

THERMOANALYTICAL STUDY OF THE PESTICIDE 3-AMINO-1,2,4-TRIAZOLE

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Abstract

Thermoanalytical study of the pesticide 3-amino-1,2,4-triazole (ATA) has been carried out, using simultaneous DTA-TG in nitrogen flow, in order to know its thermal behaviour and stability. These techniques have been further complemented using evolved gas analysis and mass spectroscopy (EGA-MS). Two different stages of ATA decomposition were observed: after the first decomposition step, a mixture of compounds is obtained, according to MS data, being the principal component a compound of molecular weight 126. It is formed by a first order reaction mechanism, according to the kinetic study, with $E_a = 124 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$. The second decomposition step takes place about 735°C, with evolution of HCN and NH₃, being the final weight loss 96%.

Keywords: DTA-TG, EGA-MS, kinetic, pesticides

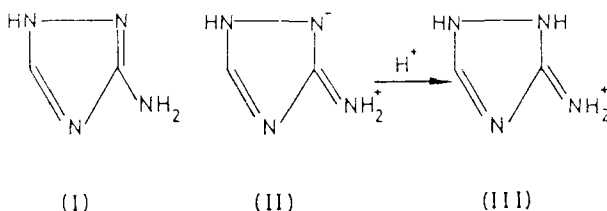
Introduction

The pesticide 3-amino-1,2,4-triazole (named amitrole, ATA, Weedazol, cytrol, amizol) was the first 1,2,4-triazole to be manufactured on a large scale from aminoguanidine formate. It is a non-selective herbicide which inhibits chlorophyll formation and regrowth from buds. Although some derivatives are more effective for some purposes, none of the more complex triazole derivatives has been able to displace aminotriazole as a neutral herbicide and defoliant of cotton. This pesticide is a basic compound that is able to protonate in aqueous solutions depending on the solution *pH*, since the *pK* is 4.14. It occurs in two desmotropic forms (I and II, Scheme 1); 3-amino-1,2,4-triazole is in the form (I) and its salts in the imino form (III).

In our laboratory, we are currently involved in some research projects on environmental problems concerning pesticides and their application in Andalusian (South Spain) agricultural soils. Some investigations on the adsorption of ATA

by the clay mineral montmorillonite have been carried out [1]. It was found that a montmorillonite–ATA complex is formed through interlamellar cations, the adsorption mechanism depending on the clay exchangeable cations. Under another point of view, ATA is also an interesting compound in materials science, since it has been proposed as raw material in the synthesis of ferromagnetic materials through formation of binuclear complexes [2]. However, the thermal behaviour of ATA alone is little understood.

Scheme 1



In the present investigation a thermoanalytical study of ATA has been carried out, using simultaneous DTA–TG in nitrogen flow in order to know the thermal behaviour and stability of ATA. These techniques have been further complemented using evolved gas analysis and mass spectroscopy (EGA–MS). A kinetic study has been also carried out applying different models to DTA–TG data.

Experimental

DTA–TG curves were simultaneously carried out at different heating rates on a Setaram high-temperature apparatus (model 92, 16–18). Samples of 30 mg of ATA (98%, Riedel) were vacuum outgassed for 30 min, and after this, flowing nitrogen (160 cm³/min) was held for 30 min. A flow of nitrogen of 16 cm³/min was hold during the runs up to 1000°C. Calcined alumina was used as a reference material and open Pt crucibles as sample holders.

Evolved gas analysis (EGA) was performed using a Leybold-Heraeus quadrupole Q100 mass spectrometer. This system permits the simultaneous recording, as a function of temperature, of several previously selected *m/z* peaks: 16 (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 and 42. A heating rate of 10 deg·min⁻¹ was used and all the experiments were recorded in vacuum. Mass spectrometry (MS) experiments using solid samples were performed using a Kratos MS80 mass spectrometer operating in electron impact mode.

Results and discussion

Figure 1 shows DTA-TG curves corresponding to the organic pesticide ATA. 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 ATA 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. It is related to kinetic features, as will be shown later. The weight loss is associated with several thermal effects on the DTA curve (Fig. 1). There is a moderate endothermic effect at 270°C, which is more easily observed in the DTA curves performed at lower heating rate (Fig. 2). Very close to this, a very sharp exothermic effect with maximum at 318°C is detected. The final temperature of the first weight loss coincides exactly with the final temperature of the later exothermic effect.

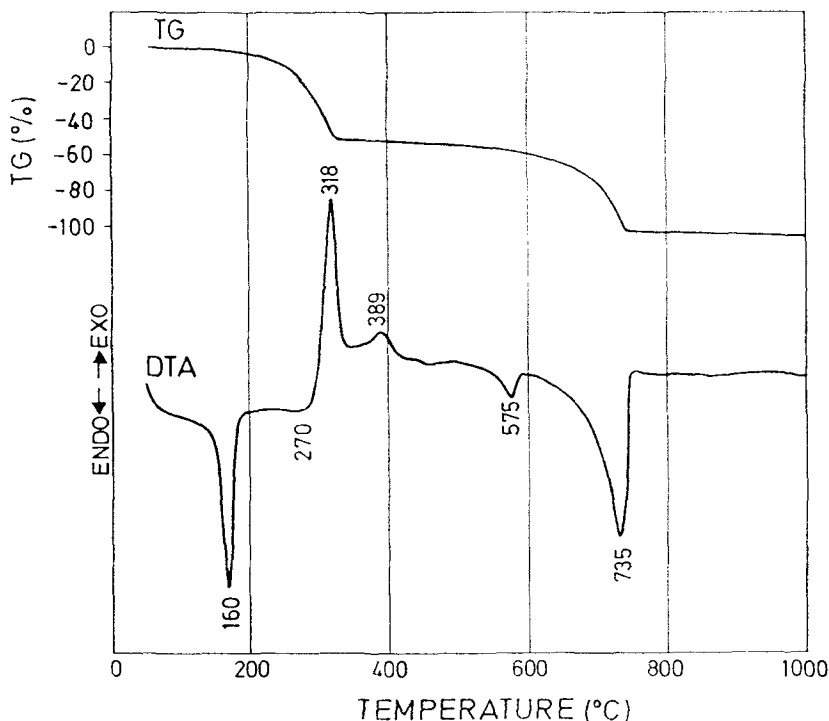


Fig. 1 DTA and TG curves of pure ATA

The products obtained before and after the exothermic peak have been studied by solid mass spectrometry and the evolution of evolved gases, to get an idea about the processes that could originate the first weight loss. The MS analysis of ATA previously heated at 340°C (Fig. 3) indicates that a mixture of com-

pounds is obtained after the first weight loss, with the principal component being a compound of molecular weight 126, together with ATA (molecular weight 84) without becoming decomposing. The analysis of evolved gases (Fig. 4) shows 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 41–42.

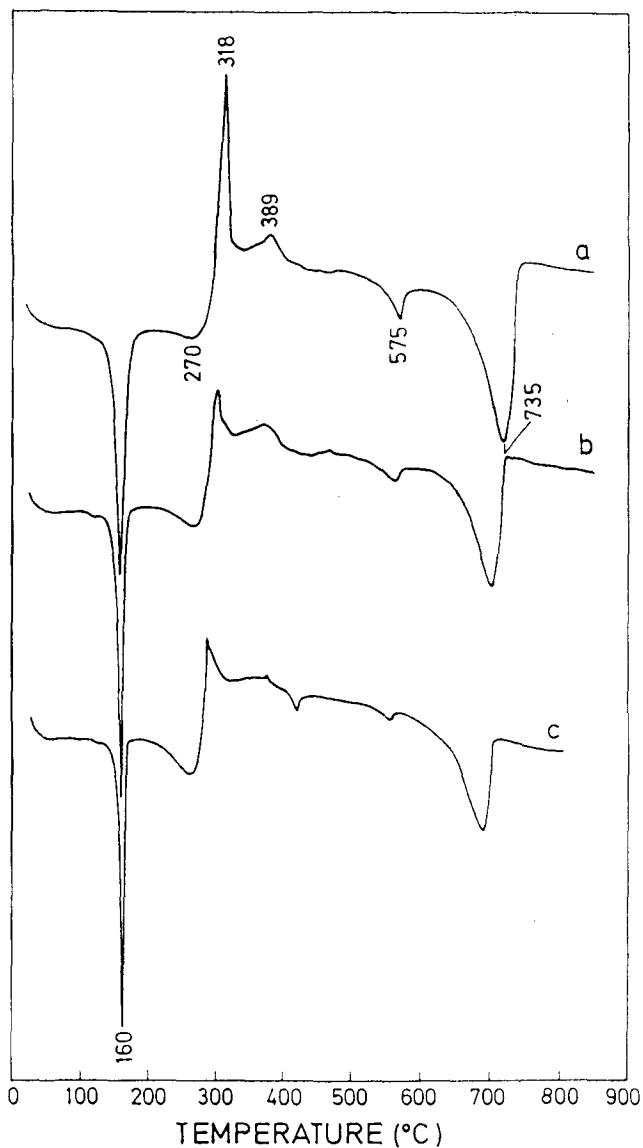


Fig. 2 DTA curves of pure ATA heated at 10(a), 5(b) and 2(c) deg·m⁻¹

The exothermic peak at 318°C could come from an exothermic reaction forming a more stable compound from other precursors. This could correspond to the formation of the compound of molecular weight 126. It is assumed that the formation of this compound needs a previous decomposition of pure ATA in some other products, which further react between them to form it. Such decomposition needs energy, so it would explain the presence of the endothermic effect observed at 270°C. Decomposition products are partially gaseous and their release gives, as a result, the weight loss observed from 220°C (Fig. 1). It is assumed that the pesticide decomposition takes place probably following the scheme 2. It gives rise to two resonant forms corresponding to a compound of molecular weight 42. It coincides with the gaseous compound detected by EGA (Fig. 4). This compound is liberated in part, but another fraction can react with ATA remaining without decomposing, giving rise to the triazole guanidine (N-(2-triazolin)-guanidine), with molecular weight 126 (Scheme 3). Probably, this compound is that one detected by mass spectrometry (Fig. 3).

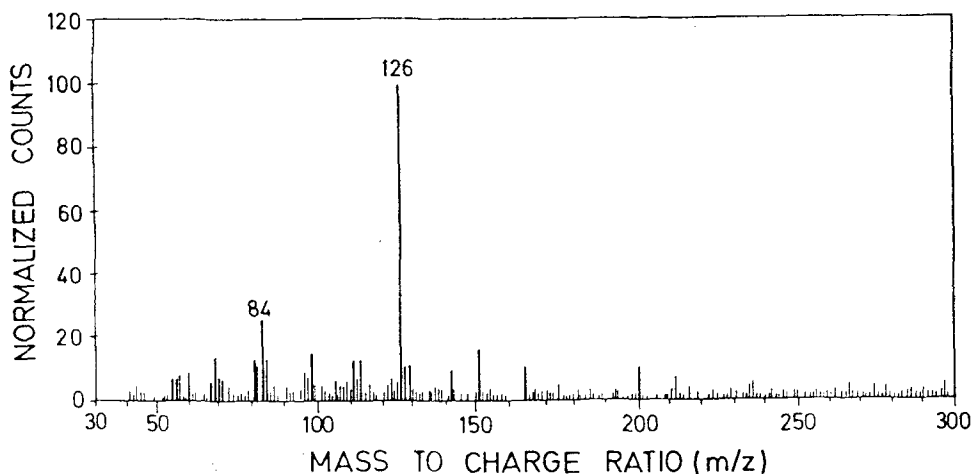


Fig. 3 Mass spectrogram for species present after heating ATA at 340°C

The exothermic effect at 318°C decreases with decreasing heating rates, becoming quite small at 2 deg·min⁻¹ (Fig. 2). It can be associated to the fact that when ATA decomposition temperature is reached, the gaseous decomposition products are liberated until the formation temperature of the new product. This interval of time is longer for low heating rates, allowing to release a higher amount of gas. It is in agreement with the higher weight loss due to gas liberation observed at lower heating rates, in comparison to the higher ones. Then, less amount of the new product of molecular weight 126 can be obtained, and the exothermic effect corresponding to this reaction is detected smaller.

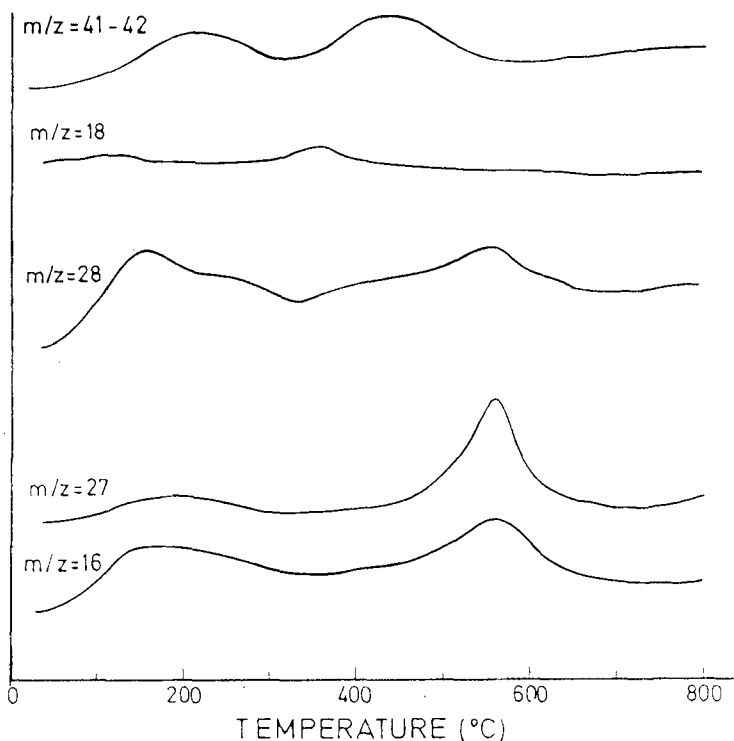
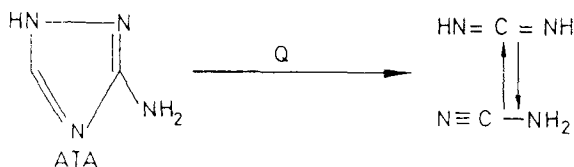
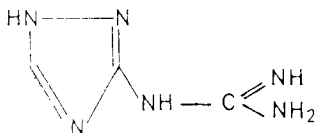


Fig. 4 Gas evolution curves obtained by thermal analysis of pure ATA. Mass peaks $m/z=16$ (ammonia), 18 (water), 27 (hydrogen cyanide), 28 (nitrogen), 41 ($\times 10$) and 42 ($\times 10$)

Scheme 2



Scheme 3



From 340°C and above, very little weight loss is observed until reaching 600°C. At this temperature the total decomposition of the organic products 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. 4). This total decomposition is accompanied by an endothermic effect with maximum at 735°C and after this point, the decomposition finishes. The weight loss obtained during the ATA heating and subsequent degradation process is 96%.

The first stage of ATA decomposition (between 220–340°C) has been kinetically analyzed because the thermal stability of ATA seems to be dependent on the kinetic parameters of this first stage, as found in other systems [3]. The Ozawa's method [4] has been used to determine the activation energy from plots of the logarithms of heating rates (β) vs. the inverse of temperature at a given conversion (from $\alpha = 0.2$ to 0.8), as shown in Fig. 5. The activation energy was calculated from the average value for the different conversions, resulting a value of $E_a = 124 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$. The Kissinger's method [5] was also applied. A plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$, being T_p the DTA peak temperature, is shown in Fig. 6. A value of $E_a = 140 \pm 8 \text{ kJ} \cdot \text{mol}^{-1}$ was obtained in well agreement with the value obtained applying the Ozawa's method.

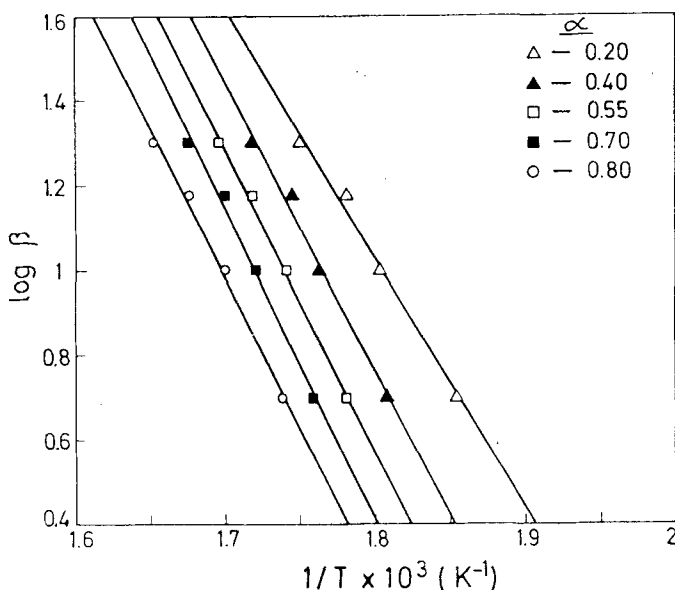


Fig. 5 Ozawa's plot of $\log \beta$ vs. the reciprocal of temperature ($\alpha = 0.2-0.8$)

Furthermore, the results obtained from kinetic analysis of these curves in the range of conversion $0.2 < \alpha < 0.8$ by means of the Coats and Redfern method [6], taking into account different $g(\alpha)$ functions, have been included in Table 1. A comparison of these results with those previously obtained by Ozawa and Kissinger methods' showed that a reasonable well agreement between the activation energies obtained from both methods can be achieved only if it is as-

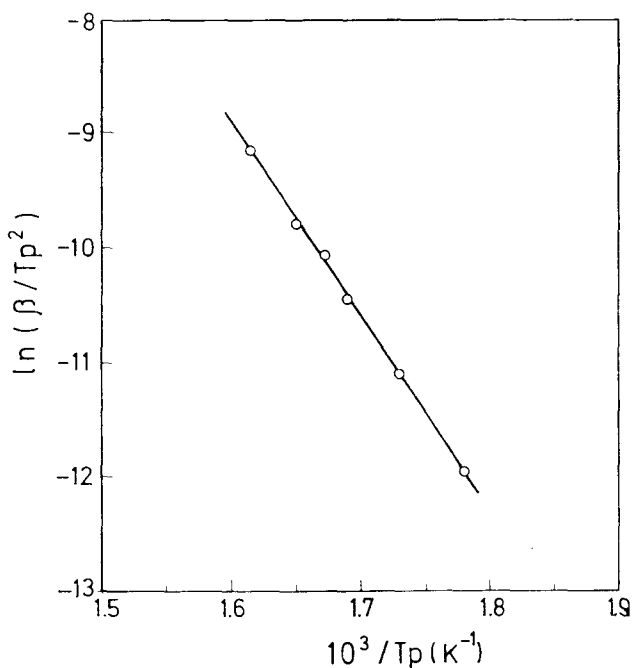


Fig. 6 Kissinger's plot of $\ln(\beta/T_p^2)$ vs. the reciprocal of the DTA peak temperature

Table 1 Kinetic parameters and correlation coefficients corresponding the first stage of ATA decomposition, calculated by means of the Arrhenius equation ($\beta = 10 \text{ deg}\cdot\text{min}^{-1}$; $\alpha = 0.10, 0.25, 0.40, 0.55, 0.70, 0.85$; $T = 533, 554, 567, 574, 581, 588 \text{ K}$)

Mechanism	$E/\text{kJ}\cdot\text{mol}^{-1}$	A/s^{-1}	r
R ₁	92.6 ± 1.7	5.9 ± 0.37	0.9993
R ₂	107.3 ± 2.8	7.4 ± 0.59	0.9987
R ₃	112.8 ± 4.1	7.9 ± 0.86	0.9974
F ₁	124.6 ± 7.2	9.1 ± 1.52	0.9935
A _{1.5}	80.0 ± 4.7	4.9 ± 1.01	0.9931
A ₂	57.7 ± 3.5	2.8 ± 0.75	0.9926
A _{2.5}	44.3 ± 2.8	1.4 ± 0.60	0.9920
A ₃	35.4 ± 2.4	0.5 ± 0.50	0.9912
A ₄	24.2 ± 1.7	-0.7 ± 0.37	0.9898
D ₁	194.5 ± 3.3	15.2 ± 0.70	0.9994
D ₂	212.6 ± 3.5	16.7 ± 0.75	0.9995
D ₃	234.9 ± 8.2	18.3 ± 1.74	0.9976
D ₄	220.0 ± 4.9	16.8 ± 1.03	0.9990

sumed that the thermal decomposition of ATA fits on F1 kinetic model. Moreover, this result is in excellent agreement with the value of $n=1$ and $E_a=130 \text{ kJ}\cdot\text{mol}^{-1}$ obtained from the Freeman and Carroll [7] method.

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This work was supported by the CICYT (project No. AMB92-0394). We thank Dr. M. A. Pradera for the MS data, and Dr. J. M. Llera for his suggestions.

References

- 1 E. Morillo, J. L. Pérez-Rodríguez and C. Maqueda, *Clay Miner.*, 26 (1992) 269.
- 2 A. Lukaszewicz, J. Michalik, J. Mikosz, L. Walis and I. Wozniak, *Mater. Lett.*, 14 (1991) 127.
- 3 M. Kamimoto, R. Sakamoto, Y. Takahashi, K. Kanari and T. Ozawa, *Thermochim. Acta*, 74 (1984) 281.
- 4 T. Ozawa, *Bull. Chem. Soc. Japan*, 38 (1965) 1881.
- 5 H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, 57 (1956) 217.
- 6 A. W. Coats and J. P. Redfern, *Nature*, 208 (1964) 68.
- 7 E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 62 (1958) 394.

Zusammenfassung — Vorliegend wird unter Einsatz simultaner DTA-TG im Stickstofffluß eine thermoanalytische Untersuchung des Pestizides 3-Amino-1,2,4-triazol (ATA) durchgeführt, um dessen thermisches Verhalten und Stabilität zu bestimmen. Diese Techniken wurden weiterhin durch Analyse der freigesetzten Gase und durch Massenspektroskopie (EGA-MS) ergänzt. Es wurden zwei verschiedene Schritte der Zersetzung von ATA beobachtet: nach dem ersten Zersetzungsschritt erhält man ein Verbindungsgemisch, wobei die Hauptkomponente laut MS-Angaben das Molekulgewicht 126 besitzt. Sie wird in einer Reaktion erster Ordnung gebildet, E_a beträgt laut kinetischer Untersuchung 1248 kJ/mol . Der zweite Zersetzungsschritt findet unter Freisetzung von HCN und NH_3 bei etwa 735°C statt, der endgültige Gewichtsverlust beträgt 96%.