, but can only be deduced by

EGA (Fig. 7). The temperature range of total release of gases from organic matter decomposition coincides completely with that of the mineral dehydroxylation approximately 550–700°C. Thus, complete gas release is made easy. Thermal decomposition of pure *AMT* and almost total weight loss (96%) is produced at higher temperatures (650–750°C), as shown in Fig. 2. This indicates that the clay mineral is catalyzing the thermal decomposition reactions of adsorbed *AMT*.

The weight loss in this second region is 10.56%. Since the weight loss from clay dehydroxylation is 3.9%, there remains 6.66% from *AMT*. It follows that there is 15.13% of *AMT* in the complex. This calculation has been confirmed by N analysis of the complex.

The third zone in the DTA of montmorillonite–*AMT* complex shows an endothermic–exothermic system corresponding to structural changes. There is an important difference compared with pure montmorillonite, since the exothermic peak is at 980°C (instead of 940°C the latter) and it is larger, sharper and better defined. This seems to indicate that the organic molecule located between the layers facilitates the recrystallization and the formation of high-temperature phases, with larger enthalpic change. These changes take place at higher temperatures. However, sintering between clay mineral layers could be impeded by carbon or residue produced after *AMT* thermal decomposition. It has been also proposed in the study of the thermal degradation behaviour of some organic complexes on synthetic micas [17].

Thermal analysis of montmorillonite–AMT mixture

Montmorillonite–*AMT* mixture prepared with a proportion of pesticide similar to that present in the complex yields TG and DTA curves which are shown in Fig. 8. A broad endothermic effect is observed at 110°C, associated with clay dehydration. Another vary sharp and well defined peak is observed at 160°C, without weight loss, corresponding to melting point of the organic compound. There is a third endothermic at 278°C which must correspond to pesticide present in the mixture, because the DTA curve of montmorillonite does not show any effect in the zone 220–340°C (Fig. 1). This is in accordance with the TG curve of pure pesticide showing a weight loss in the same region (Fig. 2). In the mixture, the weight loss in this temperature zone is 60.1% of the pesticide content, which disagrees with weight loss for pure *AMT* (50.5%). The endothermic at 278°C in the mixture coincides with that shown in pure *AMT* at 270°C, and is better observed at low heating rate than at higher rates (Fig. 3).

The exothermic effect at 318°C of *AMT*, observed at 10 deg·min^{-1}, decreases with decreasing heating rate, and is quite small at 2 deg·min^{-1}. These effects are the same as observed in the mixture, which seems to indicate that the clay mineral acts as a protection for the *AMT*. Thus, the thermal behaviour of the organic compound in the mixture is the same as if it was taking place at lower heating rate, since the heating transmission is delayed by the mineral. In connection with the above assumption, the weight loss corresponding to the pure *AMT* in this temperature range (220–340°C) is 61.6% using 2 deg·min^{-1}, which agrees with that obtained at 10 deg·min^{-1} for the montmorillonite–*AMT* mixture.

A broad endothermic DTA peak at 606°C, associated to clay dehydroxylation, is observed in the mixture (Fig. 8), while in the pure mineral this appears at 704°C. EGA curves (Fig. 9) show a gas release, coming from thermal decomposition of the organic material, which coincides with the temperature range of dehydroxylation. The gas release is facilitated by this dehydroxylation process.

It is reasonable to assume that an adsorption process of *AMT* on montmorillonite has taken place prior to dehydroxylation, since the temperature of this latter process is lower than in the pure mineral. It is very difficult to be sure about the temperature at which the adsorption process has taken place but an *AMT* adsorption would be possible after its melting point, with the formation of the complex in the melted phase. This is in accordance with previous studies of formation of clay-organic complexes by this mechanism [5].

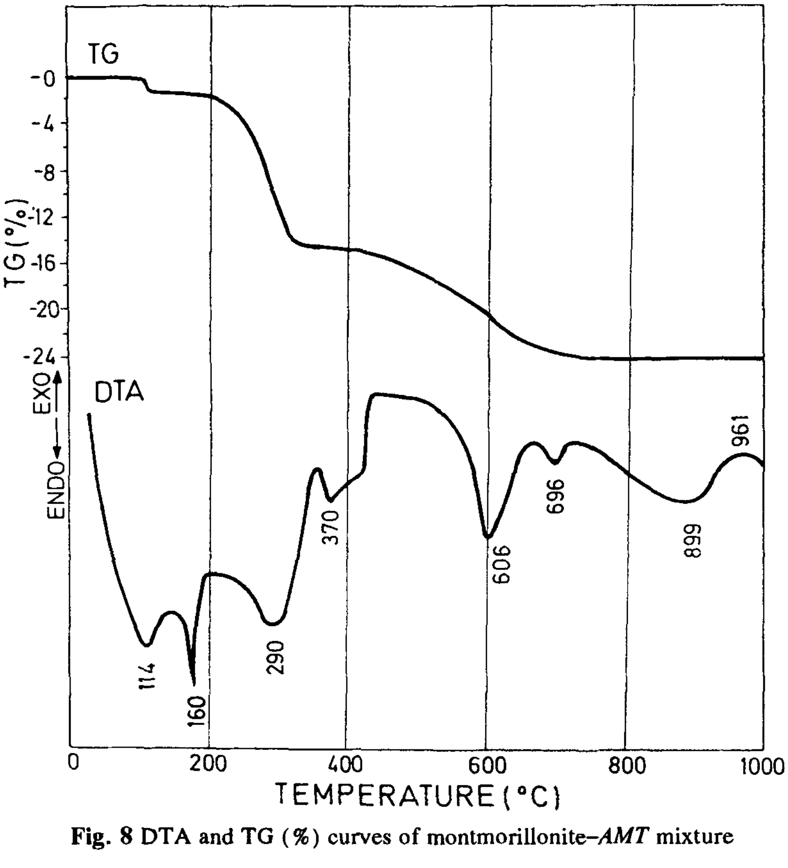


Fig. 8 DTA and TG (%) curves of montmorillonite–*AMT* mixture

Montmorillonite dehydroxylation in the mixture takes place at higher temperature than in the montmorillonite–*AMT* complex. This seems to indicate that the organic compound adsorbed is not the same in both cases. In montmorillonite–*AMT* complex the pesticide is adsorbed principally as a cation. In the complex formed after heating the physical mixture the organic compound adsorbed could be neutral *AMT* and/or a product from its decomposition.

The weight loss, which coincides with the endothermic effect about 600°C, is 39.9% of the *AMT* originally present in the mixture. This percentage plus 61.6%, from the first weight loss observed, is 101.5%, indicating that there is a percentage of water from dehydroxylation, besides decomposition gases from *AMT*.

Another endothermic effect can be observed in the DTA curve of the mixture, from water release, as confirmed by EGA (Fig. 9). This effect takes place

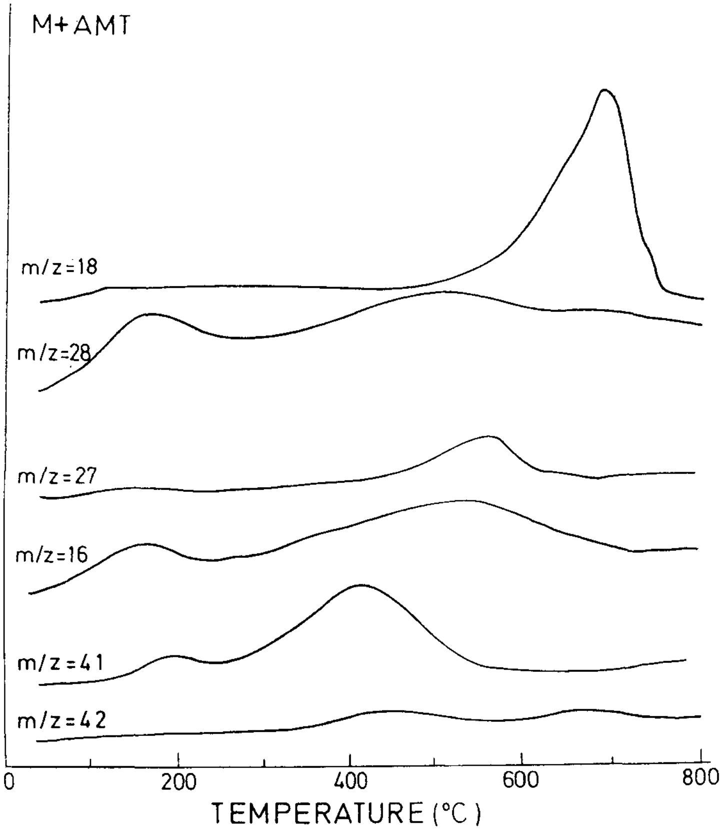


Fig. 9 Gas evolution curves obtained by thermal analysis of montmorillonite–*AMT* mixture (*M*+*AMT*). Mass peaks $m/z=16$ (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 (×10) and 42 (×10)

at 696°C, a similar temperature to that of dehydroxylation of pure montmorillonite (704°C). This suggests that part of the mineral has remained unaltered, without forming a complex. The weight loss from this effect is 1.2%, instead of the 3.9% observed in the pure mineral.

Conclusions

The results indicate that the pesticide *AMT* was adsorbed in the interlamellar space of montmorillonite, and its presence shifted the dehydroxylation peak to a lower temperature than that for the untreated clay. The clay–organic complex showed a continuous decomposition of the adsorbed *AMT* from 340 to 620°C, whereas the pure *AMT* showed a first decomposition step at lower temperature (in the range 220–340°C), with total decomposition of the organic compound at 736°C. Although the mechanism is complex, the clay seems to play a double role in thermal decomposition of adsorbed *AMT*; first of all, it acts by protecting the organic compound, since the mineral decomposition is delayed from 220 until 340°C. On the other hand, total decomposition of *AMT* is catalyzed by adsorption on the clay, taking place at 620 instead of 736°C in pure *AMT*.

The steps of *AMT* decomposition are different, and possibly the decomposition products too, depending whether or not it is adsorbed on montmorillonite. It is inferred from the comparison between EGA profiles corresponding to pure *AMT*, montmorillonite–*AMT* complex and montmorillonite–*AMT* mixture. However, under any circumstances, it is difficult to know the nature of *AMT* decomposition products, but more so in the case of being adsorbed.

The first decomposition stages of *AMT* in a physical mixture coincides with those of pure *AMT*, also showing two weight losses. However, the second weight loss takes place at lower temperatures than in pure *AMT*. It may by due to the formation of an interlamellar complex between *AMT* and montmorillonite. The pesticide has probably been adsorbed as a neutral molecule. Consequently, the montmorillonite dehydroxylation peak is observed at lower temperature than in pure montmorillonite, but it is still higher than in montmorillonite–*AMT* complex, in which the pesticide is present in the cationic form.

* * *

This work has been supported by funds of Ministerio de Educación y Ciencia, project AMB92-0394 (CICYT). We would like to thank Dr. M. A. Pradera for the Mass Spectrometry data, and Dr. J. M. Llera both from Department of Organic Chemistry, for his suggestions.

References

1 S. Yariv, Thermochim. Acta, 88 (1985) 49.
2 L. Heller-Kallai, S. Yariv and I. Friedman, J. Thermal Anal., 31 (1986) 95.
3 W. Smykatz-Kloss and L. Kaeding, Proc. 5th Intern. Solid Waste Conf., 1988, p.281.

4 S. Yariv, Thermal Analysis in the Geosciences. Springer-Verlag, Berlin 1991, p.328.
5 M. Sánchez-Camazano and M. J. Sánchez-Martín, J. Thermal Anal., (1990) 194.
6 M. C. Hermosín, J. Cornejo and J. L. Pérez-Rodríguez, Clay Miner., 20 (1985) 153.
7 W. Smykatz-Kloss, A. Heil, L,. Kaeding and E. Roller, Thermal Analysis in the Geosciences. Springer-Verlag, Berlin 1991, p.352.
8 A. K. Ghosh, N. G. Keats and G. Curthoys, J. Catal., 96 (1985) 288.
9 L. M. Parker, D. M. Bibby and R. H. Reinhold, Zeolites, 5 (1985) 384.
10 U. Shuali, M. Steinberg, S. Yariv, M. Müller-Vonmoos, G. Kahr and A. Rub, Clay Miner., 25 (1990) 107.
11 E. Morillo, J. L. Pérez-Rodríguez and C. Maqueda, Clay Miner., 26 (1991) 269.
12 R. C. Mackenzie, Differential Thermal Analysis, Academic Press, London, 1970, p.775.
13 Y. Uno, N. Kohyama, M. Sato and H. Takeshi, Proc. Int. Clay Conf. Denver 1985. The Clay Mineral Society, 1987, p.66.
14 W. Bodenheimer, L. Heller and S. Yariv, Clay Miner., 6 (1966) 167.
15 S. Yariv, M. Müller-Vonmoos, G. Kahr and A. Rub, J. Thermal Anal., 35 (1989) 1997.
16 S. Yariv, G. Kahr and A. Rub, Thermochim. Acta, 135 (1988) 299.
17 A. Oya, K. Matsunaga and S. Otani, Appl. Clay Sci., 3 (1988) 145.

Zusammenfassung — Vorliegend werden DTA- und TG-Techniken zur Untersuchung des thermischen Verhaltens von Montmorillonit in Stickstoff verwendet, welches zuvor mit Lösungen des Pestizides Aminotriazol (*AMT*) behandelt wurde. Diese Techniken wurden durch Massenspektrometrie der freigesetzten Gase (EGA-MS) ergänzt.

AMT wird im interlamellaren Raum von Montmorillonit als Kation adsorbiert. Die in vorliegender Untersuchung erhaltenen Ergebnisse zeigen, daß dies - bezogen auf unbehandelten Ton eine Verschiebung des Dehydroxylierungspeaks von Montmorillonit in Richtung niedrigerer Temperaturen auslöst. Montmorillonit schützt das adsorbierte *AMT* und verzögert den ersten Zersetzungsschritt sowie katalysiert die endgültige Zersetzung von *AMT* bei niedrigeren Temperaturen.

Die DTA-Kurve eines mechanischen Gemisches aus Montmorillonit und *AMT* unterscheidet sich von der Summe der DTA-Kurven des separat erhitzten Tonminerales und Pestizides. Die Dehydroxylierung von Montmorillonit erfolgt bei niedrigeren Temperaturen, was auf eine Komplexbildung zwischen *AMT* und dem Mineral beim Erhitzungsprozeß hinweist. Die DTA-Kurve unterscheidet sich auf alle Fälle von der des zuvor untersuchten Komplexes, was anzeigt, daß in dem durch Erhitzen des physikalischen Gemisches erhaltenen Komplex *AMT* als elektrisch neutrales Molekül oder als Zersetzungsprodukt adsorbiert wird.