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COMPARISON OF THERMOKINETIC DATA OBTAINED BY ISOTHERMAL, ISOPERIBOLIC, ADIABATIC AND TEMPERATURE PROGRAMMED MEASUREMENTS

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Abstract

In this paper isothermal, isoperibolic and adiabatic calorimeters and a Power-Compensating DSC are compared by determining kinetic data of a simple test reaction. First, the kinetic parameters were analyzed using a conventional isothermal method, based on the analytic determination of the course of reaction. Subsequently, the kinetic data of the performed reaction were determined for the different types of calorimeters by simultaneously evaluating several measurements with identical initial conditions but different temperature courses. The kinetic parameters obtained by the different calorimeters agree reasonable well, indicating the reliability of kinetic data derived from thermokinetic methods.

Keywords: calorimetry, comparison, kinetic data, kinetic evaluation, test reaction

1. Introduction

For a safe design of chemical processes a knowledge of reliable kinetic parameters of the performed reaction is essential. Therefore an exact determination of these parameters is strictly recommended. The aim of this work was to show whether the combination of modern calorimeters with appropriate methods of evaluation allows the determination of sufficient reliable kinetic data, as conventional analytic methods do. Therefore isoperibolic, adiabatic and temperature programmed thermokinetic methods were compared with a conventional isothermal method by determining kinetic parameters.

As a simple test reaction the carbamate formation from phenyl isocyanate and 2-butanol with solvent toluene was investigated under identical initial conditions, but different temperature courses.

For thermokinetic investigations it has to be proven, that no other thermal effects, e.g. phase transition, affect the supplied signal of heat power or temperature caused by the performed reaction. Therefore the reactants and their mixtures with toluene were investigated applying DSC. No thermal effects were found, so far as the reaction temperature does not exceed 120°C.

2. Types of calorimeters

The types of calorimeters with their distinguished marks and problems, concerning the further evaluation of measured data, are listed in Table 1.

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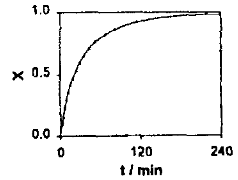
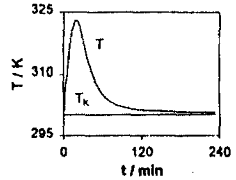
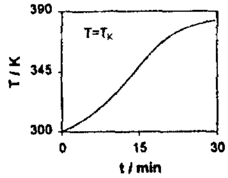
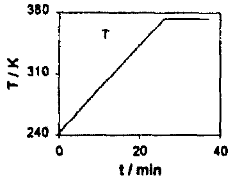
Table 1 Types of calorimeters with distinguished marks and problems

Isothermal	Isoperibolic	Adiabatic	Temperature programmed
compensation by electrical heating	constant cooling temperature	continuous re-adjustment of the ambient temperature	linear heating to a final temperature
			
analytical determination of conversion	heat transfer heat capacity	heat capacity exact compensation of heat losses	charging baseline construction
Reaction calorimeter (Köhler [1])	(Self designed)	PHI-TEC II (HEL[1])	DSC 7 (Perkin Elmer Corp.)

[1] Hazard Evaluation Laboratories

The isothermal calorimeter works with an electric compensation heater to hold the temperature constant. The analysis of the measured heat power signal revealed that a reliable thermokinetic evaluation was not possible. Therefore this calorimeter was used as an isothermal batch reactor. The progress of reaction was obtained by analyzing taken samples of the reaction mixture (Section 4.1).

The self-designed isoperibolic calorimeter operates with a constant cooling temperature. The resulting temperature rise mainly depends on the cooling conditions and kinetic data of the reaction. Therefore, above all, the heat capacity and the heat transfer has to be known exactly. This may imply some problems if the heat transfer coefficient changes during the reaction caused by a change in physical properties of the reaction mixture, especially the viscosity. To minimize this influence the stainless steel reactor is surrounded by an air gap, which, in itself, is surrounded by a brass cooling jacket. Through this jacket a coolant fluid is circulated. The air gap between the reactor and the coolant jacket strongly increases the total heat transfer resistance. Therefore, small changes of the inner heat transfer from the reaction mixture to the reactor wall should not have a significant influence on the overall heat transfer coefficient. This was proven by additional investigations of the model reaction considering the concentrations used for the thermokinetic measurements (Table 2). For the stoechiometric reaction of phenyl isocyanate and 2-butanol with the same initial concentration of 2 mol l^{-1} for both compounds (where the highest increase of viscosity is expected), an increase of the viscosity from 0.73 to 1.72 cSt was determined at 20°C during the reaction. In this range of changing viscosity no influence on the overall heat transfer coefficient was found.

The commercial adiabatic calorimeter PHI-TEC II from HEL prevents heat loss due to a controlled increase of the ambient temperature (if the pressure inside the reactor increases, the ambient pressure is elevated too). The heat produced by the chemical reaction is used entirely to heat up the reaction mixture and the reactor itself. For the evaluation of the temperature course, the knowledge of the heat capacity of the reaction mixture and reactor is required as well as the exact control of the ambient temperature.

Finally, the Power-Compensating DSC 7 from Perkin Elmer was used as a temperature programmed method. The DSC is a common tool and is described very well by several authors (e.g. [2–4]). The main problems are the correction of the primary data (e.g. deconvolution) and a correct construction of the baseline. When the mixture reacts at room temperature, as in the case of the present investigations, the charging of the capsule becomes difficult too.

3. Method of evaluation

The conventional way of determining kinetic data of an investigated reaction is well known [5, 6] and based on several isothermal measurements at different temperatures and different concentration ratios. Guided by the increasing availability of computers, several methods of evaluation were developed to determine kinetic parameters by thermokinetic measurements. Earlier methods, e.g. [7, 8], allow the determination of kinetic parameters from a single non-isothermal measurement by presetting a kinetic model of n^{th} order. Modern methods are based on the simultaneous evaluation of several measurements [9–12].

In this work an evaluation system was applied which has already been tested and described [13, 14]. This method is available as a software package and allows the treatment of isothermal and non-isothermal thermokinetic data in the same way on the basis of a set of measurements with identical initial conditions but different temperature courses. Several measurements in the form of time, temperature, conversion data sets, are simultaneously evaluated.

In the following the theoretical basis and assumptions concerning this method are described as follows.

For kinetic measurements performed in a batch mode the mass balance of compound A can be written in the form

$$\frac{1}{\nu_A}\frac{dC_A}{dt} = C_{A0}\frac{dX}{dt} = r(X,T); \quad X = \frac{C_{A0} - C_A}{C_{A0}}; \quad \nu_A = -1 \tag{1}$$

where C_A, C_{A0} and ν_A are the concentration, initial concentration and the stoechiometric coefficient of compound A. X and T are the conversion and the temperature of the reaction mixture.

If only one brutto reaction takes place all concentrations can be described by one conversion X. It can be assumed that the rate law $r(X,T)$ can be described with a temperature dependent term according to Arrhenius and a conversion dependent term $\Phi(X)$, which includes the information of the kinetic model (e.g. $\Phi(X)=(1-X)$ for a 1st order reaction)

$$r(X,T) = \underbrace{r(0,T_R)\exp(E/R(1/T_R - 1/T))}_{f(\text{temperature})} \cdot \underbrace{\Phi(X)}_{f(\text{conversion})} \tag{2}$$

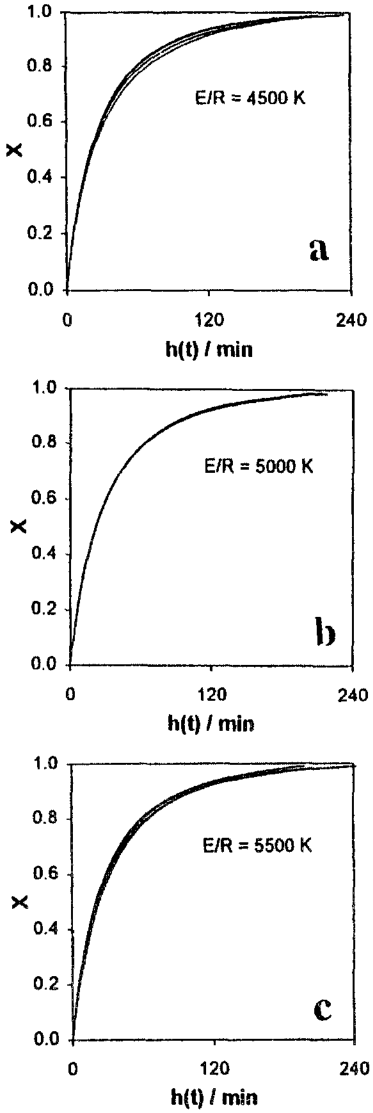


Fig. 1 a-c Optimizing the activation energy by comparing the $X(h)$ courses at different values for the activation temperature E/R. The best result for the isothermal reaction of phenyl isocyanate with 2-butanol in toluene is obtained with $E/R=5000$ K; $C_{PIC,0}=1.41$ mol l^{-1}, $C_{BuOH,0}=2.81$ mol l^{-1}

An "isothermal equivalent" reaction time h at the reference temperature T_R is defined by the following integral:

$$h = \int_0^t \exp(E/R(1/T_R - 1/T))\,dt \tag{3}$$

Now the mass balance Eq. (1) can be rearranged to an "isothermal equivalent" mass balance at the reference temperature.

$$\frac{dX}{dh} = \frac{r(0,T_R)}{C_{A0}} \Phi(X) \tag{4}$$

The right side of Eq. (4) only contains conversion X as a variable. If the correct value of the activation energy E is known, $h(t)$ can be calculated using the given t, T, X data sets from the measurements. In addition, $X(h)$ should have the same course for all measurements with the same initial conditions because the right side of Eq. (4) is independent of the temperature. As a result, the activation energy can be easily optimized by calculating and comparing the $X(h)$ courses at different activation energies as shown in Fig. 1a-c.

Subsequently, the standardized initial reaction rate $r(0,T_R)/C_{A0}$ can be obtained by extrapolating to the start of reaction at the conversion $X=0$:

$$\left.\frac{dX}{dh}\right|_{X=0} = \frac{r(0,T_R)}{C_{A0}} \cdot \underbrace{\Phi(X=0)}_{1} \tag{5}$$

Now the conversion dependent term of the reaction rate $\Phi(X)$ can be determined by numerical differentiation and standardization of the course of $X(h)$:

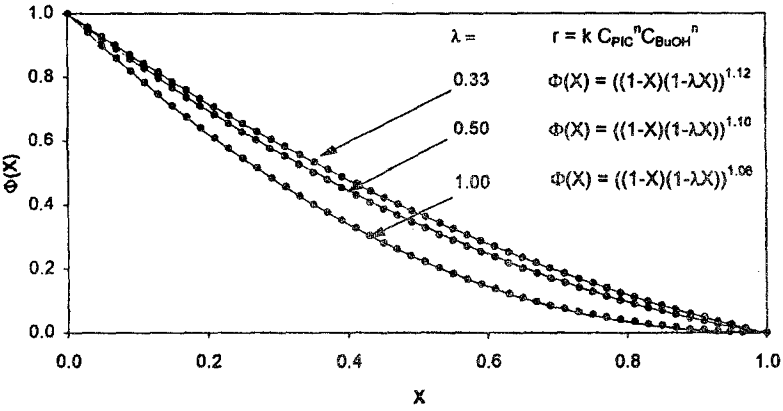


Fig. 2 Determination of a proper kinetic model by fitting $\Phi(X)$ courses which were obtained by evaluating isothermal experimental data at different ratios of initial concentrations $\lambda = C_{PIC,0}/C_{BuOH,0}$. Points: Obtained by evaluation. Lines: Result of fits

$$\Phi(X) = \frac{dX}{dh} \Big/ \frac{dX}{dh}\Big|_{X=0} \tag{6}$$

As a first result the activation energy, the standardized reaction rate and the conversion dependent term of the reaction rate $\Phi(X)$ is determined without assuming any kinetic model. In the following step, $\Phi(X)$ has to be fitted to a chosen kinetic model (for example $r{=}kC_A^n C_B^n$ for a bimolecular reaction) to obtain a proper kinetic model which is appropriate to describe the experimental data. Figure 2 shows the analysis of the $\Phi(X)$ courses which were obtained by evaluating the isothermal conventional measurements of the reaction of phenyl isocyanate with 2-butanol in toluene (Fig. 1a-c). The chosen kinetic model (Fig. 2) allows a good description of the obtained $\Phi(X)$ course.

4. Determination of time, temperature, conversion data sets from experimental data

This section describes the production of the t, T, X data sets (which are required for the evaluation method presented in section 3) from the experimental data for each type of calorimeter. The experimental conditions are given in Table 2, section 5. As a rule, at least five measurements with identical initial conditions but different temperature courses for each type of calorimeter and each ratio of initial concentrations $\lambda = C_{PIC,0}/C_{BuOH,0}$ were performed.

4.1 Isothermal conventional method

For the isothermal conventional investigations the isothermal calorimeter was used as an isothermal batch reactor. For the different ratios of initial concentrations λ=0.33, 0.50 and 1.00 at least five measurements in the range of 25 to 50°C were completed under argon atmosphere to prevent the reaction of phenyl isocyanate with moisture. First, the reactor was filled with 2-butanol and toluene and then the reaction was initiated by quickly adding phenyl isocyanate. The total reaction volume was always in the range of 85±1 ml. During the reaction about twenty samples were taken in appropriate time steps which increased with the reaction time. The samples were injected immediately into a vial with a large excess of methanol where the remaining amount of phenyl isocyanate reacted to the methyl carbamate. Subsequently, the samples were analyzed using an High Performance Liquid Chromatography system with the following set up:

Column:	RP18 (5 μ)	eluent:	60:40 methanol/water
Wave length:	220 nm	buffer:	3 mmol NaH_2PO_4
Flow:	1 ml min^{-1}	dilution:	1:1000 with methanol

To generate a close following, time related, course of conversion which can be numerically differentiated, the sequence of the single time-conversion data points were fitted according to [5]. The fitted conversion (Fig. 3) were stored together

Table 2 Results of the kinetic analysis of the reaction of phenyl isocyanate with 2-butanol in toluene at different ratios of initial concentrations $\lambda = C_{PIC,0}/C_{BuOH,0}$ obtained by different types of calorimeters. Kinetic model: $r = kC^{n}_{PIC}C^{n}_{BuOH}$

Method	$C_{PIC,0}$/	$C_{BuOH,0}$/	λ	E/	r(0, 300 K)/	n	k(300 K)·10^4/	$-\Delta H$/
	mol l^{-1}			kJ mol^{-1}	mol l^{-1} s^{-1}		mol^{1-2n} l^{2n-1} s^{-1}	kJ mol^{-1}
Isothermal	2.00	2.00	1.00	41.6	$6.31 \cdot 10^{-4}$	1.06	1.45	–
(analytic)	1.41	2.82	0.50	41.6	$6.37 \cdot 10^{-4}$	1.10	1.40	–
	1.15	3.45	0.33	41.6	$6.55 \cdot 10^{-4}$	1.12	1.40	–
				41.6		**1.09**	**1.42**	–
Isoperibolic	1.95	2.00	0.97	39.1	$5.69 \cdot 10^{-4}$	0.99	1.48	86.2
	1.42	2.83	0.50	39.1	$6.49 \cdot 10^{-4}$	1.06	1.49	86.0
	1.15	3.48	0.33	39.1	$6.63 \cdot 10^{-4}$	1.06	1.52	83.0
				39.1		**1.04**	**1.50**	**85.1**
Adiabatic	2.00	2.02	0.99	41.6	$4.49 \cdot 10^{-4}$	1.06	1.02	90.1
(PHI-TEC II)	1.42	2.82	0.50	44.1	$4.94 \cdot 10^{-4}$	1.10	1.08	81.9
				42.9		**1.08**	**1.06**	**86.0**
Temperature	1.99	1.99	1.00	39.9	$4.59 \cdot 10^{-4}$	0.94	1.26	89.4
programmed	1.42	2.81	0.51	39.9	$5.54 \cdot 10^{-4}$	0.99	1.41	83.7
(DSC 7)				**39.9**		**0.97**	**1.33**	**86.6**

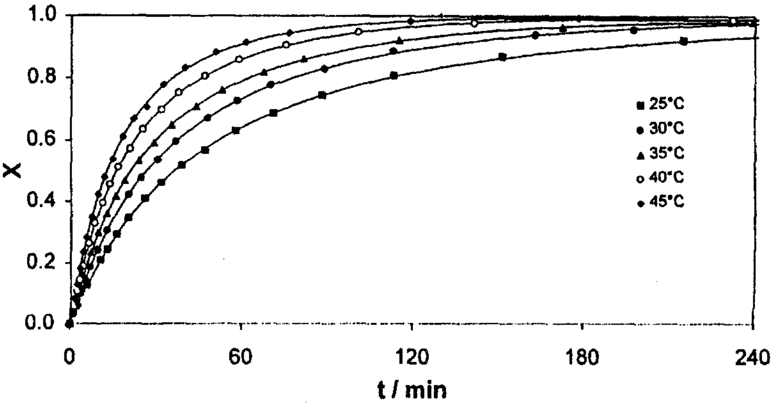


Fig. 3 Experimental (points) and fitted (lines) conversions $C_{PIC,0}=1.41$ mol l^{-1}, $C_{BuOH,0}=2.82$ mol l^{-1}

with the measured temperature in form of t, T, X data sets, which were the basis of the further evaluation as described in section 3.

The results of the isothermal conventional determination of kinetic data of the reaction of phenyl isocyanate with 2-butanol in toluene are given in Table 2.

4.2 Isoperibolic method

The isoperibolic investigations were carried out with the self-designed calorimeter described in section 2. The reaction conditions and the sequence of charging were equal to the isothermal measurements. All compounds were thermostated at the same temperature until the reaction was initiated by injecting the phenyl isocyanate into the 2-butanol-toluene mixture. The cooling temperatures were between 25 and 45°C and the reaction volume was always within the range of 45±1 ml. Finally, a sample was taken to control whether the conversion was complete and no unexpected by-products were produced. In all cases a complete reaction occurred and no by-products were discovered with the used HPLC set up described in section 4.1.

The temperature rise of isoperibolic measurements (Fig. 4) depends on the cooling conditions on the one hand and on the progress of reaction and the maximum adiabatic temperature rise $\Delta T_{\max}$ on the other:

$$\frac{dT}{dt} = \Delta T_{\max}\frac{dX}{dt} - \frac{UA}{mc_p}(T - T_K) \qquad (6)$$

The cooling term depends on the temperature difference between reactor temperature T and cooling temperature T_K and on the product of the overall heat transfer coefficient U and the heat exchange area A divided by the heat capacity of the whole system mc_p.

A typical isoperibolic temperature course is shown in Fig. 4. The short temperature decrease originating from an endothermic mixing energy of phenyl isocy-

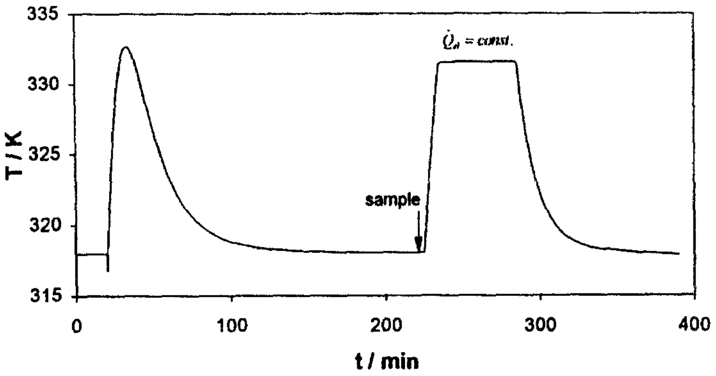


Fig. 4 Isoperibolic temperature rise of the reaction of phenyl isocyanate with 2-butanol in toluene at a cooling temperature of T_K=45°C with following calibration, $C_{PIC,0}$=1.41 mol l^{-1}, $C_{BuOH,0}$=2.82 mol l^{-1}

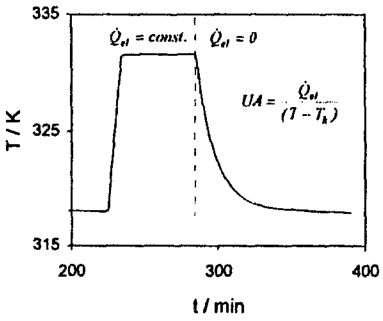


Fig. 5 Determination of *UA*

anate and the 2-butanol/toluene mixture indicates the start of reaction. The end of the reaction is reached when the temperatures of reactor and coolant are equal. After taking a sample, a calibration was performed to quantify the cooling system by applying constant electric heat power. When the reactor temperature reached a constant level *UA* is equal to the ratio of electric heat power and the temperature difference between reactor and coolant (Fig. 5).

From the cooling down curve the factor $UA/(mc_p)$ can be obtained assuming that the changes of the physical properties of the reaction mixture and the temperature have no significant effect on this constant, which is proven by the linear plot of the logarithmic temperature differences *vs.* time in Fig. 6. Usually the values of *UA* were between 0.17 and 0.18 min^{-1} and the values of $UA/(mc_p)$ were between 0.07 and 0.08 min^{-1}

Now the conversion can be calculated by integrating Eq. (6):

$$X = \frac{1}{\Delta T_{max}}\left[(T - T_k) + \frac{UA}{mc_p}\int_0^t (T - T_K)\mathrm{d}t\right] \qquad (7)$$

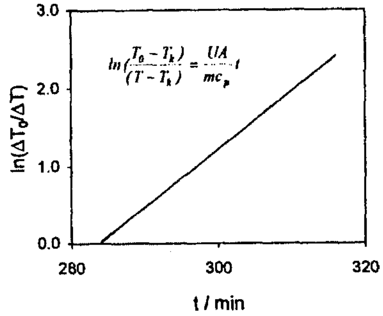


Fig. 6 Determination of $UA/(mc_p)$

The maximum adiabatic temperature rise ΔT_{max} is equal to:

$$\Delta T_{max} = \frac{UA}{mc_P} \int_0^{\infty} (T - T_K)\mathrm{d}t \tag{8}$$

Finally, the enthalpy of the reaction of phenyl isocyanate with 2-butanol in toluene can be calculated without the knowledge of the total heat capacity with Eq. (9), if UA was determined and the exact amount of phenyl isocyanate $n_{PIC,0}$ is known.

$$-\Delta H = \frac{UA}{n_{PIC,0}} \int_0^{\infty} (T - T_K)\mathrm{d}t \tag{9}$$

The results of the isoperibolic measurements, which were obtained by evaluating the t, T, X data sets are presented in Table 2 together with the results of the other methods.

4.3 Adiabatic method

The adiabatic measurements were performed in the same way as the isothermal and isoperibolic measurements concerning the reaction conditions and the charging sequence using the commercial calorimeter PHI-TEC II from the company HEL*. The test reaction was investigated with two different concentrations of phenyl isocyanate and 2-butanol respectively (Table 2). The reaction volume was always within the range of 60±1 ml. For each concentration at least five single measurements with initial temperatures between 24 and 33°C were performed. A complete reaction and absence of any unexpected by-products was checked by analyzing a final sample for each measurement. Figure 7 shows a set of measurements with identical initial conditions but different temperature courses.

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* The authors are indebted to the Schering AG for the use of this calorimeter.

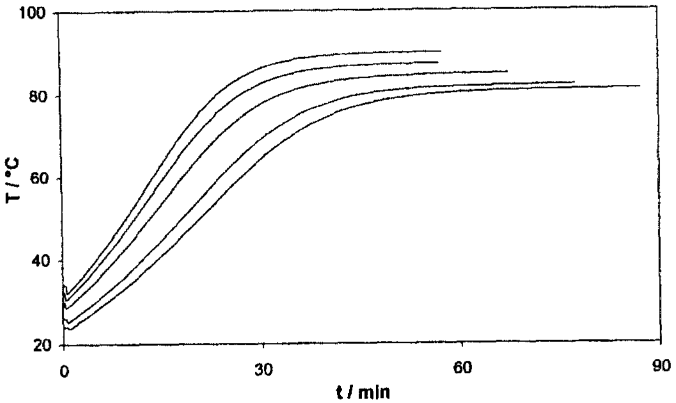

Fig. 7 Adiabatic temperature courses of the reaction of phenyl isocyanate with 2-butanol in toluene at different initial temperatures. $C_{PIC,0}=1.41$ mol l^{-1}, $C_{BuOH,0}=2.82$ mol l^{-1}

Due to the controlled increase of the ambient temperature the conversion can be obtained directly from the measured temperature rise, from the initial temperature T_0 to the final temperature T_e:

$$X=\frac{T-T_0}{T_e-T_0} \tag{10}$$

Assuming that any changes of the heat capacity caused by the rising temperature or by the changing composition of the reaction mixture are negligible, the reaction enthalpy can be calculated from the measured temperature increase:

$$\Delta T_{max}=\frac{(-\Delta H)n_{PIC,0}}{mc_p} \tag{11}$$

The results of the adiabatic investigations are presented in Table 2.

4.4 Temperature programmed method

The DSC measurements were carried out with the Power-Compensating DSC 7 from Perkin Elmer. To prevent the reaction mixture reacting before the used steel capsule is charged and positioned, a primary mixture of 2-butanol and toluene was cooled by adding liquid nitrogen until the mixture crystallized. Following this phenyl isocyanate was added. As soon as this mixture was molten it was dropped, according to Wagner [3], immediately into liquid nitrogen, where it was stored in the form of small pearls, which can be removed with a small needle to charge the capsule. Temperature scans from –40 to 120°C with linear heating rates within the range of 3 and 9 K min^{-1} was applied to investigate the test reaction with two different concentration ratios of phenyl isocyanate and 2-butanol (Table 2, section 5).

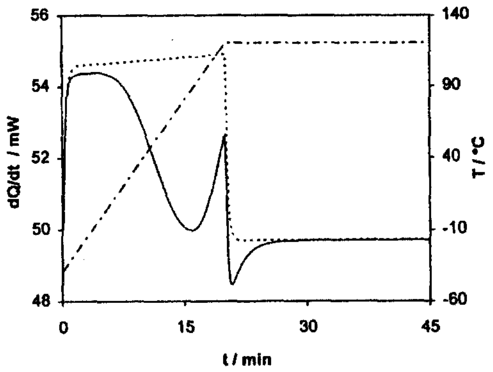

Fig. 8 DSC heat power of reaction (solid) and final mixture (dashed); 8 K $\min^{-1}$, $C_{PIC,0}$=1.41 mol l^{-1}, $C_{BuOH,0}$=2.82 mol l^{-1}

The final temperature of 120°C was held until the supplied heat power was constant. Subsequently, a scan of the final mixture with the same temperature program was recorded. The shift from linear heating to an isothermal mode causes a sudden decrease of the heat power (Fig. 8). It was assumed, that the heat capacities of reaction mixture and final mixture depend similar on the temperature. The heat power $\dot{Q}$ caused by the reaction was obtained by subtracting the DSC curves of reaction and final mixture (Fig. 9). The resulting curve shows a very small baseline shift ΔQ_{bas}.

To calculate the heat power of the chemical reaction $\dot{Q}_{ch}$ the construction of an appropriate baseline $\dot{Q}_{bas}$ is required. It was assumed that the baseline shift is caused by a change of physical properties of the reaction mixture and a corresponding baseline was constructed iteratively (Fig. 9):

$$\dot{Q}_{bas} = \dot{Q}_{bas,start} + X \cdot \Delta \dot{Q}_{bas} \tag{12}$$

The conversion itself is calculated from the ratio of the produced heat until time t and the total heat

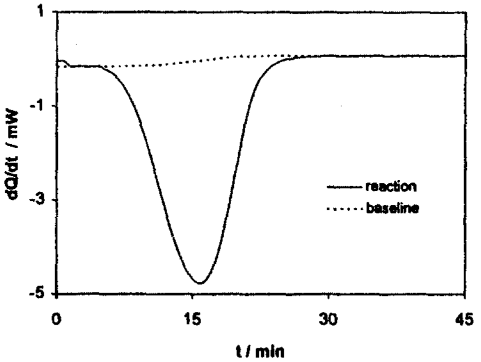

Fig. 9 Corrected DSC heat power (solid) and baseline (dashed). 8 K $\min^{-1}$, $C_{PIC,0}$=1.41 mol l^{-1}, $C_{BuOH,0}$=2.82 mol l^{-1}

$$X = \frac{\int_0^t \dot{Q}_{\mathrm{ch}} \mathrm{d}t}{\int_0^\infty \dot{Q}_{\mathrm{ch}} \mathrm{d}t} \quad \text{with} \quad \dot{Q}_{\mathrm{ch}} = \dot{Q} - \dot{Q}_{\mathrm{bas}} \tag{13}$$

where the heat power of the chemical reaction again is obtained by the difference between the corrected heat power and the baseline. Starting with a simple linear baseline the conversion is calculated according to Eq. (13). Than a new baseline is obtained considering the new conversion course. After at the most twenty iterations the baseline does not change anymore and the correct conversion course is calculated.

5. Results and discussion

The kinetic results of the thermokinetic investigations with the different types of calorimeters are presented in Table 2. Each row in Table 2 represents the results of a set of measurements with identical initial compositions. As a rule these sets consist of five single measurements with different temperature courses which were simultaneously evaluated in the form of t, T, X data sets applying the method described in Section 3. The bold letters represents the average values for the different types of calorimeters.

The obtained activation temperatures for the different thermokinetic methods are almost the same. The corresponding activation energies are within the range of E=41±3 mol l^{-1}. The kinetic model was determined as a bimolecular one, as expected. The rate constants k at 300 K are equal too within the usual range of error when determining kinetic data. However, the rate constant of the adiabatic measurements is a little lower compared to the others. The overall average values of the partial reaction orders for phenyl isocyanate and 2-butanol n=1.05 are a little higher than one. This may be due to the comparatively high concentrations applied for the present investigations.

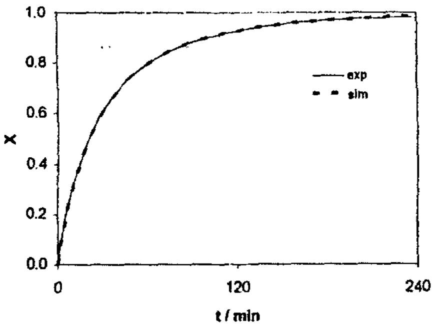

Fig. 10 Experimental and simulated course of conversion at T=308 K; isothermal method

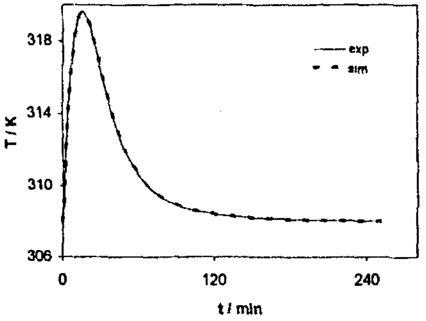

Fig. 11 Experimental and simulated temperature course with an initial temperature of $T=308$ K; isoperibolic method

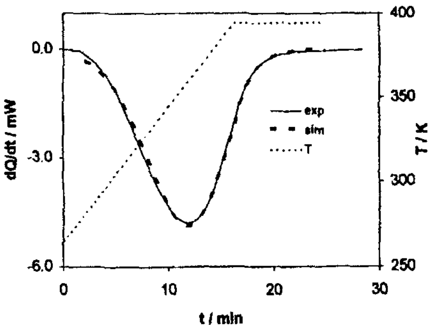

Fig. 12 Experimental and simulated course of chemical heat production (8 K min^{-1}); temperature programmed method

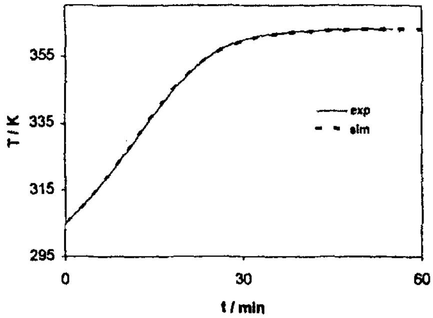

Fig. 13 Experimental and simulated temperature course with an initial temperature of $T=305$ K; adiabatic method

To validate the obtained kinetic data simulations were performed for the different types of calorimeters considering the corresponding values for each set of measurements in Table 2. The Figs 10–13 show a comparison of experimental and calculated data for the initial composition with $C_{PIC,0}=1.41$ mol l^{-1} and $C_{BuOH,0}=$

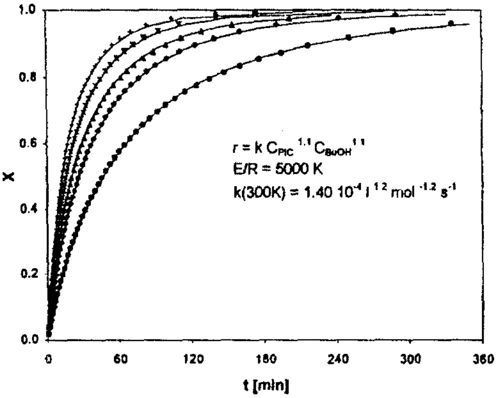

Fig. 14 Experimental (points) and simulated (lines) isothermal conversions without presetting a kinetic model, $C_{\mathrm{PIC},0}=1.41$ mol l^{-1}, $C_{\mathrm{BuOH},0}=2.82$ mol l^{-1}

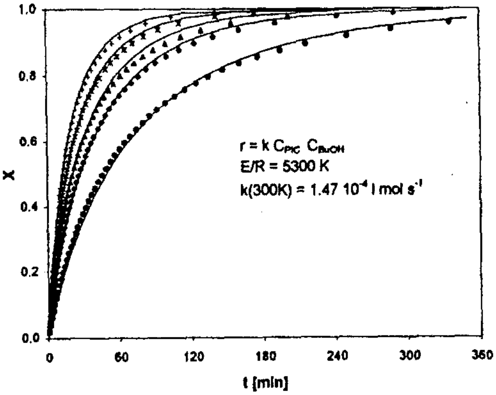

Fig. 15 Experimental (points) and simulated (lines) isothermal conversions presetting a second order model $C_{\mathrm{PIC},0}=1.41$ mol l^{-1}, $C_{\mathrm{BuOH},0}=2.82$ mol l^{-1}

2.82 mol l^{-1} respectively. The simulations match the experiments very well indicating a reliable determination of kinetic data with the evaluation method applied.

Regarding the results in Table 2, there is an indication that the test reaction is a second order reaction, because *n* is nearly equal to one. To prove this, the isothermal measurements were evaluated again with presetting a kinetic model of second order. Figures 14 and 15 show a comparison between the kinetic model with crooked orders and a strict second order model. The second order model requires a divergent activation temperature for an optimal description of the experimental data. It is obvious that the kinetic model with crooked reaction orders provides a better description of the experimental data.

Conclusion

As far as a simple homogeneous liquid phase reaction is investigated, it is possible to obtain consistent kinetic parameter sets using different types of calorimeters. Of course, it is necessary to perform and evaluate a set of measurements to get kinetic data of sufficient reliability. The reaction analyzed in this report is appropriate to test a calorimetric set up and the method of evaluation.

* * *

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List of symbols

A/m^2	heat exchange area
$C_{\mathrm{A0}}/\mathrm{mol\ l}^{-1}$	initial concentration of compound A
$C_{\mathrm{PIC,0}}/\mathrm{mol\ l}^{-1}$	initial concentration of phenyl isocyanate
$C_{\mathrm{BuOH,0}}/\mathrm{mol\ l}^{-1}$	initial concentration of 2-butanol
$E/\mathrm{J\ mol}^{-1}$	activation energy
h/s	isothermal equivalent reaction time
$\Delta H/\mathrm{J\ mol}^{-1}$	heat of reaction, reaction enthalpy
$k/\mathrm{l\ mol}^{-1}\ \mathrm{s}^{-1}$	reaction rate constant (units corresponding to a second order reaction)
λ	ratio of initial concentrations $\lambda = C_{\mathrm{PIC,0}}/C_{\mathrm{BuOH,0}}$
n	reaction order of phenyl isocyanate and 2-butanol
$n_{\mathrm{PIC,0}}/\mathrm{mol}$	initial amount of phenyl isocyanate
ν_{A}	stoichiometric coefficient of compound A
$mc_{\mathrm{p}}/\mathrm{J\ K}^{-1}$	heat capacity of the whole system (reaction mixture and reactor)
$\Phi(X)$	conversion dependent term of reaction rate
$\dot{Q}/\mathrm{W}$	heat power caused by the chemical reaction
$\dot{Q}_{\mathrm{ch}}/\mathrm{W}$	heat power of the chemical reaction
$\dot{Q}_{\mathrm{bas}}/\mathrm{W}$	baseline (heat power of the..)
$r(X,T)/\mathrm{mol\ l}^{-1}\ \mathrm{s}^{-1}$	reaction rate
$r(0,T_{\mathrm{R}})/\mathrm{mol\ l}^{-1}\ \mathrm{s}^{-1}$	initial reaction rate at a reference temperature T_{R}
τ/s	time lag constant
t/s	reaction time
T/K	temperature of reaction mixture
T_0/K	initial temperature
$T_{\mathrm{e}}/\mathrm{K}$	final temperature
$T_{\mathrm{K}}/\mathrm{K}$	cooling temperature
$\Delta T_{\mathrm{max}}/\mathrm{K}$	maximum temperature rise under adiabatic conditions
$U/\mathrm{W\ K}^{-1}\ \mathrm{m}^{-2}$	heat transfer coefficient
X	conversion

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