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Kinetic analysis of thermal decomposition in liquid and solid state of 3-nitro and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazones

Jeanina Pandele Cusu · Adina Magdalena Musuc · Dumitru Oancea

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Abstract A kinetic study on the thermal decomposition of 3-nitro and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazones was carried out. The isothermal and dynamic differential scanning calorimetric curves were recorded for solids and melts, respectively. The standard isoconversional analysis of the obtained curves from both isothermal and nonisothermal analysis suggests an autocatalytic decomposition mechanism. This mechanism is also supported by the temperature dependence of the observed induction periods. Based on the results of the model-free method from nonisothermal regime, the kinetic model was derived and the kinetic parameters were obtained by means of a multivariate nonlinear regression.

Keywords Isothermal kinetics · Isoconversional method · Induction period · Multivariate nonlinear regression · Nitro-benzaldehyde-2,4-dinitrophenylhydrazone

Introduction

When heated at high temperatures, many solid energetic compounds decompose exothermally during or after melting, indicating an increased instability of the liquid state. The literature concerning the thermal stability of various materials offers numerous examples of solids which decompose during or after melting. The kinetic studies of these systems play an important role for the explosion risks assessment. Many of the generally accepted equations for isothermal or nonisothermal kinetics were considered valid for all condensed media—crystals or melts—except those referring only to the specific characteristics of crystals. A large number of published articles dealing with exothermal decomposition after melting are based on the extension to melts of the kinetic equations derived for solids [1–4], although this approach has occasionally been criticized [1, 2].

Solid nitro derivatives have been found to decompose in the liquid phase after their melting, following a complex autocatalytic mechanism. Their exothermal decomposition in solid state is also of practical interest for hazard evaluation before melting. Chemical compounds able to decompose autocatalytically are considered more hazardous because the decomposition reactions can accelerate even under isothermal conditions during prolonged storage [5, 6]. For the decomposition of nitro compounds, the bond energy of different types of functional groups as well as their position on the aromatic ring determines the thermal stability [7, 8].

The aim of this article is to investigate the thermal behavior of 3-nitro and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazones which proved to decompose either when the solid sample is kept at constant temperatures, lower than the melting point, or after melting, during a linear heating program, unlike 2-nitro-benzaldehyde-2,4-dinitrophenylhydrazone which is stable in crystalline form [9]. The nitrophenylhydrazines are frequently used in analytical chemistry for identification of carbonyl compounds through derivatization to nitrophenylhydrazones, which are often hazardous compounds due to their exothermal decomposition at higher temperatures [10–12].

J. Pandele Cusu (✉) · D. Oancea
Faculty of Chemistry, Department of Physical Chemistry,
University of Bucharest, 4-12 Regina Elisabeta Blvd,
030018 Bucharest, Romania
e-mail: jeaninamirea@yahoo.com

A. M. Musuc
"Ilie Murgulescu" Institute of Physical Chemistry, Romanian
Academy, 202 Spl.Independentei, 060021 Bucharest, Romania

The thermal stability of synthesized and purified dinitrophenylhydrazones was investigated by differential scanning calorimetry (DSC). From the DSC curves, recorded at several heating rates, several properties such as the melting point, melting heat, melting entropy, temperature, and heat of the melt decomposition were evaluated. Isoconversional methods, Friedman [13] and Flynn–Wall–Ozawa (FWO) [14, 15] were applied to nonisothermal data measured at different heating rates yielding a significant dependence of the activation energy on conversion. From this dependence, a multi-step nature of the processes was inferred. The isothermal DSC curves for the same compounds were also used to calculate the activation parameters. The thermal behavior of these two compounds, compared with 2-nitro-benzaldehyde derivative [9], illustrates the important effect of the small structural changes on the thermal stability of related compounds.

Experimental

The thermal behavior in nonisothermal and isothermal regime of the 3-nitro and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazones was investigated using the DSC technique.

Synthesis of compounds

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

Method

The thermal stability experiments were carried out under argon atmosphere with a flow rate of 10 mL min^{-1}, using a CAHN DSC 550 differential scanning calorimeter. Instrument calibration was performed with standard indium samples of known temperatures and enthalpies of melting. The samples with masses between 1 and 1.5 mg were enclosed in aluminum crucibles with a pinhole in the lid to prevent pressure build up due to gaseous products.

The thermal behavior of compound in nonisothermal mode was followed at heating rates of 2, 4, 6, 8, 10, 15, 20, and 30 K min^{-1}. At the end of the heating process the mass of the remaining sample represents approximately 20% from its initial value.

The results from nonisothermal analysis were used to set out the solid-state temperature range. The isothermal decomposition reaction was followed up starting from several temperatures lower than the melting point. A heating rate of 20 K min^{-1} ensured a fast heating between initial and working temperature. Isothermal DSC run was stopped when no further process was observed.

The DSC curves were used to characterize the heat changes during the linear heating as well as the final mass variation and to perform the kinetic analysis of benzaldehyde-2,4-dinitrophenylhydrazones decomposition.

When heated with constant rates both compounds decompose exothermally after melting even for the lowest heating rate (2 K min^{-1}). The nonisothermal experimental curves were used to investigate the decomposition kinetics using both isoconversional (the differential Friedman and integral Flynn–Wall–Ozawa (FWO) methods) and multivariate nonlinear regression methods using the “Netzsch Thermokinetics: A Software Module for the Kinetic Analysis of Thermal Measurements” program [16, 17]. Recently, this program was used for kinetic analysis of nonisothermal and isothermal data [18–24].

The thermal behavior of solid benzaldehyde-2,4-dinitrophenylhydrazones in isothermal regime at several temperatures lower than the melting point showed that the compound exhibit an exothermal decomposition after a temperature-dependent induction period. The recorded curves were used to calculate the conversion versus time data subsequently used for kinetic analysis. The activation energy was determined using both integral and differential isoconversional methods. The overall activation energy was also evaluated from the temperature dependence of the induction period.

Results and discussion

Under linear heating, 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone show endothermal processes associated with melting, followed by exothermal decompositions. Figure 1 shows the curve of 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone for a heating rate of 10 K min^{-1}. After the endothermal process with the peak temperature $T_{\min} = 571$ K, an exothermal process appears with peak temperature $T_{\max} = 589$ K. The evaluation of peak areas gives for the exothermal process $\Delta H_{\mathrm{d}} = -1295$ J g^{-1}.

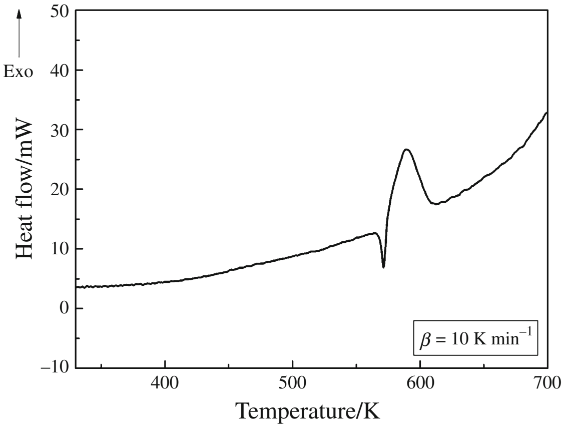

Fig. 1 DSC curve of 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

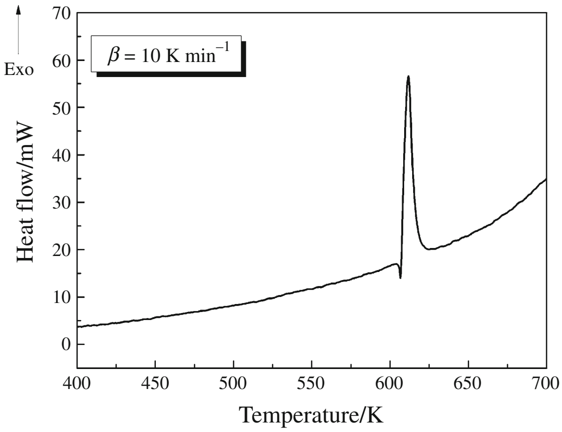

Fig. 2 DSC curve of 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

The DSC curve of 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone for a heating rate of 10 K min^{-1} is represented in Fig. 2. The curve indicates an endothermal peak, associated with the melting process at peak temperature $T_{\mathrm{min}} = 601$ K, which is immediately followed by an exothermal decomposition with peak temperature $T_{\mathrm{max}} = 612$ K and $\Delta H_{\mathrm{d}} = -1202$ J g^{-1}. It can be observed that the melting and beginning of decomposition are partly superposed for the two compounds. The corresponding melting and decomposition heats were evaluated neglecting this superposition.

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 making possible to measure correctly the melting temperature of sample and for extrapolation to zero heating rate. The melting temperatures, T_{m}, and the heats of melting, ΔH_{m} were used to calculate the melting entropies, as $\Delta S_{\mathrm{m}} = \Delta H_m / T_m$.

The results from Table 1 compared with the results obtained from previous studies for 2-nitro-benzaldehyde-2,4-dinitrophenylhydrazone ($\Delta H_{\mathrm{m}} = 68.9$ J g^{-1} (22.8 kJ mol^{-1}) and $\Delta S_{\mathrm{m}} = 43.6$ J mol^{-1} K^{-1}) [9] indicate that ΔH_{m} and ΔS_{m} tend to decrease in the order: *meta*, *ortho*, *para* NO_2 on benzaldehyde. Additionally, the melting entropies are in agreement with those reported in literature for similar compounds [23, 26, 27].

The apparent values of the activation energy for the decomposition process of the two benzaldehyde-2,4-dinitrophenylhydrazones were initially estimated using the isoconversional Friedman and FWO methods. Using the differential method according to Friedman, the regression of ln(dα/dt) versus 1/T for a given conversion, for measurements with different heating rates, gives the activation parameters according to Eq. 1 [13]:

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

where α is the conversion, dα/dt is the rate of conversion, E_{a} the activation energy, R the molar gas constant, and the subscript α indicates the values related to a given conversion.

For the integral method, according to FWO, ln(β) is analyzed as a function of 1/T, for a given conversion according to Eq. 2 [14, 15]:

$$\ln(\beta) = ct - 1.0518\frac{E_{\mathrm{a}}}{RT} \qquad (2)$$

where β is the heating rate.

For both methods, 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 for a first-order reaction with

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

Compound	T_{m}(exp)/K from DSC curves	T_{m}(exp)/K	T_{m}(literature)/K [25]	ΔH_{m}(exp)/J g^{-1}/ kJ mol^{-1}	ΔS_{m}(exp)/ J mol^{-1} K^{-1}
3-Nitro-benzaldehyde-2, 4-dinitrophenylhydrazone	568	565–568	566 (with decomposition)	93.3/30.9	54.4
4-Nitro-benzaldehyde-2, 4-dinitrophenylhydrazone	600	>573 K	593	40.9/13.5	22.5

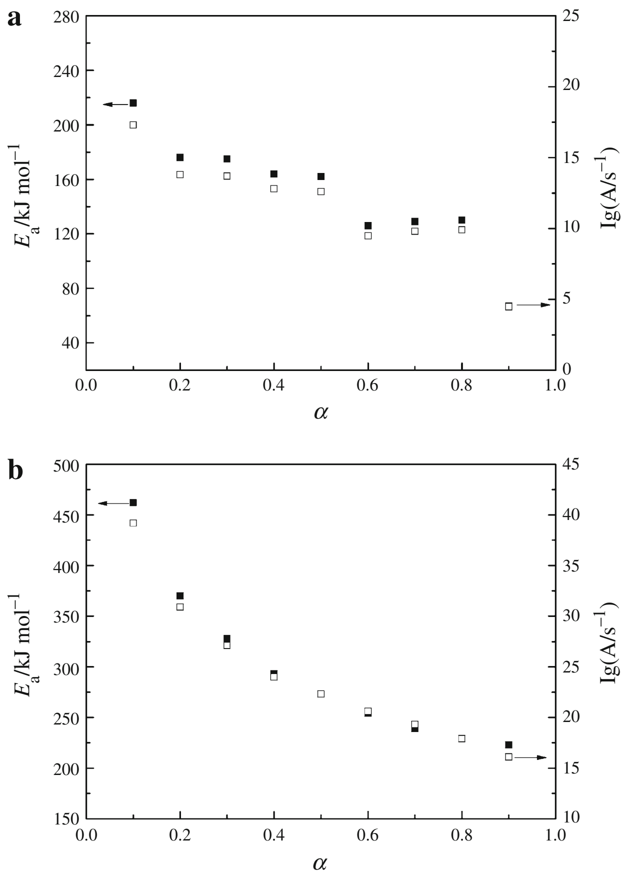

Fig. 3 **a** The Friedman analysis for the thermal decomposition of 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. **b** The FWO analysis for the thermal decomposition of 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

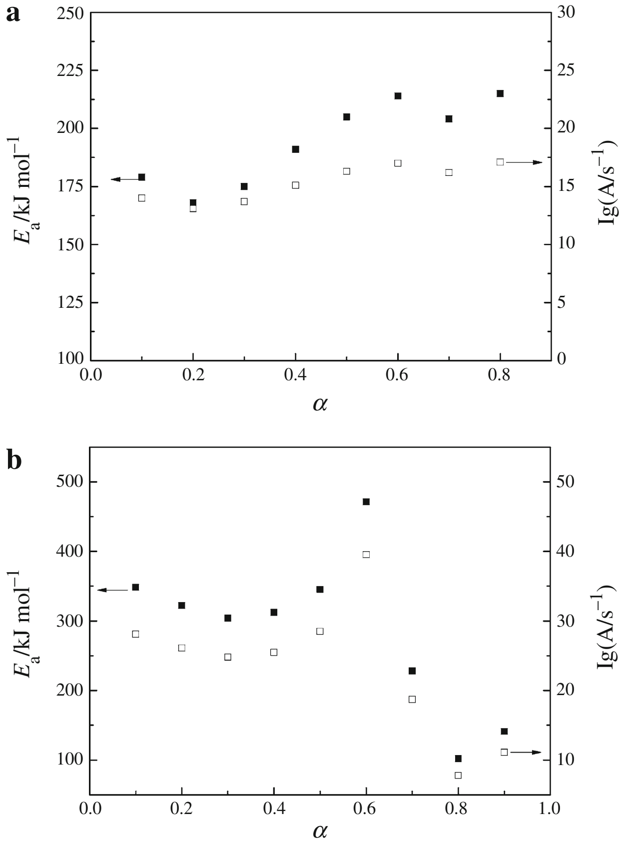

Fig. 4 **a** The Friedman analysis for the thermal decomposition of 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. **b** The FWO analysis for the thermal decomposition of 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

differential conversion function $f(\alpha) = (1 - \alpha)$ for Friedman method. According to FWO method, the frequency factor can be obtained assuming a first-order reaction with integral conversion function $g(\alpha) = -\ln(1 - \alpha)$.

The results from the above model-free analysis of the two benzaldehyde-2,4-dinitrophenylhydrazones decomposition are given in Figs. 3a, b and 4a, b.

A significant variation of the activation energy with conversion, within the significant range 5–95%, resulted from differential Friedman and integral FWO methods of analysis was observed. This result clearly shows that a multi-step mechanism must be considered for exothermal decomposition. To discriminate between different kinetic models, a multivariate nonlinear regression was applied for various possible models. This type of analysis carried out by the software Netzsch Thermokinetics applies a Runge–Kutta method in a modified Marquardt procedure. A system of differential equations based on the relevant reaction types is solved. A two-step consecutive reaction model was found for both compounds. The results of the nonlinear regression analysis for the best kinetic model (highest *F*-test) are given in Table 2. Steps 1 and 2 are of *a*th-degree autocatalytic reactions with an *n*th-order reaction (Sestak–Berggren model) (definition of kinetic model is according to the "Netzsch Thermokinetics: A Software Module for the Kinetic Analysis of Thermal Measurements" program nomenclature):

$$f(\alpha) = \alpha^a (1 - \alpha)^n \qquad (3)$$

where α is the conversion, *n* and *a* are the partial reaction orders.

Several other kinetic models available in the "Netzsch Thermokinetics" package were analyzed and rejected according to the corresponding lower *F* tests [28, 29]. These results indicate that the Sestak–Berggren equation, originally derived for crystalline compounds [30, 31] can also describe properly an autocatalytic process occurring in a liquid phase.

Additional information on the thermal decomposition of the two hydrazones can be obtained from isothermal DSC curves.

For solid-state stability study, several experiments in isothermal regime were performed. Figures 5 and 6 show

Table 2 Kinetic parameters of exothermal decomposition of investigated hydrazones

Compound	Step 1	Step 2
3-Nitro-benzaldehyde-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1} = 277 ± 0.4 log (A/s^{-1}) = 23.0 n = 1.19 a = 0.1 Correlation coefficient = 0.977	E_a/kJ mol^{-1} = 167 ± 0.2 log (A/s^{-1}) = 13.8 n = 2.78 a = 0.09
4-Nitro-benzaldehyde-2,4-dinitrophenylhydrazone	E_a/kJ mol^{-1} = 179 ± 0.5 log (A/s^{-1}) = 14.2 n = 1.34 a = 0.28 Correlation coefficient = 0.994	E_a/kJ mol^{-1} = 265 ± 0.3 log (A/s^{-1}) = 14.5 n = 2.56 a = 1.29

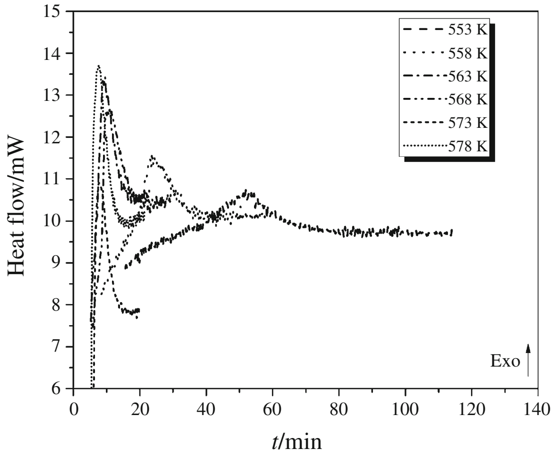

Fig. 5 The DSC curves for different isothermal decomposition experiments of 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

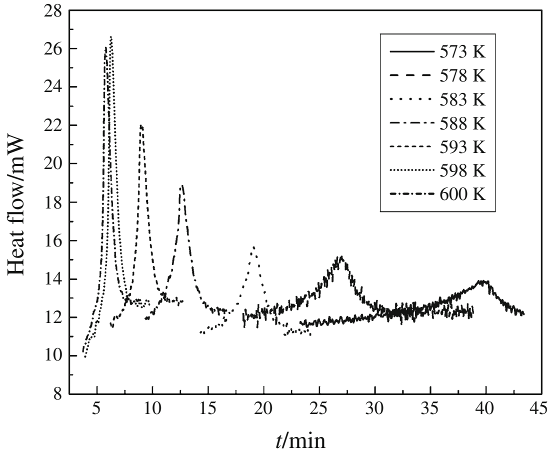

Fig. 6 The DSC curves for different isothermal decomposition experiments of 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

the DSC curves for thermal decomposition of the two hydrazones reached at several fixed temperatures. It can be observed that an exothermal peak appeared after a characteristic temperature-dependent induction period. At temperatures close to the melting point, the DSC curves present also an endothermal process associated with partial melting.

The recorded curves were used to calculate the conversion versus time data subsequently used for kinetic analysis. The $\alpha = f(t)$ isothermal experimental curves chosen at different temperatures are given in Figs. 7 and 8 for the two hydrazones.

The time values, t, measured for the same α were divided by the corresponding $t_{0.5}$ to obtain the normalized curves. The generalized reduced time plots derived from the isoconversional curves have been compared with the generalized reduced theoretical ones reported in literature [30, 32]. The reduced time plots for the various temperatures are given in Figs. 9 and 10. This pattern confirms the existence of an autocatalytic mechanism for the thermal decomposition [32]. Similar isothermal data reported in literature were analyzed using either integral or differential isoconversional methods.

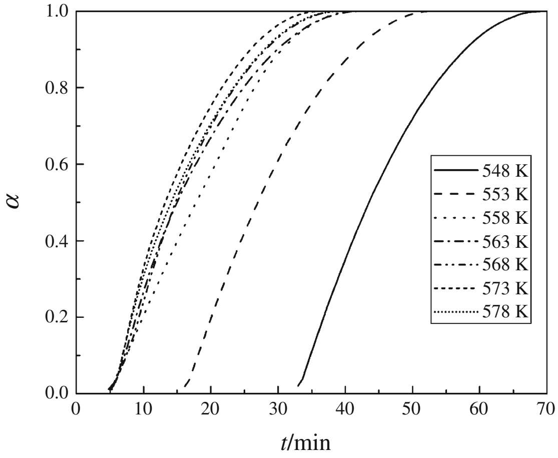

Fig. 7 Conversion versus time curves at different temperatures for 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

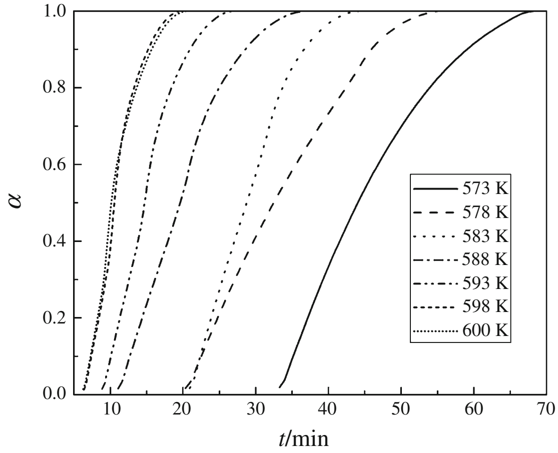

Fig. 8 Conversion versus time curves at different temperatures for 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

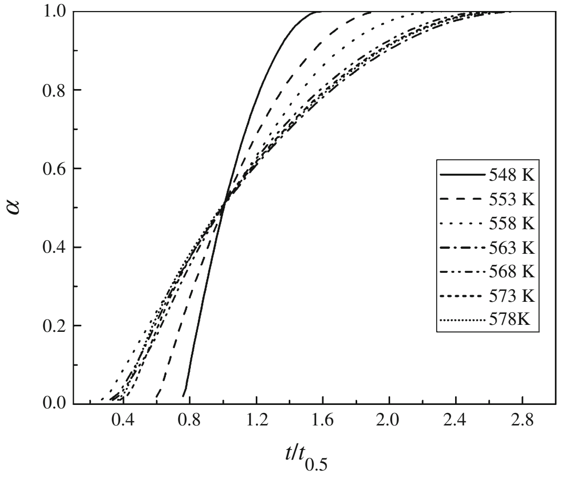

Fig. 9 Conversion versus reduced time curves at different temperatures for 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

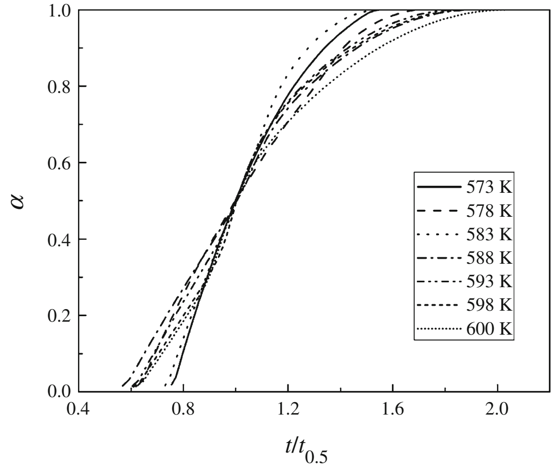

Fig. 10 Conversion versus reduced time curves at different temperatures for 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

It is known that the isothermal kinetics of condensed-state reactions can be represented by the equation [30]:

$$g(\alpha) = kt \tag{4}$$

where k is the specific rate constant and $g(\alpha)$ is an integral mathematical expression related to a mechanisms of condensed-state reactions. From isothermal DSC curves, a set of temperature T, t values were obtained for fixed values of α. By substituting $k = A\exp\left(-{}^{E_a}/_{RT}\right)$ in Eq. 4 one obtains,

$$g(\alpha) = A\exp\left(-{}^{E_a}/_{RT}\right)t \tag{5}$$

where the obtained t and T are the time and temperature values which make constant the function g(α). By using the logarithmic form of Eq. 5, one obtains

$$\ln t = -\ln A + \ln g(\alpha) + {}^{E_a}/_{RT} \tag{6}$$

The kinetic parameters of the decomposition were estimated using both the isothermal isoconversional methods. Using the integral isoconversional method, according to Eq. 7:

$$-\ln t = \ln\left(\frac{A}{g(\alpha)}\right) - \frac{E_a}{RT} \tag{7}$$

a plot of −ln t versus $1/T$ yields E_a for selected conversions, where t is the isoconversional time, A is the pre-exponential factor. The basic assumption of this method is that $g(\alpha)$ at constant conversion does not vary with temperature [33]. The intercept $\ln[A/g(\alpha)]$ is used to evaluate the frequency factor when a certain form of $g(\alpha)$ is assumed.

Using the isoconversional differential method, according to Eq. 8:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_a}{RT} \tag{8}$$

a plot of $\ln(d\alpha/dt)$ versus $1/T$ at each α yields E_a for $\alpha =$ constant. The frequency factor was also calculated from the intercept, assuming a certain form of the corresponding differential conversion function, $f(\alpha)$.

The apparent frequency factors can be also obtained from the intercepts, for each conversion, using Eqs. 7 and 8 and assuming an autocatalytic reaction with integral conversion function $g(\alpha) = [(1-\alpha)\alpha^{-1}]^{0.9} \times 0.9^{-1}$, for integral method [30, 33]. According to the differential method, the frequency factor can be obtained assuming also an autocatalytic reaction with differential conversion function $f(\alpha) = \alpha^{0.1}(1-\alpha)^{1.9}$ [30, 33]. The results are represented in Figs. 11a, b and 12a, b. The specific forms of $f(\alpha)$ and $g(\alpha)$ are introduced according to the shape of the

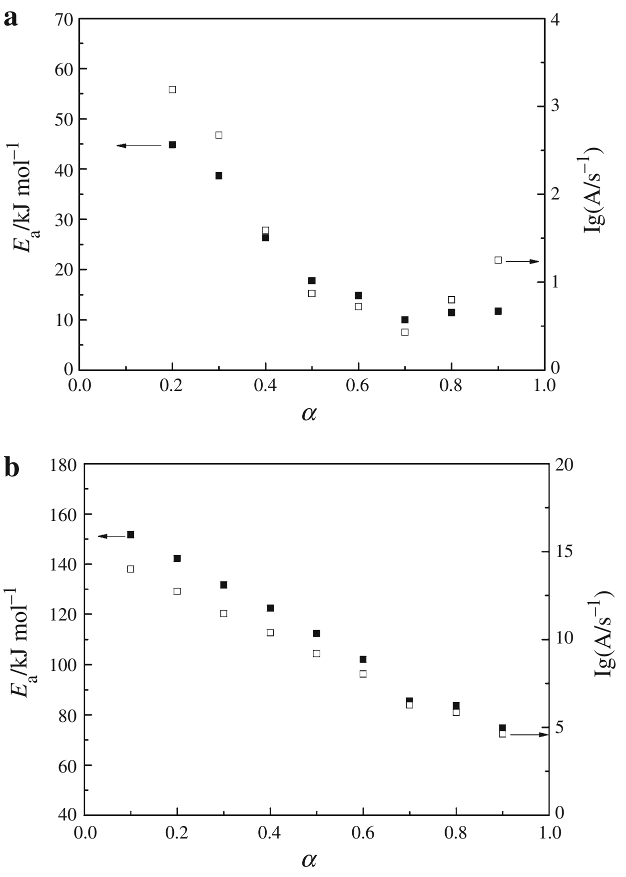

Fig. 11 **a** E_a and log(A) versus α from the isothermal isoconversional differential method for 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. **b** E_a and log(A) versus α from the isothermal isoconversional integral method for 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

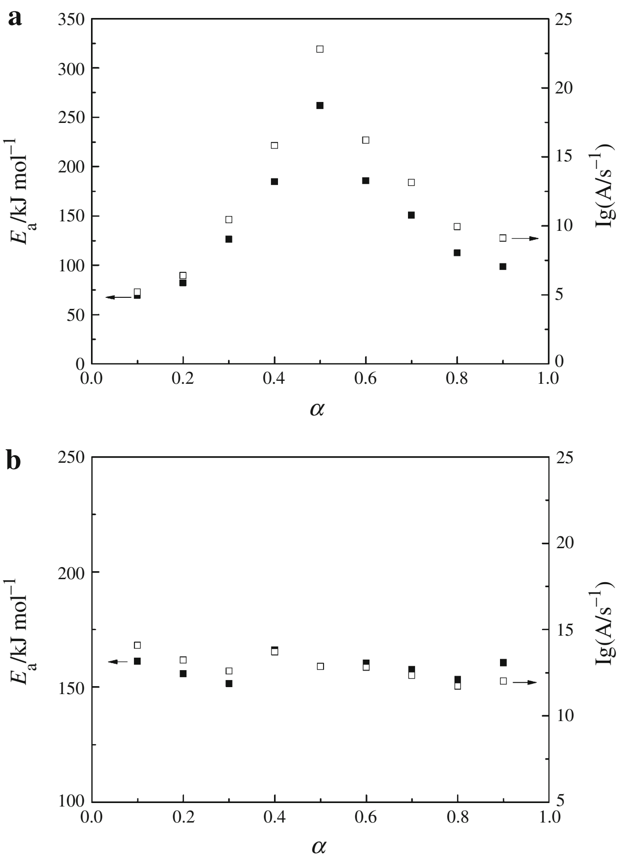

Fig. 12 **a** E_a and log(A) versus α from the isothermal isoconversional differential method for 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. **b** E_a and log(A) versus α from the isothermal isoconversional integral method for 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone

experimental curves, and also with the results obtained from the nonisothermal analysis.

Using the differential isoconversional method, the activation energy at each conversion was evaluated from the slope of the isoconversional line with a good regression coefficient (0.979–0.985) for both compounds (Figs. 11a, 12a). A significant variation of the activation energy with conversion within the significant range 10–90% can be observed. Using the integral isoconversional method, the apparent values of activation energy for each conversion was obtained with a regression coefficient within 0.879–0.968 and an error of 15% for both compounds. The results are given in Figs. 11b and 12b. A variation of activation energy with conversion, within the significant range 10–90%, was also observed.

There are some significant differences between the activation energies evaluated according to isoconversional integral and differential methods. As seen from Figs. 11 and 12, the activation energy obtained with integral method has higher values than those obtained with differential method for the 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. For the 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone, the activation energy shows a different trend. The results suggest the existence of a more complex decomposition mechanism.

Within 0.2–0.8 conversion range for 3-nitro-benzaldehyde-2,4-dinitrophenylhydrazone, the E_a dependencies are lower for isothermal as compared with nonisothermal experiments, while they are very close for 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazone. However, direct comparison between these two methods should not be made because nonisothermal method experiments cover a much wide range of temperatures (300–800 K) than those of isothermal method experiments (548–600 K).

This behavior allows inferring that more than one reaction occurs in the decomposition process for both studied compounds. The complex nature of multi-step process was proved from nonisothermal analysis.

Additional information on the overall activation energy can be obtained from the temperature dependence of the induction period (τ_{ind}). Similar dependencies were reported in literature for decomposition of other solid compounds [34–36]. Using the equation obtained by Musuc et al. [37]:

$$\ln \tau_{\mathrm{ind}} = \ln b + \frac{E_{\mathrm{a}}}{RT} \tag{9}$$

a plot of ln (τ_{ind}) versus $1/T$ should give the overall activation energy E_{a}.

The best fit (*F*-test and correlation coefficient) of experimental data was obtained using a nonlinear (parabolic) equation. The obtained activation energies have the values between 151 and 295 kJ mol^{-1}. The activation energy determined at lower temperatures has a value close to that obtained at small conversion using the isoconversional integral method.

The results of nonlinear regression and the two-step kinetic model were used to predict the reaction behavior by simulating different reaction conditions. The two studied compounds partially decompose in molten state at a temperature close to the melting temperatures after a long period of time (300 min).

Conclusions

The investigation of the thermal behavior of 3-nitro and 4-nitro-benzaldehyde-2,4-dinitrophenylhydrazones in liquid state, after the melting process, showed that both compounds exhibit an exothermal decomposition proving their hazardous nature. The results of kinetic analysis indicate the existence of specific reaction mechanisms with two autocatalytic steps for both compounds. The study of thermal behavior in solid state in isothermal regime at several temperatures lower than the melting point showed that the two compounds exhibit an exothermal decomposition after a temperature-dependent induction period. The activation energy was determined using both integral and differential isoconversional methods. The kinetic parameters obtained with the differential method allow a realistic simulation of experimental results. From the analysis of conversion-reduced time, an autocatalytic reaction model was proposed for these two compounds. The results from nonisothermal analysis are in agreement with those obtained from isothermal studies. Although the component steps present specific features, in solid and liquid states, both mechanisms imply autocatalytic steps, a characteristic of thermal decomposition of nitro compounds. The thermal decomposition in nonisothermal regime occurs in liquid phase. The presence of the reaction products in the system as impurities causes the melting point depression. Also, the presence of the reaction products in the system significantly modifies the thermal decomposition kinetics, enhancing the autocatalytic character. The selected kinetic models and the corresponding kinetic parameters of the investigated compounds enable the prediction of the reaction behavior of the system.

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