

## **THERMAL STABILITY OF SOME PESTICIDES AT THE MELTING TEMPERATURE**

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(Received April 15, 1992, in revised form March 10, 1993)

### **Abstract**

The melting process of unstable pesticides such as methomyl, atrazine, lenacil, captan, daminozide and dodine has been investigated by DSC. The influence of the heating rate on the melting enthalpy, melting temperature and cryometric determination of purity was studied. The mean rate of thermal decomposition at the melting temperature was introduced to compare the stability of the examined pesticides. The investigated pesticides may be classified into two groups. In the first group the determination of purity is independent of heating rates and in the second one the purity is dependent on the heating rates.

**Keywords:** DSC, thermal stability of pesticides

### **Introduction**

In the manufacturing, transformation, storage and purification of pesticides, the information is needed about the thermal stability of the compounds. Frequently, a number of compounds undergo degradation, polymerization and other reactions on heating. The reactions proceed at a greater rate in the liquid phase to produce impurities. Consequently, the solid-liquid equilibrium of the pure compound will change. The measurement of melting temperatures, melting enthalpies and predicted purity by cryometric method depends on the thermal history of the sample used, heating rate, chemical character of impurities (inhibitors, catalysts), conditions in the pan, pressure and kind of gas above the sample.

The aim of this paper is to study the influence of the heating rate on melting temperatures, melting enthalpies and predicted purity of unstable pesticides. The chosen compounds possessing different thermal characteristics have been taken into consideration.

## Experimental

The investigations were performed using the following pesticides:

Methomyl (S-methyl-N(methylcarbomoyloxy)thioacetamidate)) with a purity of  $P = 98.8$  mol% determined by HPLC;

Atrazine (6-chloro-N<sup>2</sup>-ethyl-N<sup>4</sup>-isopropyl-1,3,5-triazine-2,4-diamine) with a purity of  $P = 99.5$  mol% determined by HPLC and GLC;

Lenacil (3-cyclohexyl-1,5,6,7-tetrahydrocyclopentapyrimidine-2,4(3H)-dione)) with a purity of  $P = 99.9$  mol% determined by GLC;

Captan (N-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide)) with a purity of  $P = 99.9$  mol% determined by GLC;

Daminozide (N-dimethylaminosuccinamic acid) with a purity of  $P = 99.0$  mol% determined by HPLC;

Dodine (dodecylguanidinium acetate).

The pesticides were synthesized and purified in the Department of Analytical Chemistry of the Industrial Organic Chemistry Institute.

The measurements were performed on a heat-flux DSC 605 M UNIPAN calorimeter cooperating with an IBM AT computer. The authors' own (Kosinski, Ksiazczak) controlled analysis program has been used. The calibration was made using the following substances: gallium, indium, cadmium, lead, tin, zinc, naphthalene, benzoic acid. The metals used had a purity greater than 99.999% and the organic compounds greater than 99.95%. The temperature calibration was made using the melting temperature of the calibrants determined by cryometric analysis.

## Results

Calorimetric measurements of melting processes were performed using hermetic aluminium pans. The thermoanalytical curves were interpreted in the way presented in earlier papers [1–3]. During the melting process the sample was amassed near the border of the pan by surface tension. The ratio of the melting enthalpy determined in the first and the second process is nearly constant

$$\alpha = \Delta H_m^{\circ}(\text{I})/\Delta H_m^{\circ}(\text{II}) = 1.019 \quad (1)$$

It is assumed in this paper that a compound is stable when the eutectic purity ( $P$ ), melting enthalpy ( $\Delta H_m^{\circ}$ ) with the correction  $\alpha$ , melting temperatures ( $T_m$ ) of the sample in the two successive measurements performed on the same sample are constants. The cryometric interpretation of thermoanalytical curves was executed in the manner presented in earlier papers [4, 5].

**Table 1** Results of calorimetric measurements of unstable compounds for the first melting process

Pesticides	Heating rate $\beta$ / deg·min <sup>-1</sup>	Melting temperature of pure compound $T_m$ / K	Melting enthalpy $\Delta H_m^0$ / kJ·mol <sup>-1</sup>	Eutectic purity $P$ / mol%
Methomyl	0.1	351.5	20.74	97.84
	0.5	352.5	20.86	97.85
	1.0	352.7	21.07	97.96
	2.0	353.5	22.01	97.80
Atrazine	0.5	449.7	33.26	99.53
	1.0	449.9	34.64	99.56
	2.0	450.3	35.74	99.54
	5.0	451.3	36.66	99.51
	10.0	452.6	37.86	99.44
Captan	0.1	445.7	30.72	99.43
	0.5	446.4	34.93	99.39
	1.0	446.5	37.03	98.92
	2.0	447.2	36.73	99.24
	5.0	448.2	39.68	98.94
	10.0	449.8	39.70	99.24
Daminozide	0.5	415.1	47.06	96.27
	1.0	417.6	46.31	96.75
	1.5	423.5	44.29	97.36
	2.0	424.7	45.87	97.49
	3.5	428.2	46.16	98.05
	5.0	431.3	46.03	98.47
	10.0	431.2	—	98.66
Dodine	0.5	408.7	29.13	96.46
	1.0	408.7	27.87	97.51
	2.0	408.9	26.62	97.81
	5.0	409.1	26.67	98.68

For unstable compounds the percentage rate of decomposition has been calculated on the basis of the purities ( $P_1$ ,  $P_2$ ) determined in two consecutive measurements performed on the same sample and the length of the time ( $t_p$ ) taken from the beginning of the melting process to the end of the calorimetric measurement (taking the sample out of the calorimeter) as follows:

$$V = (P_1 - P_2) / t_p \quad (2)$$

It is assumed that the sample being outside the calorimeter crystallizes rapidly to stop the decomposition reaction. For the cryometric determination of eutectic

purity the beginning part of the melting process was taken. The upper limit of the melting fraction was  $F \approx 0.25$ . It was assumed that in the part of the melting taken into consideration the production of impurities is very low and the same for the two successive melting processes. For these reasons the difference ( $P_1 - P_2$ ) is equal to the amount of impurities produced during the first melting process in the length of time ( $t_p$ ).

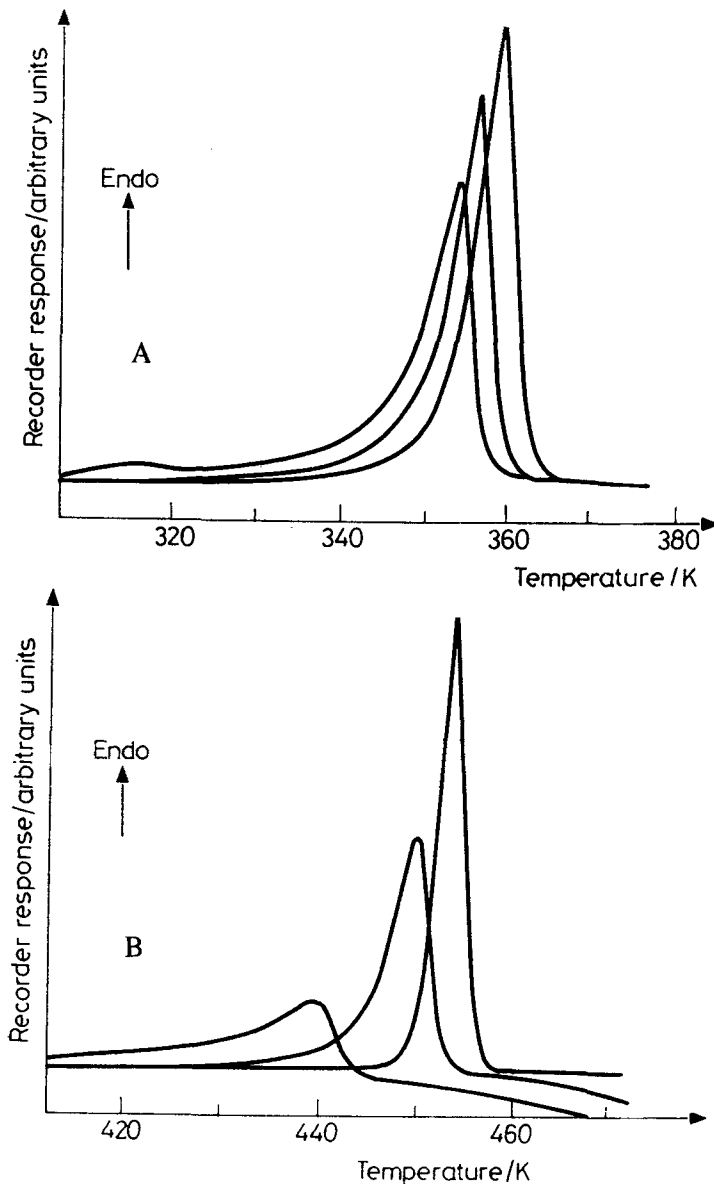
The melting temperatures of the pure compound ( $T_m^o$ ), eutectic purity ( $P$ ), melting enthalpy ( $\Delta H_m^o$ ) for different heating rates ( $\beta$ ) are listed in Table 1. The simplest relations for the mentioned parameters ( $T_m^o$ ,  $P$ ,  $\Delta H_m^o$ ) with the heating rate ( $\beta$ ) or the length of the melting time ( $t$ ) are collected in Table 2. The length of the melting time ( $t$ ) is taken from the start of the peak to the end of the same peak.

**Table 2** Relationships between eutectic purity ( $P$ ), melting temperature ( $T_m^o$ ), melting enthalpy ( $\Delta H_m^o$ ) and melting process time ( $t$ ) or heating rate ( $\beta$ )

Pesticides	Relationships	Unit
Methomyl	$P = 97.9 \pm 0.1$	mol%
	$T_m^o = (0.95 \pm 0.022)\beta + (351.7 \pm 0.2)$	K
	$\Delta H_m^o = (-0.0146 \pm 0.010)t + (21.9 \pm 0.6)$	$\text{kJ}\cdot\text{mol}^{-1}$
	$V = 0.10$	$\%\text{min}^{-1}$
Atrazine	$P = 99.52 \pm 0.08$	mol%
	$T_m^o = (0.304 \pm 0.015)\beta + (449.6 \pm 0.07)$	K
	$\Delta H_m^o = (-0.454 \pm 0.018)t + (39.3 \pm 0.2)$	$\text{kJ}\cdot\text{mol}^{-1}$
	$V = 0.11$	$\%\text{min}^{-1}$
Captan	$P = 99.2 \pm 0.2$	mol%
	$T_m^o = (0.380 \pm 0.036)\beta + (446.1 \pm 0.2)$	K
	$\Delta H_m^o = (-0.270 \pm 0.050)t + (41.1 \pm 1.0)$	$\text{kJ}\cdot\text{mol}^{-1}$
	$V = 0.25$	$\%\text{min}^{-1}$
Daminozide	$P = (-2.13 \pm 0.20) / \beta + (98.77 \pm 0.11)$	mol%
	$T_m^o = (-15.50 \pm 1.1) / \beta + (433.2 \pm 0.6)$	K
	$\Delta H_m^o = 45.9 \pm 1.1$	$\text{kJ}\cdot\text{mol}^{-1}$
	$V > 6$	$\%\text{min}^{-1}$
Dodine	$P = (-1.13 \pm 0.19) / \beta + (98.66 \pm 0.22)$	mol%
	$T_m^o = 408.8 \pm 0.3$	K
	$\Delta H_m^o = (0.101 \pm 0.015)t + (25.6 \pm 0.4)$	$\text{kJ}\cdot\text{mol}^{-1}$
	$V = 0.08$	$\%\text{min}^{-1}$

Figure 1A shows the three consecutive melting DSC curves for the same sample of methomyl at a heating rate  $\beta = 2 \text{ deg}\cdot\text{min}^{-1}$ . The height of the consecutive thermoanalytical curves decreases. The third thermoanalytical curve possesses an additional small and broad peak. The changes of the consecutive

peaks indicate that methomyl is unstable at the melting temperature to undergo a thermal decomposition reaction. The melting enthalpy in successive calorimetric measurements is decreased by about 9%. The eutectic purities are:  $P_2^1 = 97.81\%$ ,  $P_2^2 = 95.26\%$ ,  $P_2^3 = 93.26\%$ . The subscript indicates the heat-



**Fig. 1** Comparison of the successive melting processes performed on the same sample of methomyl (A) and atrazine (B) at  $\beta = 2 \text{ deg}\cdot\text{min}^{-1}$

ing rate and the superscript indicates the number of consecutive measurements performed on the same sample. The last value of purity may be burdened with a large uncertainty because of the large amount of the impurities produced. The mean value of the decomposition rate is  $V = 0.01\% \text{ min}^{-1}$ . The extrapolated melting temperature ( $\beta \rightarrow 0$ ) of pure methomyl is  $T_{\text{mE}}^{\circ} = 351.7 \text{ K}$ . The extrapolated melting enthalpy ( $t \rightarrow 0$ ) is  $\Delta H_{\text{mE}}^{\circ} = 21.9 \pm 0.6 \text{ kJ} \cdot \text{mol}^{-1}$ . The decrease in melting enthalpy with the increase of the melting process time ( $t$ ) indicates that the decomposition reaction is exothermic.

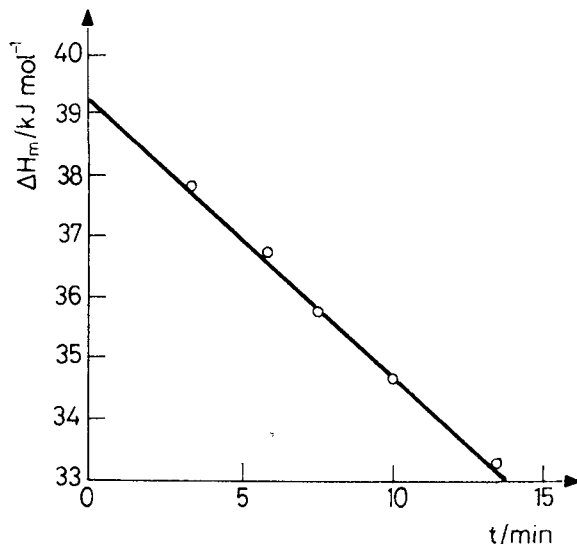


Fig. 2 Relationship between the melting enthalpy of atrazine and the melting time

The three DSC curves taken of the same sample of atrazine at a heating rate  $\beta = 2 \text{ deg} \cdot \text{min}^{-1}$  are shown in Fig. 1B. The melting enthalpy obtained for the second measurement is decreased by about 12%; for the third by 54%. The predicted eutectic purities for these DSC curves are:  $P_2^1 = 99.54\%$ ,  $P_2^2 = 98.02\%$ ,  $P_2^3 = 91.72\%$ . The changes of the melting enthalpy and the purity suggest that atrazine undergoes a decomposition reaction during melting. The mean value of the decomposition rate is  $V = 0.11\% \text{ min}^{-1}$ . The relationship between the melting enthalpy for the first scan and the length of the melting time ( $t$ ) is shown in Fig. 2. The parameters of these linear relations are listed in Table 2. The extrapolated melting enthalpy is  $\Delta H_{\text{mE}}^{\circ} = 39.3 \pm 0.2 \text{ kJ} \cdot \text{mol}^{-1}$  and extrapolated melting temperature of pure atrazine is  $T_{\text{mE}}^{\circ} = 449 \pm 0.1 \text{ K}$ .

Figure 3A shows two curves for the first melting process of lenacil for the heating rate  $\beta = 5 \text{ deg} \cdot \text{min}^{-1}$ . The curves exhibit two peaks. The first one is due to a melting process and the second one is due to the vaporization process of

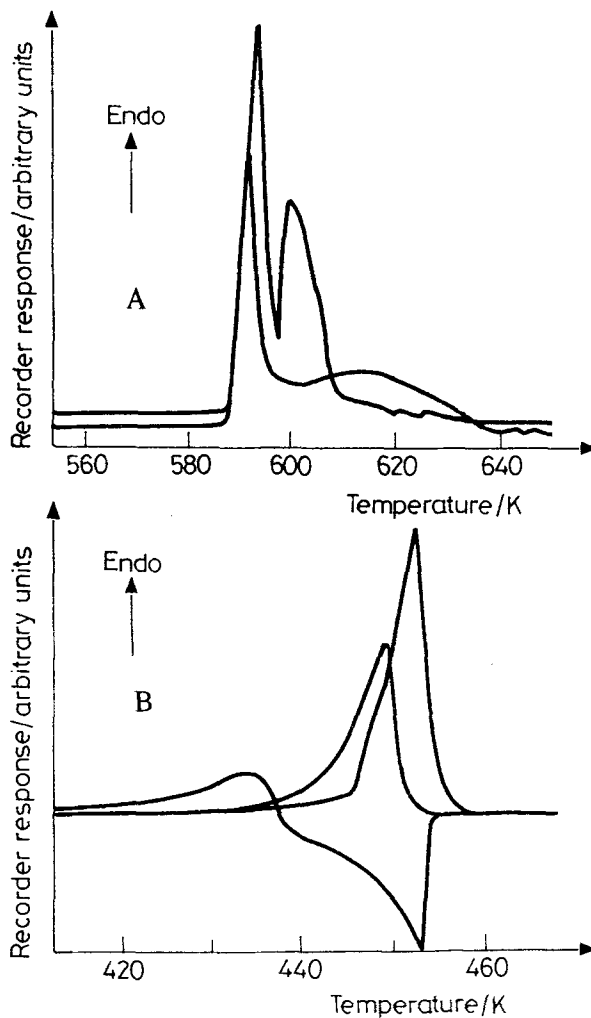
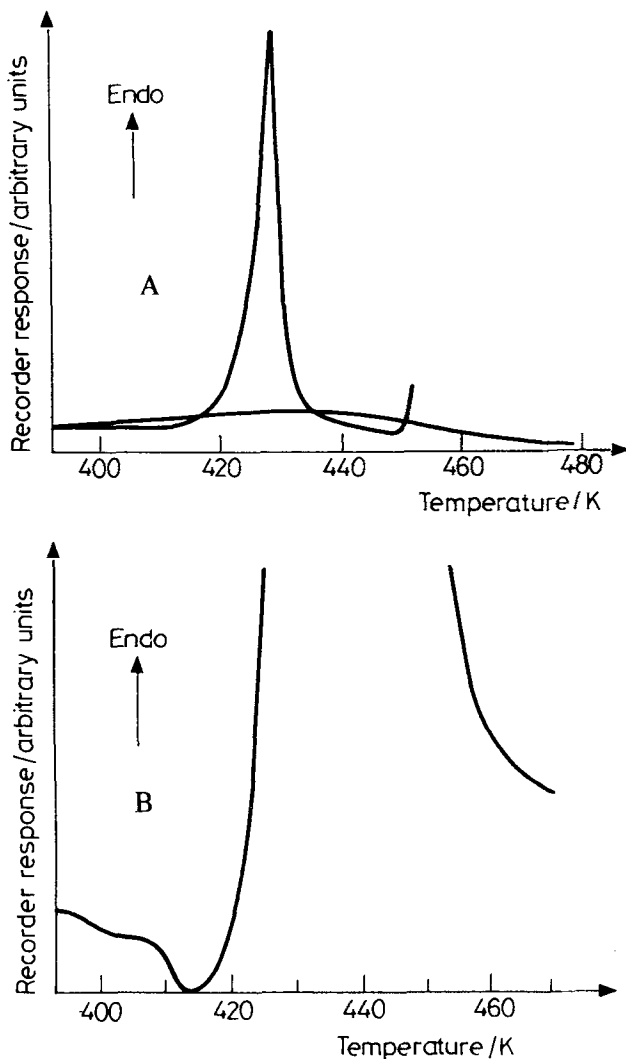


Fig. 3 (A) DSC curves for the different samples of lenacil. (B) Comparison of the successive melting processes performed on the same sample of captan

volatile impurities produced by the thermal decomposition. The attempt to perform calorimetric measurements for lower heating rates failed because the hermetic pans were also split. The estimated melting enthalpy is  $\Delta H_m = 59.81 \text{ kJ}\cdot\text{mol}^{-1}$  at the heating rate  $\beta = 5 \text{ deg}\cdot\text{min}^{-1}$ . The predicted eutectic purities are  $P_1^I = 99.94\%$  and  $P_2^I = 99.95\%$  and are consistent with the purity determined by GLC (99.9%). The agreements of purities at different heating rates suggest that the decomposition reaction proceeds at a higher rate for the greater

melted fraction of the sample than for the smaller fraction considered in the prediction of purity.

In Fig. 3B are presented three successive melting curves of captan for the same sample at  $\beta = 2 \text{ deg}\cdot\text{min}^{-1}$  which indicate the great influence of the decomposition reaction on the next melting process. The melting enthalpy in the second melting process is decreased by about 45%. The purities of the next



**Fig. 4** (A) Comparison of the successive melting processes of daminozide at  $2 \text{ deg}\cdot\text{min}^{-1}$ .  
(B) Base line of daminozide the melting indicates a thermal decomposition before the melting DSC peak



melting process are:  $P_1^2 = 99.24\%$ ,  $P_2^2 = 94.59\%$ ,  $P_3^2 = 83.59\%$ . The mean value of the rate of decomposition is  $V = 0.25\% \text{ min}^{-1}$ . The results of the first melting process for different heating rates are listed in Table 1. The purity of captan is independent of the heating rate  $P = 99.2 \pm 0.2\%$  and is lower than the one obtained by GLC.

Figure 4A shows the DSC curves for the two consecutive melting processes for the same sample of daminozide. It can be seen that the sample is nearly

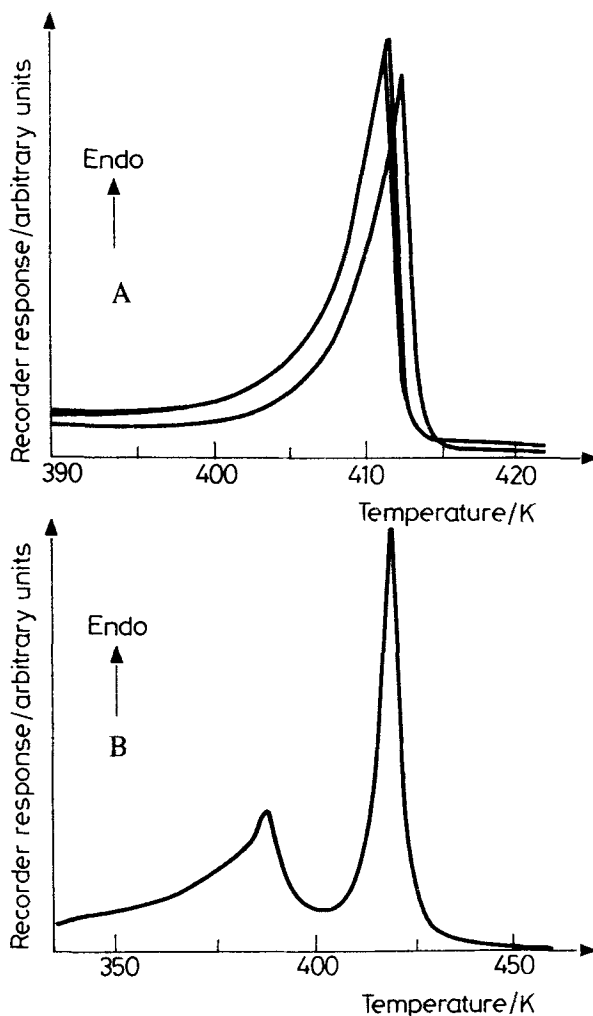


Fig. 5 (A) Comparison of the three successive melting processes performed on the same sample of dodine at the heating rate  $\beta = 1 \text{ deg}\cdot\text{min}^{-1}$ . The fat DSC curve represents both the second and third melting processes. (B) DSC curve for dodine at  $\beta = 5 \text{ deg}\cdot\text{min}^{-1}$

completely decomposed after the first measurement. The peak of the second melting process is small and broad.

Figure 4B shows the changes of the base line before the melting peak indicating that the production of impurities occurs at the start of melting. The eutectic purity depends strongly on the heating rate. For this reason the error of the purity determination of daminozide increases with increasing melting process time. The extrapolation of the purity to zero of the melting time ( $1/\beta \rightarrow 0$ ) gives  $P_E = 98.8 \pm 0.1\%$ . This value is consistent with the purity  $P = 99.0\%$  obtained by HPLC. In this case the melting enthalpy is burdened with a large uncertainty because of the irregularity of the base line before and after the melting peak due to the decomposition process. It was assumed that the melting enthalpy of daminozide is independent of the length of the melting time  $\Delta H_{mE}^0 = 45.9 \pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ . The melting temperature depends strongly on the heating rate and the value extrapolated to zero melting time ( $1/\beta \rightarrow 0$ ) is  $T_{mE}^0 = 433.2 \pm 0.6 \text{ K}$ . The results obtained at the heating rate  $\beta = 0.5 \text{ deg}\cdot\text{min}^{-1}$  were not taken into account because of the large concentration of impurities.

Figure 5A shows three consecutive DSC runs performed on the same sample of dodine at  $\beta = 1 \text{ deg}\cdot\text{min}^{-1}$ . The fat curve represents the second and third process to point out that the decomposition reaction is reversible. After the first melting process the sample achieves an equilibrium state (dodine with produced impurities). The decrease of melting enthalpy for the second melting process is 10.3%. The purities determined by analysis of successive melting process are  $P_1^1 = 97.69\%$ ,  $P_1^2 = 96.48\%$ ,  $P_1^3 = 96.46\%$ . The mean rate of decomposition is  $V = 0.08\% \text{ min}^{-1}$ . The eutectic purity depends strongly on the heating rate which is shown by the relationships collected in Table 2. The results for  $\beta = 5 \text{ deg}\cdot\text{min}^{-1}$  were not taken for the calculations of the relations for  $P$  and  $T_m^0$  because the solid-solid transition peak is near the liquid-solid transition to hinder reliable interpretations of the curve. The mentioned transitions are presented in Fig. 5B. The extrapolated melting enthalpy is  $\Delta H_{mE}^0 = 25.6 \text{ kJmol}^{-1}$ . The melting temperature of dodine is  $T_{mE}^0 = 408.8 \pm 0.3 \text{ K}$  and is independent of the heating rate.

## Conclusions

The cryometric analysis of all the investigated pesticides was made only up to the molten fraction  $F \approx 0.25$ . It can be assumed that the determined eutectic purities of captane, methymol, atrazine, lenacil are independent of the heating rate. Probably, thermal decomposition reactions of the mentioned pesticides proceed with great rates for molten fractions greater than  $F \approx 0.25$ . The purities of daminozide and dodine depend strongly on the heating rate. Thermal decomposition occurs for a very small molten fraction of the sample. The decrease of

the melting enthalpy for methomyl, atrazine, lenacil, daminozide with the melting time indicates that the thermal decomposition is exothermic. The thermal decomposition of dodine is endothermic. Introducing the mean decomposition rate at the melting point is useful in technological operations on the liquid phase to allow to predict impurity productions. The mean decomposition rate increases in the following sequence: dodine < methymol < atrazine < captan < daminozide.

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We thank dr. T. Krasiejko for his help. This work was supported by the Ministry of Education.

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**Zusammenfassung** — Mittels DSC wurde der Schmelzvorgang von instabilen Pestiziden, wie z.B. von Methomyl, Atrazin, Lenacil, Captan, Daminozid und Dodine untersucht. Es wurde der Einfluß der Aufheizgeschwindigkeit auf Schmelzenthalpie, Schmelztemperatur und auf die cryometrische Bestimmung des Reinheitsgrades untersucht. Zum Stabilitätsvergleich der untersuchten Pestizide wurde die mittlere Zersetzungsgeschwindigkeit bei Schmelztemperatur eingeführt. Die untersuchten Pestizide können in zwei Gruppen unterteilt werden. In der ersten Gruppe ist die Reinheitsbestimmung unabhängig von der Aufheizgeschwindigkeit, in der zweiten ist sie davon abhängig.