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Thermal stabilities of some benzaldehyde 2,4-dinitrophenylhydrazones

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Abstract The thermal stability of some benzaldehyde 2,4-dinitrophenylhydrazones has been studied using DSC technique. The crystalline solids are thermally stable and start to decompose after melting. Non-isothermal DSC curves, recorded at several heating rates, were used to evaluate the melting properties and the kinetics of thermal decomposition. Both isoconversional and model fitting methods were used for the evaluation of the kinetic parameters. Based on the results of the model free method, a kinetic model was derived and the kinetic parameters were obtained by means of a multivariate non-linear regression. A good agreement between the experimental and fitted data was found.

Keywords Benzaldehyde 2,4-dinitrophenylhydrazones · Differential scanning calorimetry · Exothermal decomposition · Multivariate non-linear regression

Introduction

The derivatives of 2,4-dinitrophenylhydrazone [2,4-DNPH] type have acquired special relevance for the analysis of carbonyl compounds such as aldehydes and ketones [1, 2]. Identification of carbonyls by their 2,4-DNPHs are made by column and thin-layer chromatography. Some 2,4-DNPH derivatives are analyzed by direct Gas–Liquid Chromatography (GLC). An important aspect with regards to the GLC separation of the 2,4-DNPH derivatives lies in their thermal stabilities. As the column temperature required in GLC separation is quite high, artifacts or double peaks occasionally appeared in the chromatograms revealing possible decomposition phenomena [3] of these energetic compounds. Moreover, an increasing interest has been observed during recent years concerning hydrazones due to their coordinative capabilities and physiological activities.

The aim of this article is to study the thermal decomposition of some benzaldehyde 2,4-dinitrophenylhydrazones in isothermal and non-isothermal regime. The derivatives are obtained from the condensation of 2,4-dinitrophenylhydrazine with the corresponding carbonyl compounds (benzaldehyde and its 4-methyl, 4-methoxy and 2 nitro derivatives) as follows (Fig. 1).

The conjugation of the benzaldehyde aromatic ring with C=N double bond, as well as the substituent effect, are expected to markedly influence the thermal stabilities of these compounds. The presence of nitro group on the aromatic ring frequently induces thermal instability, a characteristic feature of aromatic derivatives [4–8]. The hazards associated with this instability have been thoroughly analyzed in many scientific works [9–11]. DNPH is also thermally unstable and decomposes exothermally both in solid and molten state following a multi-step autocatalytic mechanism [12, 13].

The thermal stability of synthesized and purified hydrazones was investigated by differential scanning calorimetry (DSC) under isothermal and non-isothermal conditions. From DSC curves, recorded at several heating rates, several properties such as the melting point, the melting heat, the temperature, and heat of decomposition

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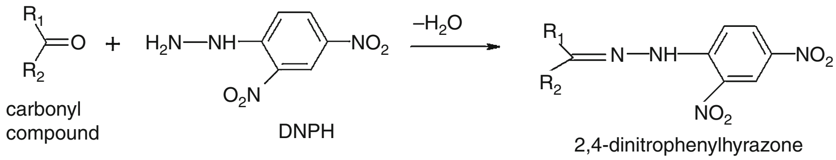

Fig. 1 DNPH and its condensation product with a carbonyl compound

were evaluated. The kinetic parameters of their decomposition were obtained by isoconversional differential Friedman [14] and integral Flynn–Wall–Ozawa (FWO) [15, 16] methods and the reaction model was validated by means of a multivariate non-linear regression analysis. The activation energy was also determined using two equation based on the variable heating rate method, by differential Kissinger [17] and integral Ozawa [18] isoconversional methods. Investigation of the kinetics and mechanism of thermal decomposition of studied compounds can provide valuable information on the behavior of their hazardous nature.

Experimental

To the clear solution, obtained by warming of 2,4-dinitrophenylhydrazine (25 mmol) in 10-mL concentrated hydrochloric acid and 250 mL ethanol, the carbonyl compound (25 mmol) was added and heated just to boiling. The reaction mixture was cooled to room temperature and was filtered and recrystallized from ethanol or glacial acetic acid. The compounds were purified by double recrystallization.

The benzaldehyde 2,4-dinitrophenylhydrazones were insoluble, at room temperature, in all common solvents used for recrystallization; they were simply washed on the filter with boiling ethanol.

The thermal stability experiments were performed using a CAHN DSC 550 differential scanning calorimeter, within the temperature range 298–800 K. The samples of approximately 1 mg were held in aluminum crucibles with a pinhole in the lid to prevent pressure build up due to gaseous products. All experiments were made in argon atmosphere with a 10 mL min^{-1} flow rate. Heating rate of 2, 4, 6, 8, 10, 15, 20, and 30 K min^{-1} were used. At the end of the heating process, the mass of the remaining sample represents approximately 25% from its initial values.

The calibration of temperature and peak area of DSC was carried out using sample (2 mg) of two pure substances (indium and tin) in closed aluminum crucibles at the same heating rates as in the experiments.

The melting temperatures were determined both in open capillary tubes using an electric STUART SMP3 Melting Point Apparatus and also from DSC curves.

Measurements of the depression of the melting point [19] of a sample are often used to determine its purity [20]. Melting endotherms, recorded using DSC are used to recognize the occurrence of melting and to measure the melting temperatures of sample. The melting endotherms for pure substance are very sharp [21]. The presence of an impurity in the sample generally lowers the melting point and also broadness the melting range, giving a boarder DSC endotherms.

The thermal behavior of compounds in isothermal mode was followed at several temperatures lower than the onset melting temperatures. No decomposition was identified after 2 h and more than 30% of sample was vaporized.

The experimental DSC curves were used to determine the characteristic melting and decomposition properties and to investigate the decomposition kinetics using the ‘‘Netzsch Thermokinetics: A Software Module for the Kinetic Analysis of Thermal Measurements’’ program [22, 23], which include initially a model free analysis according to isoconversional Friedman and FWO methods, followed by non-linear regression analysis in order to determinate the multi-step nature and kinetics of decomposition. The "Netzsch Thermokinetics" software was subsequently used to predict the stability of the investigated compounds in molten state using the kinetic parameters and kinetic models obtained by non-linear regression as starting values. Recently, [24–27] this program was used for kinetic analysis of non-isothermal and isothermal data.

Results and discussion

Depending on the structure of the compound the decomposition of the studied derivatives occurs after melting and exhibits an exothermal peak.

For 10 K min^{-1} heating rate, benzaldehyde-2,4-dinitrophenylhydrazone shows an exothermal peak located at 585 K, after the melting process located at 515.7 K (Fig. 2).

The presence of –NO_2 group on the molecule of benzaldehyde engenders important changes of the thermal stability. The DSC curve, at 10 K min^{-1} heating rate, of 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone (Fig. 3) shows a melting process, located at 525.5 K (peak temperature) followed by exothermal decomposition. It can be

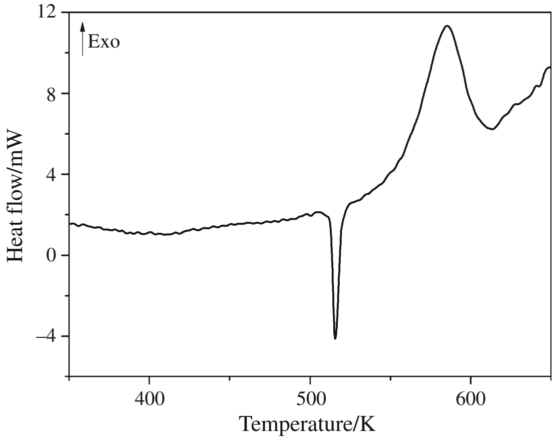

Fig. 2 The DSC curve of benzaldehyde-2,4-dinitrophenylhydrazone

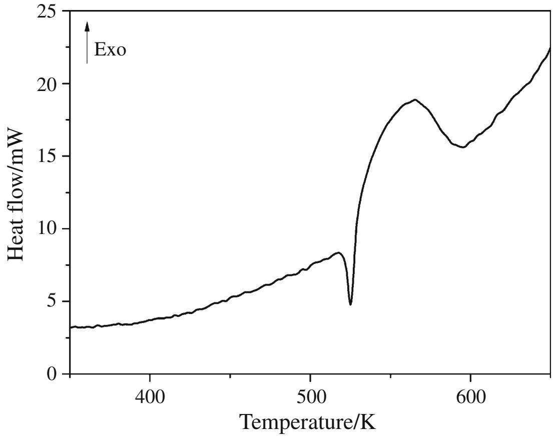

Fig. 3 The DSC curve of 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone

observed that the melting and the beginning of the decomposition process are partially overlapped.

For linear heating 4-methylbenzaldehyde-2,4-dinitrophenylhydrazone decomposes exothermally after its melting. The exothermal process with the maximum temperature at 579.9 K (peak temperature) follows the endothermal process, for a heating rate of 10 K min^{-1} (Fig. 4).

The DSC curve of 4-methoxybenzaldehyde-2,4-dinitrophenylhydrazone given in Fig. 5 (for 10 K min^{-1} heating rate) shows an endothermal process located at 530.7 K followed by an exothermal one with maximum at 586.4 K.

The melting properties and the decomposition heats, ΔH_d of the investigated compounds are given in Table 1. The melting temperatures, determined from extrapolation to zero of the heating rates, are listed in Table 1 together with literature data. The observed melting endotherms of the studied compounds are sharp indicating the purity of the synthesized compounds. The melting temperatures, T_m, and the heats of melting, ΔH_m were used to calculate the melting entropies, as $\Delta S_\mathrm{m} = \Delta H_\mathrm{m}/T_\mathrm{m}$.

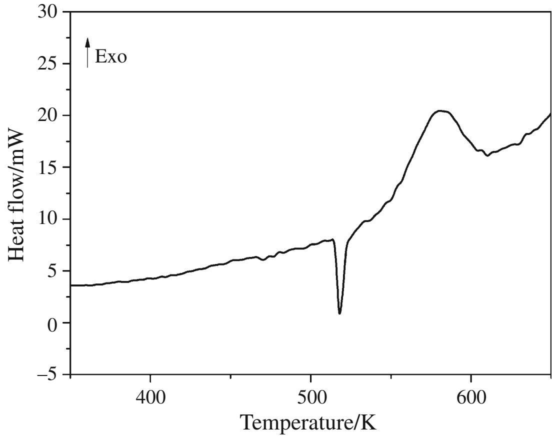

Fig. 4 The DSC curve of 4-methylbenzaldehyde-2,4-dinitrophenylhydrazone

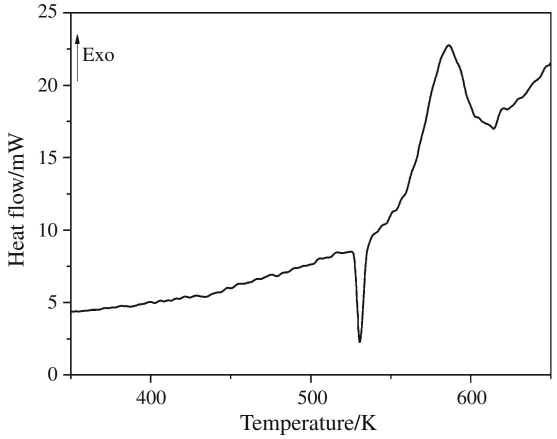

Fig. 5 The DSC curve of 4-metoxybenzaldehyde-2,4-dinitrophenylhydrazone

The results indicate that ΔH_m and ΔS_m tend to decrease with addition of a NO_2, methyl or methoxy groups on the benzaldehyde. In addition, the values of melting entropy are in agreement with those reported in literature for similar compounds [10, 29, 30].

The recorded curves were used to calculate the conversion versus temperature data subsequently used for kinetic analysis of the decomposition process using the "Netzsch Thermokinetic" program. The apparent values of the activation energy of the decomposition processes of investigated 2,4-dinitrophenylhydrazones were initially estimated using the isoconversional Friedman and FWO analysis, as a first approximation. Using the differential method according to Friedman [14], the regression of ln $(\mathrm{d}\alpha/\mathrm{d}t)$ versus $1/T$ for a given conversion, α, for measurements with different heating rates, gives the activation parameters according to Eq. 1:

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha} = \ln[Af(\alpha)] - \frac{E_\mathrm{a}}{RT} \qquad (1)$$

Table 1 The properties of investigated 2,4-dinitrophenylhydrazones derivatives

Compound	T_m(exp)/K from DSC curves	T_m(exp)/K	T_m(lit)/K [28]	ΔH_m(exp)/ J g^{-1}	ΔS_m(exp)/ J $mol^{-1}K^{-1}$	ΔH_d(exp)/ J g^{-1}
Benzaldehyde-2,4-dinitrophenylhydrazone	513.6	512–514	512–514	182.88	75.9	1137.2
2-Nitrobenzaldehyde-2,4-dinitrophenylhydrazone	522.7	528–530	523[a]	68.97	28.1	1605.4
4-Methylbenzaldehyde-2,4-dinitrophenylhydrazone	515.6	515–517	507	162.72	67.3	1223.0
4-Methoxybenzaldehyde-2,4-dinitrophenylhydrazone	524.0	522–524	526[a]	52.21	21.2	1257.0

[a] Decomposition

where α is the conversion, *t* the time, *T* the temperature, E_a the activation energy, and *R* the ideal gas constant. The activation energy was determined from the slope of isoconversional line and the frequency factor *A* was determined from the intercept. The frequency factor is calculated for a first-order reaction with differential conversion function $f(\alpha) = (1 - \alpha)$.

For the integral method according to FWO [15, 16], lnβ is analyzed as a function of 1/*T*, for a given conversion according to Eq. 2:

$$\ln \beta = ct - 1.0518\frac{E_a}{RT} \tag{2}$$

where β is the heating rate and *ct* is a constant. The activation energy E_a was determined from the slope of isoconversional line and the frequency factor *A* was determined from the intercept. The frequency factor is calculated assuming a first-order reaction with integral conversion function $g(\alpha) = -\ln(1 - \alpha)$.

The result of isoconversional Friedman and FWO analysis for studied compounds are given in Tables 2, 3, 4, 5. The apparent values of activation energy for each conversion were obtained with an error of ±20%.

From Tables 2 and 3, it follows that the activation energy has a high value at the beginning of decomposition due to the influence of the melting process. Since the activation energy is approximately the same for various conversions within the significant range 10–90%, it can be assumed that the thermal decomposition of benzaldehyde 2,4-dinitrophenylhydrazone and 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone is likely to occur as a single-step reaction.

A significant variation of the activation energy with conversion, within the significant range 15–90% was observed using both model free methods (within the experimental errors of 20%) for the thermal decomposition of 4-methylbenzaldehyde-2,4-dinitrophenylhydrazone and 4-methoxylbenzaldehyde 2,4-dinitrophenylhydrazone (Table 4 and 5). This result clearly shows that at least two-steps must be considered for the exothermal peak.

Table 2 Kinetic parameters for the thermal decomposition of benzaldehyde-2,4-dinitrophenylhydrazone

Conversion/α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg (A/s^{-1})	E_a/kJ mol^{-1}	lg (A/s^{-1})
0.05	183 ± 20.6	14.1	189 ± 28.6	14.4
0.10	164 ± 11.4	12.5	184 ± 21.3	14.0
0.20	163 ± 8.63	11.6	176 ± 15.8	13.5
0.30	153 ± 6.94	12.1	172 ± 12.9	13.1
0.40	157 ± 8.66	11. 9	169 ± 11.2	12.9
0.50	154 ± 6.37	11.9	166 ± 9.98	12.7
0.60	154 ± 5.28	11.6	164 ± 9.32	12.6
0.70	150 ± 12.8	11.7	163 ± 8.50	12.5
0.80	151 ± 18.4	11.8	161 ± 7.63	12.4
0.90	132 ± 13.2	10.1	161 ± 8.31	12.4
0.95	136 ± 14.0	10.5	160 ± 8.41	12.4

Table 3 Kinetic parameters for the thermal decomposition of 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone

Conversion/α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg (A/s^{-1})	E_a/kJ mol^{-1}	lg (A/s^{-1})
0.05	225 ± 63.6	19.4	325 ± 42.3	28.8
0.10	218 ± 34.9	18.7	280 ± 35.8	24.5
0.20	188 ± 12.9	15.7	242 ± 24.6	20.8
0.30	160 ± 4.69	13.0	242 ± 24.6	18.6
0.40	166 ± 10.1	13.5	219 ± 16.6	16.6
0.50	141 ± 9.15	11.1	198 ± 10.2	15.3
0.60	119 ± 16.3	9.15	185 ± 6.30	14.2
0.70	139 ± 12.8	11.0	174 ± 4.62	13.3
0.80	130 ± 11.5	10.1	164 ± 5.24	12.6
0.90	117 ± 11.9	8.99	148 ± 5.52	11.8
0.95	90.5 ± 32.5	6.63	141 ± 5.97	11.1

The activation energy of the 2,4-dinitrophenylhydrazones were also determined form DSC curves using the differential Kissinger method [17] according to equation:

Table 4 Kinetic parameters for the thermal decomposition of 4-methylbenzaldehyde-2,4-dinitrophenylhydrazone

Conversion/α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg (A/s^{-1})	E_a/kJ mol^{-1}	lg (A/s^{-1})
0.05	157 ± 12.74	12.0	166 ± 17.9	12.4
0.10	142 ± 35.50	10.6	162 ± 10.1	12.2
0.20	187 ± 12.98	14.9	159 ± 5.53	12.0
0.30	153 ± 18.22	11.8	156 ± 3.46	11.9
0.40	140 ± 6.67	10.6	154 ± 3.29	11.7
0.50	142 ± 10.39	10.8	153 ± 4.46	11.7
0.60	139 ± 15.96	10.5	152 ± 6.33	11.6
0.70	122 ± 8.59	9.03	149 ± 7.89	11.3
0.80	122 ± 14.75	9.05	146 ± 9.50	11.0
0.90	115 ± 21.26	8.42	140 ± 12.0	10.6
0.95	122 ± 32.06	9.15	137 ± 15.0	10.3

Table 5 Kinetic parameters for the thermal decomposition of 4-methoxylbenzaldehyde 2,4-dinitrophenylhydrazone

Conversion/α	Friedman analysis		FWO analysis	
	E_a/kJ mol^{-1}	lg (A/s^{-1})	E_a/kJ mol^{-1}	lg (A/s^{-1})
0.05	64.3 ± 35.2	3.11	195 ± 16.0	15.0
0.10	121 ± 20.9	8.61	182 ± 7.80	13.9
0.20	146 ± 14.2	11.0	170 ± 4.11	12.9
0.30	135 ± 22.3	12.1	162 ± 3.39	12.2
0.40	157 ± 6.61	11.5	160 ± 3.23	12.1
0.50	150 ± 10.1	11.5	157 ± 3.59	11.9
0.60	149 ± 22.9	10.6	156 ± 3.53	11.9
0.70	139 ± 13.4	10.7	156 ± 4.01	11.9
0.80	140 ± 9.90	9.86	155 ± 4.31	11.8
0.90	131 ± 23.8	9.26	154 ± 6.19	11.8
0.95	124 ± 12.7	6.87	151 ± 8.55	11.6

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{AR}{T}\right) - \frac{E_a}{RT_{\max}} \qquad (3)$$

where β is the heating rate and $T_{\max}$ is the peak temperature of a DSC scan at that rate. In the experiments, $T_{\max}$ at various heating rate were collected, and values of $\ln\left(\frac{\beta}{T_{\max}^2}\right)$ were plotted against $\frac{1}{T_{\max}}$. The activation energy, E_a, was determined from the linear regression assuming that the term $\ln\left(\frac{AR}{T}\right)$ was constant.

Using the Ozawa method [18], the regression of $\lg\beta$ versus $\frac{1}{T_{\max}}$ at various heating rates, gives the activation energy from the slope according to Eq. 4:

$$\lg\beta = ct - 0.4567\frac{E_a}{RT_{\max}} \qquad (4)$$

where *ct.* is a constant. The results are listed in Table 6.

To discriminate between different kinetic models, a multivariate non-linear regression was applied on the dynamic DSC measurements, at different heating rates, in order to identify the possible number of reaction steps and to evaluate the corresponding kinetic parameters. The most probable kinetic model is chosen for highest *F* test and the best correlation coefficient [31, 32].

The activation parameters of exothermal decomposition of investigated compounds were listed in Table 7. The kinetic models assumed for each step were of the Prout-Tompkins equation (named as 'model a', Eq. 5) and Sestak-Berggren model (named as 'model b', Eq. 6) [33, 34]:

$$f(\alpha) = (1-\alpha)^n(1+K_{\mathrm{cat}}\alpha) \qquad (5)$$

$$f(\alpha) = \alpha^a(1-\alpha)^n \qquad (6)$$

where α is the conversion, K_{cat} is the catalytic constant, n and a are the partial reaction orders.

Several other kinetic models available in the Netzsch Thermokinetics pack were analyzed and rejected according to the corresponding lower *F* tests.

The obtained parameters can be used for prediction of the stability of these compounds in molten state. By comparing the activation energies of decomposition with those obtained using model free methods a good agreement is observed.

There are some significant differences between the activation energies evaluated according to isoconversional integral and differential methods. The qualities and drawbacks of these methods were critically discussed by Vyazovkin [35]. Although the integral method introduces systematic errors in the evaluated activation energies, it is less sensitive to

Table 6 The activation parameters obtained from Kissinger and Ozawa methods

Compound	Kissinger		Ozawa		Temperature range/K
	E_a/kJ mol^{-1}	Correlation coefficient	E_a/kJ mol^{-1}	Correlation coefficient	
Benzaldehyde-2,4-dinitrophenylhydrazone	170 ± 0.5	0.989	171 ± 0.3	0.990	556–605
2-Nitrobenzaldehyde-2,4-dinitrophenylhydrazone	148 ± 0.2	0.995	150 ± 0.4	0.996	535–581
4-Methylbenzaldehyde-2,4-dinitrophenylhydrazone	146 ± 0.3	0.993	147 ± 0.1	0.994	558–605
4-Methoxybenzaldehyde-2,4-dinitrophenylhydrazone	155 ± 0.6	0.993	156 ± 0.2	0.993	562–606

Table 7 Kinetic parameters of exothermal decomposition of investigated 2,4-dinitrophenylhydrazones

Compound	Kinetic parameters		
Benzaldehyde-2,4-dinitrophenylhydrazone	$E_a/\mathrm{kJ\ mol^{-1}} = 158 \pm 0.6$		
	lg $(A/\mathrm{s^{-1}}) = 12.3$		
	$f(\alpha)$—model a		
	Correlation coefficient = 0.995		
2-Nitrobenzaldehyde-2,4-dinitrophenylhydrazone	$E_a/\mathrm{kJ\ mol^{-1}} = 140 \pm 0.8$		
	lg $(A/\mathrm{s^{-1}}) = 11.1$		
	$f(\alpha)$—model a		
	Correlation coefficient = 0.991		
4-Methylbenzaldehyde-2,4-dinitrophenylhydrazone	Step 1	Step 2	
	$E_a/\mathrm{kJ\ mol^{-1}} = 154 \pm 0.3$	$E_a/\mathrm{kJ\ mol^{-1}} = 245 \pm 0.4$	
	lg $(A/\mathrm{s^{-1}}) = 12.0$	lg $(A/\mathrm{s^{-1}}) = 13.6$	
	$f(\alpha)$—model a	$f(\alpha)$—model a	
	Correlation coefficient = 0.995		
4-Methoxybenzaldehyde-2,4-dinitrophenylhydrazone	Step 1	Step 2	Step 3
	$E_a/\mathrm{kJ\ mol^{-1}} = 155 \pm 0.4$	$E_a/\mathrm{kJ\ mol^{-1}} = 257 \pm 0.3$	$E_a/\mathrm{kJ\ mol^{-1}} = 456 \pm 0.6$
	lg $(A/\mathrm{s^{-1}}) = 12.1$	lg $(A/\mathrm{s^{-1}}) = 12.6$	lg $(A/\mathrm{s^{-1}}) = 2.13$
	$f(\alpha)$—model a	$f(\alpha)$—model b	$f(\alpha)$—model a
	Correlation coefficient = 0.991		

experimental noise. A comparative study of these methods is expected to discriminate between their prediction powers of measured data.

The obtained activation energies are in good agreement with those reported in literature (110–300 kJ mol^{-1}) for similar nitro compounds decomposing by an autocatalytic mechanism [10, 12, 13, 36–38].

The kinetic parameters were used to predict the time evolution of thermal decomposition of studied compounds in molten state using "Netzsch Thermokinetics" program. For benzaldehyde-2,4-dinitrophenylhydrazone and 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone at 513 and 523 K, respectively the total reaction occurs in 300 min for the first compound and 90 min for the second one. The 4-methylbenzaldehyde-2,4-dinitrophenylhydrazone and 4-methoxybenzaldehyde-2,4-dinitrophenylhydrazone partially decomposes in molten state at a temperature close to the melting temperatures, in the same conditions.

Conclusions

The thermal stability of four benzaldehyde 2,4-dinitrophenylhydrazones was studied by DSC technique. The experimental curves recorded at several heating rates were analyzed by model free Friedman and FOW methods, and also using two equations based on the variable heating rate method, by differential Kissinger and integral Ozawa methods. The strong dependence of the activation energy on the conversion imposed the use of a multi-step kinetic model only for 4-methylbenzaldehyde and for 4-methoxybenzaldehyde-2,4-dinitrophenylhydrazones. Benzaldehyde-2,4-dinitrophenylhydrazone and 2-nitrobenzaldehyde-2,4-dinitrophenylhydrazone show a single-step reaction. Its actual form was established using a multivariate non-linear regression method. The results of thermal analysis show that the compounds first melts and, while in liquid form, decomposition starts with the degradation of the molecule to gaseous products and a solid residuum. The isothermal analysis indicate a good stability of benzaldehyde 2,4-dinitrophenylhydrazones in solid state. The differences observed in their thermal decompositions can be attributed to the substituent effect on the aromatic ring of the carbonyl compounds. Their thermal decomposition is associated with the liquid state, a common characteristic of many nitro compounds. This behavior can be attributed among other structural properties, to the acquired transitional and rotational degrees of freedom of molecules in the melt as compared to the solid state.

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