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Thermal degradation of triazine herbicides substituted by Cl. Identification of triazine degradation products

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Abstract

The thermal degradation of biologically active triazines, whose Cl substituent is bonded to the heterocyclic ring, is a multi-stage process. The final products are high molecular compounds. Investigations of these compounds were performed using the thermogravimetric method (TG) at the temperature range from ambient temperature to about 850 K using the *Q* technique and labyrinth crucibles. MALDI TOF spectrometry and elementary analysis were also used to confirm the degradation products' structures. The compounds identified after the measurement were identified as dealkylation products, compounds with removed amino group and high molecular weight products.

Keywords: Triazine herbicides; Thermogravimetry; MALDI TOF spectrometry; Degradation; Dealkylation

1. Introduction

The biologically active triazines that were examined in this work had the six-member ring substituted symmetrically or unsymetrically with nitrogen atoms, *N*-alkylamino groups and Cl substituent. Their thermal behavior was observed using thermogravimetry. It can be expected that one step of the degradation process of these compounds includes dealkylation leading to the amino groups. Tadic and Ries [1] concluded that heating of some triazines up to the temperature of 513 K causes decomposition with the evolution of gaseous olefins. The experimental data obtained by the authors shows that in the case of atrazine more propylene is produced than ethylene. The presence of R–Cl compounds after triazine degradation were also detected and four stages degradation of atrazine was described by Matuschek et al. [2]. The detailed mechanism of the thermal behavior of amino groups during heating was described in literature concerning melamine. This mechanism can be applied to predict thermal degradation mechanism in the case of triazines. Costa and Camino [3] showed that thermal changes take place in melamine when it is heated to above 873 K due to two different mechanisms, both of which lead to the formation of high molecular products. The first mechanism yields products in the form of condensed rings, the second one yields polymeric products, whose triazine rings are bonded by amino bridges. During thermal changes melamine forms three different polymeric compounds known as: melem, melam and melon.

The presence of amino groups and the Cl substituent enable high molecular weight products to form. Triazines can be applied during the synthesis of polymers in the reaction of two C1 substituted chlorotriazines and diamines. Such a reaction takes place in ambient temperature and leads to the formation of poliamines [4] and the elimination of HCl.

Rodante et al. [5] have examined the thermal changes of some triazines using the thermogravimetric method (TG) and DSC. They pointed to evaporation as the main process that takes place. Thermal degradation in the liquid phase was observed only in the case of cyanazine, anilazine and metribuzin. The investigations were carried out with a simultaneous analysis of volatile products using the mass spectrometry method. Our examinations of atrazine and its metabolite's thermal degradation [6,7] using thermogravimetric method in labyrinth crucibles, which hindered the investigated substance from evaporating, showed

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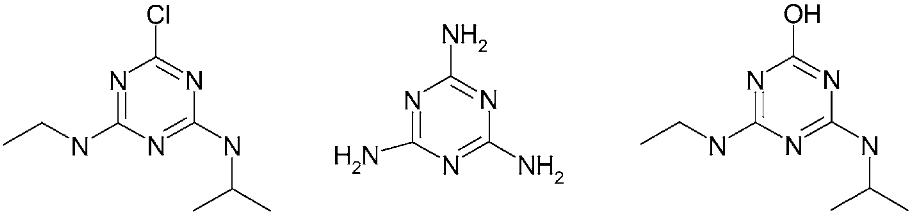
that it is possible to obtain and interpret the complex TG curves. These curves showed that the mechanism of thermal changes of triazines is complicated and multi-step. The shape of TG curves is determined by the type of crucible used and process control: heating rate and mass loss rate. There is no reliable information in literature concerning the behavior of substituted triazines at high temperatures. This was the reason to begin systematic investigations using thermoanalytical methods. The aim of this work is to apply thermal methods for substituted triazines containing the Cl substituent and to examine the influence of the different substituents on the reactions that occur in high temperatures.

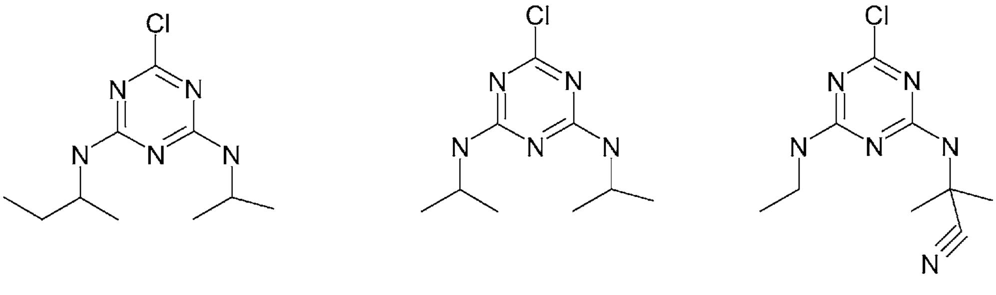
2. Experimental

Triazines with purity of above 99% that are manufactured by the Institute of Industrial Organic Chemistry as certified reference materials were used in measurements. These compounds were used in the examination of: atrazine (6-chloro-N^2-ethylo-N^4-isopropylo-1,3,5-triazine-2,4-diamine) and known metabolites of atrazine: atrazine-desethyl (6-chloro-*N*-(1-methylethyl)-1,3,5-triazine-2,4-diamine), atrazine-deisopropyl (6-chloro-*N*-ethyl-1,3,5-triazine-2,4-diamine), hydroxyatrazine (4-ethylamino-6-[(1-methylethyl)amino]-1,3,5-triazine-2-(1*H*)-on), atrazine desethyl-deisopropyl (6-chloro-1,3,5-triazine-2,4-diamine), melamine (2,4,6-triamine–6-triazine) and other Cl substituted triazines like: 6-chloro-N^2, N^4-diisopropyl-1,3,5-triazine-2,4-diamine (propazine), 6-chloro-N^2-ethyl-N^4-sec-butyl-1,3,5-triazine-2,4-diamine (sebuthylazine), 6-chloro-N^2, N^4-diethyl-1,3,5-triazyne-2,4-diamine (simazine), 2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile (cyanazine). The aim of examining melamine was to determine the role of amino groups in thermal changes of triazines. The structures of these compounds are presented in Fig. 1 so that it will be easier to understand the thermal changes under discussion.

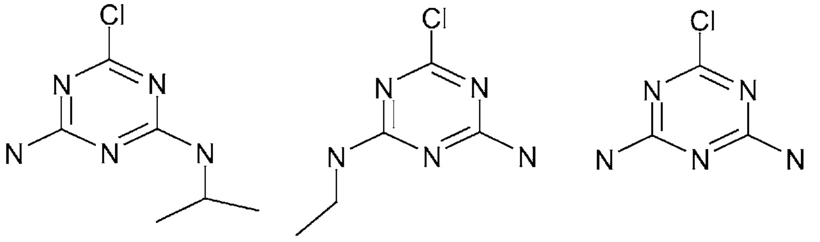
Measurements using the *Q* method (quasi-isothermal, quasi-isobaric) of thermogravimetry were carried out in labyrinth crucibles on the MOM Budapest Derivatograph PC with the heating rate of 5 K/min and with mass loss $Q = 0.1$ mg/min. Use of platinum labyrinth crucibles lowers the evaporation rate and the evolution of volatile



Atrazine Melamine Hydroxyatrazine



Sebuthylazine Propazine Cyanazine



Desethylatrazine Desisopropylatrazine Desethyl-desisopropylatrazine

Fig. 1. Structures of the investigated triazines.

products from the reaction phase. Measurements were performed in inert atmosphere under Ar in the temperature range of 50–500 °C. The choice of measurement conditions selected for thermogravimetric analysis was based on earlier published [8] results.

The content of C, H, N in products obtaining after thermal changes was determined by elementary analysis using the Perkin Elmer Model PE Series II CHNS/O analyzer. The MALDI TOF method with a nitrogen laser source with the wavelength of 227 nm was used to determine mass distribution. The Kratos Kompakt Maldi 4 apparatus was used in these measurements (a single laser pulse lasted 3 ns and had a positive polarity; accelerating voltage was 20 kV; 200 impulses per spectrum).

3. Results

The thermogravimetric analysis of atrazine and its metabolites served to determine the share of individual substituents in the triazine ring during high temperature measurements. These measurements were performed with a constant heating rate and controlled mass loss $Q = 0.1$ mg/min. In this technique the growth of temperature can be halted when mass loss exceeds $Q = 0.1$ mg/min. Sustaining a specified temperature allows a particular reaction to finish in roughly the lowest possible and constant temperature. These conditions help differentiate the steps of thermal change. Two selected compounds were investigated to identify the role of particular substituents in thermal changes. Fig. 2 presents TG curves obtained for atrazine, its metabolites and melamine. The number of non-volatile high molecular compounds can be determined by an analysis of mass loss at particular temperatures. When the mass loss is lower, the amount of high molecular products is greater. The increase of molecular mass of degradation products at high temperatures lowers the vapor pressure and makes more difficult evaporation in measurement conditions. The value of mass loss in final temperature can be used to determine the polymerization efficiency of the examined compound.

All the curves presented in Fig. 2 are multi-stage and some stages are joint for particular compounds. The difference in reactivity between the Cl substituent and the OH substituent can be determined by comparing TG curves for atrazine (curve 2) and hydroxyatrazine (curve 1) presented in Fig. 2. Decomposition of hydroxyatrazine is a one-step process. It takes place in much higher temperatures and yields considerable amounts of volatile products. The multi-stage thermal process in the case of atrazine is reflected in the jumps in the TG curve. The first step is connected with the reactivity of the Cl and NH_2 substituents [6]. The presence of volatile HCl causes the mass losses. The non-volatile compound has a polymeric structure. The presence of the alkyl group in the alkylamino substituent lowers the temperature change of the first step as can be seen from the comparison of the TG curves of atrazine (curve 2), desethylatrazine (curve 3) and desethyldesisopropylatrazyne (curve 5). A comparison of these three curves and the TG curve of melamine (curve 4) shows that the second step of thermal changes takes place in similar temperature ranges. Melamine is subjected to deamination that leads to the formation of high molecular compounds in this temperature range. This comparison indicates that deamination is the second step visible as a jump on the TG curve of thermal degradation for atrazine and its metabolites. In the case of hydroxyatrazine (curve 1) deamination can be observed and takes place in a narrow temperature range. The great mass loss in the case of hydroxyatrazine indicates that dealkylation is accompanied by the evaporation of low molecular products. This suggests the conclusion that the rate of the reaction, which leads to the formation

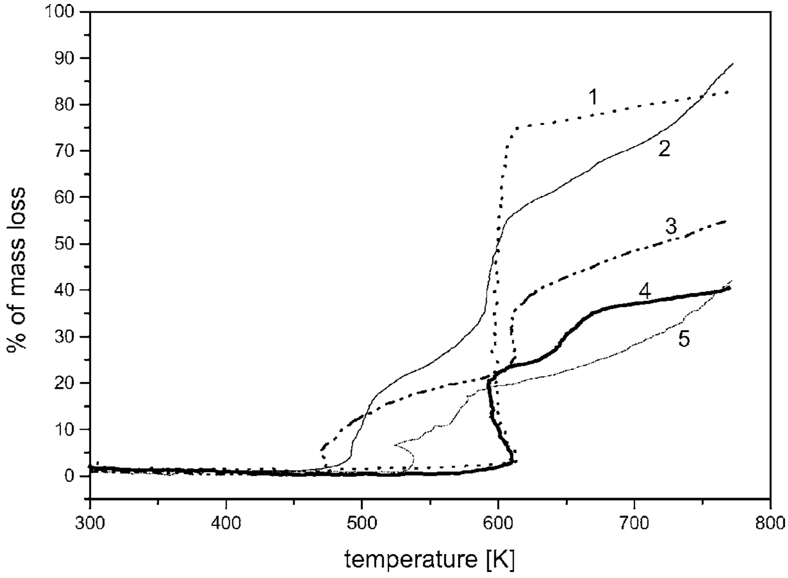


Fig. 2. TG curves of atrazine metabolites and melamine (1-hydroxyatrazine, 2-atrazine, 3-desethylatrazine, 4-melamine, 5-desethyldesisopropylatrazine.

Table 1
Results of elementary analysis of thermal degradation products of desisopropyloatrazine after TG measurement at final temperatures 500 and 772 K

Element	%N	%H	%C	%Cl
Calculated from molecular formula	40.32	4.03	36.56	20.45
Products obtained at 500 K	42.70	4.56	36.06	12.16
Products obtained at 772 K	54.68	2.14	40.36	0.7

of high molecular products, is slower than the evaporation of volatile low molecular products. The next step of deamination attributed to crosslinking is visible in the melamine TG curve. The same step, connected with mass loss is also visible in the same temperature range for atrazine and its dealkilated metabolites on the TG curves when the scale is reduced. The reactivity of Cl, OH and NH_2 as well as their ability to form high molecular products can be estimated by taking into consideration the results of comparing TG curves for atrazine and its dealkylated metabolites with melamine and hydroxyatrazine. The Cl substituent presents the greatest reactivity, whereas the OH group the smallest reactivity. The results of mass loss observed for 750 K suggest that if the amount of alkyl groups in the molecule is smaller the mass fraction of non-volatile products is higher. This observation complies with the interpretation of the steps in the TG curves. Analyses of the thermal degradation products after TG measurements were performed to confirm the observations discussed above. The final temperatures of the measurements were chosen as to allow the determination of products for every step of the reaction. Simultaneously analyses of degradation products were carried out during isothermal conditioning in chosen temperatures.

MALDI TOF was used to examine degradation products of desethylatrazine after TG measurements for two final temperatures 500 and 772 K. Elementary analysis was additionally performed. The first temperature comprises the first step of decomposition (in Fig. 2, curve 3) and the second is the final measurement temperature. The content of C, H, N and Cl was determined. Table 1 presents the percentage content of elements calculated theoretically for desisopropylatrazine; average values for measurements performed for samples after TG analysis at temperature 500 and 772 K.

Results of the analysis show that Cl content in the sample gradually decreases before 500 K. At 772 K the loss of Cl is almost complete. This result confirms the conclusion that the first step of mass loss visible on the TG curve corresponds to the release of HCl.

The measurement was carried out up to the final temperature of 572 K to determine the products of chemical changes in atrazine that undergo in every step (before the second step on TG curve). Atrazine was also conditioned in solid phase in a closed crucible at a temperature of 435 K for 7 h to examine the thermal decomposition products by using the MALDI TOF method to determine the resolution of molecule mass. The mass resolutions of atrazine that was stored for 7 h at temperature 435 K and after the TG measurement at 572 K are presented in Figs. 3 and 4 respectively. The difference between consecutive peaks was 14 D (g/mol).

The MALDI TOF spectra show that the high molecular structures were folded in many fragments. In the case of the sample stored in lower temperature the mass resolution consists of groups of peaks. The difference between peak maxima was 179 D. This molecular mass responds to a

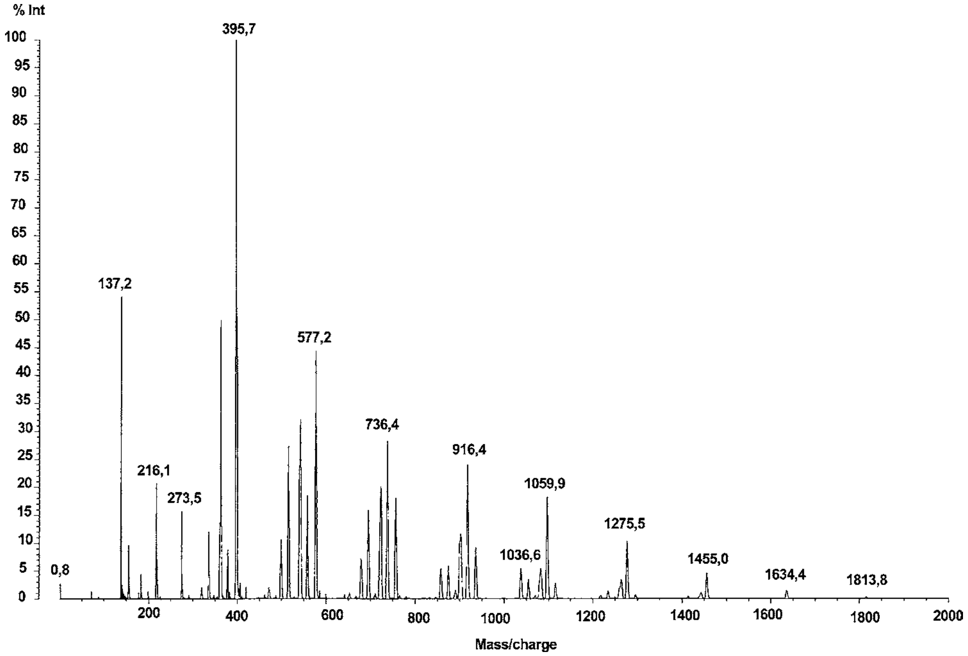


Fig. 3. MALDI TOF spectra of atrazine conditioned at 435 K for 7 h in the closed sample pan.

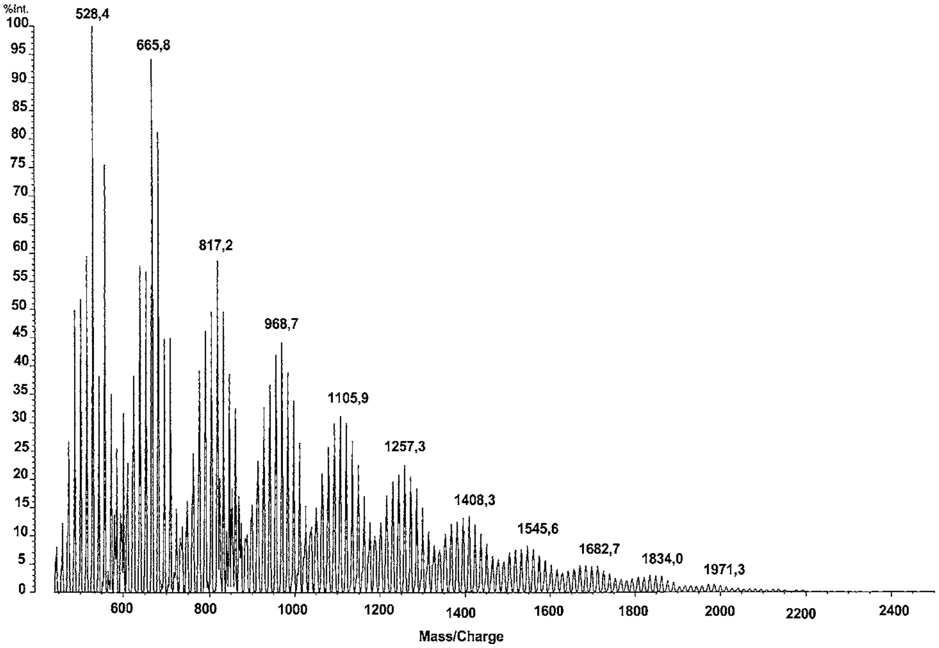


Fig. 4. MALDI TOF spectra of decomposition products of atrazine after TG analysis at 572 K.

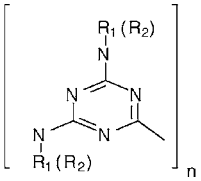
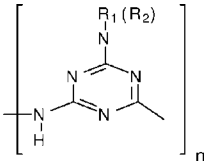
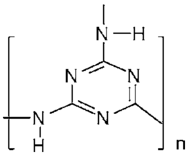
ring structure without Cl, but with both alkylamino groups. This structure was presented in Table 2 and described as structure I.

The resolution of molecular mass for the atrazine sample obtained after the TG measurement until 572 K shows that differences between maxima of molecular masses in particular groups of peaks occur and are equal 137 or 151 D. This structure was specified as structure II and also placed in Table 2. These results show that both alkyloamino groups: ethyl and isopropyl undergo dealkylation with equal probability. When the isopropyl group is detached the mer mass is 137 D, whereas when the ethyl group is detached the mer mass is 151 D.

The lack of Cl in the mer structure is observed even after conditioning the atrazine sample at 435 K. Information obtained from molecular mass resolution suggests that high molecular products with several rings bonded with –NH– bridges are formed after the thermal degradation of atrazine. At higher temperatures (up to 572 K) the mer structure lacks one alkyl group.

The temperature range of the second jump on the TG curves of atrazine and its metabolites is close to the tempera-

Table 2
The structural changes of mer in particular steps of thermal degradation and calculated mass losses for atrazine

The number of degradation step (structure number)	Chemical formula	Mass loss for particular step (%)
1. Elimination of HCl (structure I)		16.92
2. Elimination of first alkyl (structure II)		37.28
3. Elimination of second alkyl (structure III)		53.41
4. Forming of condensed ring (structure IV)	$C_3N_3H_{3/2}$	63.37

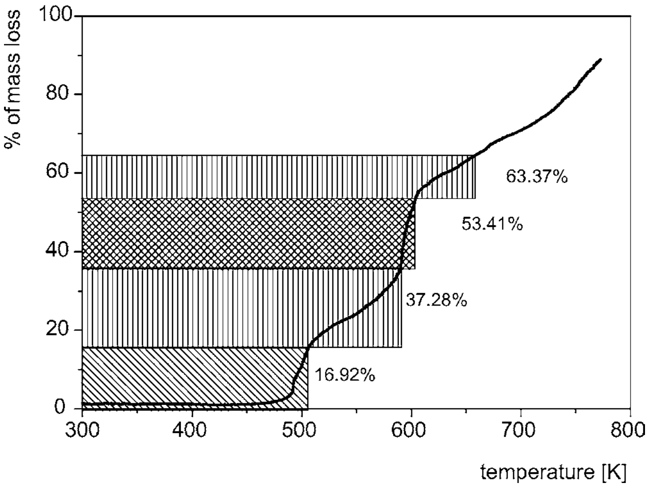


Fig. 5. TG curve of atrazine and calculated mass losses (%) based on the structures of different mer presented in Table 2.

ture range of the first jump on the TG curve of melamine. The proposed structure of this product is similar as the structure of the mer after deamination and is described as structure III in Table 2. The molecular mass of this mer is 100.5, the predicted weight loss of melamine mass is about 20% and complies with the mass loss determined from the TG curve. In the case of melamine condensed structures the molecular formula is $C_6N_6H_3$. The formula for one molecule of melamine can be formally expressed as $C_3N_3H_{3/2}$. The mass loss for melamine calculated according to the considered structure is equal about 37% and complies with the experimental value calculated from TG curve 4, presented in Fig. 2.

The following sequence of thermal degradation steps of atrazine and other triazines containing Cl substituents is proposed based on the above-discussed independent results:

1. Elimination of hydrogen chloride and formation of the mer corresponding to structure I.
2. Elimination of alkyl groups and formation of the mer corresponding to structure II.
3. Deamination, formation of the mer corresponding to structure III.
4. Formation of condensed structure ($C_6N_6H_3$) and formation of the mer corresponding to structure IV.

The percent of mass loss in the case of the above-mentioned four mer structures was calculated with the assumption that the participation of terminal groups is negligible. The structure of mer I and examples of atrazine mass loss calculations are presented in Table 2. Fig. 5 presents the TG curve of atrazine and calculated steps of mass losses based on proposed mer structures for particular steps of thermal changes (marked rectangular areas). The steps of mass losses visible on the TG curve comply with calculations based on the proposed mechanism of thermal changes.

Table 3 presents the mass losses of the examined triazines calculated according to mer structures presented in Table 2. The characteristic changes in TG curves presented in Fig. 2 comply with the values of particular steps described in Table 3.

The TG curve for simazine is presented in Fig. 6, whereas Fig. 7 presents two superimposed TG curves, for sebuthylazine and propazine respectively. The mass losses calculated for particular stages are consistent with experimentally obtained values. Small shifts on TG curves can be the effects of the evaporation of examined compounds and of the incomplete evolution of gaseous products from the reaction vessel during measurements. Slow evaporation of volatile products in measurement conditions influences the sharpness of the observed multi-step thermal processes on TG curves.

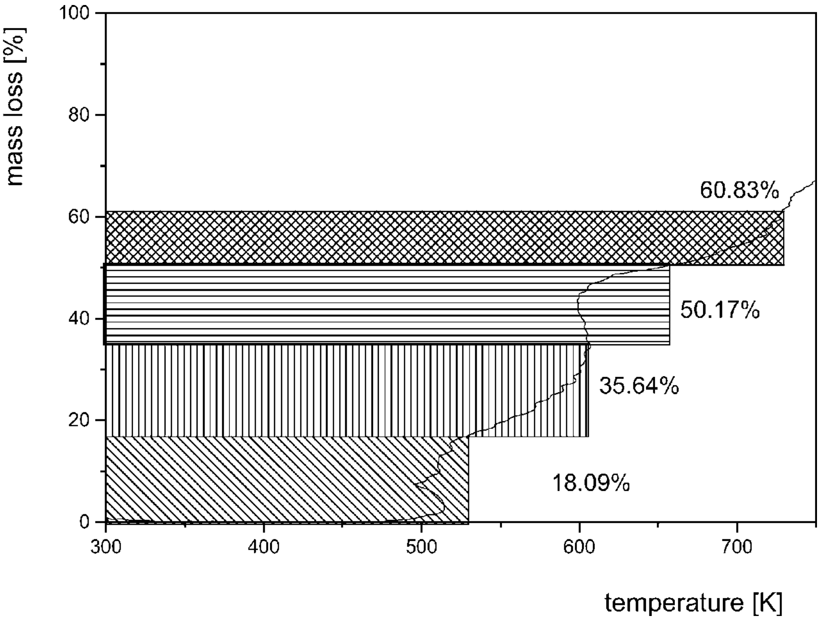


Fig. 6. The TG curve of decomposition of simazine and calculated mass losses (%) based on the structures of different mer presented in Table 2.

Table 3
Theoretical mass losses (%) in particular steps for Cl substituted triazines

Name of compound	Mass loss at I step (%)	Mass loss at II step (%)	Mass loss at III step (%)	Mass loss at IV step (%)
Atrazine	16.92	37.28	53.41	63.37
Simazine	18.09	35.64	50.17	60.83
Sebuthylazine	15.89	38.14	56.25	65.61
Propazine	15.89	38.61	56.25	65.61
Terbuthylazine	15.89	38.14	56.25	65.61
Cyanazine	15.16	38,91	58.25	67.18
Melamine	–	–	20.32	37.36
Desethylatrazine	19.47	48.58	–	57.89
Desisopropylatrazine	21.08	42.23	–	54.49
Desethyldesisopropylatrazine	25.15	–	–	45.72

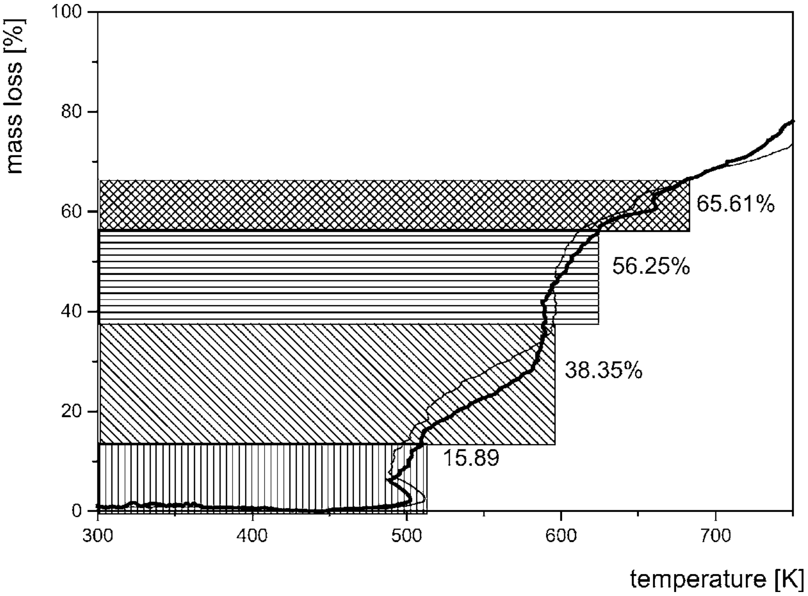


Fig. 7. The TG curve of propazine (thin line) and sebuthylazine (thick line) and calculated mass losses (%) based on the structures of different mer presented in Table 2.

4. Conclusions

Thermal degradation of triazines substituted by Cl examined up to 750 K proceeded in four stages and included such processes as elimination of HCl, dealkylation, deamination and formation of condensed structures. The steps mentioned above were established based on the comparable analysis of TG curves, MALDI TOF spectrometry and elementary analysis of decomposition products and samples taken after different steps of thermal degradation. Thermal degradation of triazines substituted by Cl and alkylamino groups leads to the formation of high molecular compounds. The products of the thermal degradation of toxic Cl substituted triazines can be converted into water insoluble and environmentally safe products.

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