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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

KINETIC ON-LINE EVALUATION OF CHEMICAL REACTIONS

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Abstract

A computer program was developed for kinetic evaluations of calorimetric experiments to predict the further reaction run under adiabatic conditions. Kinetic modeling is based on elementary reaction steps whose rate laws form a set of differential equations. For the continuous parameter optimization time-temperature data and their derivatives are used. A special calorimeter of the ACTRON series with safety equipment was applied to investigate the kinetics of chemical reactions and to test kinetic on-line evaluations. In the paper, examples for the reaction of *n*-propanol with *o*-chlornitrobenzene and for the alcoholysis of phenyl isocyanate are given.

Keywords: calorimetry, kinetics, on-line, optimization, software

Introduction

A detailed investigation of the kinetics of a normal reaction system does not require the application of techniques for on-line evaluations. The recognition of the main reaction steps and the determination of the corresponding activation parameters are easier and often more reliable when evaluations are executed off-line. But on the one hand, automatic on-line calculations applied as screening methods can reduce the necessary time expense and on the other hand they open manifold opportunities in the area of process control in chemical plants.

Frequently, incidents in plants are caused by thermal hazards owing to a runaway reaction. After the so-called point of no return an industrial reactor becomes out of control because its heat exchange is lower than the heat generation by an exothermic reaction that could be the desired primary reaction or an undesired secondary reaction. A comparison of the actual reaction run with the expected one and further its prediction as a result of a parameter optimization enable a risk assessment of an imminent hazard.

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A few methods for the kinetic control of chemical reaction have been developed by several workers [1–3].

1) Data fitting using functions that approximate simple kinetic processes
2) Evaluation of first and second derivatives of measured data
3) Data analyses using neuronal networks, partly supported by additional information about an assumed kinetic model
4) Model based non-linear regressions

The first two methods are relative easy to realize but they allow only a limited prediction of the further reaction run. On the other hand, the last two methods are more time expensive and they require a considerable computational effort, but the predictable range enlarges. In this paper, examples for the application of the fourth method on homogeneous reactions are given.

Mostly, differential scanning calorimeter (DSC) and accelerating rate calorimeter (ARC) [4, 5] were used for thermal kinetic hazard evaluations. The authors applied a new type of an adiabatic calorimeter [6] to control the reaction of *n*-propanol with *o*-chlornitrobenzene and the alcoholysis of phenyl isocyanate. Because of the special equipment of this calorimeter, reaction runs can be observed beyond the point of no return.

Software

Especially for the realization of kinetic on line evaluations we extended the well-tried software package TA-kin [7, 8]. This program communicates with the calorimeter software via dynamic data exchange (DDE). Instead of parallel processing on one computer it is possible to separate both programs if a Microsoft network is available. Otherwise, a generous equipment of the computer with random access memory (RAM) is necessary. For the experiments we used a single computer with a Pentium 90 processor and 32 Mbyte RAM.

The kinetic software performs the data evaluation by non-linear regression [9, 10] including the numerical integration [10] of the rate

$$\xi_{\mathrm{j}} = v k_{\mathrm{j}}(T_{\mathrm{R}}) \prod_{\mathrm{i}=1}^{\mathrm{M}} c_{\mathrm{i}}^{n_{\mathrm{j,i}}} \tag{1a}$$

$$\text{with} \quad c_{\mathrm{i}} = \frac{1}{v}\left(n_{\mathrm{i,o}} + n_{\mathrm{i,add}} + \sum_{\mathrm{j}=1}^{\mathrm{R}} \nu_{\mathrm{j,i}} \xi_{\mathrm{j}} \right)$$

$$k_{\mathrm{j}}(T_{\mathrm{R}}) = \exp\left(\ln k_{\mathrm{o,j}} - \frac{E_{\mathrm{A,j}}}{R T_{\mathrm{R}}} \right)$$

$$\dot{T}_R = -\frac{\sum_{j-1}^{R}\Delta H_j\xi_j}{C_p} - \frac{1}{\tau_R}(T_R - T_U) \tag{1b}$$

$$T_s = -\frac{1}{\tau_S}(T_S - T_R) \tag{1c}$$

equations and the heat balance equation given in Eqs (1a–c).

In the isoperibol mode the heat exchange between the calorimeter and its environment is characterized by a reactor time constant τ_R (1b). Furthermore, a correction of the measured temperature with a sensor time constant can be considered by Eq. (1c) [11].

Calorimeter

The precision calorimeter ACTRON 5 with safety scenario equipment [6] represents the experimental basis for the reactions described in the next section. Its very fast safety pumps are the main components of the safety scenario equipment. They work simultaneously, one empties the reactor whilst the other purges it with cold solvent. In this way, kinetic evaluations become possible even under conditions that characterize a case of a runaway reaction.

By the ACTRON software the working mode can be easily changed from isoperibol to adiabatic. The working volume of the calorimeter can be varied between 30 and 70 ml. The reactor itself is alternatively constructed of Teflon, glass or stainless steel.

Experiments

First, a simple second order reaction was chosen to examine the equipment and procedures of on-line evaluations. The reaction of phenyl isocyanate with 2-butanol shown in Fig. 1 was carried out in toluene under adiabatic conditions. This reaction owns a rather low thermal risk because of its low activation energy and medium reaction enthalpy.

As an example for earlier investigations of this reaction using an isoperibol calorimeter and HPLC-technique the Fig. 2 demonstrates a batch reaction run [12]. Based on the obtained activation parameters and reaction enthalpy we repeated the kinetic evaluation as on-line parameter optimization with the adi-

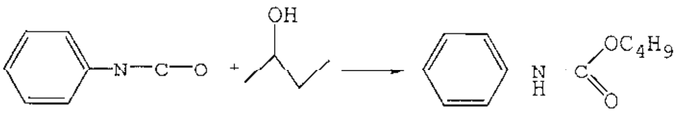

Fig. 1 Reaction of phenyl isocyanate with 2-butanol

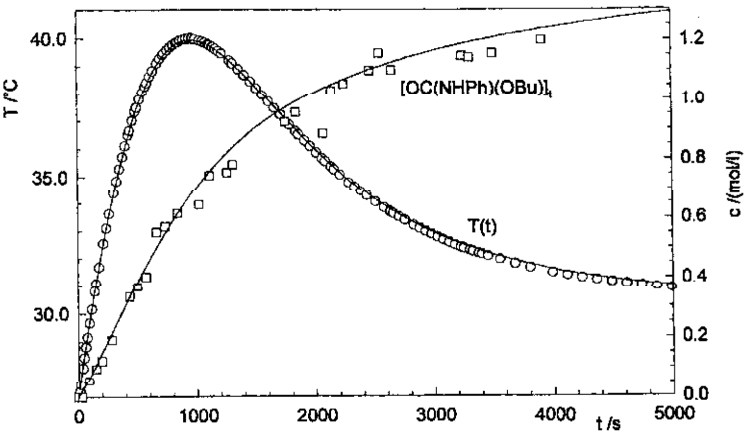

Fig. 2 Kinetic off-line evaluation of the reaction from Fig. 1. An isoperibol calorimeter was used to perform batch reactions. The kinetic parameters are listed in Table 1, the reaction enthalpy equals to –84.3 kJ mol^{-1}, the heat of mixing equals to 292 J. o – measured temperature $T(t)$, □– measured product concentration $c(t)$, simulated data are plotted by solid lines

abatic ACTRON calorimeter equipped with a Teflon reactor in semi-batch technique. A typical evaluation result shows Fig. 3 in which the experimental reaction time reached 2000 s. After each optimization a forward simulation using the estimated parameters, see Table 1, is executed. The listed parameters as well as the agreement of measurement and simulation demonstrate that no changes in reaction kinetics or non-chemical conditions arise.

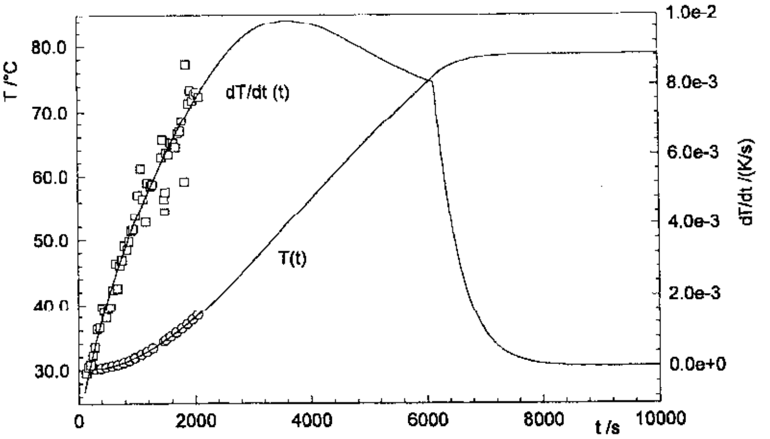

Fig. 3 Kinetic on-line evaluation of the reaction from Fig. 1. The adiabatic ACTRON calorimeter was used to perform semi-batch reactions with dv/dt=0.1 ml min^{-1} and Δt=6000 s. o – measured temperature $T(t)$, □ – measured temperature derivatives dT/dt (t), simulated data are plotted by solid lines

Table 1

	off-line evaluation	on-line evaluation			
		at 1000 s	at 1500 s	at 2000 s	at 2500 s
$\ln k_u$	7.22	0.344	8.09	7.47	5.79
$E_A/(\mathrm{kJmol^{-1}})$	39.6	22.4	42.0	40.4	36.1
$k(30°\mathrm{C})/[(\mathrm{mol\ l^{-1}})^{-1}\mathrm{s}^{-1}$	2.09e–4	1.97e–4	1.93e–4	1.94c–4	1.97e–4
$\Delta T/\mathrm{K}$	13	2.3	5.0	8.6	12.5

On the contrary, more dramatic temperature courses are observed if the reaction of *o*-chloronitrobenzene with alkaline *n*-propanol is carried out. Depending on several experimental factors the complex reaction system can respond very sensible to changes of the conditions with unexpected heat generation rates [13]. This is caused by the occurrence of a high exothermic reduction of the nitro

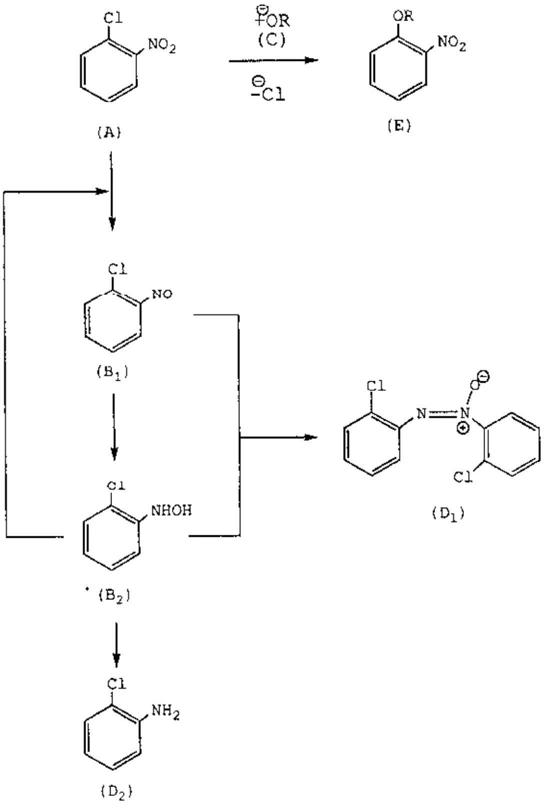

Fig. 4 Reactions in the system *o*-chloronitrobenzene + ROH + NaOH

group after an induction period that does hardly contain information about this sudden event. The main reaction steps that seem to control the behavior of the system are given schematically in Fig. 4. Only the harmless substitution of chlorine to form alkoxy compounds, see first line in Fig. 4, is the desired reaction in the chemical industry. Therefore, an early recognition of a possible thermal explosion caused by considerable conversions within the reduction ways could prevent the reactor that is dimensioned for rather low heat production rates from rupture.

A simplified kinetic model was formed for the kinetic on-line evaluations. A set of four differential rate laws was taken into consideration.

0) Substitution that results in E by consuming A and C

1) Initiation as formation of an autocatalytic acting compound B_1 consuming A

2) Autocatalytic accumulation of B_1

3) Termination by condensation of B_1 and B_2 to D_1, or by further reduction of B_2 to D_2, resp.

Figure 5 shows the result of an on-line parameter optimization 700 s after reaction start. A simple second order model for the substitution (zeroth step only) was used to test the agreement of the experiment and the expected reaction run that contains the primary substitution only. The measured temperature curve is well described by this model, but its derivatives show the opposite trend than the simulated curve d*T*/d*t*. This observation could be interpreted as an already underlying formation of reduction products.

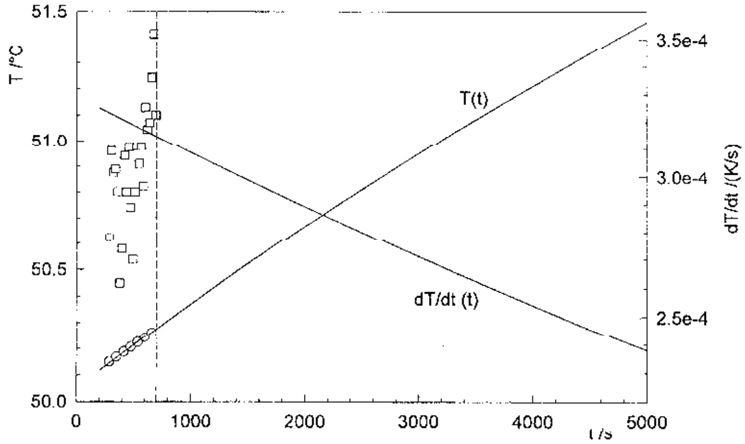

Fig. 5 Kinetic on-line evaluation of the substitution reaction from Fig. 4. The adiabatic ACTRON calorimeter was used to perform batch reactions. o – measured temperature *T*(*t*), □ – measured temperature derivatives d*T*/d*t* (*t*), simulated data are plotted by solid lines

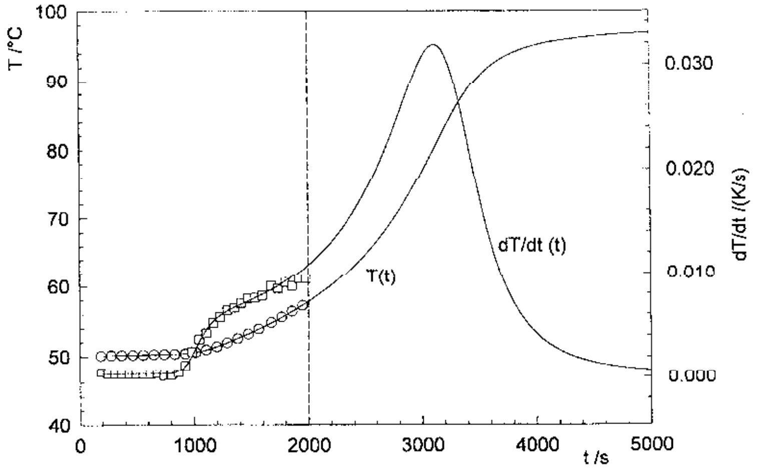

Fig. 6 Kinetic on-line evaluation of the complex reaction system from Fig. 4. The adiabatic ACTRON calorimeter was used to perform batch reactions. o – measured temperature $T(t)$, □ – measured temperature derivatives dT/dt (t), simulated data are plotted by solid lines

In Fig. 6, 1000 s after reaction start a significant change in the course of temperature derivatives arises. The possibility of easy switching between several user-defined reaction models within the evaluation software allows an uncomplicated variation of the applied model. For the evaluation 2000 s after reaction start the four-step model mentioned above was introduced. Because of the high correlation of the activation parameters k_0 and E_A in rather small temperature ranges [14] only the activation energies have been optimized. The forward simulation plotted by solid lines in Fig. 6 predicts a maximal heat production rate at TMR=3100 s. The complex system resulted in three main statements about the behavior of the reduction path.

1) The initiation is temperature catalyzed, i.e. this reaction has a rather high activation energy

2) The autocatalytic accumulation of B_1 has a relative high rate constant

3) The main chemical heat release is provided by the termination reactions.

Conclusions

The kinetic controlled calorimetric experiments show that non-linear evaluations based on real chemical kinetic models are possible whilst the reaction run is more and more completed. Particularly complex reactions require a detailed knowledge about the structure of the system, i.e. black box evaluations will not be successful.

Symbols

Symbol	Name	Context	Unit
t	time		s
ξ	amount of conversion	$d\xi = dn_i/\nu_i$	mol
ν	stoechiometric coefficient		
c	concentration		$\mathrm{mol\ l^{-1}}$
k_o	frequency factor		$\mathrm{(mol\ l^{-1})^{1-n} s^{-1}}$
E_A	activation energy		$\mathrm{kJ\ mol^{-1}}$
ΔH	reaction enthalpy		$\mathrm{kJ\ mol^{-1}}$
n	amount of substance		mol
	(partial) reaction order		
R	gas constant	R=8.31441E–3	$\mathrm{kJ\ mol^{-1} K^{-1}}$
	count of chemical reactions		
M	count of reaction components		
v	filled reactor volume		l
C_p	filled reactor heat capacity		$\mathrm{J\ K^{-1}}$
k	reaction rate constant	$k = k_o \exp(-E_A/RT)$	$\mathrm{(mol\ l^{-1})^{1-n} s^{-1}}$
K	heat exchange coefficient		$\mathrm{J\ K^{-1} s^{-1}}$
τ_S	sensor time constant		s
τ_R	reactor time constant	$\tau_R = C_p/K$	s
T_S	sensor temperature		°C
T_R	reactor temperature		°C
T_U	cooling temperature		°C
TMR	time to maximum rate		s

References

1 L. Hub, Dissertation, Zürich 1975.

2 B. Schenker and M. Agarwal, AIChE (1993).

3 E. M. Assaf and R. Giordano, Chem. Eng. Sci., 51 (1996) 3107.

4 J. M. Dien, Chimia 48 (1994) 542.

5 D. I. Townsend and J. C. Tou, Thermochim. Acta, 37 (1980).

6 K. Heldt, H. L. Anderson, B. Hinz and A. Kemmler, J. Thermal Anal., 49 (1997) 1647.

7 H. L. Anderson, A. Kemmler and R. Strey, Thermochim. Acta, 271 (1996) 23.

8 H. L. Anderson, A. Kemmler and R. Strey, J.Thermal Anal., 47 (1996) 543.

9 D. W. Marquardt, J. Soc. Indust. Appl. Math., 11(1963) 431.

10 W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, 'Numerical Recipes in Pascal', Cambridge University Press 1990.

11 H. L. Anderson, R. Strey, A. Kemmler and K. Heldt, J. Thermal Anal., 48 (1997) 769.

12 K. Heldt, H. L. Anderson, B. Hinz and Th. Willms, J. Thermal Anal., 52 (1998) 203.

13 B. Hinz and H. L. Anderson, J. Thermal Anal., 47 (1996) 435.

14 H. L. Anderson, R. Strey, A. Kemmler and D. Haberland, J. Thermal Anal., 49 (1997) 1565.