

Thermal stabilities of new synthesized *N*-methoxy-polynitroanilines derivatives

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Abstract The thermal decomposition of new *N*-methoxy-polynitroanilines was studied using the differential scanning calorimetry (DSC) method. The characteristic melting parameters were measured and the activation parameters of the most probable kinetic models of thermal decomposition were determined using a multivariate non-linear regression method. All investigated compounds followed an autocatalytic decomposition mechanism. Depending on the number and position of substituents on the aromatic ring the thermal decomposition occurs in one, two or three steps.

Keywords Exothermal decomposition · Kinetic analysis · Multivariate non-linear regression · *N*-methoxy-polynitroanilines

Introduction

The kinetics of the decomposition reactions of nitro compounds is an important step in risk analysis and the assessment of potential hazard during their production, transportation and storage. The presence of even one nitro group on the aromatic ring is sufficient to decrease the thermal stability of these compounds. The experimental and

theoretical analysis of the thermal decomposition of nitro compounds in different conditions gives valuable information on the time evolution of the process. Depending on the compound and on the experimental conditions, the thermal decomposition can occur in solid or liquid phase. The presence of different types of functional groups, such as $-\text{NH}-\text{O}-\text{CH}_3$ or/and $-\text{CN}$ functions on the aromatic ring containing nitro groups induces a supplementary instability of the molecule. It has been found that for the decomposition of nitro compounds the bond energy of different types of functional groups and their position on the aromatic ring determine the thermal stability. A large amount of literature data has been reported on the decomposition of polynitroaromatic compounds and many attempts to correlate their thermal decomposition kinetics with molecular structure and thermal stability [1–7] were advanced. For a large number of nitro compounds reported in literature the autocatalytic multi-step decomposition [8–10] was found as a frequent feature.

The aim of this paper was to study the thermal behavior of several less characterized *N*-methoxy-polynitroanilines [11], with unknown thermal properties, using DSC method. Synthesis of *N*-methoxy-polynitroaniline derivatives has been intensively studied in recent years, due to their chromogenic properties with numerous applications in analytical and preparative chemistry. On the other hand, these compounds may be oxidized to persistent free radicals, which may be intermediates in self-nitration processes.

From the DSC curves, recorded at various heating rates, several properties such as the melting temperature, the melting heat and the melting entropy, the average overall heat of the decomposition and the maximum peak temperatures can be obtained. The kinetic analysis started with the isoconversional Friedman [12] and Flynn–Wall–Ozawa (FWO) methods [13, 14]. This analysis indicated a

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variation of the activation parameters during the progress of reaction. The suggested multi-step nature of the processes was subsequently substantiated using a multivariate regression analysis.

Experimental

The thermal stabilities of the following compounds derived from *N*-methoxy-anilines were evaluated: *N*-methoxy-2, 4-dinitroaniline, *N*-methoxy-2, 6-dinitroaniline, *N*-methoxy-2, 4, 6-trinitroaniline, *N*-methoxy-2-cyano-4, 6-dinitroaniline, *N*-methoxy-3-cyano-4, 6-dinitroaniline, *N*-methoxy-4-cyano-2, 6-dinitroaniline. The synthesis and characterization by UV-VIS and NMR spectra and by pK_a measurements were reported in literature [11, 15].

The experiments were carried out using a CAHN DSC 550 differential scanning calorimeter, between 25 and 300 °C. Samples of 0.9–1.3 mg were placed in aluminum crucibles with a pinhole in the lid. All experiments were made in argon atmosphere with a 10 mL min⁻¹ flow rate. Heating rates of 2, 2.5, 5, 10 and 15 K min⁻¹ were used. At the end of the process the residual mass was approximately 35% from its initial value. The calibration of temperature and peak area of DSC was carried out using samples (2 mg) of two pure substances (indium and tin) in closed aluminum crucibles at the same heating rates as in experiments.

The experimental DSC curves were used to determine the characteristic melting and decomposition properties and to investigate the decomposition kinetics using the “Netzsch Thermokinetics” program [16, 17], 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 thermal behavior of all *N*-methoxy-polynitroanilines in isothermal mode was followed at several temperatures lower than the onset melting temperatures. No decomposition was identified after one hour and more than 60% of sample was vaporized.

Results and discussion

An examination of the DSC curves shows that, depending on the structure of the compound, the decomposition of the samples occurs before or after melting and exhibits a single or several exothermal peaks. For 10 °C min⁻¹ heating rate, *N*-methoxy-2, 4-dinitroaniline shows two separate exothermal peaks located at 120 °C for the first process and 256.7 °C for the second one, after the melting process located at 101 °C (Fig. 1a). The DSC curve of *N*-methoxy-2, 6-dinitroaniline (Fig. 1b) shows a melting process,

located at 113 °C (peak temperature), followed by a complex exothermal decomposition. The DSC curve of *N*-methoxy-2, 4, 6-trinitroaniline from Fig. 1c shows two exothermal peaks between 90 and 150 °C followed by a strong exothermal peak with maximum at 270.9 °C (Fig. 1c).

The presence of –CN group on benzene ring engenders important changes of the thermal stability. The DSC curves of *N*-methoxy-2-cyano-4, 6-dinitroaniline, *N*-methoxy-3-cyano-4, 6-dinitroaniline and *N*-methoxy-4-cyano-2, 6-dinitroaniline are given in Fig. 2a–c.

For linear heating *N*-methoxy-2-cyano-4, 6-dinitroaniline decomposes exothermally after its melting. Two exotherms with the maximum temperatures at 150.8 °C (for the first peak) and 279.3 °C (for the second peak) follows the endothermal process located at 146.7 °C (peak temperature), for a heating rate of 10 °C min⁻¹.

N-methoxy-3-cyano-4, 6-dinitroaniline decomposes without apparent melting exhibiting two separate exothermal peaks with the maximum temperatures at 159.5 and 265.7 °C (for a heating rate of 10 °C min⁻¹, Fig. 2b).

The DSC curve of *N*-methoxy-4-cyano-2, 6-dinitroaniline given in Fig. 2c shows one exothermal peak with the maximum temperatures at 123.5 °C.

The melting properties of the investigated compounds are given in Table 1. The melting temperatures, determined from extrapolation to zero of the heating rate, are listed in Table 1 together with literature data [11]. The melting temperatures, T_m , and the melting heats, ΔH_m were used to calculate the melting entropies, as $\Delta S_m = \Delta H_m/T_m$.

The results indicate that ΔH_m and ΔS_m tend to decrease with addition of a CN group on the aromatic ring. Additionally, the values of melting entropy are in agreement with those reported in literature for similar nitro compounds [18, 19].

The next step was to perform the kinetic analysis of decomposition process. This was accomplished using the “Netzsch Thermokinetic” program. The apparent values of the activation energy of the decomposition processes of *N*-methoxy-polynitroanilines were initially estimated using the isoconversional Friedman [12] and FWO [13, 14] analysis, as a first approximation. Using the differential method according to Friedman, the regression of $\ln(d\alpha/dt)$ vs. $1/T$ for a given conversion, α , for measurements with different heating rates, gives the activation parameters according to Eq. 1:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (1)$$

where α is the conversion, t the time, T the temperature, E_a the activation energy and R the gas constant. The activation energy was determined from the slope of isoconversional line and the frequency factor A was determined from the

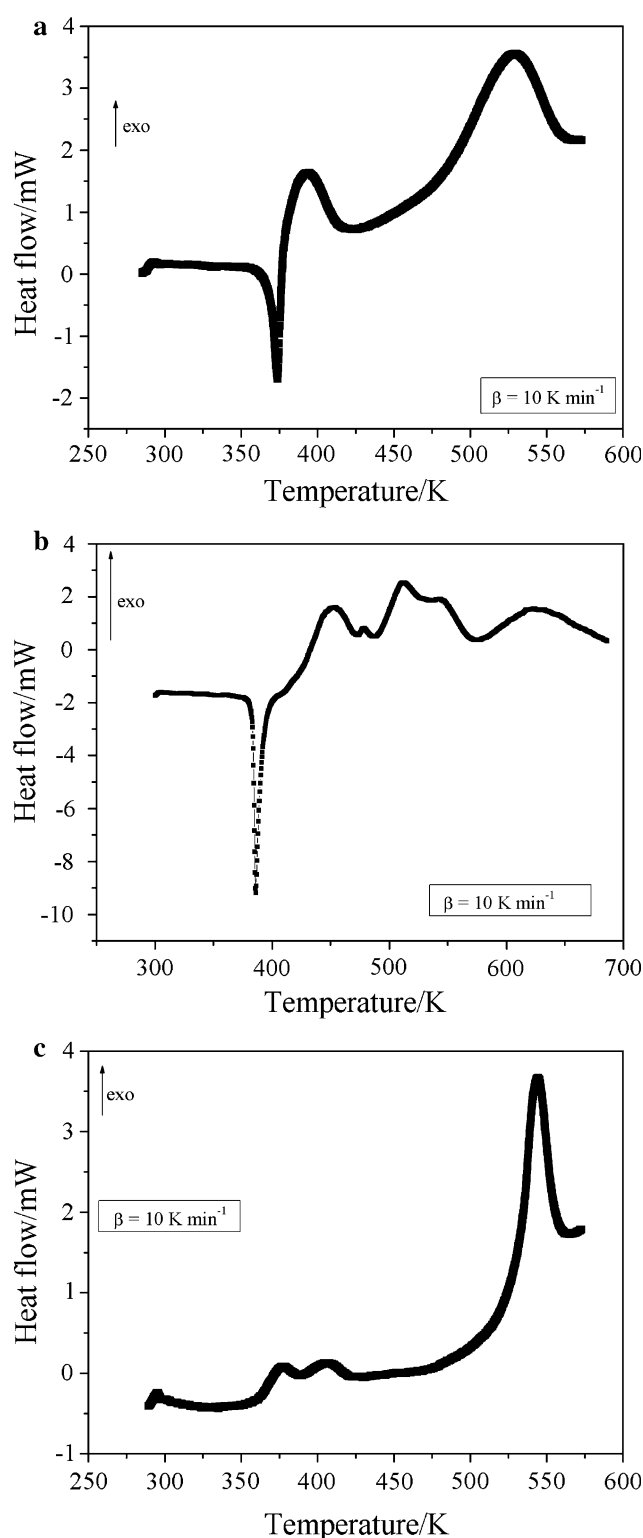


Fig. 1 **a** The DSC curve of *N*-methoxy-2, 4-dinitroaniline. **b** The DSC curve of *N*-methoxy-2, 6-dinitroaniline. **c** The DSC curve of *N*-methoxy-2, 4, 6-trinitroaniline

intercept. The frequency factor is calculated for a first-order reaction with differential conversion function $f(\alpha) = (1 - \alpha)$ [16, 17].

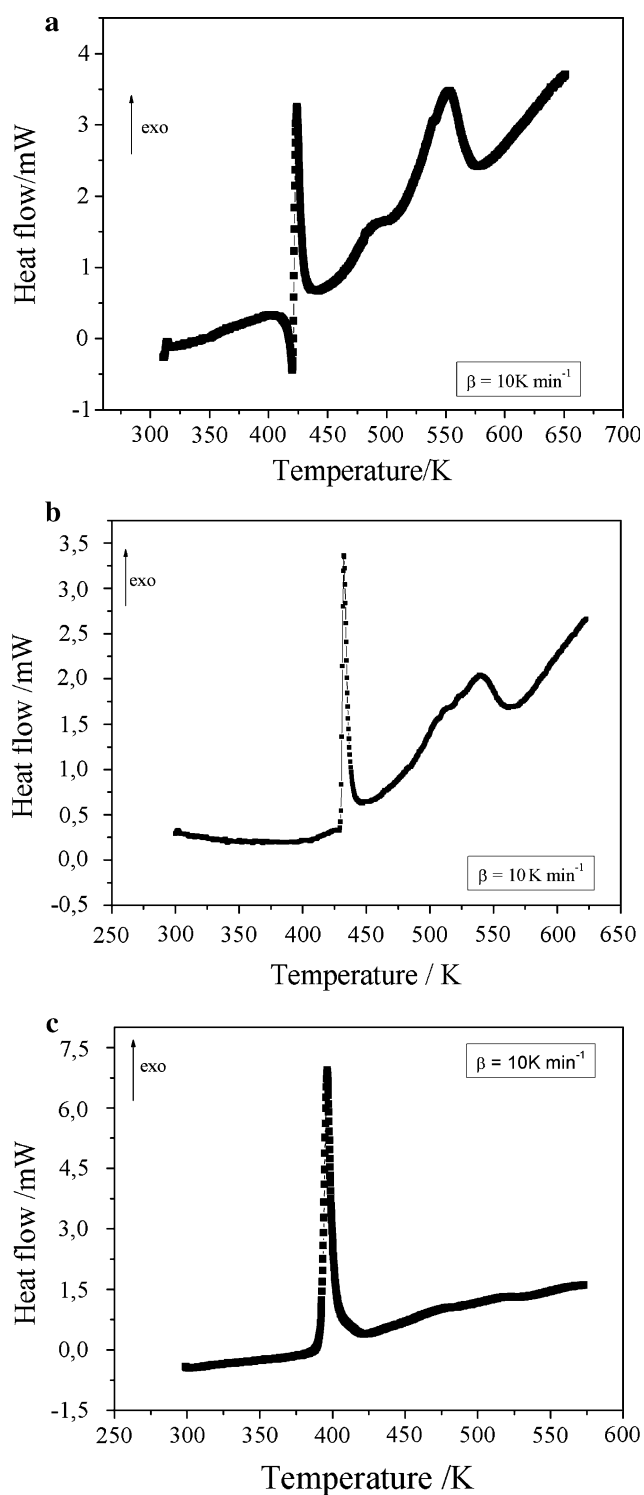


Fig. 2 **a** The DSC curve of *N*-methoxy-2-cyano-4, 6-dinitroaniline. **b** The DSC curve of *N*-methoxy-3-cyano-4, 6-dinitroaniline. **c** The DSC curve of *N*-methoxy-4-cyano-2, 6-dinitroaniline

For the integral method according to FWO, $\ln \beta$ is analyzed as a function of $1/T$, for a given conversion according to Eq. 2 [13]:

Table 1 The melting properties of investigated *N*-methoxy-polynitroaniline derivatives

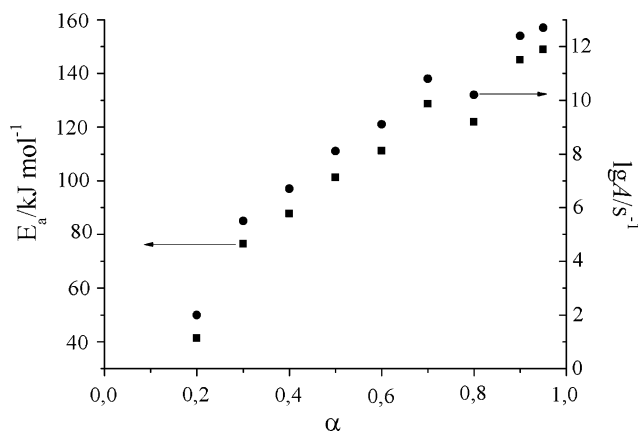
Compound	$T_m(\text{exp})$ (°C)	$T_m(\text{lit})$ (°C) [9]	$\Delta H_m(\text{exp})$ (J g ⁻¹)	$\Delta S_m(\text{exp})$ (J mol ⁻¹ K ⁻¹)
<i>N</i> -methoxy-2, 4-dinitroaniline	86.8	112.0	57.07	33.8
<i>N</i> -methoxy-2, 6-dinitroaniline	109.8	115.0	113.5	63.2
<i>N</i> -methoxy-2, 4, 6-trinitroaniline	–	165.0	–	–
<i>N</i> -methoxy-2-cyano-4, 6-dinitroaniline	145.1	142.0	21.4	12.2
<i>N</i> -methoxy-3-cyano-4, 6-dinitroaniline	–	160.0	–	–
<i>N</i> -methoxy-4-cyano-2, 6-dinitroaniline	–	135.0	–	–

$$\ln \beta = ct - 1.0518 \frac{E_a}{RT} \quad (2)$$

where β is the heating rate. 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 Friedman analysis for *N*-methoxy-2, 4, 6-trinitroaniline (for the third exothermal peak) is given in Fig. 3. The apparent values of activation energy for each conversion were obtained with an error of 20%.

A significant variation of the activation energy with conversion, within the significant range 10–90% was observed using both model-free methods, (within the experimental errors of 20%) for several exothermal processes, for thermal decomposition of investigated *N*-methoxy-polynitroanilines. These results clearly indicate that at least two-steps must be considered for those exothermal processes. Since the activation energy is approximately the same for various conversions within the significant range 10–90% (within the mentioned experimental errors) using both Friedman and Flynn–Wall–Ozawa methods, for the first decomposition process of *N*-methoxy-2, 4-dinitroaniline and *N*-methoxy-2, 6-dinitroaniline, respectively, it can be assumed that the thermal decomposition is likely to occur as a single-step reaction.

**Fig. 3** The Friedman analysis for thermal decomposition of *N*-methoxy-2,4,6-trinitroaniline

The existence of a linear correlation between $\ln A$ and E_a (the compensation effect), very frequently reported in literature [20–25], was verified:

$$\ln A = a + bE_a \quad (3)$$

where a and b are constants. The activation energy (E_a) of exothermal decomposition of studied compounds was determined using the Coats-Redfern method [26]:

$$\ln \frac{g(\alpha)}{T^2} \cong \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (4)$$

where

$$g(\alpha) = \int_0^\alpha \frac{1}{f(\alpha)} d\alpha \quad (5)$$

The values of the pre-exponential factor (A) were calculated under the assumption of the autocatalytic Sestak-Berggren model [27]:

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

Using the Eq. 3 the existence of the compensation effect between values of E and $\ln A$ obtained by Coats-Redfern method was checked. For all investigated compounds the obtained results did not confirm the existence of the compensation effect.

The kinetic analysis was expanded performing a multi-variate non-linear regression analysis on the dynamic DSC measurements at different heating rates to identify the possible number of reaction steps and to evaluate the corresponding kinetic parameters. The most probable kinetic model was chosen for highest F -test and the best correlation coefficient [28, 29]. A two or/and three steps mechanism was accepted as the most probable for the thermal decomposition of the studied *N*-methoxy-polynitroaniline compounds, for each exothermal peak.

The kinetic models assumed for each step were of an n -th order reaction with autocatalysis, Sestak-Berggren model (Eq. 6) [27] (named model 1) and the Prout-Tompkins equation (Eq. 7) (named model 2) [30]:

$$f(\alpha) = (1 - \alpha)^n (1 + K_{\text{cat}}\alpha) \quad (7)$$

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

Table 2 Kinetic parameters of thermal decomposition of *N*-methoxy-polynitroanilines derivatives

Compound	First exothermal process			Second exothermal process		
	E_a /(kJ mol ⁻¹)	A/s^{-1}	r	E_a /(kJ mol ⁻¹)	A/s^{-1}	r
<i>N</i> -methoxy-2, 4-dinitroaniline	103.8 ± 0.9	1.58E + 12	0.989	99.1 ± 0.3	2.0E + 08	0.997
	$f(x)$ —model 1			125.0 ± 0.8	2.0E + 10	
<i>N</i> -methoxy-2, 6-dinitroaniline*	49.8 ± 0.6	5.01E + 04	0.947	126.3 ± 0.6	2.0E + 09	0.981
	$f(x)$ —model 1			120.0 ± 0.7	7.94E + 08	
				$f(x)$ —model 2 for both processes		
<i>N</i> -methoxy-2, 4, 6-trinitroaniline**	142.0 ± 0.3	1.3E + 12	0.995	—	—	—
	140.0 ± 0.4	1.0E + 10				
	$f(x)$ —model 2 for both processes					
<i>N</i> -methoxy-2-cyano-4, 6-dinitroaniline***	93.1 ± 0.6	5.01E + 10	0.985	176.4 ± 0.8	1.26E + 15	0.996
	129.2 ± 0.8	3.98E + 14		180.0 ± 0.7	1.58E + 15	
	First process—model 2			$f(x)$ —model 2 for both processes		
	Second process—model 1					
<i>N</i> -methoxy-3-cyano-4, 6-dinitroaniline	127.5 ± 0.3	1.0E + 12	0.936	81.9 ± 0.6	2.0E + 05	0.987
	128.9 ± 0.4	7.9E + 08		94.9 ± 0.7	3.2E + 08	
	132.5 ± 0.3	2.0E + 11		$f(x)$ —model 1 for both processes		
	$f(x)$ —model 2 for all processes					
<i>N</i> -methoxy-4-cyano-2, 6-dinitroaniline	120.1 ± 0.5	1.0E + 15	0.988	—	—	—
	87.0 ± 0.6	1.58E + 09				
	83.2 ± 0.2	5.01E + 09				
	$f(x)$ —model 2 for all processes					

*The first exothermal process was considered between 403 and 472 K and the second one between 472 and 552 K. The third exothermal process is not completed for all heating rates and temperature range limitation of DSC CAHN 550

**The kinetic analysis for the first two exothermal processes, between 358 and 421 K temperature range, do not lead to activation parameters with real physical significance

***The first exothermal process was considered between 420 and 443 K and the second one between 462 and 581 K

The activation parameters of exothermal decomposition of investigated compounds were listed in Table 2.

Several other kinetic models available in the “Netzsch Thermokinetic” package were analyzed and rejected according to the above criteria.

From Table 2 it results that the presence of a third nitro group or of a -CN group on the aromatic ring changes significantly the overall decomposition process. The activation energies (80–180 kJ mol⁻¹) and pre-exponential factors (1.0E + 10–1.0E + 15 s⁻¹) are closer to those reported in literature for similar nitro compounds which decompose exothermally following a multi-step autocatalytic mechanism [31–33]. The results are in good agreement with those reported by Zeman et al. [34–36] for thermal decomposition of *N*-substituted 2, 6-dinitroanilines using DTA method. They predicted on the basis of experimental analysis an increase in the thermal stability due to the increasing volume of the *N*-alkyl substituent of *N*-monosubstituted derivatives of 2, 4-dinitroanilines. It follows from the results of their paper [34] that this leads to the formation of more rigid activated complexes in the

thermal decomposition of *N*-alkyl-2, 4-dinitroanilines than the 2, 6-dinitro analogues. They found that only *N*-methoxy-2, 4-dinitroaniline has an approximately planar molecule and the others are nonplanar. Similarly, a relationship of this type was found for the *N*-methoxy-polynitroaniline derivatives studied in this paper on the basis of the calculated activation energies and the decomposition temperature range.

Conclusions

From the analysis of experimental DSC curves of *N*-methoxy-polynitroanilines it can be concluded that in the series of di- and tri- *N*-substituted compounds, di-*N*-substituted ones are more stable according to the onset decomposition temperatures and activation energies. The results of the kinetic analysis indicate the existence of complex reaction mechanisms of thermal decomposition of these compounds. All compounds followed a multi-step autocatalytic reaction. The exothermal decomposition

temperatures (for the first exothermal peak) of investigated compounds clearly show that the thermal sensitivity increases in the order *N*-methoxy-4-cyano-2, 6-dinitroaniline, *N*-methoxy-2, 4-dinitroaniline, *N*-methoxy-2, 6-dinitroaniline, *N*-methoxy-2-cyano-4, 6-dinitroaniline, *N*-methoxy-3-cyano-4, 6-dinitroaniline, *N*-methoxy-2, 4, 6-trinitroaniline. The differences in thermal stability of *N*-methoxy-polynitroanilines derivatives are due to both the electronic and steric effects of the functional groups present on the aromatic ring.

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References

- Rongzu H, Desuo Y, Hongan Z, Shengli G, Qizhen S. Kinetics and mechanism of the exothermic first-stage decomposition reaction for 1,4-dinitro-3,6-bis(trinitroethyl)glycoluril. *Thermochim Acta*. 2002;389:65–9.
- Brown ME. Thermal analysis of energetic materials. *Thermochim Acta*. 1988;148:521–31.
- Vogel K, Widmann G. Investigating safety aspects by thermal analysis. *J Therm Anal*. 1989;35:329–34.
- Pickard JM. Application of rigorous nonlinear regression to the decomposition kinetics of explosives. *Thermochim Acta*. 1989;149:301–15.
- Grewer Th, Frurip DJ, Harrison BK. Prediction of thermal hazards of chemical reactions. *J Loss Prev Proc Ind*. 1999;12:391–8.
- Zeman S. Thermogravimetric analysis of polynitro arenes. *J Therm Anal Calorim*. 2001;65:919–33.
- Ksiazczak A, Ksiazczak T, Zielenkiewicz T. Influence of purity on the thermal stability of solid organic compounds. *J Therm Anal Calorim*. 2004;77:233–42.
- Long GT, Brems BA, Wight ChA. Autocatalytic thermal decomposition kinetics of TNT. *Thermochim Acta*. 2002;388:175–81.
- Chervin S, Bodman GT. Phenomenon of autocatalysis in decomposition of energetic chemicals. *Thermochim Acta*. 2002;392–393:371–83.
- Bon-Diab L, Fierz H. Autocatalytic decomposition reactions, hazards and detection. *J Hazard Mater*. 2002;93:137–46.
- Stanciu C, Constantinescu T, Caproiu MT, Zarna N, Carageorghopol A, Caldararu H, et al. Self-nitration of *N*-alkoxy-dinitroanilines as result of oxidation processes. *Rev Roum Chim*. 1997;42:395–400.
- Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Applications to a phenol plastic. *J Polym Sci*. 1963;6C:183–95.
- Ozawa T. A new method of analyzing thermogravimetric data. *Bull Chem Soc Jpn*. 1965;38:1881–6.
- Flynn JH, Wall LA. General treatment of the thermogravimetry of polymers. *J Res Nat Bur Stand*. 1966;70A:487–523.
- Beteringhe A. QSPR study on pKa values of *N*-methoxy-poly-nitroaniline. *Cent Eur J Chem*. 2005;3(4):585–91.
- Opfermann J. Kinetic analysis using multivariate non-linear regression. I. Basic concepts. *J Therm Anal Calorim*. 2000;60:641–58.
- Flammersheim H-J, Opfermann JR. Kinetic evaluation of DSC curves for reacting systems with variable stoichiometric compositions. *Thermochim Acta*. 2002;388:389–400.
- Ranga Reddy S, ManikYamba P. Linear free energy relationship in reactions between diphenyl amine and benzyl bromides. *J Chem Sci*. 2006;118(3):257–60.
- Fukuhara K, Akisue M, Matsuura H. Melting of the all-trans planar modification of triblock oligomers α -*n*-alkyl- ω -*n*-alkoxyoligo(oxyethylene)s. *Chem Lett*. 2001;30(8):828–30.
- Brown ME, Galwey AK. The significance of "compensation effects" appearing in data published in computational aspects of kinetic analysis: ICTAC project, 2000. *Thermochim Acta*. 2002;387:173–83.
- Budrugaec P, Segal E. Non-isothermal kinetics of reactions whose activation energy depends on the degree of conversion. *Thermochim Acta*. 1995;260:75–85.
- Budrugaec P, Segal E. On the compensation effect at the form of the differential conversion function. *J Therm Anal Calorim*. 1998;53:269–83.
- Budrugaec P, Segal E. On the apparent compensation effect found for two consecutive reactions. *J Therm Anal Calorim*. 2000;62:227–35.
- Norwicz J, Musielak T. Compensation law again. *J Therm Anal Calorim*. 2007;88(3):751–5.
- Dias DS, Crespi MS, Ribeiro CA, Fernandes JLS, Cerqueira HMG. Application of non-isothermal cure kinetics on the interaction of poly(ethylene terephthalate)—alkyd resin paints. *J Therm Anal Calorim*. 2008;91(2):409–12.
- Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature*. 1964;201:68–9.
- Sestak J, Berggren G. Study of the kinetics of the mechanism of solid-state reactions at increasing temperatures. *Thermochim Acta*. 1971;3:1–12.
- Mandel J. The statistical analysis of experimental data, Chap. 6–7. New York; 1984.
- Marinoiu V, Stratula C, Petcu A, Patrascioiu C, Marinescu C. Metode numerice aplicabile in ingineria chimica, Ed.Tehnica 1986.
- Brown ME, Dollimore D, Galwey AK. Comprehensive chemical kinetics. vol. 22. Amsterdam: Elsevier; 1980.
- Brill TB, James KJ. Kinetics and mechanisms of thermal decomposition of nitroaromatic explosives. *Chem Rev*. 1993;93:2667–92.
- Duh YS, Lee C, Hsu CC, Hwang DR, Kao CS. Chemical incompatibility of nitrocompounds. *J Hazard Mater*. 1997;53:183–94.
- Brill TA, James KJ. Thermal decomposition of energetic materials. 662. Reconciliation of the kinetics and mechanisms of TNT on the time scale from microseconds to hours. *J Phys Chem*. 1993;97:8759–63.
- Zeman S, Zemanova E. Possibilities of applying the Piloyan method of determination of decomposition activation energies in the differential thermal analysis of polynitroaromatic compounds and their derivatives Part VI. Relationships found between chromatographic and thermal analysis data for *N*-substituted 2,6-dinitroanilines. *J Therm Anal Calorim*. 1981;20:87–92.
- Zeman S, Dimun M, Truchlik S. The relationship between kinetic data of the low-temperature thermolysis and the heats of explosion of organic polynitro compounds. *Thermochim Acta*. 1984;78:181–209.
- Zeman S. Possibilities of applying the Piloyan method of determination of decomposition activation energies in the differential thermal analysis of polynitroaromatic compounds and of their derivatives Part I. Polymethyl and polychloro derivatives of 1,3,5-trinitro-benzene. *J Therm Anal*. 1979;17(1):19–29.