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THERMAL DECOMPOSITION OF TRIAZINE HERBICIDES II. 6-Chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine (atrazine) and its metabolites

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Abstract

Thermal degradation of atrazine and its metabolites has been investigated using a thermogravimetric technique (TG) with the application of three types of crucibles: opened, Knudsen type and labyrinth type, and non-isothermal DSC method, using hermetically closed and opened alumina sample pans. The great influence of decomposition conditions (the crucible type) on thermal degradation was observed. TG analysis showed that the degradation process of atrazine took place in three stages. The increase of amino groups in triazine ring increases the amount of non-volatile thermal degradation products by association. The presence of chlorine substituent facilitates the forming of products with low volatility. Hydroxyatrazine decomposes only in one stage process. The dealkylation process observed in hermetical sample pans (DSC) was two-stage and in open sample pans one-stage process.

Keywords: atrazine, DSC, metabolites, TG, thermal decomposition

Introduction

The investigations aiming at establishing the mechanism of thermal degradation of triazine herbicides have been performed for 6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine (atrazine) and its metabolites: 6-chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine (desethylatrazine), 6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine (deisopropylatrazine), 4-ethylamino-6[(1-methylethyl) amino]-1,3,5-triazine-2(1H)-one (hydroxyatrazine) and 6-chloro-1,3,5-triazine-2,4-diamine (desethyl-deisopropylatrazine).

Atrazine is a selective triazine herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, christmas trees, and other crops, and in conifer reforestation plantings. It is also used as a non-selective herbicide on non-cropped industrial lands. It is a very persistent compound. Atrazine can be transformed into metabolites by dechlorination and dealkylation of ethyl and isopropyl groups. In a soil, acid-catalysed chemical process leads to hydrolysis of atrazine

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forming hydroxyatrazine [1]. Hydroxylated analog of atrazine has lower solubility in water. This compound can contaminate drinking water. The hydrolysis is an important detoxification route for atrazine, because hydroxyanalogs are not toxic to aquatic plants [2]. N-dealkylation is mediated by microorganisms, but it is also possible to obtain the dealkylation products by abiotic process i.e. using δ-MnO_2 as a catalyst [3]. The dealkylation occurs also during the photodegradation reactions, using Fenton reagent [4] and ozonolysis [5]. The content of dealkylation products and reaction rate are different for biological and abiotic process.

Thermal degradation of triazine herbicides was investigated using pyrolysis [6]. The decomposition mechanism is similar to degradation of esters by Chugayev reaction and undergoes by cyclic transition state, dealkylation and elimination of olefines. The mechanism was proposed basing on quantitative determination of olefines, released from the reaction phase.

The investigations on application of thermal methods for determination thermal stability of pesticides have been made and presented in [7]. The kinetic model of thermal degradation of cyanazine (2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile) was elaborated and presented in part I [8].

The aim of this work is the determination of atrazine and its metabolites thermal degradation mechanism in liquid phase. The different conditions of experiment were applied. The metabolites were used to determine the influence of substituents on thermal stabillity of atrazine.

Experimental

The investigations were performed using the differential scanning calorimeter, heat flux, DSC-605, all samples with heating rate 2 K min^{-1}, using two types of alumina sample pans: hermetically sealed under pressure of ~1.3 kPa, and pans with pin holes (0.05 mm ID). For TG measurements by Q technique Derivatograph PC, MOM Budapest (using labyrinth crucibles), thermobalance TG-50/TA-4000 by Mettler (using Knudsen crucibles with holes 0.5 mm ID) and TG/DTA apparatus (SDT 2960 TA Instruments) (open crucibles) were used. The measurement was carried out in air atmosphere. The triazines used in the measurement were obtained and purified in the Institute of Organic Industrial Chemistry to obtain analytical standards with purity not less than 99.0%.

Results and discussion

TG measurements were performed in different crucibles to determine the influence of conditions on the shape of thermogravimetric curve. Figure 1 presents the typical shape of DTA and TG curves obtained in open crucibles (II and I respectively).

The mass loss (%) begins in the melting temperature and increases monotonically. The endothermic peaks observed on the DTA curve confirm that mass loss is caused mainly by the sample evaporation. In the terminal phase of decomposition a

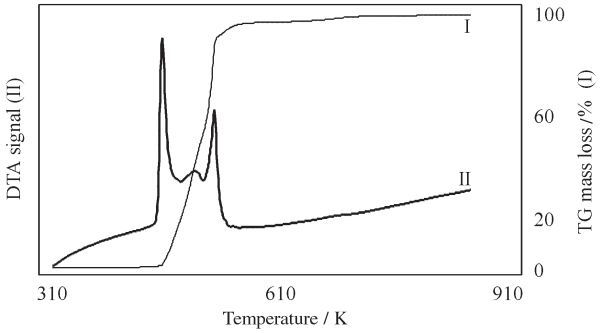

Fig. 1 TG (I) and DTA (II) curves of thermal degradation of atrazine in the open crucible

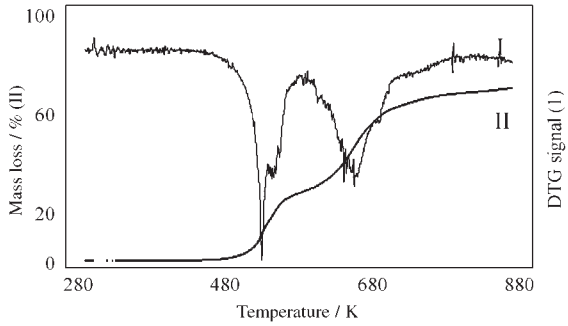

Fig. 2 DTG (I) and TG (II) degradation curves of atrazine in Knudsen cell (ϕ=0.5 mm)

small amount of non-volatile thermal decomposition products appears. The quick evaporation of examined substance in open crucibles does not allow to observe the thermal degradation in liquid phase. For the purpose of diminishing the rate of evaporation, the Knudsen cells were applied. DTG (I) and TG (II) curves are presented in Fig. 2. There are two distinguished steps of thermal decomposition, confirmed by two peaks maxima in the DTG curve.

In order to decrease the influence of mass evaporation on the total mass loss during the measurements, the labyrinth crucibles were applied. For optimizing experimental conditions the influence of heating rate (β) changes of at the constant rate of mass loss Q=0.1 mg min^{-1} on the shape of TG curve was examined. The results were presented in Fig. 3. The measurements were performed at heating rates β=2, 5 and 10 K min^{-1}. The increase of temperature of the decomposition beginning was observed with the increase of β. This temperature is lowered in the course of the decomposition due to the effect of Q technique action.

TG curves are converging for higher degree of conversion with different heating rate β applied. It is worth mentioning that TG curves for β=5 and 10 K min^{-1} show the characteristic oscillations, but for β=2 K min^{-1} the curve is smooth. In our opinion, it is connected with clogs of throughput of volatile decomposition products in the labyrinth. For small heating rate β=2 K min^{-1} the flow of degradation products is small,

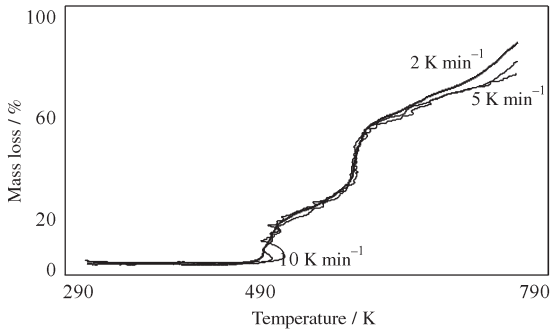

Fig. 3 TG degradation curves for the following three heating rates β=2 K min^{-1}; 5 K min^{-1} and 10 K min^{-1} with constant Q=0.1 mg min^{-1} in labyrinth crucible, using Q technique

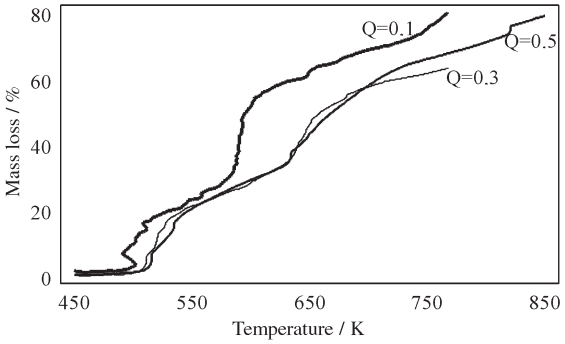

Fig. 4 TG degradation curves obtained with different rates of mass loss Q; Q=0.1, 0.3, 0.5 mg min^{-1}

which ensures the continuity of flow. The investigations on the influence of mass loss rate (Q) on the shape of TG curve were carried out. The results are presented in Fig. 4. The characteristic jumps on TG curve, attributed to steps of degradation are not well distinguishable for the great rate of mass loss change Q (Q=0.5 mg min^{-1}). If the Q diminishes, the rate of mass loss connected with evacuation of gaseous products is significant. Taking that into account, the measurements for in Q=0.1 mg min^{-1} were performed. The changes of mass loss for particular steps were determined by linear extrapolation of the part of TG near the jump in the curve. It was considered that the jump of mass loss is connected with evolving of volatile products, occurring during thermal decomposition related to given decomposition step. The calculation results are collected in Table 1. The first step of thermal decomposition is probably attributed to removing the alkyl groups. In the case of removing the ethyl group to form ethylene the theoretical mass loss is 13.5 and 20.0% for removing the isopropyl group to form isopropylene. The value of mass loss of the both mentioned groups is about 33.5% in the case of removing the ethyl and isopropyl group. This is a good agreement with experimental value 32.9% for the first and second step. The experimental

value ascribed to I step (about 16.5%) suggests that the removal of isopropyl group plays the predominant role. The third step relates to removing the chlorine. Trace amounts of chlorine were only detected by elementary analysis of samples after the measurements (the final temperature 775 K). The mass loss of alkyl and chlorine group is 49.0% and this value is consistent with the experimental value 54.0%. A little higher experimental result is due to the evaporation of investigated sample during the measurement. The similar steps are observed in the case of the degradation of atrazine metabolites. The dealkylation of atrazine could be confirmed by the examination of desethylatrazine and desisopropylatrazine. The next steps should be attributed by chlorine separation. The results are presented in Table 2.

Table 1 Temperatures (K) and mass losses (%) for steps of atrazine thermal degradation with Q=0.1 mg min^{-1}

	Sample 1		Sample 2		Sample 3		Average	
	T/K	Mass loss/%	T/K	Mass loss/%	T/K	Mass loss/%	T/K	Mass loss/%
I step	508.54	15.85	517.48	17.46	507.53	16.26	511.18	16.52
II step	584.71	31.33	585.51	33.34	587.23	34.16	585.81	32.94
III step	603.69	53.76	601.52	52.89	607.25	55.35	604.15	54.00

Table 2 Temperatures (K) and mass losses (%) for thermal decomposition steps of atrazine metabolites

Sample name	Decomposition temperature/K	Mass loss/%	Mass loss group elimination
Desethyldesiso-propylatrazine	546.430	4.94628	
	553.538	12.3906	
	625.962	17.8846	
Desethylatrazine	609.303	23.9760	Theoret. 22.99%-isopropyl group
	611.935	35.6595	18.71%-Cl
Desisopro-pylatrazine	599.154	25.8357	Theoret. 16.86%-ethyl group
	604.028	32.9668	20.34%-Cl
Hydroxyatrazine	606.344	74.2048	

Figure 5 presents the TG curves of atrazine metabolites degradation. It can be concluded as shown in Fig. 5 that with increase in amount of free amino group, the amount of non-volatile products is growing. It is worth mentioning that the introduction of hydroxy group instead of Cl causes the one-step degradation is almost without non-volatile products. A big jump in the TG curve at 600 K proves that degradation can undergo with triazine ring cleavage. It is the argument that chlorine group in the molecule contributes to forming of non-volatile products.

Some DSC experiments were made in order to carry out the decomposition of atrazine in open (the hole diameter is 0.05 mm ID) and hermetically closed sample pans. In hermetically closed sample pans the decomposition is a multi-step process.

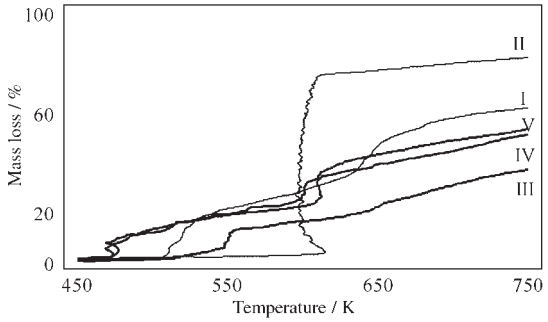

Fig. 5 TG degradation curves of atrazine metabolites; I – atrazine; II – hydroxyatrazine; III – desethyldesisopropylatrazine; IV – desisopropylatrazine;

We suppose that in this condition the reaction phase goes to the thermodynamic equilibrium state causing the setback of decomposition process. During the next step the decomposition process is released, in higher temperatures, by the association to form non-volatile products, insoluble in reaction phase. In the case of open sample pan, the gaseous decomposition products leave the reaction phase, which causes non impeded decomposition process. Additionally in open sample pan the small exothermal effect. After the melting process is observed and probably it is associated with the influence of air (oxygen) on atrazine. Figure 6 presents two typical decomposition DSC curves of atrazine, using hermetic and open sample pan. It was observed that in the case of decomposition of atrazine metabolites, performed in close sample pans, the decomposition curves was also complex and multi-step.

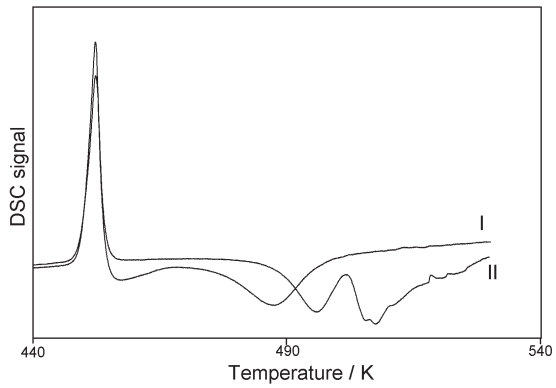

Fig. 6 DSC degradation curves of atrazine in open sample pan (I) and hermetically closed sample pan (II)

TG and DSC results indicate that the stability of investigated compounds decrease in the following order: hydroxyatrazine<desethyldesisopropylatrazine<atrazine<desethylatrazine and desisopropyloatrazine. The increased stability of atrazine in comparison to indicate some contributions of steric effects of alkyl groups on the dealkylation processes.

Conclusions

The conditions of thermal decompositions of triazine sample have an influence on the shape of termogravimetric curve. It is closely connected with the type of crucible used for measurement and proper interpretation of decomposition process. In order to achieve the most reliable results, the evaporation rate of atrazine should be significantly less than the mass loss due to the degradation. The reaction of decomposition in hermetic sample pans can be impeded because the decomposition products are in termodynamic equilibrium. The Cl substituent in triazine molecule has conclusive influence on dealkylation and association (polymerization) to form of non-volatile products. It was observed that the increase of non-substituted amino group faciliates forming non-volatile decomposition products by association.

References

1 L. E. Ericson and K. H. Lee, Crit. Rev. in Environ. Sci. Tech., 19 (1998) 46.
2 W. Mersie, J. Liu and C. Seybold, Weed Sci., 46 (1998) 480.
3 M. A. Cheney and J. Y. Shin, Coll. and Surfaces A, 137 (1998) 267.
4 M. E. Balmer and B. Sulzberger, Environ. Sci. Tech., 33 (1999) 2418.
5 F. J. Beltran, J. Rivas and B. Acedo, J. Environ. Sci. Health B, 34 (1999) 449.
6 Z. D. Tadic and S. K. Ries, J. Agr. Food Chem, 19 (1971) 1.
7 A. Książczak and T. Książczak, J. Thermal Anal., 41 (1994) 1153.
8 K. Drożdżewska, A. Książczak and T. Książczak, J. Therm. Anal. Cal., 60 (2000) 103.