Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 445 (2006) 160–167

thermochimica acta

www.elsevier.com/locate/tca

Evaluation of microcalorimetric measurements in terms of information content for decomposition reactions

S. Fischer[*], G. Krahn, B. Reimer

Institute of Environmental Technology, Department of Engineering Sciences, Faculty of Mathematics, Natural Sciences and Technology,
Martin-Luther-University Halle-Wittenberg 06099 Halle (Saale), Germany

Abstract

Decomposition reactions of liquids and solids can be observed by the heat development using microcalorimetric methods. By determination of the released heat flow for heating up a sample, it is possible to get details to answer safety relevant questions.

For reactions *n*th order the overall activation energy and the accompanying frequency factor can be determined, provided that the heat release is determined by the rate of a single reaction step. Researches have been carried out whether these parameters are useable for safety technical specifications.

Autocatalytic affected decomposition reactions are connected with special problems. This affects the experimental examination or interpretation of results, and also the precise identification of beginning decomposition reactions in technical reactors. The application of microcalorimetric measurements on decomposition reactions is described and associated problems are pointed out.

The conclusions from thermoanalysis data alone are not sufficient in the final consequence for safety technical assessments.

Keywords: Decomposition; Exothermal reaction; Autocatalysis; Adiabatic induction time; Activation energy; Thermal stability

1. Introduction

In a reactor, the danger exists for a runaway reaction with exothermic reaction systems. A consequence of this is a pressure increase as a result of the emergence of gases and the spontaneous evaporation of system components. Hazardous consequences are to be expected, if the decomposition of a thermally unstable component is released by rising temperatures.

The calorimeter delivers information about the thermal stability of reaction mixtures and substances with small amounts of masses and an acceptable effort.

It is possible to study the planned synthesis reaction thermoanalytically. Such investigations are preferably carried out in reaction calorimeters with reaction volumes in the milliliter range.

On the other hand, microcalorimeters, which are operating with a volume of a few microliter, are used for examinations of secondary reactions, i.e. for decomposition processes preferably. It is possible to get an overview about the onset temperature of the decomposition and the released quantity of heat with dynamic methods.

Decomposition reactions can also be investigated by a constant device temperature that means under isoperibolic conditions. The induction times, which are required to reach the maximum reaction velocity, can be determined under these conditions. Valuable safety technical information can be defined by the experimental definable dependence of these induction times of the temperature.

The German Guideline “TRAS 410” [1] suggests three methods for the definition of a safe maximum temperature for substances and reaction mixtures for a technical reactor.

The boundary temperature (T_{exo}) is defined as follows:

- the temperature which is 100 K below the onset temperature of a DSC measurement with a heating rate between 1 and 10 K/min,
- the temperature of the adiabatic decomposition temperature after 24 h ($\mathrm{ADT}_{24\,\mathrm{h}}$) reduced for 10 K,
- the temperature where the heat production of the system is reaching 0.1 W/kg reduced for 10 K.

---

[*] Corresponding author. Tel.: +49 3461 462164; fax: +49 3461 462710.
E-mail address: sabine.fischer@iw.uni-halle.de (S. Fischer).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.10.002

Nomenclature

A	area
$\mathrm{ADT}_{24\,\mathrm{h}}$	adiabatic decomposition temperature after 24 h
C_A; C_B	concentration of the component A and B, respectively
c_p	heat capacity
D	correction factor
E	activation energy
k	reaction rate constant
k_0	heat transfer coefficient
k_∞	preexponential factor
K	constant
M	molar mass
P_max	maximum heat flow [W kg^{-1}]
Q_G	overall heat of decomposition
$Q_\mathrm{z}(t)$	heat of decomposition to time t
R	universal gas constant
t_ad	adiabatic induction time
t_iso	isoperibolic induction time
T	temperature
T_max	temperature of the heat flow maximum
T_onset	start temperature of the decomposition
U	conversion
V	volume
β	heating rate
κ	cooling-constant
ρ	density
τ	dimensionless induction time
Φ	phi-factor

Some authors (Keller [2], Steinbach [3], Pastre’ [4]) found that these rules do not fit in all cases.

There are many methods for the estimation of kinetic parameters (Ozawa [5], Kissinger [6], ASTM E 698 [7], Göllnitz [8,9], Grewer [10], Constantinou [11], CISP Software [12], NETZSCH Software [13,14], AKTS Software [15–17], TA-kin [18]). A distinction is drawn between linear and non-linear modulation. If these kinetic data are applied for the determination of the adiabatic induction time, substantial differences can appear for decomposition reactions with autocatalytic character. The goal of this investigation is to detect a method for the application of autocatalytic decomposition reactions. Detailed overviews for the safety assessment for chemical processes and autocatalytic reactions are given by Steinbach [19] and Grewer [20].

2. Experiments, materials and methods

A power compensated DSC (SETARAM model DSC 141) was used for all measurements.

The thermal decomposition of 2-bromo-2-nitro-1,3-propanediol was investigated here as an example. The reaction was measured under dynamic conditions with different heating rates (1–10 K min^{-1}) in the range of 40–300 °C and also under isoperibolic conditions with different storage temperatures (152–172 °C). The measurements were carried out in sealed pressure resistant, gilded steel crucibles. The experiments were carried out with a sample mass of 5 and 10 mg for dynamic and isoperibolic tests, respectively. No weight loss was detected by weighing the crucibles before and after the tests.

An empty capsule was used as reference. The DSC equipment was temperature and enthalpy calibrated by the melting peaks of indium. The determination of the peak boundaries is a subjective decision but the baseline should be continuous. A linear baseline correction was used.

The 2-bromo-2-nitro-1,3-propanediol (CAS-Nr: 52-51-7) was delivered by FLUKA, with a degree of purity more than 98%. The substance was used in the delivered condition.

3. Results and discussion

Information about the thermal behaviour of substances can be achieved with DSC measurements with little operating effort. These data are used for the characterization of decomposition reactions. Furthermore, the determination of safety relevant parameters is possible, as well as the estimation of kinetic parameters like activation energy and frequency factor of simple reactions.

3.1. Dynamic test operations

The following parameters are important in a dynamic test operation (scanning):

- the initiation temperature of the exothermic decomposition reaction (onset temperature, T_onset) is the point where the heat flow curve leaves the baseline,
- the temperature of the maximum heat flow (T_max),
- the heat of decomposition (Q_G) which provides important information about the expected consequences.

How the requested parameters are determined, is described in Fig. 1.

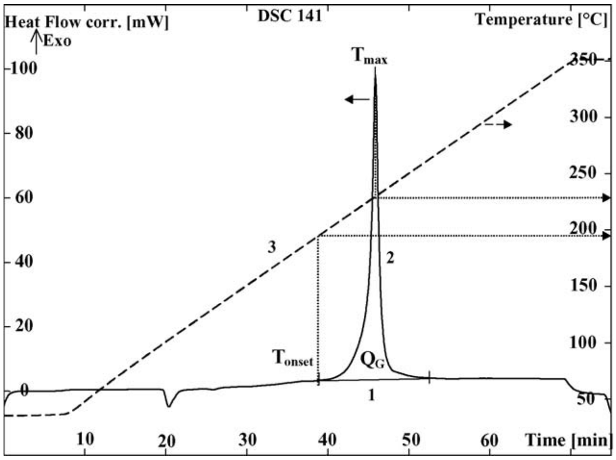

Fig. 1. Dynamic measured DSC curve of 2-bromo-2-nitro-1,3-propanediol with 5 K/min heating rate (T_onset = 190 °C; T_max = 230 °C; Q_G = −2760 J g^{-1}; 1–constructed baseline; 2–heat flow curve; 3–ambiance temperature).

The heat of decomposition is determined by the area below the exothermal curve in relation to a baseline.

Barton [21] is pointing out the fact that mistakes can be caused by a horizontal baseline, especially at higher temperatures in dynamic operations. For the determination of the correct baseline, the reacted sample has to be subjected to an identical temperature program. In this way, the determined heat flow curve is used as a baseline.

Regarding TRAS 410 [1] the defined “boundary temperatures” (T_{exo}) for a technical reactor can be applied by the following rule:

> “If the maximum temperature in a technical reactor is at least 100 K below the onset temperature which is determined by a screening-DTA, the danger of a decomposition reaction does not exist”.
>
> Detailed examinations of these issues have been investigated by Pastre’ et. al. [4]. They compare adiabatic measurements with values from the 100 K rule.

The results of thermoanalytical measurements are strongly influenced by the test conditions like experiences have shown. The shift of the curves, like the onset temperatures and the temperature of maximum heat flow, by an increasing heating rate is demonstrated in Fig. 2.

Hazards can result from a mistake in the determination of the exothermic boundary temperature by the onset temperature (according to the TRAS 410 [1]). A heating rate in the range of 1 to 10 K/min is provided in the TRAS 410 [1], but in this range fluctuations of 20 K are possible.

The basic advantage of the 100 K rule is the necessity of a single and simple experiment. However, it is not possible to get kinetic information and the shown influence of the heating rates might be cause of errors.

Other factors influencing the measurement results are the experimental conditions of the measuring cell and the kind of sample container (material, heat capacity, heat conduction). Impurities of the sample or appearing endothermic effects can impair the measurement results. If open crucibles are used it is possible that an exchange of substance and heat with the environment and a loss of autocatalytic active substances takes place. Cronin and Nolan [22] have examined the influence of the sample mass, the container material, endothermic effects and the heating rate.

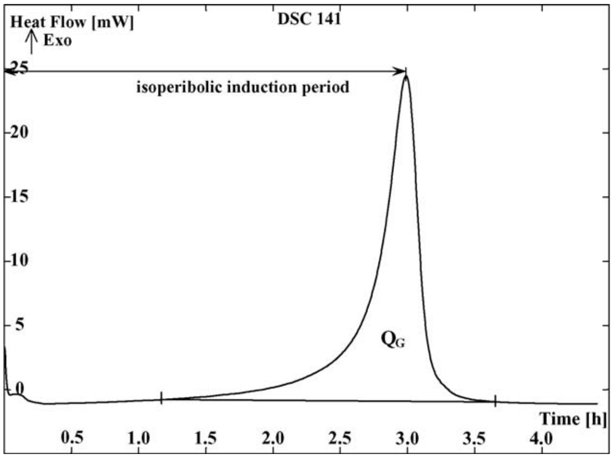

Fig. 3. Isoperibolic measured DSC curve of 2-bromo-2-nitro-1,3-propanediol at 160 °C storage temperature (isoperibolic induction time = 2.98 h; $Q_G = -2208\,\mathrm{J\,g^{-1}}$).

3.2. Isoperibolic test operation

Further relevant safety conclusions are available from isothermal or isoperibolic tests. A DSC measurement determined under isoperibolic conditions is given in Fig. 3.

The heat of decomposition can be determined from the area below the curve. Additionally, the isoperibolic induction time can be determined.

This is the period from the time point when a given storage temperature is reached and ending when the maximum heat flow occurs. The maximum heat flow rate and the maximum heat flow are coinciding at an explosive decomposition.

Fig. 4 shows the results of isoperibolic measurements at different storage temperatures.

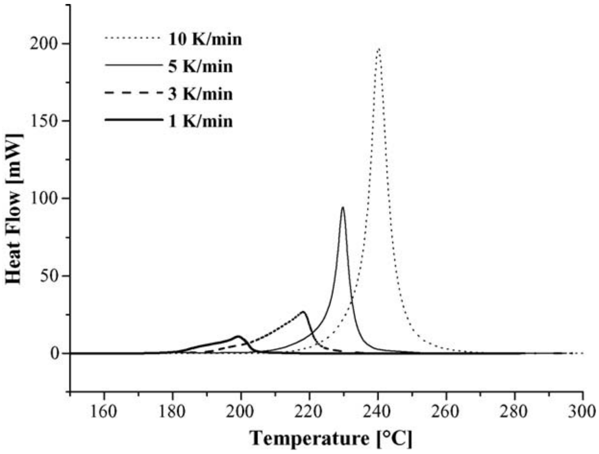

Fig. 2. Dynamic measured DSC curve of 2-bromo-2-nitro-1,3-propanediol with different heating rates.

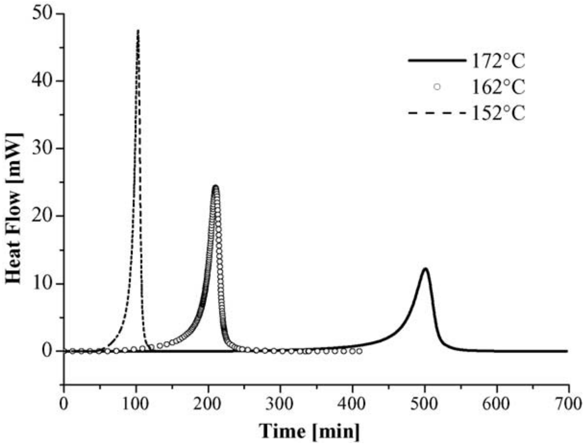

Fig. 4. Isoperibolic measured DSC curves of 2-bromo-2-nitro-1,3-propanediol at different storage temperatures.

Obviously, the decomposition peak is decreasing with decreasing storage temperatures and increasing induction times.

The conditions in a technical reactor can not be considered as isoperibolic. The most hazardous situation is to expected under adiabatic conditions and is characterized by considerably shorter induction times.

Therefore, the question arises, how far the described experimental data can be utilized for qualified safety engineering conclusions. The adiabatic induction time, at a given storage temperature, delivers the important information with regard to the time, which is available to take suitable preventive actions in emergency cases. Additionally, the ambient temperature can be determined, where the maximum heat flow is reached after exactly 24 h under adiabatic conditions. This is a recognized characteristic parameter for the comparative evaluation of the stability of substances and reaction mixtures.

Göllnitz and Reimer have [8,9] developed a method for the extrapolation of adiabatic induction times from isoperibolic induction times. For this procedure the cooling-constant κ is necessary, which characterizes the heat loss of the equipment.

$$\kappa = \frac{k_0 A}{V\rho c_p \Phi} \tag{1}$$

All quantities of the article are described in the nomenclature at the end of the article.

The dimensionless induction time is defined by the product of the cooling-constant and the isoperibolic induction time.

$$\tau = t_{\text{iso}}\kappa \tag{2}$$

By the following correlation the dimensionless induction time can be assigned to a Semenov number.

$$\tau = \sum_{i=1}^{\infty} \frac{(i-1)!}{i^! Se^!} \tag{3}$$

The Semenov number is a dimensionless parameter, which represents the ratio between the heat power and the heat loss power of a reaction system.

$$Se = \frac{(\mathrm{d}\dot{Q}_{\text{reaction}}/\mathrm{d}T)}{(\mathrm{d}\dot{Q}_{\text{loss}}/\mathrm{d}T)} = \frac{Q_G V M k_\infty E}{k_0 A R T_0^2} \exp\left(-\frac{E}{RT_0}\right) \tag{4}$$

The adiabatic induction time can be determined by the Semenov number, the cooling constant and the Φ-factor. The Φ-factor characterizes the heat accumulation power of all internals in the reaction vessel.

$$\Phi = 1 + \frac{(c_p m)_{\text{inert}}}{(c_p m)_{\text{reaction}}} \tag{5}$$

The enlargement of the Φ-factor causes an extension of the induction time.

$$t_{\text{ad}} = \frac{1}{Se\kappa\Phi} \tag{6}$$

This extrapolation model is only applicable for zero-order reactions.

For isoperibolic or isothermal storage tests it is possible to carry out an isokinetical conversion representation, and the kind of kinetics can be estimated qualitatively.

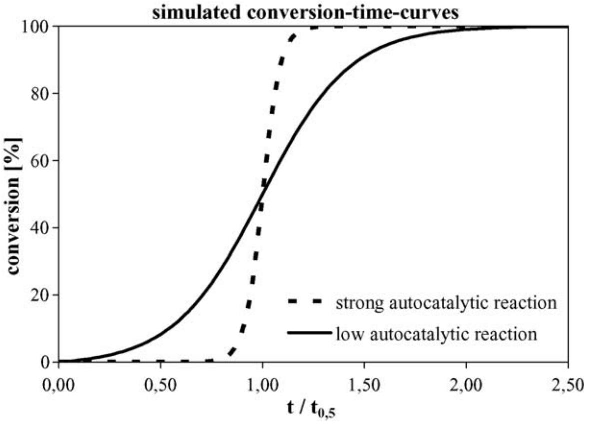

Fig. 5. Isokinetical conversion representation for 2 simulated reactions.

This representation is based on the fact that the conversion is determined as the ratio of the decomposition energy at a time t in relation to the energy of the complete decomposition and is represented beyond a reduced time.

Fig. 5 shows a representation for two reactions with different degrees of autocatalysis.

This representation enables an evaluation whether decomposition proceeds with the equal mechanism in the examined temperature range or not. It is an indication of the same mechanism if the curves of a substance show the same course by different temperatures. Otherwise, a change of the reaction mechanism is assumed.

Apart from the estimation can be decided, if decomposition shows an autocatalytic behaviour and what is its magnitude. In Fig. 5 the conversion curves indicate the typical course for vigorous autocatalytic decompositions exemplarily. Besides, it appears that the exothermal conversion proceeds in a short time interval.

For illustrating this interrelationship, Fig. 6 depicts simulated DSC measurements as an example of a low and vigorous autocatalytic decomposition, respectively.

The curve of a strong autocatalytic reaction shows the appearance of the exothermal signal only after a long duration of storage and directly before the decomposition. Therefore, the reaction acceleration in the decomposition is caused by the enrichment of

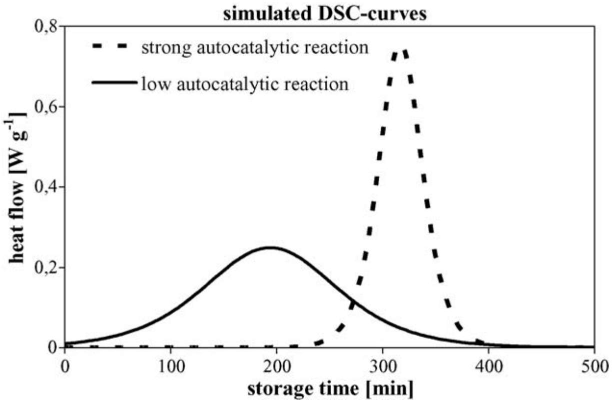

Fig. 6. Diagram of isoperibolic storage of simulated DSC curves.

an autocatalytic substance but not by the thermal accumulation. On the other hand, the low autocatalytic reaction shows a slowly ascending curve during the whole induction time. This slowly ascending curve is due to a correlation of thermal accumulation and an enrichment of autocatalytic substances.

Kinetic examination on the base of storage tests require much time. The question arises, if the first indications of the present kinetic can be determined on the bases of dynamic tests. This question shall be answered later.

3.3. Determination of kinetic parameters

If there is a well-defined rate equation of the reaction, the heat production rate can be calculated as follows:

$$\dot{Q}_{\text{reaction}} = f(C)\Delta H k_{\infty} \exp\left(-\frac{E}{RT}\right) \tag{7}$$

Critical or non-critical states can be determined by simulation, provided that a model equation for the cooling power of a reactor is available.

Furthermore, the adiabatic induction time can be calculated for a zero-order reaction for a given temperature T_0 if the kinetic parameters are available [19].

$$t_{\text{ad}} = \frac{RT_0^2 c_{\text{p}}}{EQ_{\text{G}}k_{\infty}} \exp\left(\frac{E}{RT_0}\right) \tag{8}$$

The start or ambient temperature and the adiabatic induction time are corresponding parameters. Using these parameters it is possible to estimate the time which is available for countermeasures for a given reaction system.

Both, dynamic and isoperibolic tests are used for the determination of kinetic constants.

- The dynamic methods assume that there exists a functional connection between the temperature of the maximum rate and the heating rate.
- Four different methods are used for isoperibolic measurements.
    - Provided that the following connection between the conversion and the heat of reaction is realized: $U(t) = Q_{\text{Z}}(t)/Q_{\text{G}}$ a calculation of the kinetic parameters can be executed, using the induction times for different temperatures.
    - For autocatalytic reactions the rate constants of isothermal tests can be determined by the help of the difference between the time of the maximal reaction rate and the half time of the reaction at different temperatures.
    - Based on storage tests the kinetic parameters can be determined from the adiabatic induction time and the associated storage temperature.
    - Estimation of kinetic parameter with nonlinear methods.

3.3.1. Dynamic methods

At least three tests at different heating rates are necessary for the determination of kinetic parameters.

Ozawa [5] assumed in his approach the existence of a linear correlation between the maximum temperature and the logarithm of the heating rate, for a first order reaction.

$$\log\beta = \log\left(\frac{k_{\infty}E}{R}\right) - 2.315 - 0.4567\frac{E}{RT_{\max}} \tag{9}$$

From the slope of this linear function the activation energy can be determined.

The analysis method presupposes the same conversion at the maximum of the curve at different heating rates.

A similar method has been developed by Kissinger [6] which uses the following linear equation for the determination of the activation energy.

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = \ln\left(\frac{k_{\infty}R}{E}\right) - \frac{E}{RT_{\max}} \tag{10}$$

Another procedure is described in ASTM E 698-79 [7]. Based on this method the logarithm of the heating rate is applied in a first step against the reciprocal maximum temperature. An approximate value for the activation energy is calculated by the slope of the linear function multiplied by the universal gas constant and a factor. For the estimation of the correct value an approximation procedure is described. Accordingly, the value $E/(RT)$ is calculated and a correction factor D is determined by a given table. By this factor D, the activation energy is determined again by the following equation:

$$E = 2.303\frac{R}{D}\frac{\text{d}\log\beta}{\text{d}(1/T_{\max})} \tag{11}$$

This sequence is continued till a sufficient high adjustment of the activation energy is reached. Accordingly, the preexponential factor can be calculated:

$$k_{\infty} = \frac{\beta E \exp(E/RT_{\max})}{RT_{\max}^2} \tag{12}$$

The previously named methods are based on the linearization of a model after logarithmic transformation. The kinetics are created by using Arrhenius context and nth-order reaction mechanism. The alternative approach to kinetics evaluation is based on non-linear optimization. This is discussed in detail in the following chapter.

3.3.2. Isoperibolic methods

By an isoperibolic mode of operation some problems can be avoided, which appear within the dynamic calorimetry as a result of the scan about greater temperature area. Stationary conditions adjust under isoperibolic conditions. For this reason the signal can be assigned more unambiguously to the chemical reaction.

Kinetic parameters can be estimated using the mathematical correlation between adiabatic induction time and start temperature.

Grewer [10] has developed an estimation method for kinetic parameters of autocatalytic reactions which uses isothermal DSC-measurements.

We use the isothermal procedure under the assumption that the temperature varies from our isoperibolic DSC measurements only slightly.

For this purpose the following rate equation is used:

$$-\frac{\mathrm{d}C_\mathrm{A}}{\mathrm{d}t} \approx \frac{\exp(kt)}{(1+\beta\exp(kt))^2}; \tag{13}$$

Presupposition for the application of this method is that,

- the reaction rate increases exponentially,
- the heat flow curve is symmetrically to the maximum of the curve and
- the following equation is applicable to the maximum reaction rate:

$$\beta\exp(kt_\mathrm{max}) = 1 \tag{14}$$

Three experiments at different temperatures are necessary, from which the rate constant is determined using the difference between the moment of the maximum reaction velocity and the half-life time:

$$k = \frac{\ln(\sqrt{8}+3)}{\Delta t_{1/2}} \tag{15}$$

The rate constant of every isoperibolic experiment can be determined by this formula.

The determination of activation energy and frequency factor results from the Arrhenius-Plot:

$$\ln k = \ln k_\infty - \frac{E}{RT} \tag{16}$$

Another possibility to determine kinetic parameters from isoperibolic experiments assumes that between the conversion and the heat of reaction the following correlation exists:

$$U(t) = \frac{Q_\mathrm{Z}(t)}{Q_\mathrm{G}} \tag{17}$$

On the other hand, it must be considered that the reaction velocity and the heat flow are proportional:

$$\frac{\mathrm{d}U}{\mathrm{d}t} \sim \frac{\mathrm{d}Q}{\mathrm{d}t} \tag{18}$$

The rate constant of a first order reaction can be determined by using thermoanalytical measurements as followed:

$$R_G = \frac{\mathrm{d}Q/\mathrm{d}t}{\int_o^t(\mathrm{d}Q/\mathrm{d}t)/\mathrm{d}t} \tag{19}$$

The integral below the fraction stroke is determined by the area under the exothermic curve at time interval d*t*.

The activation energy and the frequency factor can be determined from the reaction rate constants at different temperatures with well known methods.

The application of the isothermal test method for the decomposition of nitromethane is described by Constantinou [11]. The kinetic evaluation is based on the following equation:

$$\frac{\mathrm{d}U}{\mathrm{d}t} \sim \frac{\mathrm{d}Q}{\mathrm{d}t} = f(1-U)\cdot k_\infty \cdot \exp\left(\frac{-E}{R\cdot T}\right) \tag{20}$$

For the kinetic function *f*(*1–U*), which is characterized by an autocatalytic mechanism, exist miscellaneous methods. By a non-linear regression the test can determine which kinetic function corresponds most suitably with the experimental data.

The activation energy can also be calculated from the function, which describes the dependence of the maximum heat flow on the temperature:

$$\ln P_\mathrm{max} = \ln K - \frac{E}{R}\left(\frac{1}{T}\right) \tag{21}$$

Göllnitz [8,9] (chapter 3.2) determined the adiabatic induction times and represented the adiabatic induction time logarithmically against the reciprocal start temperature. Based on the slope of the linear function the activation energy and the frequency factor can determined:

$$\ln t_\mathrm{ad} = \ln\left(\frac{RT_0^2 c_\mathrm{p}\Phi}{EQ_G k_\infty}\right) + \frac{E}{RT_0} \tag{22}$$

The method is called as “classic method” in the paper.

This method is limited substantially by the assumptions of a zero-order reaction and the Semenov model (homogeneous temperature distribution), so that an application for decomposition reactions with complex mechanisms is disputed. The aim is to extend this method in regard to autocatalytic decomposition reactions.

The alternative approach to kinetically evaluation is based on non-linear optimization. Detailed discussion of this complicated matter is beyond the scope of this paper. It can be referred to some publications [23–25,18]. The main idea of this approach is that the complete model of a process is used for evaluation of reaction kinetics instead of the linearized form. During the non-linear optimization is considered only the time as independent variable. The kinetic parameters are estimated on the basis of the non-linear Least Square Method by using numerical optimization. Unfortunately these methods are rather complex in use and cannot be applied without specialized software [26]. The Formal Kinetics program (ForK) [25,27], developed by ChemInform Ltd., can serve as example of the commercial software. It was used for the exemplary evaluation of a non-linear kinetic in this article.

Additional commercial software is available like the NETZSCH Advanced Software [13,14] and Advanced Thermokinetics Software (AKTS) [15–17].

3.4. Example

Substantial differences arise at the calculation of the kinetic parameters with the indicated methods. Table 1 represents a comparison of the activation energies, the preexponential factors and the adiabatic decomposition temperatures after 24 h for the substance 2-bromo-2-nitro-1,3-propanediol calculated with different methods.

The results of the dynamic experiments have shown high agreement. This is not surprising, because the evaluation methods are based on the integral form of the rate equation. That means they possess a common basis.

No conformance is observed if a comparison with the results of isoperibolic measurements takes place.

Table 1
Kinetic parameters of 2-bromo-2-nitro-1,3-propanediol from different evaluation methods

Calculation method	Operation mode	E (kJ/mol)	k_∞ (min^{-1})	ADT$_{24\,h}$ (°C)
Ozawa	Dynamic	91	9.00×10^8	61
Kissinger	Dynamic	87	2.69×10^8	61
ASTM E 698–79	Dynamic	87	2.25×10^8	63
ForK	Dynamic	85	3.38×10^8	84
Classic method	Isoperibolic	150	1.26×10^{16}	93
Grewer	Isoperibolic	97	6.80×10^{10}	41
Constantinou	Isoperibolic	110	9.21×10^{10}	50
ForK	Isoperibolic	102	3.05×10^{11}	107

Therefore, the use of these parameters for calculations cannot be recommended, such as for the adiabatic decomposition temperature. Differences from up to 66 K are the result.

Also, the estimation of the kinetic parameters with non-linear methods shows no congruent results. However, a good agreement occurs for the non-linear modulation of the dynamic attempts with the linear methods.

The estimation of rate equations for decomposition reactions by thermoanalytic methods meets some principal difficulties:

- For the decomposition reaction of solids, other mechanisms might be responsible than for the decomposition of liquids.
- Solids and liquids are in each case heterogeneous system; in addition to a condensed phase, always a gas phase appears. Thermoanalytical methods assume homogeneous reactions, so that the temperature gradients as well as the heat and material transportation processes are ignored.
- Both phases are changing their masses and volumes during the conversion.
- The results are strongly affected by the experimental conditions. So the heating rate influences the results of dynamic measurements. Referring to a large scale process the informative capability is also limited by the test mass. Furthermore, the sampling can be problematic because of inhomogeneous mixtures.

Additional problems in the evaluation of reaction curves arise if no fitting of the curves with models of reactions of *n*th order is possible. Frequently, a sigmoid behaviour is observed that formally can be described by an autocatalytic rate equation. Such reactions are characterized by the fact that no heat accumulation exists and/or only a very low conversion appears. Therefore, the acceleration of the reaction in the decomposition is caused by the enrichment of an autocatalytic substance but not by thermal accumulation.

For the estimation of the kinetic parameters of such difficult decomposition reactions the application of linear methods is not to be recommended, because it requires the consideration of the degree of conversion and the temperature as independent variables. In many cases this assumption turns out to be very rough. The reaction rate depends exponentially on temperature and therefore changes significantly even at small temperature variations. As a result the influence of small errors in parameters is magnified dramatically.

Consequently, such linearization methods can only be applied to simple single state models. In such cases, the application of a simple kinetic model can lead to unsafe safety engineering statements.

In contrast to the main idea of the non-linear method the complete model of a process is used for kinetics evaluation instead of linearized form and only time is considered as independent variable.

The most important advantages of the non-linear method are the applicability to various classes of kinetic models and to complex multi stage models as well as the use of experimental data obtained at various temperature modes.

4. Conclusions

Concerning examinations by microcalorimetric methods the following aspects should be considered:

- The examination of small substance masses impairs the informative capability concerning to a large scale process. The sample collection is problematic by inhomogeneous mixture of substances.
- The results depend always on the temperature program and the heating rate, respectively. To create comparable conditions, trials for isoperibolic tests should be conducted with equal heating rates.
- The thermoanalytical models are generally developed for homogeneous reactions. But decomposition reactions, which arise usually in heterogeneous systems, are characterized by preceding melt or evaporation processes. The application on decomposition reactions is problematic, because they are characterized by a heterogeneous run of the reaction.
- In the heterogeneous kinetic the temperature distribution, heat and mass transportation processes, as well as diffusion processes play a decisive role.
- At microcalorimetric measuring methods a direct temperature measurement does not take place in the sample. Therefore, no accurate information on the actual temperature inside the sample is available. Only a sensor in the bottom of the sample crucible measures the temperature. Consequently, temperature gradients exist in the crucible. Hence, heat losses must be accepted through the heat transfer of the sample to the crucible material and to the sensor.
- The linear estimation methods for kinetic parameters do not work for autocatalytic decomposition reactions. Not even the

use of non-linear adjustments in modern programs is always successful. The kinetic modulation from DSC measurements with different storage temperatures is partly difficult and time-consuming. Moreover, simple and fast methods are often used in the industry.

The application of microcalorimetric measurements on decomposition reactions was presented and the coherent problems were pointed out.

In the final consequence the information basing only on microcalorimetric measurements are not sufficient for safety technical decisions.

In conclusion, it is to ascertain that a rough estimate can be obtained using microcalorimetry for the start temperature and the violence of the decomposition reaction as well as the induction time. These are useful data for the identification of thermal hazards.

References

[1] German guidelines, Technische Regel für Anlagensicherheit TRAS 410—Erkennen und Beherrschen exothermer chemischer Reaktionen, 2000.
[2] A. Keller, D. Stark, H. Fierz, E. Heinzele, K. Hungerbühler, J. Loss Prev. Process. Ind. 10 (1997) 31–41.
[3] J. Steinbach, Safety Assessment for Chemical Processes, Wiley-VCH, Weinheim, 1999.
[4] J. Pastre, U. Wörsdörfer, A. Keller, K. Hungerbühler, J. Loss Prev. Process Ind. 13 (2000) 7–17.
[5] T. Ozawa, J. Therm. Anal. 2 (1970) 301–324.
[6] H.E. Kissinger, J. Res. Nat. Bur. Stds. 57 (1956) 217.
[7] ASTM: Standard Test Method for Arrhenius Kinetic Constants for thermally unstable Materials; Designation: E 698–79, 1979.
[8] R. Göllnitz, B. Reimer, Chemie Ing. Technik 72 (6) (2000) 641–644.
[9] R. Göllnitz, B. Reimer, Chem. Eng. Technol. 24 (5) (2001) 462–466.
[10] T. Grewer, Thermochim. Acta 225 (1993) 165–176.
[11] C.P. Constantinou, Int. J. Chem. Kinet. 26 (1994) 1151–1166.
[12] CISP Thermal Safety Software Series, Fork User Guide.
[13] E. Kaisersberger, J. Opfermann, Laborpraxis 4 (1992) 360–364.
[14] J. Opfermann, J. Therm. Anal. Cal. 60 (2000) 641–658.
[15] B. Roduit, Thermochim. Acta 355 (2000) 171–180.
[16] B. Roduit, Thermochim. Acta 388 (2002) 377–387.
[17] B. Roduit, Ch. Borgeat, B. Berger, P. Folly, B. Alonso, J.N. Aebischer, F. Stoessel, J. Therm. Anal. Cal. 80 (2005) 229–236.
[18] H.L. Anderson, A. Kemmler, R. Strey, J. Therm. Anal. 47 (1996) 543–557.
[19] J. Steinbach, Safety Assessment for Chemical Processes, Wiley-VCH, Weinheim, 1999.
[20] T. Grewer, Thermal Hazards of Chemical Reactions, in: Industrial Safety Series, vol. 4, Elsevier, Amsterdam, 1994.
[21] J.M. Barton, Thermochim. Acta 71 (3) (1983) 337–344.
[22] J.L. Cronin, P.F. Nolan, J. Hazard. Mater. 14 (1987) 293–307.
[23] H. Anderson, A. Kemmler, R. Strey, Thermochim. Acta 271 (1996) 23–29.
[24] A. Kossoy, E. Koludarova, J. Loss Prev. Process Ind. 8 (4) (1995) 229–235.
[25] A. Kossoy, A. Benin, Report on the Fall Meeting of the DIERS Users Group, Pittsburgh, USA, 1997.
[26] H. Anderson, A. Kemmler, R. Strey, Thermoch. Acta 271 (1996) 23–29.
[27] A. Kossoy, V. Belohvostov, A. Ahmedshin, The First International Conference Reaction hazards assessment and vent sizing (RHV 99), Saint-Petersburg, Russia, 1999.