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Thermochimica Acta 392–393 (2002) 371–383

thermochimica acta

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Phenomenon of autocatalysis in decomposition of energetic chemicals

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Abstract

Kinetic equations of decomposition of several nitrobenzene (NB) derivatives were developed from isothermal DSC data. The mechanism of decomposition of all chemicals appeared to be autocatalytic with a slow first-order initiation reaction. Reaction orders, activation energies, and frequency factors of both (autocatalytic and initiation) reactions were determined for all chemicals. It was demonstrated that:

- utilization of a kinetic model with two parallel reactions (first-order initiation reaction and autocatalytic reaction) that have different activation energies accounts for the change in chemical behavior sometimes observed at low temperatures;
- reaction orders of the autocatalytic reaction are directly associated with the isothermal DSC curve shapes;
- elevated temperature aging of chemicals that decompose autocatalytically results in small to very significant reductions in their subsequent thermal stability.

Keywords: Decomposition; Kinetics; Autocatalysis; Isothermal; Nitrobenzene

1. Introduction

Characterization of decomposition reactions of energetic chemicals is vital for developing safe chemical manufacturing processes and assessing the stability of chemicals under various conditions, e.g. storage and transportation. Differential scanning calorimetry (DSC) is widely used for studying thermal decomposition of chemicals. Relating the experimentally obtained decomposition characteristics to safety recommendations for specific situations is a challenging process. However, when kinetic equations of decomposition developed from experimental data are available, they can be used for quantitative prediction of decomposition under a variety of conditions. This significantly increases the accuracy of thermal hazard assessment and supports the development of a safe but not overly conservative process. The kinetics of decomposition are also important in assessing the potential of materials for thermal explosion during drying, storing, shipping and handling operations.

Chemicals that decompose autocatalytically are considered more hazardous because these reactions can accelerate even under isothermal conditions during prolonged storage. Therefore, for assessing thermal hazards and determining the necessary precautionary measures, it is important to identify the decomposition mechanism. All tetrazoles studied earlier [1] appeared to have an autocatalytic decomposition mechanism with various autocatalytic reaction orders (0.7–2.2). The current study is targeted at investigating the decomposition of nitrobenzenes, and

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PII: S0040-6031(02)00122-3

drawing generic conclusions about the phenomenon of autocatalysis.

The detailed objectives of this study were:

- determining the decomposition mechanism of the nitrobenzene chemical class;
- deriving kinetic equations for four representatives of this class that demonstrated significantly different decomposition curves in scanning DSC experiments;
- using the derived kinetic equations for predicting chemical behavior under various conditions;
- establishing a relationship between the derived kinetic equations and the DSC curve shapes to provide a foundation for estimating certain kinetic parameters from DSC curve shapes;
- studying and predicting the effects of aging of chemicals on their subsequent thermal stability.

2. Experimental

DSC experiments were conducted using the TA Instruments Model 2910 differential scanning calorimeter. The sample size was approximately 1 mg. The sample was inserted into a glass capillary [2], after which the capillary was centrifuged and sealed under nitrogen. The DSC experiments were conducted isothermally (for at least three different temperatures) and in a scanning mode at 10 °C/min heating rate. The instrument was calibrated using a dedicated 1 mg indium standard in a glass capillary at 1 °C/min heating rate for the isothermal experiments and at 10 °C/min heating rate for the scanning experiments. The cell constant, onset slope and temperature correction factors are automatically updated by the TA2200 DSC computer. Plotting for exothermic reactions was as upward deflection of the curve peak from the baseline.

3. Results and discussion

The method [1] that was used to derive kinetic equations of decomposition of nitrobenzenes is based on utilization of the results of at least three isothermal DSC experiments. Use of the isothermal technique is strongly recommended, especially for the investigation of new reactions where the reaction mechanism is not known. The advantage of an isothermal approach is greater simplicity of data interpretation, generation of more reliable kinetic data, and broader applicability. This is because the isothermal method eliminates temperature as a variable in each measurement so that the level of ambiguity in the interpretation of data is reduced. The method utilized consists of the following steps [1]:

1. Collecting experimental data in the form of heat flow versus time from isothermal DSC experiments at three or four different temperatures.
2. Converting the experimental DSC data into conversion versus time data using DSC Isothermal Kinetics Data Analysis Program Part 1.
3. Fitting a specific kinetic equation to the concentration versus time data using Batch CAD Rate Program.
4. Calculating rate constants at the experimental temperatures using Batch CAD Rate Program.
5. Determining activation energy and frequency factor from the temperature dependence of the rate constant.
6. Verifying the kinetic equation by simulating decomposition of the chemical under different conditions using the derived kinetic equation and Batch CAD Reaction Program and comparing the simulation results to experimental curves.

Decomposition of four nitrobenzene derivatives was studied at several isothermal temperatures to develop kinetic equations. The overlays of the isothermal DSC curves are presented in Figs. 1–4. It can be seen that all four nitrobenzenes exhibited acceleration of the heat flow rate under isothermal conditions, which indicates the reactions are autocatalytic in nature. The main characteristic feature of an autocatalytic reaction is that one of the reaction products catalyzes the reaction, hence the rate of the reaction is proportional not only to the reactant concentration, but also to the product concentration. Another feature of autocatalytic decomposition is that it requires a certain initial concentration of the catalyst present to trigger the autocatalytic reaction. The catalyst can be either introduced into the reaction zone (which is not typical for decompositions), or a parallel slow *n*th order reaction can generate the necessary catalyst to trigger the autocatalytic reaction. The following kinetic model will represent the described reaction mechanism.

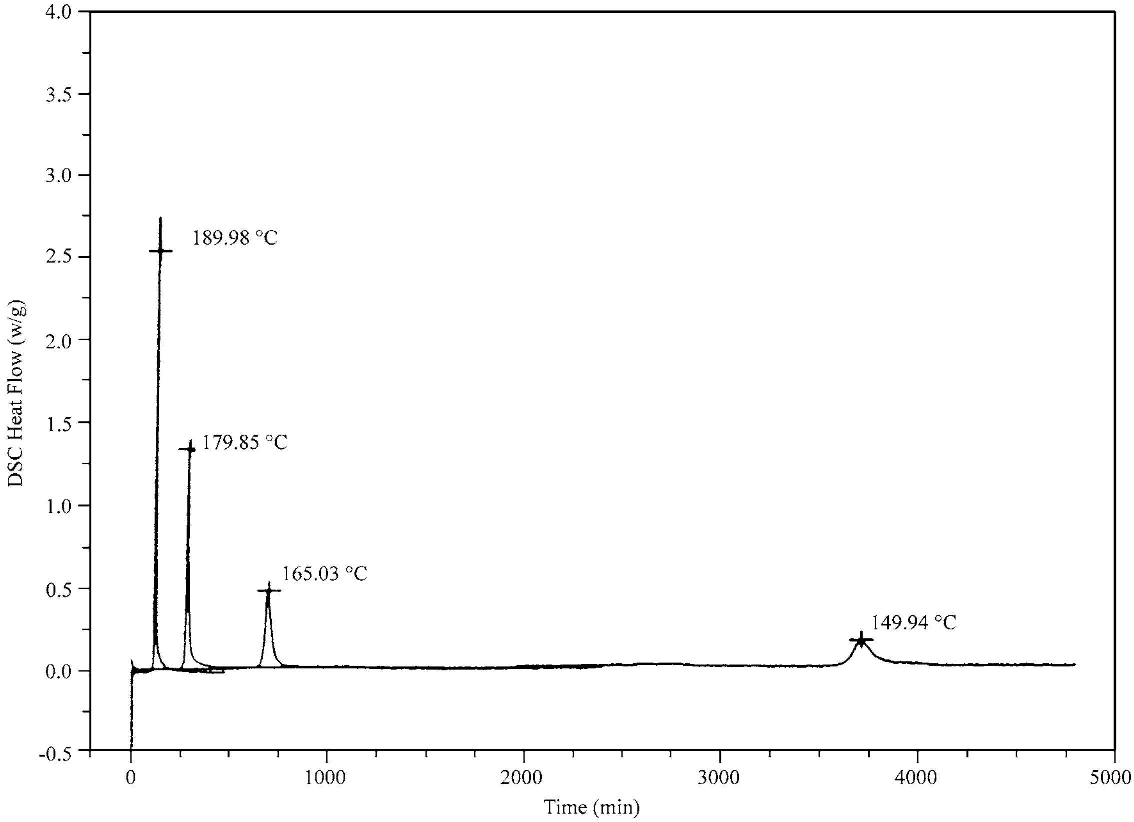

Fig. 1. Isothermal DSC curves of 2-benzyloxy-5-chloro-4-nitroaniline (Chemical 1) decomposition at four temperatures (isothermal test temperatures are printed with each curve).

Reaction scheme:

$$\text{Autocatalytic reaction}: \quad \mathrm{A} + \mathrm{B} \Rightarrow 2\mathrm{B} + \mathrm{D} + \cdots \tag{1}$$

$$\text{Initiation reaction}: \quad \mathrm{A} \Rightarrow \mathrm{B} + \mathrm{D} + \cdots \tag{2}$$

Kinetic model:

Autocatalyticreaction :

$$r_1 = k_1 C_\mathrm{A}^m C_\mathrm{B}^n, \quad k_1 = A_1 \exp\left(\frac{-E_1}{RT}\right) \tag{3}$$

Initiation reaction :

$$r_2 = k_2 C_\mathrm{A}, \quad k_2 = A_2 \exp\left(\frac{-E_2}{RT}\right)() \tag{4}$$

where

C_A, C_B are the concentrations of the reactant and the product/catalyst; r_1, r_2 are the rates of the autocatalytic and initiation reactions; k_1, k_2 are the rate constants of the autocatalytic and initiation reactions; m, n are the reaction orders with respect to the reactant and the catalyst; E_1, E_2 are the activation energies of the autocatalytic and initiation reactions; A_1, A_2 are the frequency factors of autocatalytic and initiation reactions.

In order to derive decomposition kinetics, the following parameters of the model have to be determined for each chemical n, m, E_1, A_1, E_2, A_2. The calculations were performed using the isothermal DSC experiments for each chemical (Figs. 1–4) according to the method previously reported for tetrazoles [1]. The derived kinetic equations were verified by predicting decomposition in a scanning DSC experiment (for all chemicals), isoageing and subsequent decomposition of the residues (for three chemicals), and decomposition in accelerating rate calorimeter (for one chemical). All

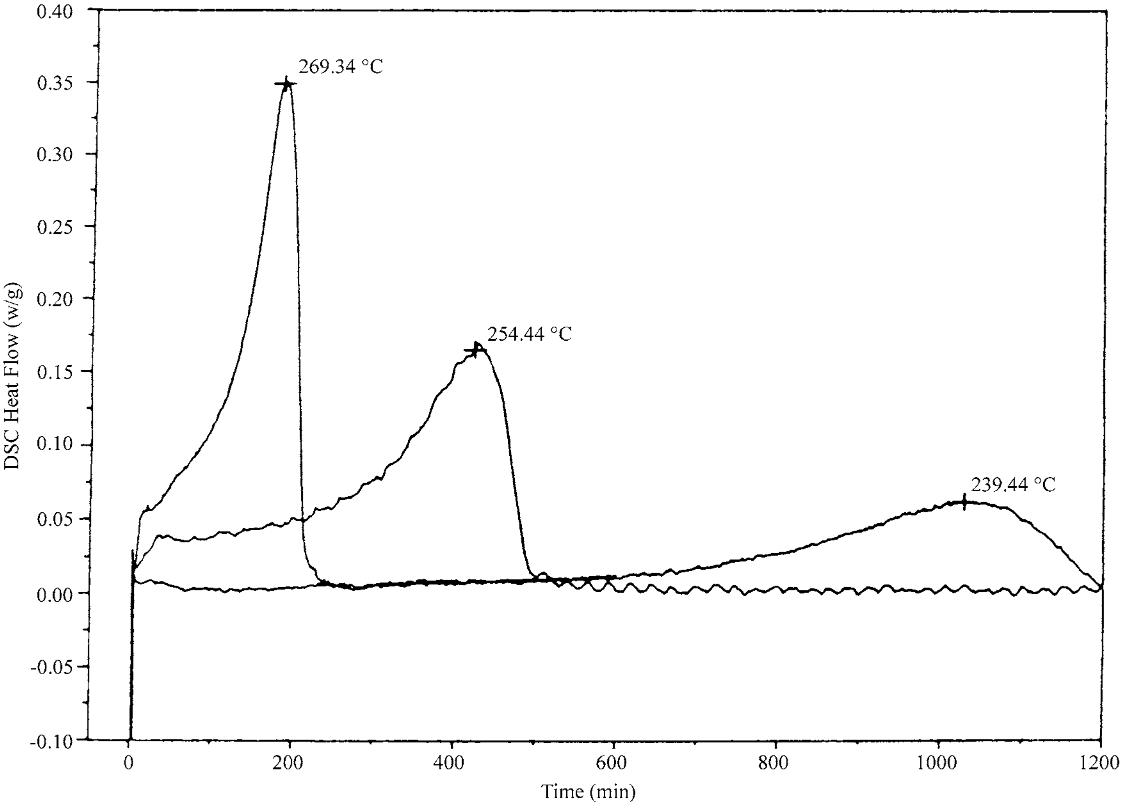

Fig. 2. Isothermal DSC curves of 3-chloro-4-nitrobenzoic acid (Chemical 2) decomposition at three temperatures (isothermal test temperatures are printed with each curve).

parameters of the derived kinetic models for the four chemicals are summarized in Table 1.

3.1. Relationship between the decomposition kinetics and DSC curve shape

Kinetic models allow prediction of thermal response under widely different conditions. Isothermal DSC curve shape is indicative of decomposition kinetics. Understanding the relationship between the kinetics and isothermal curve shape may allow screening level prediction of plant hazards from isothermal DSC curves. Following are some examples of the relationship between isothermal DSC curve shape and the associated kinetic models.

For instructional purposes an overlay plot (Fig. 5) was prepared showing a single isothermal DSC curve for each of the four nitrobenzenes. For decompositions

Table 1
Kinetics of decomposition of nitrobenzene derivatives

Number	Molecular weight	Autocatalytic reaction				Initiation reaction	
		m	n	E_1 (kJ/mol)	A_1 (s^{-1})	E_2 (kJ/mol)	A_2 (s^{-1})
1	279	2.3	1.5	118	1.38E + 10	172	9.84E + 11
2	202	0.5	1.8	113	5.28E + 6	157	3.23E + 10
3	141	0.6	0.8	149	1.67E + 9	294	2.58E + 19
4	202	0.6	0.6	128	6.80E + 8	155	3.20E + 4

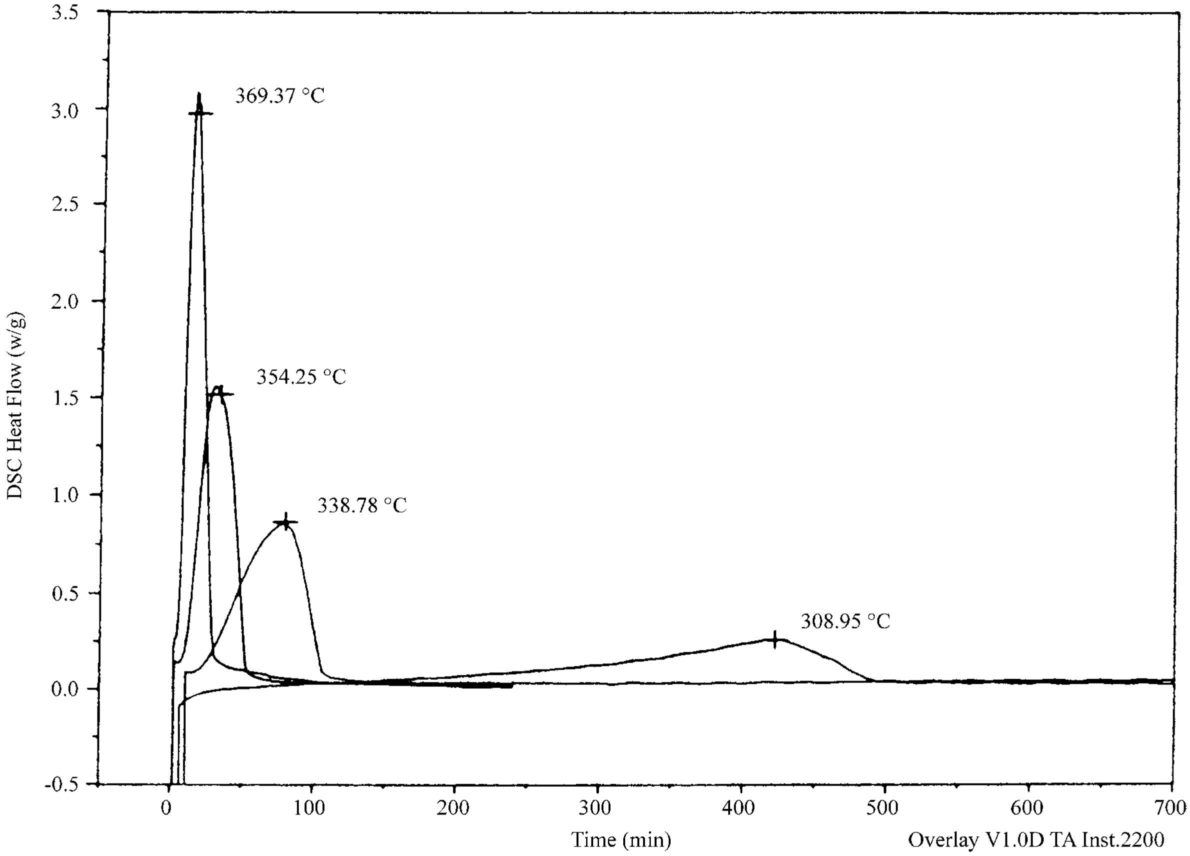

Fig. 3. Isothermal DSC curves of *p*-fluoronitrobenzene (Chemical 3) decomposition at four temperatures (isothermal test temperatures are printed with each curve).

with high reaction orders (m, $n > 1$) the isothermal heat flow curve will yield a narrow and sharp peak, which will have a concave curvature of its onset and return to baseline regions (Figs. 1 and 5, curve 1). These decomposition reactions usually have a distinct, long induction period with no measurable heat flow, after which the decomposition starts to accelerate and goes to completion in a relatively short period of time. For autocatalytic decompositions with reactant (m) and catalyst (n) reaction orders less than one, the isothermal heat flow curve will yield a broader shallow (dome-shaped) peak, which will have a convex curvature of its onset and return to baseline regions (Figs. 4 and 5, curve 4). These decomposition reactions usually start to occur as soon as the chemical is exposed to an elevated temperature without any significant induction period.

A symmetrical isothermal heat flow curve (Fig. 4) is an indication of autocatalytic decomposition with equivalent reaction orders with respect to the catalyst and the reactant ($m = n$). Asymmetric curves result from autocatalytic decompositions for which there are significantly different reactant (m) and catalyst (n) reaction orders. As an example, curve 2 (Fig. 5) illustrates the case when $n \gg m$, which results in a long, gradual leading edge of the decomposition exotherm followed by a sharp return to baseline. The mirror image of curve 2 (Fig. 5) is possible when $m \gg n$.

A measurable positive heat flow at the very beginning of isothermal DSC experiments indicates that the initiation reaction (r_2) has a relatively high rate under experimental conditions and occurs simultaneously with the autocatalytic decomposition throughout the

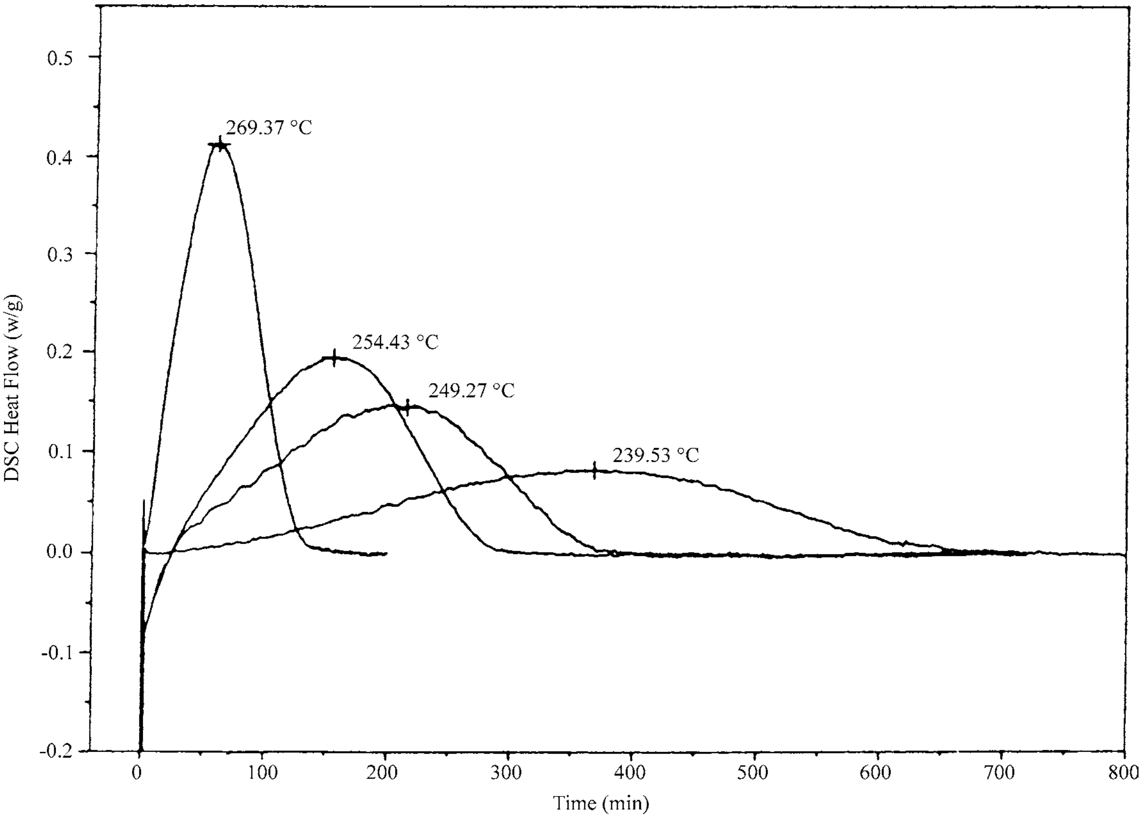

Fig. 4. Isothermal DSC curves of 5-chloro-2-nitrobenzoic acid (Chemical 4) decomposition at four temperatures (isothermal test temperatures are printed with each curve).

experiments (Figs. 2, 3 and 5) curves 2 and 3. This means that the heat flow curve recorded during isothermal or regular DSC experiments is a combination of rates of two competing reactions: initiation and autocatalytic, whose ratio can change depending upon their activation energies and experimental conditions. The exact rate of the initiation reaction throughout the isothermal and scanning DSC experiments of Chemical 2 can be seen on its simulated decomposition curves (Figs. 6 and 7). It is clear from the scanning DSC reaction rate plot that the autocatalytic reaction became measurable only at temperatures higher than 330 °C, when the overall reaction rate curve began to deviate from the initiation reaction rate curve. It was predicted that a large part of the chemical decomposed by the initiation reaction during the scanning DSC experiment (40%), as well as the isothermal DSC runs (19–24%). At reduced isoage temperatures the predicted amount of chemical decomposed by the initiation reaction would decrease. This would occur because the higher activation energy of the initiation reaction would cause a more rapid decrease in the reaction rate with temperature. Theoretically at a low enough temperature the entire reaction would occur according to the autocatalytic mechanism, and at a high enough temperature the initiation reaction could be dominant. This would dramatically alter the decomposition heat flow curve, which could be wrongly interpreted as a change in reaction mechanism. In DSC runs at higher scanning rates, the percentage of the chemical decomposed by the initiation reaction would be higher.

By analyzing the overlay of scanning DSC curves of the four nitrobenzenes (Fig. 8), we can see that similar information about autocatalytic reaction orders could be obtained from the scanning DSC curves (assuming

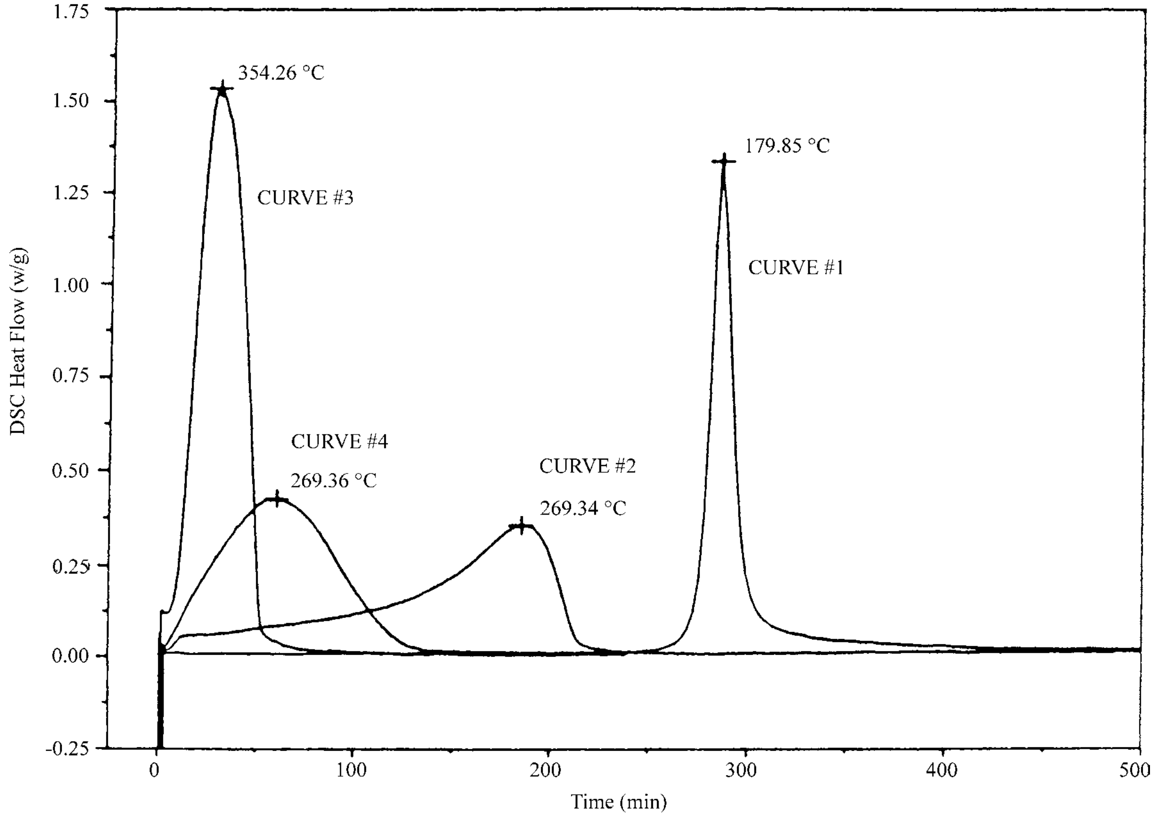

Fig. 5. Overlay of isothermal DSC curves of four nitrobenzenes: curve 1 – 2-benzyloxy-5-chloro-4-nitroaniline, curve 2 – 3-chloro-4-nitrobenzoic acid, curve 3– *p*-fluoronitrobenzene, curve 4 – 5-chloro-2-nitrobenzoic acid (isothermal test temperatures are printed with each curve).

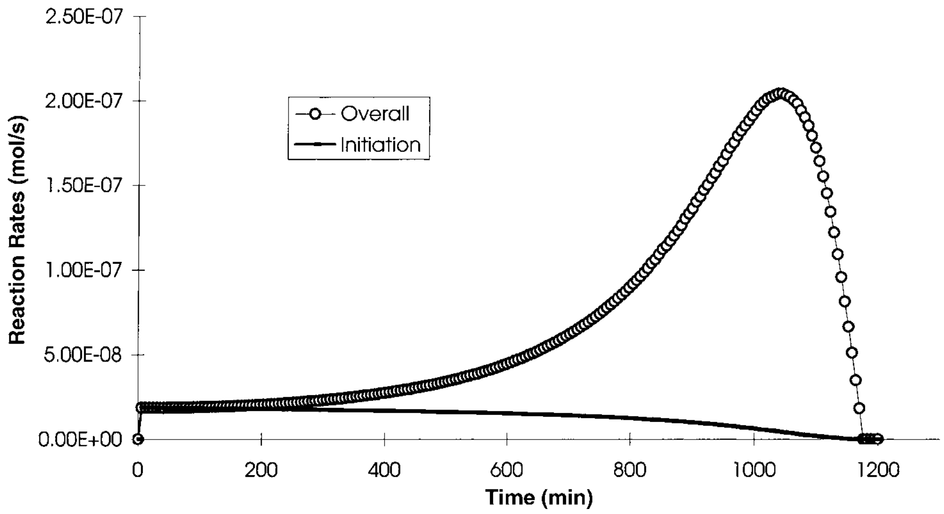

Fig. 6. Simulated rates of the initiation and overall reactions during isothermal DSC test at 241 °C of 3-chloro-4-nitro-benzoic acid (Chemical 2).

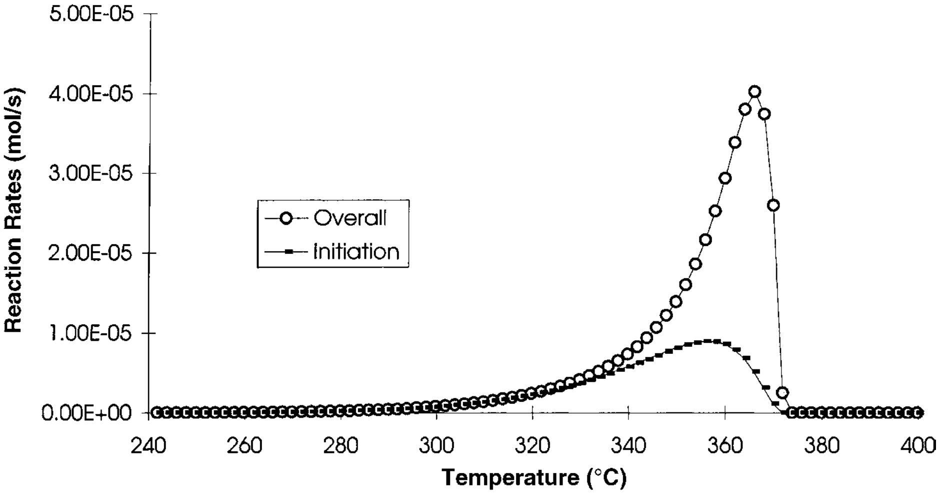

Fig. 7. Simulated rates of the initiation and overall reactions during a scanning DSC test of 3-chloro-4-nitrobenzoic acid (Chemical 2).

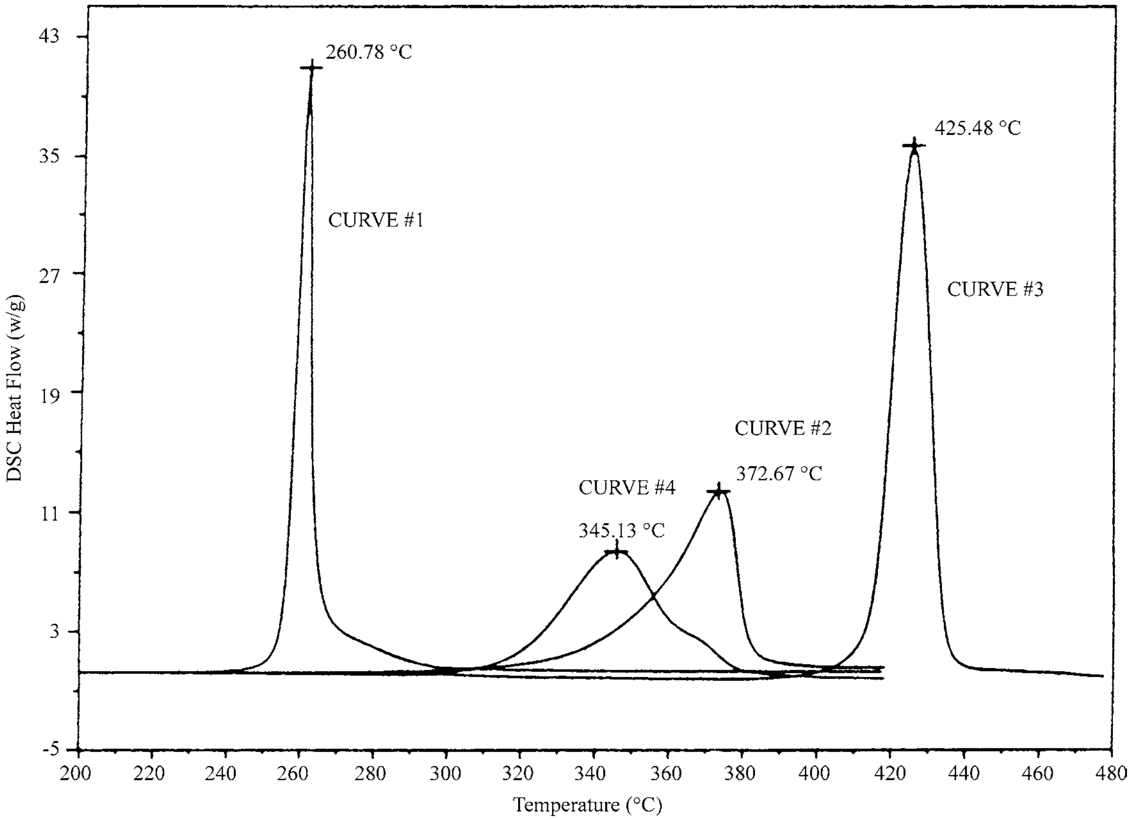

Fig. 8. Overlay of scanning DSC curves of four nitrobenzenes: curve 1 – 2-benzyloxy-5-chloro-4-nitroaniline, curve 2 – 3-chloro-4-nitro-benzoic acid, curve 3– *p*-fluoronitrobenzene, curve 4 – 5-chloro-2-nitrobenzoic acid (decomposition peak temperatures are printed with each curve).

we know that decomposition mechanism is autocatalytic). Curve 1 would represent high reaction orders, curve 4 would represent low and equal reaction orders, curve 2 would represent a low reactant and a high catalyst reaction order. However, to distinguish between the relative rates of the initiation and autocatalytic reactions and to determine the effect of the initiation reaction on the overall reaction rate does not appear to be possible from the scanning DSC curves.

The existing opinion is that the scanning DSC curve shapes are related to the activation energies of decomposition reactions, i.e. high activation energy reactions yield a narrow, sharp peak of significant heat flow in a scanning DSC test and low activation energy reactions yield a broad, shallow peak in the same test. For autocatalytic decompositions, it appears that the reaction orders of the autocatalytic reaction have an even greater effect on the DSC curve shape.

3.2. Effect of low-temperature aging of chemicals on their subsequent thermal stability

Chemicals that decompose autocatalytically are susceptible to thermal aging effects to varying degrees. Understanding these effects in detail becomes increasingly important as longer and more adiabatic operations are considered, or when the thermal history of a raw material is not well defined.

An interesting phenomenon was observed from the testing of the residues obtained from isothermal experiments of Chemicals 1 and 2. The scanning DSC on the residues showed lower decomposition onset and peak temperatures (Figs. 9 and 10). This demonstrates that, although, there was no measurable reaction during the low-temperature isothermal runs, a slow decomposition was occurring and a certain amount of the catalyst was produced. Hence, when the

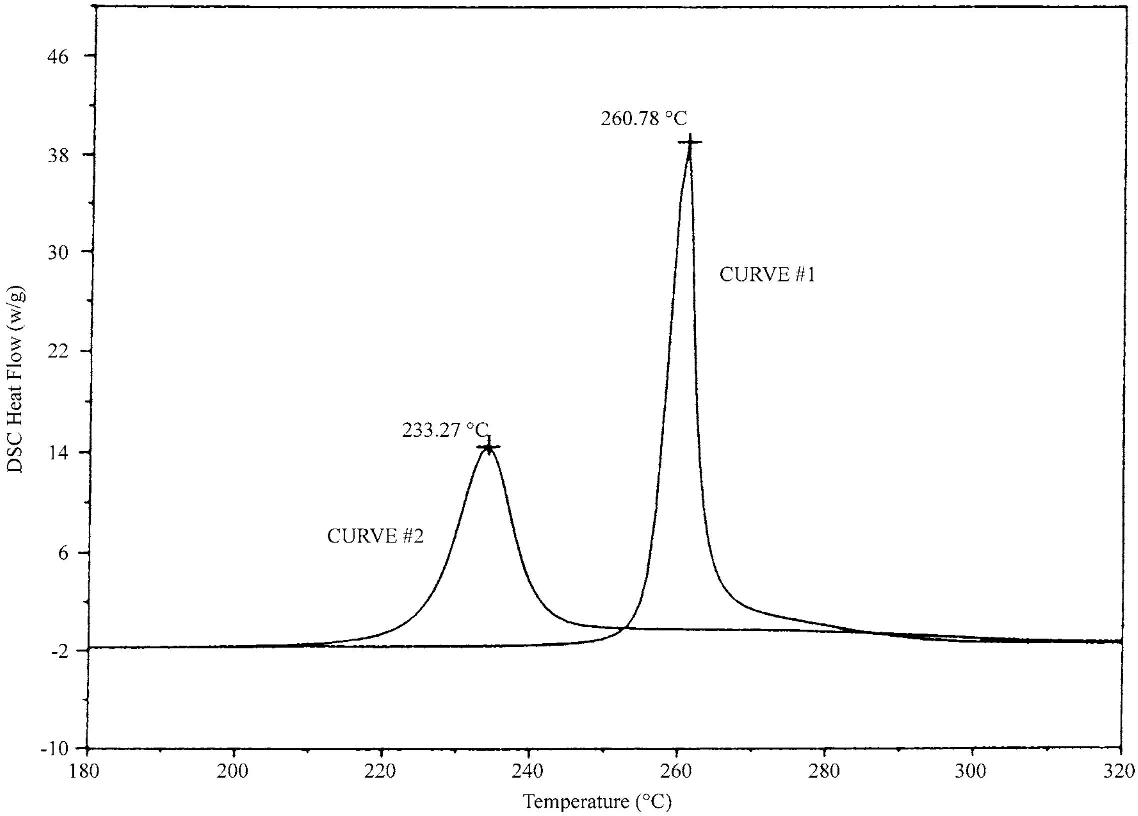

Fig. 9. Overlay of scanning DSC curves of the original (curve 1) and isoaged at 155 °C for 48 h (curve 2) samples of 2-benzyloxy-5-chloro-4-nitroaniline (Chemical 1).

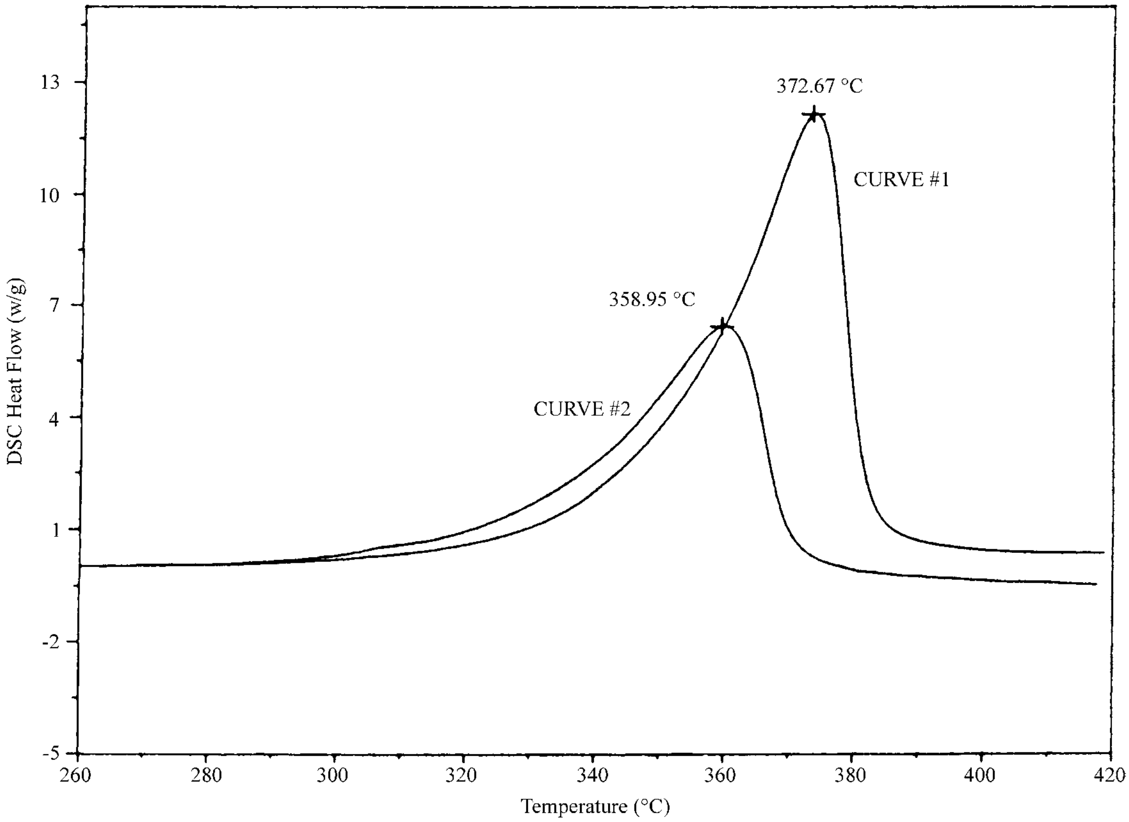

Fig. 10. Overlay of scanning DSC curves of the original (curve 1) and isoaged at 271 °C for 2 h (curve 2) samples of 3-chloro-4-nitrobenzoic acid (Chemical 2).

samples were subjected to elevated temperatures during the scanning DSC experiments on the residues, the catalyst accelerated the decomposition and shifted its onset to lower temperature.

Both isoages were simulated using the derived kinetic equations of decomposition and the amount of the catalyst that could have been formed during the isoages was determined. These catalyst concentrations (3% for Chemical 1 and 30% for Chemical 2) were assumed to be present prior to the scanning DSC measurements of the respective isoage residues. Simulated scanning DSC curves assuming different concentrations of the catalyst at the beginning of the experiments (from 0 to 30%) were overlaid with the original (unaged sample) curve in Figs. 11 and 12 to study the effect of the initial catalyst concentration on the thermal stability of these chemicals. In Fig. 11, the original curve and the 3% catalyst concentration curve should be compared to the curves presented in Fig. 9. In Fig. 12, the original curve and the 30% catalyst concentration curve should be compared to the curves presented in Fig. 10. Both simulations predict the experimental results quite accurately.

The predicted changes in scanning DSC decomposition parameters of the nitrobenzenes as a function of the concentration of the catalyst present at the beginning of the simulated scanning DSC experiment are summarized in Table 2.

Analyzing the simulation results summarized in Table 2 and the DSC curves overlaid in Figs. 9–12, it can be seen that the largest decrease in both the decomposition onset and peak temperatures were observed for Chemical 1, which has the highest reaction orders and an insignificant contribution from the initiation reaction in the overall reaction rate. Moreover, a very small amount of the catalyst (<3%) caused

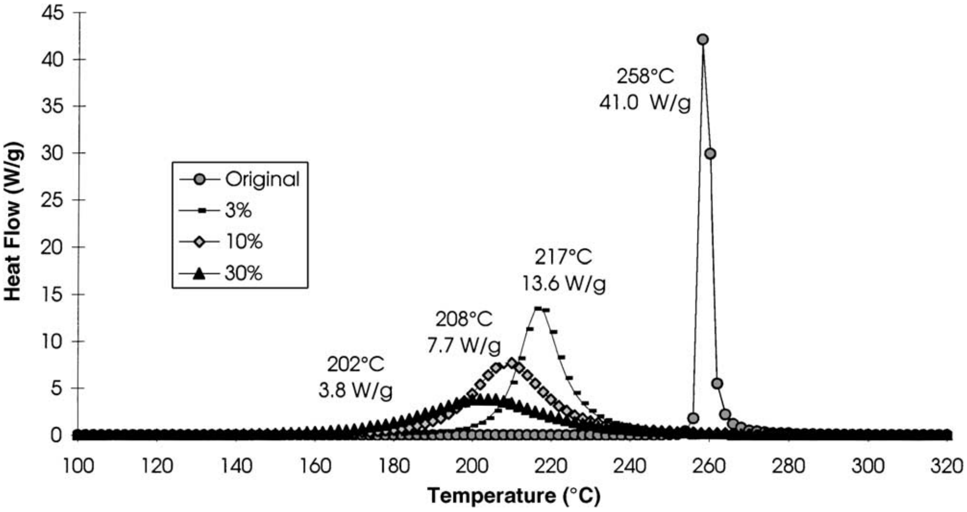

Fig. 11. Overlay of simulated scanning DSC of 2-benzyloxy-5-chloro-4-nitroaniline (Chemical 1) original sample and hypothetical samples containing 3, 10, 30% of the catalyst/product.

a significant change in the decomposition curve. The influence of the catalyst concentration on the decomposition characteristics decreases with increase in the catalyst concentration. The significant impact of the small amount of catalytic impurity on the chemical decomposition is caused by high reactant and catalyst reaction orders (m, n), which increase the influence of the concentration change on reaction rate.

When analyzing the effect of catalyst concentration (aging) on decomposition with low reactant and catalyst reaction orders (Chemicals 3 and 4), it can be seen that the presence of the product/catalyst results in a smaller, but still significant drop in the decomposition onset temperature, while the peak temperature is much less influenced. The decomposition curves are broadened with an increase in the amount of catalyst present. The less substantial change in the decomposition peak temperatures of the isoaged samples is predicted because of the low (m, $n < 1$) reaction orders of the autocatalytic reaction, which decreased

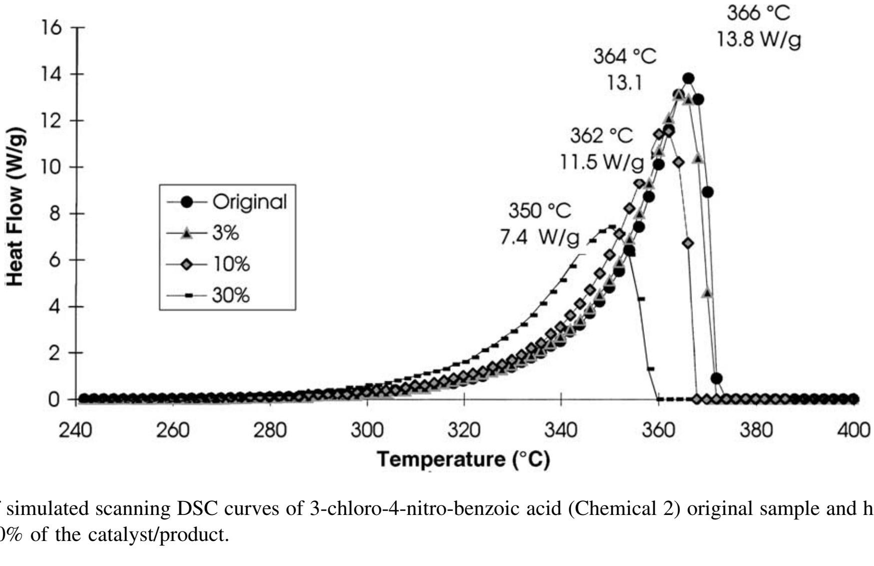

Fig. 12. Overlay of simulated scanning DSC curves of 3-chloro-4-nitro-benzoic acid (Chemical 2) original sample and hypothetical samples containing 3, 10, 30% of the catalyst/product.

Table 2
Effect of the initial catalyst concentration on the change in decomposition onset and peak temperatures

Number	Conversion by initiation reaction in scanning DSC (%)	ΔT_o (°C)[a]			ΔT_p (°C)		
		3%	10%	30%	3%	10%	30%
1	0.22	47	90	102	41	50	56
2	40	0	3	16	2	4	16
3	10	40	53	66	8	12	20
4	0.0003	36	47	56	7	10	18

[a] Difference in decomposition onset/peak temperature between the sample containing an assumed concentration of the catalyst.

the influence of the change in catalyst concentration on reaction rate.

The effect of aging is almost completely eliminated when the initiation reaction has a significant rate under the experimental conditions and competes with the autocatalytic reaction (Chemical 2, 40% conversion by initiation reaction in a scanning DSC run). Presence of 3–10% of the catalyst had practically no effect on the DSC curves. Even 30% of the catalyst concentration triggered only a 16 °C drop in both the onset and the peak temperatures. Apparently, a substantial change in the decomposition temperature of the iso-aged sample does not occur because the initiation reaction (which is not influenced by the presence of the catalyst and would result in a higher decomposition onset temperature when performed on partially decomposed sample) dominates at low temperatures (Fig. 7) and has a relatively significant rate throughout the entire decomposition (40% of the chemical decomposes by the initiation reaction).

Summarizing the discussion, it can be concluded that the chemicals most influenced by thermal aging are those that have high reactant and catalyst reaction orders and a very low rate of initiation reaction under aging conditions. Lower reaction orders, as well as increased initiation reaction rates will minimize the impact of chemical aging on subsequent thermal stability.

4. Conclusions

Kinetic equations of decomposition have been derived for four representatives of the nitrobenzene class of chemicals. All chemicals demonstrated an autocatalytic reaction mechanism with a range of reaction orders (0.5–2.3) and activation energies of the initiation and autocatalytic reactions.

Utilization of a kinetic model with two parallel reactions (first-order initiation reaction and autocatalytic reaction) can account for the change in chemical behavior sometimes observed at low temperatures without the need to assume a change in reaction mechanism. Different activation energies of the competing initiation and autocatalytic reactions will result in a temperature dependent change in the relative contributions of each reaction into the overall heat flow rate. This change in chemical behavior has sometimes been interpreted incorrectly as a change in reaction mechanism.

It was demonstrated that the shape of isothermal and, to a lesser extent, scanning DSC curves appear to be a good indicator of the reaction orders of autocatalytic reaction. It was also shown that the initiation reaction can have a significant rate under experimental conditions and can be competing with the autocatalytic reaction.

It was determined that the aging of autocatalytically decomposing chemicals can lead to a significant decrease in the subsequent decomposition onset and peak temperatures. This is most predominant for chemicals with high reactant and catalyst autocatalytic reaction orders and very low rates of initiation reaction under experimental aging conditions.

Autocatalytically decomposing chemicals present additional thermal hazard due to their varying susceptibility to aging effects. Prolonged storage of these types of chemicals under elevated temperatures, even if much lower than the measured decomposition onset temperature, can decrease the thermal stability of the chemical and lead to a hazardous situation during storage or subsequent use.

Acknowledgements

The authors would like to thank Paul R. kingsley for carrying out the experimental work necessary to complete this project.

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