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APPLICATION OF AN ADIABATIC PRECISION CALORIMETER IN THE FIELD OF ORGANIC REACTIONS

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Abstract

Adiabatic calorimetry is a suitable method for investigations of reactions because the generated heat remains completely in the reactor. For the investigation of organic reactions, the adiabatic precision calorimeter ACTRON 5 is used. The alcoholyses of phenyl isocyanate and 1,2-butyleneoxide were investigated. The temperature-time course was estimated by means of the nonlinear program TA-kin. Inclusion of the concentration-time course in the estimation procedure led to an increase in the reliability of the parameters. Probes were taken during isoperibolic measurements and were analysed by means of HPLC.

Keywords: adiabatic calorimetry, alcoholysis, non-linear kinetic evaluation program, phenyl isocyanate

Introduction

Calorimetric methods are often used to evaluate thermodynamic and kinetic parameters and reaction mechanisms. Highly developed commercial devices are available, and experiments may be executed automatically. It is possible to study the influence of many parameters of chemical reactions by the investigation of small samples. The computerization of experiments controls and guarantees the constancy of selected reaction conditions. The parameters can be obtained by suitable non-linear evaluation procedures.

For investigation of chemical reactions, isoperibolic calorimetry is often used. In this case, the reactor temperature is measured at constant ambient temperature. From a technical point of view, this method is the simplest: the ambient temperature can be adjusted and regulated by means of a thermostat. However, a disadvantage of this method is the necessary correction of the heat flux according to the equation of TIAN. The heat generated in an exothermic reaction on the one side remains partly in the reactor, raising its temperature, and flows on the other side to the surroundings. The flowed heat can be determined only by means of calibration. Therefore, isoperibolic calorimetry requires very precise calibration.

In comparison with isoperibolic calorimetry, adiabatic calorimetry has considerable advantages: the generated heat remains completely in the reactor and therefore correction of the heat flux according to the equation of TIAN is not necessary. The reaction heat can be determined directly from the maximum temperature

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change in the reactor corresponding to the heat capacity. Further, it is possible to determine the heat capacity directly by means of adiabatic calorimetry.

In isothermal calorimetry, the generated heat flows completely to the surroundings, while the reactor temperature remains constant.

The adiabatic precision calorimeter ACTRON 5

For the investigation of chemical reactions, the precision calorimeter ACTRON 5 [1, 2] has been used; this can be switched from isoperibolic to adiabatic working mode by software command. Figure 1 shows the schematic construction of the calorimeter. The apparatus works in the range from 10 to 180°C. In order to realize a high temperature stability of $1\cdot10^{-4}$ K, the calorimeter is equipped with a double thermostat. The inner thermostat consists of a liquid bath, while the outer one is an air thermostat in order to regulate the ambient temperature for the liquid thermostat. In adiabatic working mode, the bath temperature follows the temperature in the reactor by 1 mK. The greatest temperature gradient is 1.5 K min^{-1}.

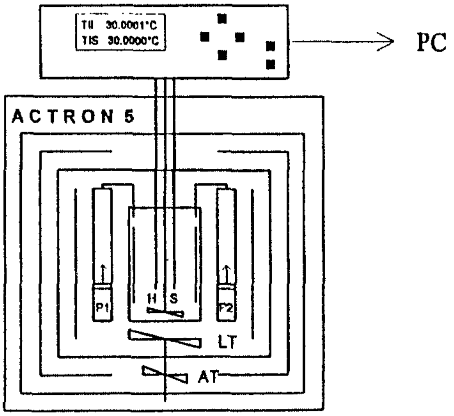


Fig. 1 Schematic construction of ACTRON 5

The working volume of the reactor can be chosen between 30 and 100 ml. The reactor is constructed of Teflon, glass or stainless steel (possibly gilded). In the reactor, there are a temperature sensor, a calibration heater, a stirrer and tubes to change the atmosphere or to add the second and further reaction components. The addition of the components is performed by precision burette pumps located in the same bath as the reactor. Therefore, all components have the same temperature before mixing. The rate of addition can be programmed freely.

The ACTRON device receives its commands through a personal computer, which communicates the micro-computer in the device itself.

Software package TA-kin

To investigate thermodynamic and kinetic activation parameters, the software package TA-kin developed in our group was used [3]. The activation parameters are determined by means of the Marquardt-Levenberg algorithm by minimization of the sum of deviation squares (SDS).

The program TA-kin v 3.3 allows a free definition of the reaction rate law via the reaction equation. The kinetics of the reaction is described as a simple or complex reaction; moreover, the software package can be applied to both homogeneous and heterogeneous reactions.

The import of the measured data as an ASCII file is easy by means of a special procedure. In the program, many useful functions are available to edit the data in the desired form, e.g. as a shortened file. Graphical data processing is possible too. It is sometimes difficult to find starting values for the parameter estimation because of their correlation by the compensation effect [3, 4]. In real experiments, the minimum of SDS lies in a ditch ('Banana Valley'). To the right and to the left of the ditch, plateaus with constant level are formed [5]. If the starting values are located on such a plateau, it becomes difficult for the estimation algorithm to find the direction of the vector to minimize the SDS. Therefore, a special function of searching for suitable starting values has been included in the program. In a selected interval of $\ln k_0$ and E_A, the procedure runs for random pairs of these parameters. In this way, determined start parameters are introduced in the non-linear optimization procedure.

Besides the kinetic parameter determination from one experimental data set, the overall evaluation of several data sets is possible. An advantage arises if not only the temperature-time signal, but also concentration-time information is used.

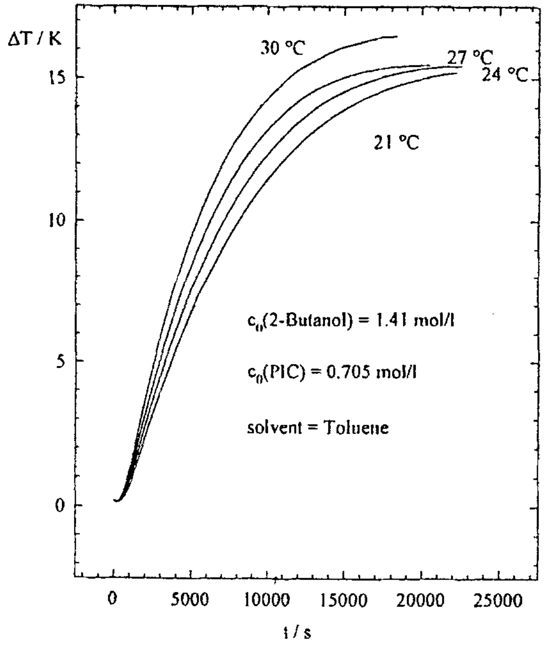
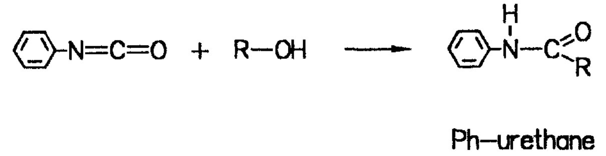


Fig. 2 2-Butanolysis of phenyl isocyanate under adiabatic semi-batch conditions by varying of the starting temperature $[2\text{-BuOH}]_0 = 1.41$ mol l^{-1}; $[PIC]_0 = 0.705$ mol l^{-1}

Alcoholysis of phenyl isocyanate

The alcoholysis of phenyl isocyanate leads to phenylurethanes. This is a well-defined (only one product) and strongly exothermic reaction that is widely used for the detection of alcohols. Therefore, the reaction for calorimetric investigation is very useful. The reaction runs as a second-order rate law [6]:



The reaction of phenyl isocyanate with 2-butanol was carried out in toluene as solvent. In some experiments, pyridine was used as catalyst.

For these investigations, the adiabatic calorimeter ACTRON 5 was applied and the reaction was carried out under semibatch conditions.

Calorimetric curves are shown in Fig. 2. They were recorded by varying the starting temperature for a phenyl isocyanate concentration of about 0.705 mol l^{-1}. The solution of phenyl isocyanate was added during 20 min at a rate of 0.8 ml min^{-1}. The alcohol was present in the reactor in 2-fold excess.

At the reaction start, an endothermic mixing peak of about ~60 mK appears. Therefore, the reaction is handled as a competitive reaction consisting of two pro-

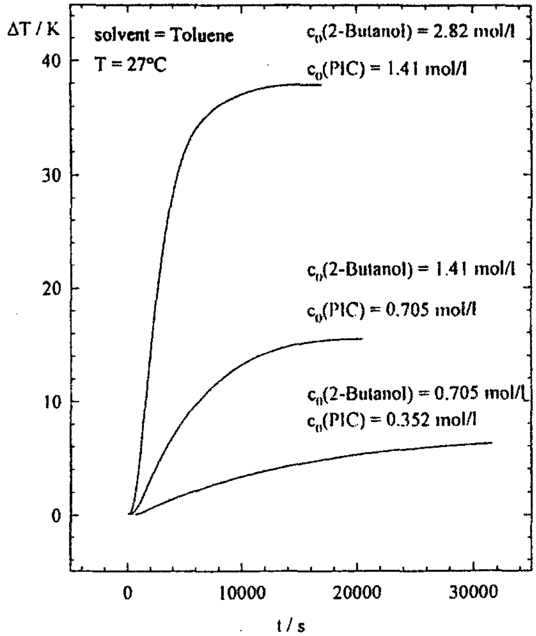


Fig. 3 2-Butanolysis of phenyl isocyanate under adiabatic semi-batch conditions at 27°C by varying of the concentrations

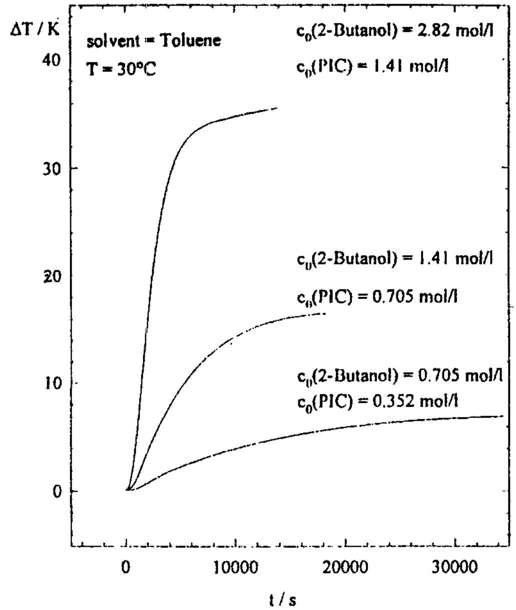


Fig. 4 2-Butanolysis of phenyl isocyanate under adiabatic semi-batch conditions at 30°C by varying of the concentrations

cesses. The mixing is computed as a first-order reaction without energy of activation, whereby the reaction heat is constant during the addition of phenyl isocyanate. The duration of mixing is defined by its rate constant.

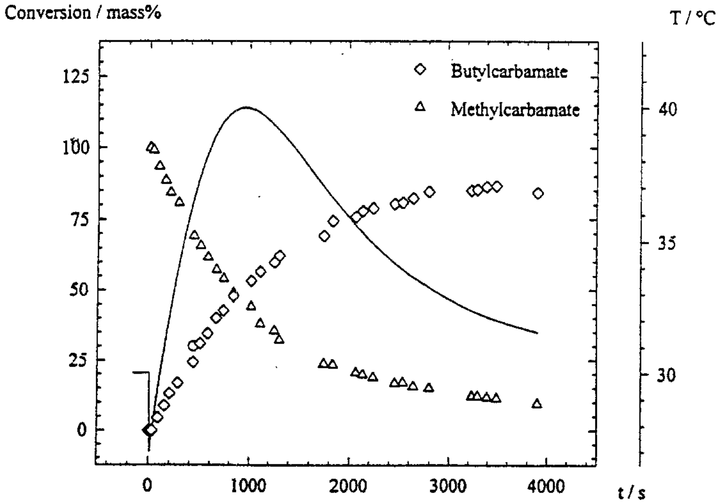


Fig. 5 2-Butanolysis of phenyl isocyanate under isoperibolic batch conditions, temperature-time- and concentration-time-course [2-BuOH]$_0$=1.41 mol l^{-1}; [PIC]$_0$=0.705 mol l^{-1}; Cat.=pyridine; T=30°C

Figures 3 and 4 show calorimetry curves involving variation of the phenyl isocyanate concentration at 27 and 30°C, respectively. The corresponding activation parameters are given in Table 1.

Table 1 Results of the kinetic evaluation of the adiabatic experiments shown in Figs 2 to 4

T/	$c_{(PIC)}$ /	$c_{(2\text{-}BuOH)}$ /	$\ln k_0$	E_A	$\Delta_R H$/
°C	mol l^{-1}			kJ mol^{-1}	
21	0.705	1.410	8.72	43.48	–66.71
24	0.705	1.410	10.08	47.01	–72.91
27	0.705	1.410	10.76	48.87	–70.68
30	0.705	1.410	7.24	40.16	–68.27
27	1.410	2.820	2.78	28.81	–81.66
27	0.705	1.410	10.76	48.87	–70.68
27	0.352	0.705	17.47	65.84	–59.67
30	1.410	2.820	5.23	35.04	–75.42
30	0.705	1.410	7.24	40.16	–68.27
30	0.352	0.705	16.436	63.44	–62.34
overall: 21 24 27	1.410	2.820	6.71	38.7	–79.43

Use of concentration-time courses

Evaluation of the temperature-time curves and of the concentration-time course in an overall iteration routine increases the reliability of the parameters. Therefore, probes were taken during the reaction of phenyl isocyanate with 2-butanol, while the reaction was running under isoperibolic conditions. The second component (solution of phenyl isocyanate) is added in batch mode. The reactivity of the probes is quenched by methanol, followed by HPLC analysis using a reversed phase C18 column with a mixture of 85% methanol, 15% water and 3 mmol NaH_2PO_4 as mobile phase at a flow rate of 1 ml min^{-1}.

Figure 5 shows the calorimetric curves for the reaction of phenyl isocyanate catalysed by pyridine, and the concentration-time courses for butyl carbamate (reaction product) and methyl carbamate. The concentration of methyl carbamate represents the remaining concentration of phenyl isocyanate.

In Fig. 6, the results of an overall evaluation of both data sets by means of TA-kin are shown. The results of isoperibolic experiments with analytical values of concentration are given in Table 2.

Table 2 Results of the kinetic evaluation of the isoperibolic experiments performed like the experiment shown in Fig. 5

T/	$c_{(PIC)}$ /	$c_{(2\text{-}BuOH)}$ /	$c_{(Cat.)}$ /	$\ln k_0$	E_A	$\Delta_R H$/
°C		mol l^{-1}			kJ mol^{-1}	
20	1.410	2.820	–	5.64	36.05	–96.08
25	1.410	2.820	–	3.36	30.20	–90.74
30	1.410	2.820	–	6.09	37.10	–98.32
30	1.410	2.820	–	6.09	37.10	–98.32
30	0.705	1.410	–	16.03	62.18	–91.15
30	0.352	0.705	–	6.99	39.98	–86.66
30	1.410	2.820	–	6.09	37.10	–98.32
30	1.410	2.820	0.1	7.45	40.01	–82.56
overall:						
20						
25	1.410	2.820	–	8.65	43.62	–92.14
30						

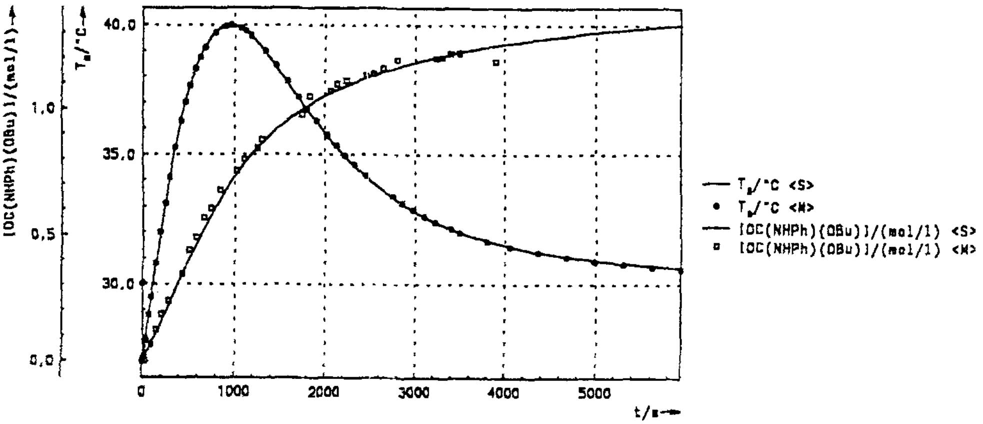


Fig. 6 Results of the overall evaluation of the curve shown in Fig. 5 by means of TA-kin

Alcoholysis of oxirane

A thermoanalytical investigation was made of the alcoholysis of 1,2-butyleneoxide with ethanol in excess and sodium hydroxide as catalyst.

According to the literature [7], the basic catalysis with alcohol in excess leads only to monoether. Therefore, it can be described as a reaction of second order.

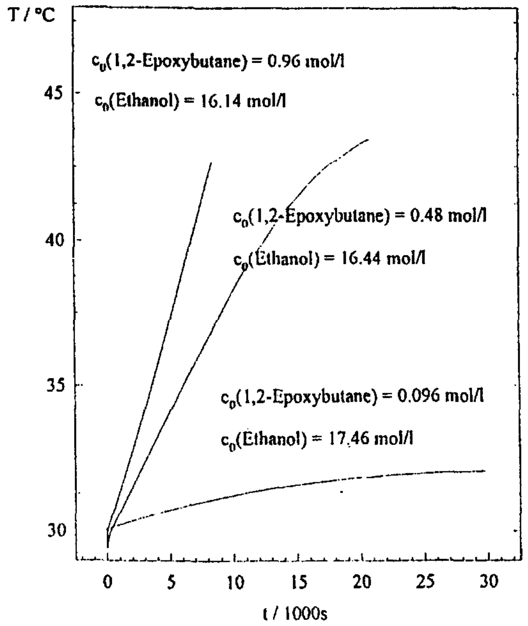
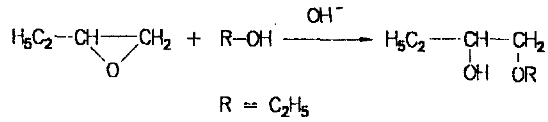


Fig. 7 Ethanolysis of 1,2-butylenoxide with sodium hydroxide as catalyst under adiabatic semi-batch conditions at 30°C by varying of the concentrations

The basic oxirane alcoholysis yields two ether isomers, with preferential formation of 1-ethoxybutan-2-ol.



The reactions were carried out under adiabatic conditions at a starting temperature of 30°C by varying the concentration (Fig. 7). For this reaction, E_A and $\ln k_0$ were found to 62.2 kJ mol^{-1} and 12.1. The heat of reaction proved to be –69.9 kJ mol^{-1}.

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