

## **THERMAL DECOMPOSITION OF TRIAZINE HERBICIDES**

### **I. 1,2-(4-chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile (cyanazine)**

*K. Drożdżewska<sup>1</sup>, A. Książczak<sup>2</sup> and T. Książczak<sup>2</sup>*

<sup>1</sup>Analytical Department, Institute of Industrial Organic Chemistry, Annopol 6, 03-236 Warsaw

<sup>2</sup>Department of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw  
Poland

#### **Abstract**

Cyanazine was taken as an example for investigations under the influence of different conditions on thermal decomposition of triazine herbicides. DSC measurements were carried out under atmospheric pressure and hermetically closed, under pressure 1.3 kPa. The influence of the pressure on the constant reaction rate of decomposition of cyanazine was discussed. It was also proved that the predicted reaction constant rates from isothermal and non-isothermal measurements are consistent.

**Keywords:** cyanazine, DSC, kinetics, thermal stability

#### **Introduction**

Cyanazine is a herbicide, used for weed control applied pre-emergency to the crop for broad beans, maize and peas, post emergency in barley and wheat during the early tillering stage in combination with hormone weedkillers for the control of broad-leaved weeds. This herbicide is also used in other plants like cotton, flowers, forestry, potatoes, soybeans and sugarcane. The degradation of this compound in environment was investigated by some authors [1–3]. In the presence of mineral acids or bases the CN group of cyanazine is the primary point of hydrolysis. In weak acids solutions Cl group becomes labile [1]. In water, after 35 days, there was found 60% of N-deethylcyanazine, 0.8% cyanazine amide and 0.3% N-deethylcyanazine amide [2]. The mechanism of degradation in acid and alkaline solution is different. Although the final product is the same (2-hydroxy-4-carboxyisopropylamino-6-ethylamino-1,3,5-triazine), in alkaline solution was found the other intermediate (2-chloro-4-amidoisopropylamino-6-ethylamino-1,3,5-triazine).

For the purpose of environmental studies and residual analyses, there is a need for production and certification of pure analytical standard of this compound with purity not less than 99%. This type of standards are produced in Analytical Department of Institute of Industrial Organic Chemistry. The cost of production of standard and its certification is

relatively high. For economical purposes, it is important to predict the different factors determining the thermal stability of this compound. The decomposition process is always connected with enthalpy changes and the growing content of impurities and it is the reason why DSC method found the application in stability tests [4–6]. The main purpose of this work is to determine the influence of thermal conditions during the process of thermal decomposition on the kinetic parameters of cyanazine.

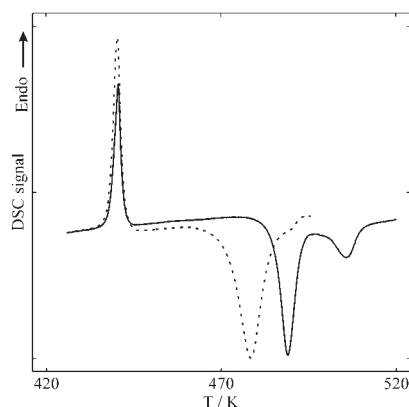
## Experimental

The two types of differential scanning calorimeters were used in the investigation of thermal decomposition: the heat flow microcalorimeter (DSC 605 UNIPAN Poland), used for non-isothermal measurements and the power-compensation (DSC-7 Perkin Elmer) in the case of isothermal experiments. Two processes were analysed: the process solid-liquid equilibria (cryometric method), which is very sensible for purity changes and exothermal decomposition in the liquid phase. The measurements were performed using three types of alumina sample pans : hermetically sealed under pressure of ~1.3 kPa, pans with pinholes (0.05 and 0.4 mm ID). The masses of compound, used in the experiments were low (approximately 3 mg) and higher (about 13 mg). The isothermal measurements were performed in sample pans with pinholes 0.05 mm ID [7]. Cyanazine was prepared and purified in the Analytical Department of Institute of Industrial Organic Chemistry (Warsaw). Purity was determined by the cryometric and chromatographic method and was 99.4%.

## Results and discussion

For the covered pans with the lid hole 0.4 mm ID, the values of decomposition enthalpy were low (about 36 kJ mol<sup>-1</sup>). For the pans with pinholes with lower diameter (0.05 mm ID) the values of enthalpy were greater (85 kJ mol<sup>-1</sup>). For the pans hermetically sealed, the enthalpy values varied from 75 to 128 kJ mol<sup>-1</sup>. The variation in enthalpy changes could be caused by not quite hermetically closing. The highest value of enthalpy should be attributed to the decomposition in fully hermetically closed pan. The relatively small value of enthalpy, obtained in the case of pans with lid hole of 0.4 mm ID shows that heat losses are significant and these results were not taken into consideration in further analyses.

Figure 1 presents an example of two decomposition curves, obtained in two different sample pans. The first curve is plotted for the sample placed in the pan with lid hole 0.05 mm ID (dashed line) and the second curve is obtained for the hermetically closed pan (solid line). The process of decomposition begins about 10 K earlier in the open system than in the case of the hermetically closed sample pan. It is worth mentioning that pressure in the beginning of process was 1.3 kPa in the hermetically closed system and 103 kPa in the open system (atmospheric pressure). The direct comparison of both decomposition curves given in Fig. 1 shows that growth of the pressure promotes the decomposition process of cyanazine.

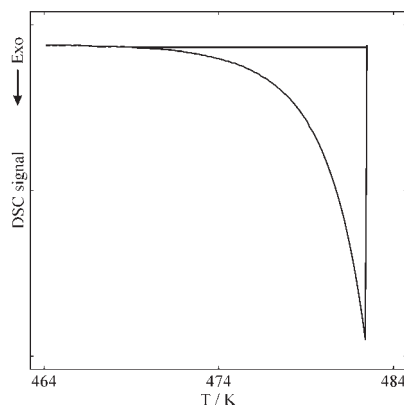


**Fig. 1** The DSC curves of melting and decomposition process of cyanazine in the hermetic pan — and in the pan with lid hole 0.05 mm ID - - -

The kinetic models, adequate for the description of the decomposition process in the liquid phase were applied for the interpretation of the obtained decomposition peaks. The experimental data were the best described by the first order reaction. All obtained data are collected in Table 1. The activation energy  $E_a$  and pre-exponential factor ( $A$ ) are placed in the second and third column respectively. The beginning temperature of decomposition process is placed in the fourth column and in the last column there are the values of constant rates of reaction (for 278.2 K). It is worth mentioning that the activation energy  $E_a$  increases with growing the value of the beginning decomposition temperature.

The method of partial decomposition of great mass samples is used to improve the accuracy of determination of the kinetic parameters. The beginning of the decomposition curve of great mass sample of cyanazine and method of heat reaction determination is presented in Fig. 2. During the thermal decomposition of larger masses, the internal pressure is growing, leading to the decompression of the sample pan. It is seen on the graph as a large endothermic peak. The horizontal line was led from the last measured point before the decompression of the sample pan and vertical line was generated by extrapolation of the baseline before the decomposition. The area calculated between these two lines and the curve gives the thermal effect of partial decomposition. Knowing the heat of the whole decomposition  $\Delta H_D$  estimated from the run performed for the small masses, enabled us to determine the reaction rate in the beginning of decomposition. Taking into consideration that the degree of conversion ( $\alpha_p$ ) determined by calculation based on the area of responding the partial decomposition, the method of calculation of the real degree of conversion ( $\alpha$ ) is based on the equation:

$$\alpha = \alpha_p \frac{\Delta H_C}{\Delta H_D} \quad (1)$$



**Fig. 2** DSC curve of partial decomposition of cyanazine. Straight lines present the way of determination of the heat effect of partial decomposition

where  $\Delta H_C$  is an enthalpy of partial decomposition, evaluated by the method presented in Fig 2. This method allows the kinetic study for small degree of conversion. For the partial decomposition presented in Fig. 2 the degree of conversion  $\alpha$  is between 0.004–0.018. Two last results, presented in Table 1 were obtained by using the method of partial decomposition in hermetically sealed pans. In the case of total decomposition reaction, the low limit of degree of conversion was constant and it was equal to  $\alpha=0.02$ . The values of the activation energy obtained for partial decomposition were in good agreement with total results of  $E_a$  for the total decomposition performed in pans with a lid hole. To analyse the data presented in Table 1 the question is about the reason for thermal sensibility of decomposition phenomena on the change of the beginning conditions of this process.

Let us consider that the decomposition of cyanazine is in agreement in the first order reaction and the degradation products act as catalysts of the process. We can express the whole reaction rate by the equation:

$$\frac{d\alpha}{dt} = k_1(1-\alpha) + k_2(1-\alpha)\alpha \quad (2)$$

where  $k_1$  and  $k_2$  are reaction rate constants of the first order and that of the auto-catalytic reaction respectively. In Eq. (2) it was considered that the sample and its decomposition products are soluble in one phase. During the real degradation process, the volatile products appear. Taking into consideration that the concentration of catalytic gaseous products is constant, the pseudo-first rate equation is obtained:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^*)(1-\alpha) \equiv k(1-\alpha) \quad (3)$$

These catalytic volatile products, after degradation have limited solubility  $\alpha^*$  and for excess amount of these products, the auto-degassing process occurs [4]. The

first part of the Eq. (3) given in brackets, depends on the temperature and thermodynamic properties of the reaction phase. If the constants of the reaction rate  $k_1$  and  $k_2$  could be defined by Arrhenius equation, the relation between the first part of equation and temperature could be given by the relation:

$$k \equiv k_1 + k_2 \alpha^* = A_1 e^{-E_{a1}/RT} + \alpha^* A_2 e^{-E_{a2}/RT} \equiv A e^{-E_a/RT} \quad (4)$$

where  $A_1, A_2, A$  are pre-exponential factors,  $E_{a1}, E_{a2}, E_a$  are the activation energy for the first-rate reactions, autocatalytic and global reaction respectively. The value  $E_a$  depends not only on kinetics, but also on the thermodynamic factors like relation between the solubility of volatile catalyst ( $\alpha^*$ ) and the temperature. Equation (3) shows why the catalytic reactions of decomposition in the liquid phase are often described by the pseudofirst-order equation. The concentration of catalytic volatile products in the reaction phase depends not only on the temperature but also on the pressure in the sample pan.

Figure 3 presents the isothermal decomposition curve, obtained for cyanazine sample at 478 K, closed in the pan with lid hole 0.05 mm ID. For the isothermal measurements the constant rate of decomposition  $k$  was  $0.0073 \text{ s}^{-1}$  established for the first order model. The kinetic parameters, calculated for the isothermal and non-isothermal mode and the reaction-rate constants for the temperature 478.2 K were placed in Table 1. The agreement between the results exists only in the case of measurements performed in open systems (0.05 mm ID) and partial decompositions. It leads to the conclusion that the decomposition mechanism is similar in both cases. The temperature value in isothermal measurements is among the values obtained for non-isothermal experiments.

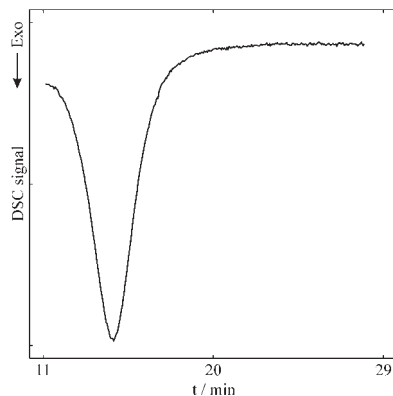
**Table 1** The kinetic parameters for the thermal decomposition of cyanazine (scanning rate  $\beta = 2 \text{ K min}^{-1}$ )

Sample mass /mg	$E_a/\text{kJ mol}^{-1}$	$\ln A/\text{s}^{-1}$	$T_{\text{onset}}/\text{K}$	$k_{(478.2)} \cdot 10^{-3}$
4.12	885.52	213.01	484	0.054
1.07	800.00	191.72	483	0.068
6.35	747.64	180.30	481	0.394
3.00	543.21	130.77	473	2.668
2.96*	549.14	133.19	471	6.747
5.70*	618.13	150.39	472	5.743
12.61**	630.40	154.18	474	11.592
12.44**	631.83	154.13	475	7.694

\*The alumina pan with lid hole,  $\phi = 0.05 \text{ mm ID}$

\*\*The calculations were made by partial decomposition method

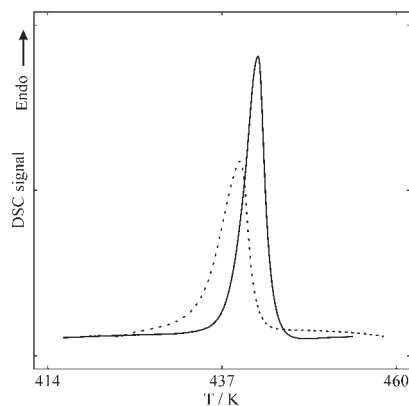
The investigations of thermal behaviour of cyanazine were also performed in the area of melting. The scanning rate was  $\beta = 2 \text{ K min}^{-1}$ . The beginning temperature was below the melting temperature. The final temperature ( $T_k$ ) was chosen to give small



**Fig. 3** DSC curve of the isothermal decomposition of cyanazine in the pan with lid hole 0.05 mm ID at temperature 478.2 K

degree of conversion. The purity change was determined by cryometric method. The cryometry data are collected in Table 2. The purity change ( $\Delta p$ ) responds to the degree of conversion ( $\alpha$ ). Attempts were made for the prediction of purity changes based on the kinetic parameters, presented in column 2 and 3 in Table 1. The results were not in agreement. The content of impurities after melting determined by calorimetry is much lower than in reality [4] although for calculations the kinetic parameters for the mass sample 12.61 were taken, resulting in the high value of constant reaction rate. It leads to the conclusion that the kinetic parameters used are not suitable for the correct prediction of the thermal production of impurities in the area beyond the temperature range, used for the determination of kinetic parameters.

The subsequent DSC melting curves of cyanazine, performed on the same sample are presented in Fig. 4. It can be seen that the baseline is straight after melting which proves that there are no additional processes with enthalpy changes, accompa-



**Fig. 4** Subsequent melting of cyanazine, performed on the same sample; first run —, second run - - -

nying melting. The melting peak in the second run is much lower and shifted towards lower temperatures. It is caused by the growing amount of impurities. It is also shown, there is a small exothermic peak in the temperature range before the second melting. It is probably due to 'defreezing' the active products of thermal decomposition, produced during the first run until  $T_k=456.6$  K. This effect is about  $\Delta H=-0.21$  kJ mol<sup>-1</sup> and the calculated growth of impurities is 2.27 mol%.

**Table 2** The purity changes ( $\Delta p$ ) of cyanazine samples during the heating with the heating rate 2 K min<sup>-1</sup> from  $T_m^0=438.8$  K to the final temperature ( $T_k$ )

$T_k/K$	$\Delta p=\alpha$	$\alpha_{(Pred.)}^* \cdot 10^{-4}$
452.06	$7.7 \cdot 10^{-3}$	1.04
450.95	$5.4 \cdot 10^{-3}$	0.68
455.83	$2.51 \cdot 10^{-2}$	4.24

\*For prediction were used the kinetic data for mass sample 12.61 mg Table 1 (see text)

The same effect was also measured for the sample heated to final temperature  $T_k=477.2$  K. The growth of impurities was 6.14 mol% and exothermal effect was  $\Delta H=-3.089$  kJ mol<sup>-1</sup>. It can lead to the conclusion that active products are generated as the result of the thermal decomposition of this sample. Taking these observations into account, the value of enthalpy of the beginning stage of the thermal decomposition was established. Two effects were used in calculation: the enthalpy of the partial decomposition in the first run and subsequent exothermic effect in the second run. The growth of impurities was taken also into consideration. The calculated final effect was 89 kJ mol<sup>-1</sup> and it was in agreement with results based on the enthalpy, determined from the area of the peak of the whole decomposition. It confirms that the thermal effects of the beginning reactions and reactions of degradation products are in agreement.

## Conclusions

The obtained results confirm that values for kinetic parameters of cyanazine depend on the conditions of thermal decomposition. The constant of the reaction rate in a closed pan under diminished pressure 1.3 kPa is about 100 times less than in the case of a pan with a pinhole (under atmospheric pressure). The observed changes of decomposition rate constants are caused by the solubility of catalytic gaseous products. The increase of pressure under the reaction phase in the pan causes the growth of concentration of volatile catalytic products in the liquid reaction phase and values of the reaction rate constant (Eq. 3). These observations lead to the conclusion that storage of the liquid cyanazine under reduced pressure improves its thermal stability.

## References

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