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APPLICATION OF A NEW TYPE OF SAFETY CALORIMETER

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Abstract

Safety production in chemical plants is a high-priority task, especially as concerns reactions which can change mechanism suddenly under defined conditions, e.g. from a simple well-defined to an undesired autocatalytic reaction. An example of this kind, the reaction of chloronitrobenzene with alkaline alcohol, was investigated with the new adiabatic precision calorimeter ACTRON 5, designed with a safety concept. It is shown that the reaction can be interrupted safely under predicted conditions.

Keywords: adiabatic calorimetry, chloronitrobenzene, non-linear kinetics, sodium thiosulfate

Introduction

The improvement of safety in chemical plants is a task of high priority for basic science and technology. This aim includes the increase of production under a defined reaction course and optimization of the safety conditions. This is important for environmental protection. For a given reaction, it is possible to reduce the amounts of by-products of reactions and the energy necessary for the process.

For the optimization of reactor conditions, an exact knowledge of the kinetic and thermodynamic reaction parameters is necessary. To ensure reactor safety, the course of the reaction in hazardous situations is needed. Early recognition of a hazardous situation is of high priority.

Calorimetric methods are often used for the determination of kinetic and thermodynamic parameters of reactions and processes. It is possible to simulate the production course in laboratories by calorimetry. Provided that the apparatus constants of the used production reactor are known, the results can be scaled up.

For an estimation of the hazardous potential of chemical reactions, adiabatic calorimetry is a suitable method, because a runaway reactor behaves like a quasi-adiabatic one. By definition of adiabatic calorimetry, the heat generated by an exothermic reaction remains completely in the reactor. The calorimeters used for the investigation of safety processes are characterized by a high resolution and reproducibility, besides functions which guarantee to stop the reaction in hazardous situations under the control of software or at the command of the operator. Therefore, it is possible to prevent damage of the expensive measuring devices and also to acquire data beyond the point-of-no-return.

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An adiabatic precision calorimeter with safety concept

The precision calorimeter ACTRON 5 with safety scenario concept is a calorimeter with the functions given above. The calorimeter is based on the adiabatic precision calorimeter ACTRON 5 [1, 2]. Figure 1 schematically outlines the construction. Optionally, the ACTRON 5 can be equipped with a safety package, which allows the investigation of reactions in the danger area. The calorimeter is equipped with 3 precision burette pumps. All pumps are connected to the reactor. The second reaction component can be added during the reaction, as can a catalyst or a stopper (inhibitor). The rates of addition of the components can be programmed without limitation. Since the pumps and reactor are located in the same bath, all the reaction components have the same temperature as the contents of the reactor.

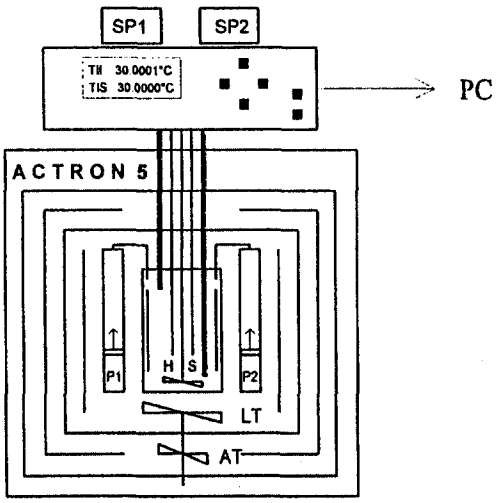

Fig. 1 Schematic construction of the ACTRON 5

The working volume of the reactor can be selected between 30 and 70 ml. The reactor is constructed of Teflon, glass or stainless steel (possibly gilded). In the reactor are a temperature sensor, a calibration heater and a stirrer. Beyond it, the reactor is connected with two safety pumps to empty the reactor contents into a cold solvent outside the calorimeter and to rinse the reactor with cold solvent. The safety pumps can be activated in hazardous situations or under pretended conditions in 2 s. In this way, many reactions can be stopped safely.

An interpretation of the recorded data of the interrupted reaction is possible by means of the software package TA-kin v. 3.3 [3]. For the determination of kinetic activation parameters, non-linear optimization procedures involving minimization of the sum of deviation squares (SDS) are used.

The on-line investigation of kinetic parameters during the reaction is important too. Therefore, it is possible to forecast hazardous situations. Starting of the safety pumps then prevents undesired incidents.

Examples

To demonstrate the effects of the safety pumps, two reactions were carried out in the adiabatic calorimeter. The reactions were stopped by starting the safety pumps, whereby the pumps were activated under pretended conditions, e.g. maximum temperature limit.

The reaction of sodium thiosulfate with hydrogen peroxide runs as a second-order rate law at temperatures below room temperature [4].

$$2Na_2S_2O_3 + 4H_2O_2 \rightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O$$

The reactor contained 30 ml of 0.1 *N* sodium thiosulfate solution. 9 ml of 0.8 *N* hydrogen peroxide was added at a flow of 2 ml min^{-1}. Figure 2 shows calorimeter curve with a starting temperature of 20°C, the end of addition of the second component being indicated by a mark line. For estimation of the activation parameters, the program TA-kin was used. E_A and ln k_0 were found to be 77.6 kJ mol^{-1} and 27.7. The heat of the reaction was –546.6 kJ mol^{-1}.

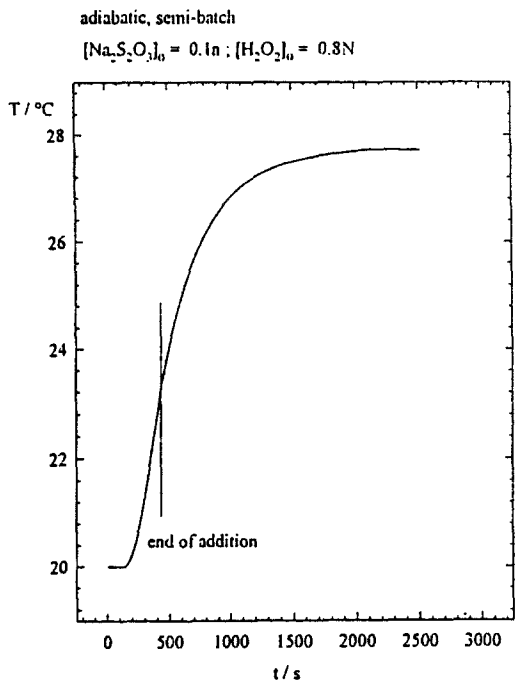

Fig. 2 Calorimetric curve of the reaction of $Na_2S_2O_3$ with H_2O_2

Figure 3 shows the calorimeter curves of the same reaction, but in this case the reactions were stopped by emptying the reactor. In the case of curve 1, the safety pumps were activated under the condition that the rate of temperature increase in the reactor exceeds 1 K min^{-1}. Curve 2 demonstrates a reaction stopped under the

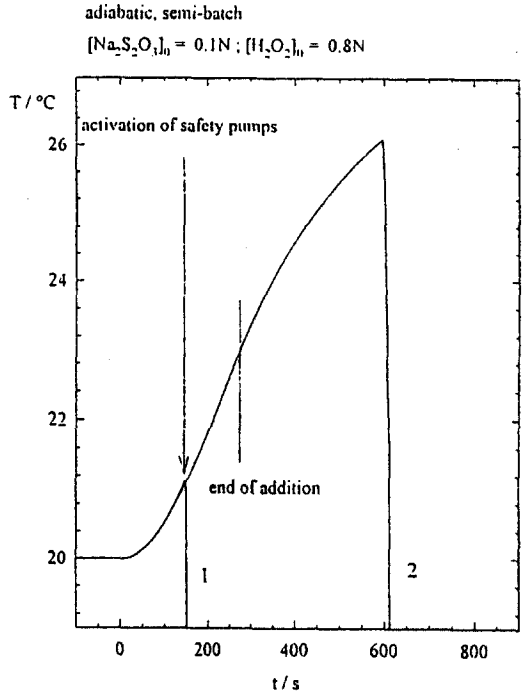

Fig. 3 Calorimetric curves of the interrupted reaction of $Na_2S_2O_3$ with H_2O_2

condition that the temperature in the reactor exceeds 26°C. Both reactions were evaluated with the program TA-kin. The founded activation parameters are given in Table 1.

In the reaction of chloronitrobenzene with alkaline alcohol, the product alkoxynitrobenzene is formed. This reaction is performed in several chemical plants. Besides the substitution of chlorine by an alkoxy group, the undesired reduction of the nitro group is possible, then azoxybenzenes are formed. The reaction course depends on several conditions, e.g. concentrations and temperature [5, 6].

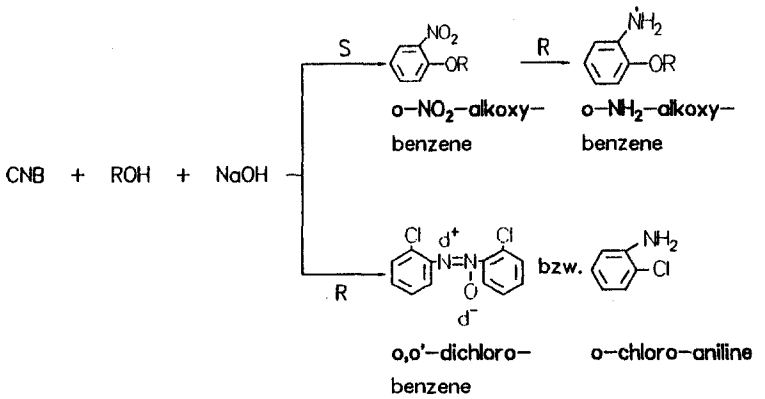

Table 1 Results of kinetic evaluation of the adiabatic experiments shown in Figs 2 and 3

Conditions	$\ln k_o$	E_A	$\Delta_R H$
		kJ mol^{-1}	
non-interrupted	27.70	77.63	-546.6
interrupted at 26°C	26.70	75.29	-582.0
interrupted at 1 K min^{-1}	(27.70)	77.58	(-546.6)

The sudden change from the substitution to the reduction was the reason for an incident in Griesheim/Germany in 1992.

To test the safety pumps of this calorimeter, the undesired reduction was provocated by suitable conditions. The reactor contained a solution of *n*-propanol with sodium or potassium hydroxide. A solution of *o*-chloronitrobenzene in *n*-propanol was added as last component. The reaction temperature was about 80°C.

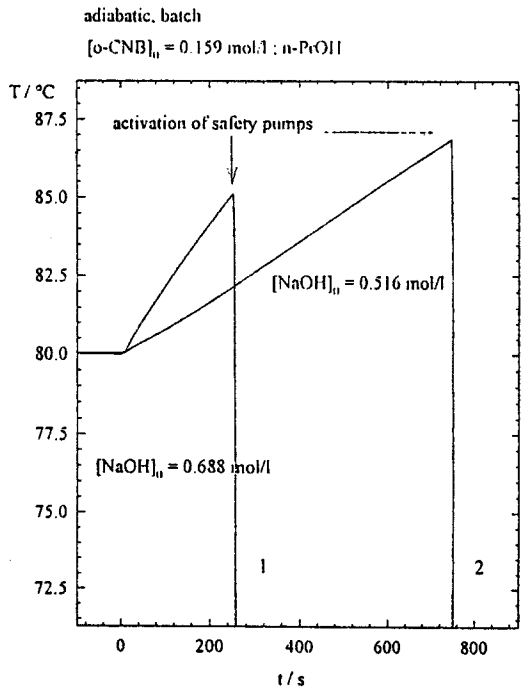

Fig. 4 Calorimetric curves of the interrupted reaction of *o*-chloronitrobenzene with *n*-propanol and NaOH

Figure 4 shows the calorimeter curves of the reactions with sodium hydroxide. In the case of curve 1, the safety pumps were activated by a temperature of about 85°C in the reactor. The curve indicates a high rate of temperature increase of about 1.3 K min^{-1}. In the case of the second experiment (curve 2), the concentration of sodium hydroxide was reduced. The rate of temperature in this case reached only

0.5 K min^{-1}. At a reactor temperature of about 87°C, the reaction was stopped by automatic activation of the safety pumps.

The influence of the nature of the alkali metal hydroxide is to be seen in Fig. 5. Both reactions were stopped by a reactor temperature of about 85°C. In the case of NaOH (curve 1), this temperature was reached after 251.5 s, while the reaction with KOH (curve 2) needed 975.7 s. This is an example of the difference in hazardous potential when NaOH or KOH is used.

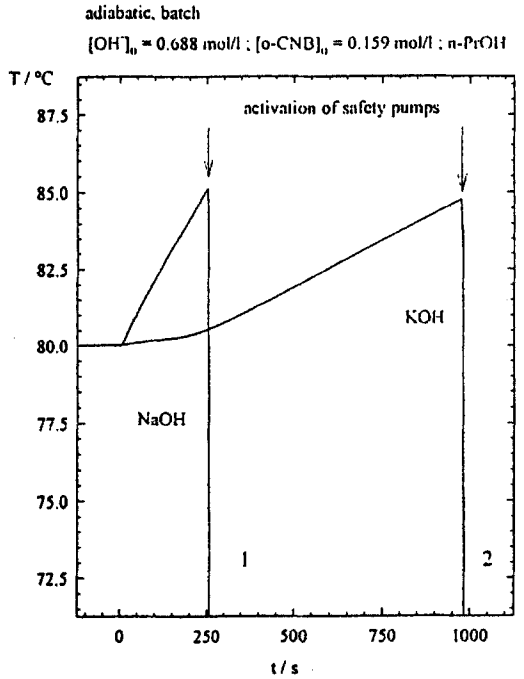

Fig. 5 Calorimetric curves of the interrupted reaction of *o*-chloronitrobenzene with *n*-propanol and NaOH (1) or KOH (2)

Analysis of the reaction mixtures with HPLC confirmed the substitution and reduction products, but also residual *o*-chloronitrobenzene. That indicates the interrupted character of the reaction.

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