A DSC STUDY OF THE THERMAL DECOMPOSITION OF 2–METHOXYAMINO–3, 5–DINITRO–PYRIDINE

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abstract: The thermal decomposition of 2–methoxyamino–3, 5–dinitro–pyridine was investigated by differential scanning calorimetry. Kinetics of the exothermal decomposition was initially analyzed using the model-free Friedman method. The best kinetic model and the kinetic parameters were obtained by means of a non-linear regression analysis using the "Netzsch Thermokinetics" program. It corresponds to a three step mechanism consisting in melting followed by a two-step decomposition process.

Introduction

Synthesis of N-methoxy-derivatives was a subject of real interest during the last years due to their interesting acid – base and chromogenic properties [1]. Their oxidation leads to relatively stable free radicals, assumed to be possible intermediates in the related disproportionation (self-nitration) reactions. On the other hand, the presence of nitro groups on the aromatic ring frequently induces thermal instability, a characteristic feature of nitro derivatives. The hazards associated with this instability have been thoroughly analyzed in many scientific works [2÷4]. Among numberless nitro derivatives, 2–methoxyamino–3, 5–dinitro–pyridine is a solid recently synthesized [5] with unknown thermal properties, offering new insights into the structure – stability relationship.

Experimental

2–methoxyamino–3, 5–dinitro–pyridine is a product recently synthesized and purified [5]. The experiments designed to check its thermal stability were carried out using a CAHN DSC 550 differential scanning calorimeter, operated in non-isothermal regime. The DSC curves were recorded between 25 and 300°C, with five heating rates between 2 and 15°C/min. Amounts of 0.9 - 1.3 mg of the compound in sealed aluminum crucibles with a pinhole in the lid were used. At the end of the process the residual mass represents approximately 30% of the initial mass.

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The kinetic parameters of the thermal decomposition were obtained using the "Netzsch Thermokinetics" software program [6,7].

Results and Discussion

Under linear heating, 2-methoxyamino-3, 5-dinitro-pyridine shows an endothermal effect associated with the melting process, immediately followed by an exothermal decomposition. Several experiments performed in isothermal conditions at temperatures slightly lower than the melting temperature indicate a good stability of this compound in solid state. Its thermal decomposition is consequently associated with the liquid state, a common characteristic of many nitro compounds. This behavior can be attributed, among other things, to the acquired translational and rotational degrees of freedom of molecules in the melt as compared to the solid state. Fig. 1 shows the DSC curve at 10°C/min heating rate. Similar results were obtained for all the other heating rates, used for the deconvolution of the recorded signals. The results indicate a melting temperature of 126.8°C (determined from extrapolation to zero heating rates) and a melting heat of 47.7 J/g or 10.21 kJ/mol. The corresponding melting entropy is of 25.5 J/mol K. The average overall heat of the decomposition reaction is of 315.6 J/g or 67.53 kJ/mol and the maximum temperatures for the decomposition reaction are between 132.4°C and 143.8°C for heating rates of 2 to 15°C/min.
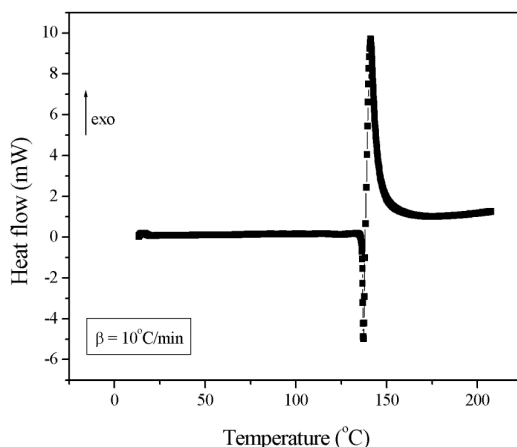

Fig. 1 *The DSC curve of 2-methoxyamino-3, 5-dinitro-pyridine.*

From Fig. 1 it can be observed that the melting process and the beginning of decomposition are partially superposed. The corresponding melting and decomposition processes were preliminarily evaluated neglecting this superposition.

The activation energy was initially evaluated using the isoconversional Friedman method [8]. Using this method, the regression of $\ln(d\alpha/dt)$ against $1/T$ for a given conversion, for measurements with different heating rates, gives the activation parameters according to eq. (1) [8]:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \text{constant} - \frac{E_a}{RT} \tag{1}$$

where α is the conversion, t is the time, T is the temperature, E_a is the activation energy and R is the gas constant.

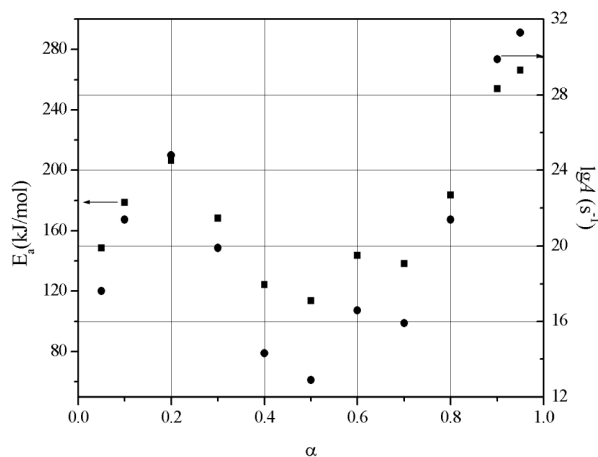The results from this model are given in Fig. 2.

Fig. 2 *The activation parameters dependence on the conversion according to the Friedman method*

A significant variation of the activation energy with conversion, within the significant range 10-90% was observed. It can be also observed that both the activation energy and pre-exponential factor exhibit a visible pattern. This result shows that at least two-steps must be considered, for the exothermal decomposition of 2-methoxyamino-3, 5-dinitro-pyridine.
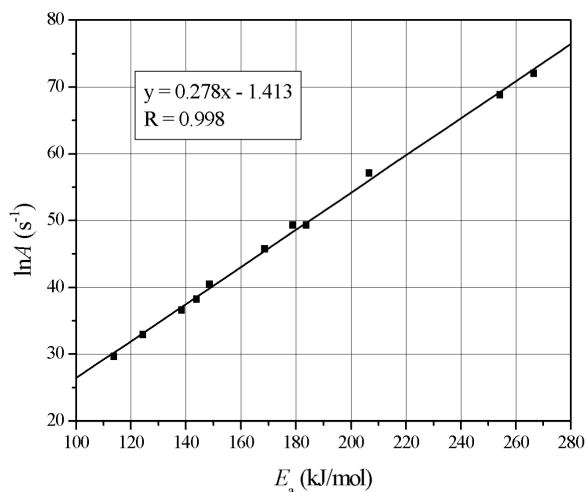

Fig. 3 *Compensation effect of the kinetic parameters from differential Friedman method.*

The results given in Fig. 3 indicate the existence of a linear correlation between ln$A$ and E (the compensation effect), very frequently reported in literature [9-12]:

$$\ln A = a + bE \qquad (2)$$

where a and b are constants. A straight line fits the data with a good correlation coefficient (Fig. 3), suggesting that the overall rate constant can be expressed only by a single activation parameter. The slope of the straight line is given by the reciprocal of the product ($R \cdot T_i$), where T_i is the isokinetic temperature. Since the abscissa was given in kJ/mol, the isokinetic temperature can be calculated as $T_i = 10^3/(8.31 \cdot 0.278) = 433K$ or $160^{\circ}C$. It can be seen that the obtained value is within the temperature range of the decomposition reaction (see Fig. 1), attesting its real physical significance, frequently questioned in the pertinent literature. Such a relationship constitutes the basis of another new approach of the non-isothermal kinetic analysis of solid decomposition [9÷12].
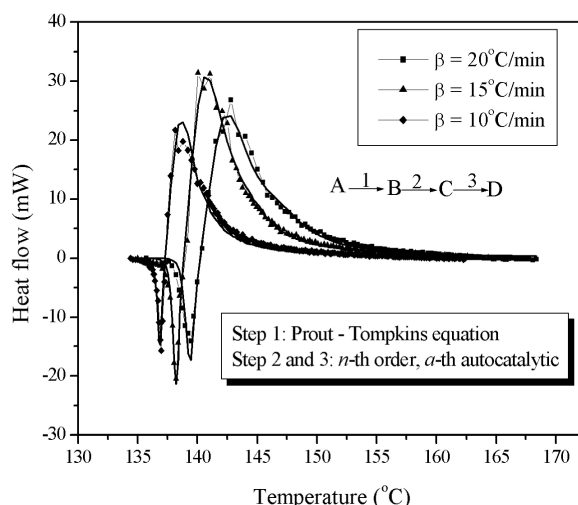

Fig. 4 *Best fit of non-linear regression analysis for selected heating rates.*

Table 1. Results of non-linear regression analysis

Kinetic parameters for the three step process		
A $\xrightarrow{1}$ B $\xrightarrow{2}$ C $\xrightarrow{3}$ D		
Step 1	Step 2	Step 3
Melting	Decomposition	Decomposition
E_1/(kJ·mol^{-1}): 158.8±0.7	E_2/(kJ·mol^{-1}): 55.4±0.2	E_3/(kJ·mol^{-1}): 131.3±0.4
Lg(A$_1$/s^{-1}): 20.1	Lg(A$_2$/s^{-1}): 6.7	Lg(A$_3$/s^{-1}): 15.4
	n_2: 1.7	n_3: 2.1
	a_2: 0.8	a_3: 0.2
	contribution: 64%	contribution: 36%
Correlation coefficient: 0.987		

Step 1: $f(\alpha) = \alpha(1-\alpha)$, Prout – Tompkins equation [15]

Step 2 and 3: $f(\alpha) = \alpha^a (1-\alpha)^n$, *a*-th degree autocatalytic reaction with a *n*-th order reaction (expanded Prout – Tompkins equation) [15]

The next step in the kinetic analysis was to perform a non-linear regression analysis in order to evaluate the kinetic parameters of the decomposition. The best kinetic model was chosen for the best correlation coefficient and for highest F-test [13,14]. The non-linear regression analysis was applied to the thermal decomposition of 2-methoxyamino-3, 5-dinitro-pyridine taking into account the partial overlap of the melting and decomposition processes. The results of the kinetic analysis are given in Fig. 4 and Table 1.

The melting process is approximated by a Prout–Tompkins equation and the decomposition process as a two-step consecutive reaction with *a*-the degree autocatalytic reaction with an *n*-th order reaction type.

Conclusions

The study of the thermal decomposition of 2-methoxyamino-3, 5-dinitro-pyridine showed an exothermal process after melting. The experiments revealed that the two processes (endothermal and exothermal) are partially overlapped. The results of kinetic analysis show that 2-methoxyamino-3, 5-dinitro-pyridine decomposes through two consecutive steps. The mechanism is autocatalytic, a characteristic of thermal decomposition of compounds with nitro groups in their molecules [16-19].

Acknowledgements

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