Investigation of run-away reactions by precision calorimetry[1]

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Abstract

Investigations in chemical safety are necessary in case that the reaction course depends on changes of the reaction conditions sensitively. To break off a conversion in a hazardous situation, the precision calorimeter ACTRON 5 is equipped with two safety pumps. They empty and rinse the reactor with cold solvent. The pumps will be activated automatically. For testing the calorimeter the complex reaction of chloronitrobenzene with alkalined alcohol was used and break off at predefined conditions. The possibility of the kinetic estimation of these break-off files is shown. © 1998 Elsevier Science B.V.

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1. Introduction

Run-away reactions are strongest in cases of explosion and detonation. They characterize processes with high exothermic reaction heats. Why is its use recommended in investigation of these processes in precision calorimeters?

The aim and efforts in the field of chemical safety are to prevent accidents in chemical laboratories and plants. Besides, we have to consider the economical point of view, e.g. an increased turnover or selection of one reaction. Only in case where all processes in the reactor are well known, including the thermodynamic and kinetic reaction parameters, it is possible to solve these problems effectively. The parameters could be determined with high precision by a laboratory tester. The measuring technique is available commercially. Only when the exact parameters of the reactor and activation are known, the temperature, concentration or pressure course can be simulated in larger reactors. The determination of the reactor parameters is sometimes difficult and not sure.

Investigation is more difficult in a case where the reaction course deviates from the normal region. Therefore, we have to work in a part of reaction which is not accessible to get data.

To guarantee a safe run of the reaction, the parameters will be determined under normal conditions and increased by a 'safety factor'. Generally this is sufficient.

Now, it is possible to get the reaction data with a high precision and in dangerous reaction area as well. Modern safety calorimeters should stop the reaction in hazardous situations by crossing predefined limiting values of the reactor state.

2. Experimental and results

For the investigation of reactions with dangerous potential, the adiabatic precision calorimeter ACTRON 5 was used [1,2]. This calorimeter is characterized by a thermal resolution of ca. 1×10^{-4} K. To guarantee the high thermal stability of ca. ± 0.2 mK, in non-thermostatized laboratories too, this device is equipped with two thermostats. Thus, the outer air thermostat controls the temperature of the surroundings of the inner liquid thermostat.

In adiabatic mode, the bath temperature closely follows the temperature of the reactor. To add the second as well as further reaction components, the calorimeter contains three precision burette pumps. All pumps are connected with the reactor. Since the reactor and the burette pumps are located in the same bath, differences in the temperature of the reaction components before being added in the reactor can be neglected. This is very important in case of adiabatic reactions in the semi-batch mode.

To rapidly stop the reaction in hazardous situation the calorimeter is equipped with two safety pumps (Fig. 1). One of these, the suction pump, transmits the content of the reactor in the cold solvent outside the calorimeter and the other, the pressure pump, presses the cold solvent into the reactor to rinse it. If the temperature of the reactor or the increase of the temperature cross a predefined limiting value, the pumps will be activated automatically.

Fig. 2 shows the regime of the pump. Approximately 2 s after recognizing a hazardous situation, the suction pump will be activated and will begin to
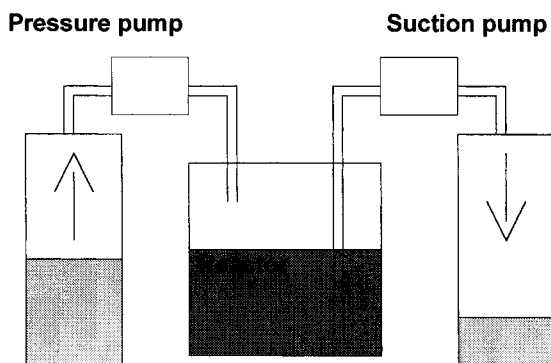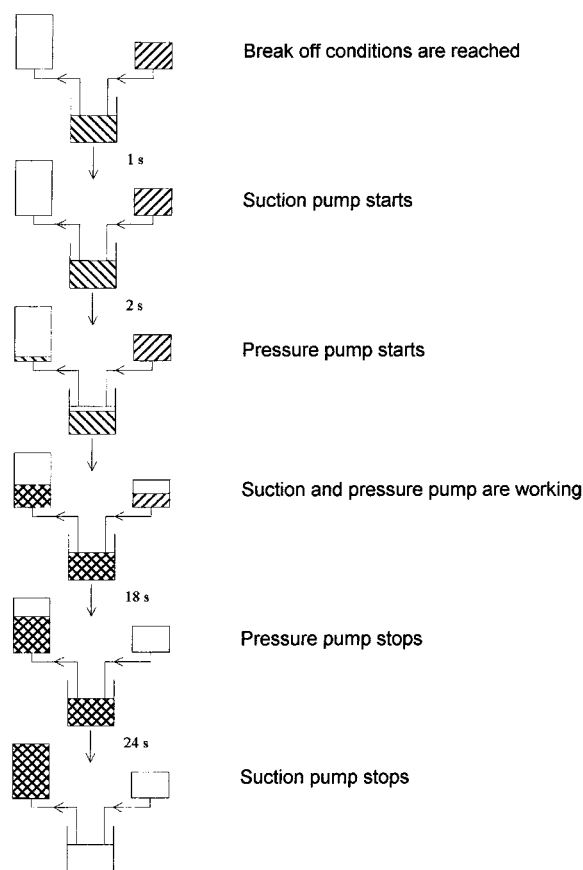
The regime of the safety pumps

Fig. 2. Regime of the safety pumps: suction pump on the left side, pressure pump with cold solvent on the right side, and reactor in the middle.

Fig. 1. Safety pumps of the precision calorimeter ACTRON 5.

empty the reactor. The pressure pump starts 2 s later to pump the cold solvent into the reactor. In this way, the content of the reactor will be diluted and hence the rate of the reaction will decrease rapidly. Therefore the reaction leaves the dangerous region. After the deactivation of the pressure pump, the suction pump evacuates the rest of the diluted solution of the reactor.

Investigation of hazardous potential of chemical reactions is very important in case of complex reactions, especially if the reaction course depends very sensitively on changes in the reaction conditions, for example the reaction of chloronitrobenzene (CNB) with alkalined alcohol.
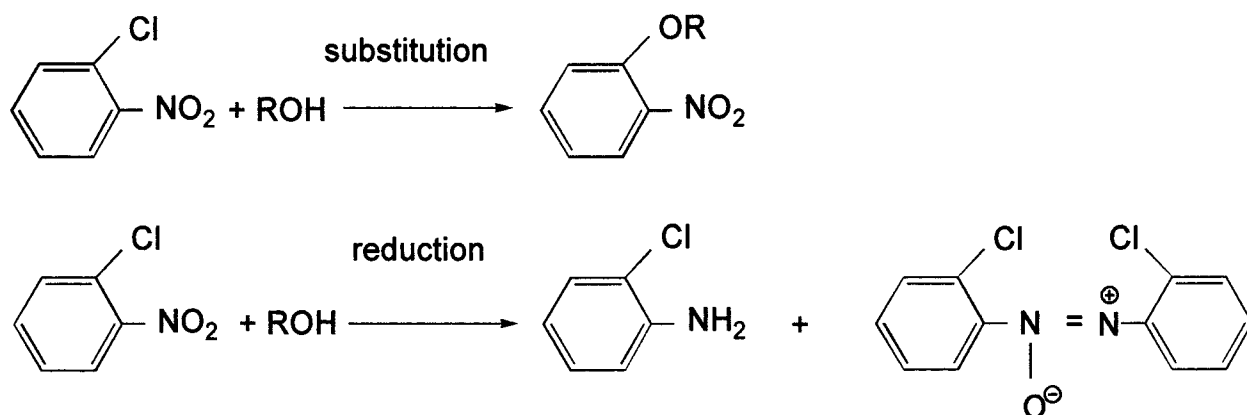
Therefore the desired harmless reaction is the substitution of chlorine by alkoxy group. It is used in chemical plants. By relatively small changes in reaction conditions, the reaction branches out to an autocatalytic, high exothermic reduction of the nitro group. This reaction course depends strongly on the kind and concentration of the reaction components, initial temperature and concentration of oxygen in the atmosphere above the solution [3–5].

Obviously, the reduction is initiated by radicals. Probably radicals will be formed during the substitution. It will be prohibited by oxygen. The reduction starts if the concentration of oxygen is too small to destroy the radicals.

Both reaction steps show a different temperature course; the reduction is characterized by a high exothermic reaction heat.

The reaction of *o*-CNB with alkalined alcohol was investigated by the adiabatic precision calorimeter ACTRON 5. To proof switching on and off the safety pumps, different reaction conditions were chosen in such a way that the reduction of the nitro group occurs.

Fig. 3 characterizes the influence of the concentration of *o*-CNB on the hazardous potential of the reaction with sodium hydroxide in *n*-propanol. On increasing the concentration of *o*-CNB, the hazardous potential grows. Reactions were definitely stopped when the temperature of the reactor became higher than 85°C. Fig. 3 shows, in case of a CNB-concentration of ca. 0.159 mol/l, that the safety pumps were activated not before the end of the reaction. The hazardous potential at this point is relatively low as compared with the other two curves. For the double
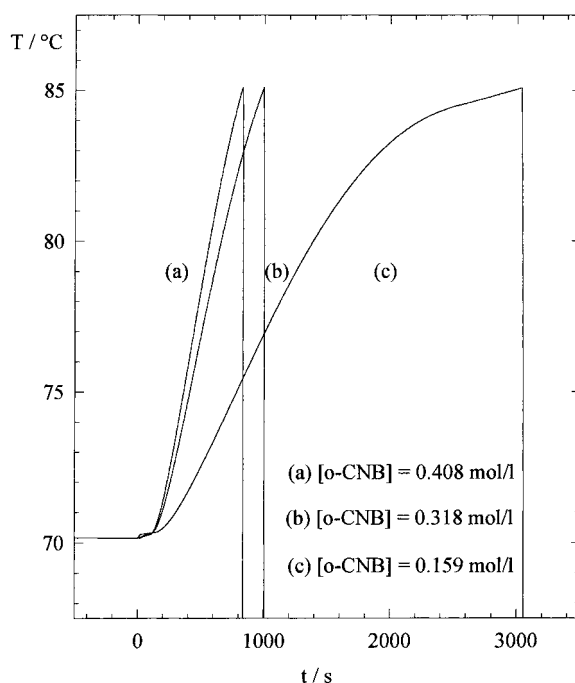
Fig. 3. Influence of the starting concentration of *o*-chloronitrobenzene; $[NaOH]_0 = 0.688$ mol/l; *n*-PrOH; $T = 70°C$. Break-off conditions: maximum temperature 85°C; maximum temperature increase 3000 mK/min.

concentration of chloronitrobenzene, the reaction was stopped in the region of rapid temperature increase. This fact demonstrates the sensitivity of the reaction course to changes in the reaction conditions.

The reaction mixture at the time of activation of the safety pumps was analyzed by HPLC. It could detect
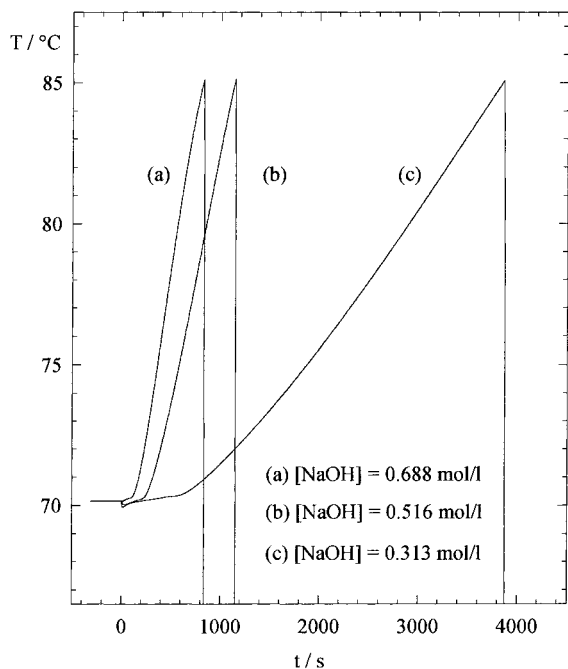
Fig. 4. Influence of the starting concentration of sodium hydroxide; $[o\text{-CNB}]_0=0.408$ mol/l; n-PrOH; $T=70°C$. Break-off conditions: maximum temperature 85°C; maximum temperature increase 3000 mK/min.

Fig. 5. Influence of the alcohol; $[\text{NaOH}]_0=0.313$ mol/l; $[o\text{-CNB}]_0=0.318$ mol/l; $T=60°C$. Break-off conditions: maximum temperature 75°C; maximum temperature increase 3000 mK/min.

products of substitution, e.g. o-nitro-n-prop-oxyether and of reduction, e.g. o-chloroaniline and o,o'-dichloroazoxybenzene as well as o-CNB.

Fig. 4 demonstrates the influence of sodium hydroxide on the reaction course. An increase in the concentration of hydroxide leads to a higher hazardous potential. When initial concentration rises by 65% the time for the reaction to stop reduces from 3850 to 1150 s.

The hazardous potential also depends on the alcohol applied. Fig. 5 shows interesting results for the investigation of reactions with n- and i-propanol at ca. 60°C. A glance at the curves reveals that n-propanol is characterized by a higher hazardous potential than i-propanol. Once the reaction starts, a small endothermic mixing peak appears and the calorimetric curve shows a short period of substitution. Approximately after 3500 s the reduction dominates. At a limiting temperature of 75°C, the reaction was automatically stopped because of activation of the safety pumps. In comparison the substitution period of i-propanol is
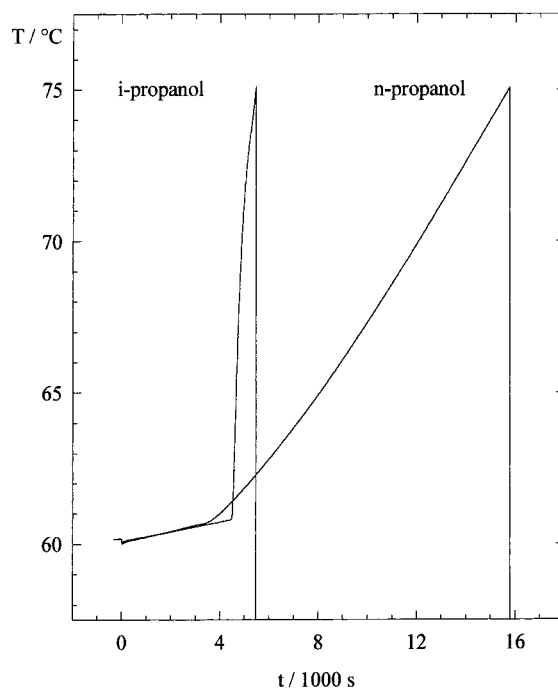
longer (4050 s), thereafter, the reduction leads to a higher temperature jump. Thus, the safety pumps were activated approximately 10 000 s earlier than in the case of n-propanol. Hence, it is proved that i-propanol is marked by a higher hazardous potential.

All examples demonstrate that investigation of hazardous reactions with the calorimeter are satisfactory. The reactions can be stopped automatically by starting the safety pumps. After recording all data before the break off, it is possible to estimate the activation parameters, including the range of high-level reaction rate.

To test the possibility of estimating the thermodynamic and kinetic parameters of the break-off reaction, the alcoholysis of phenyl isocyanate (1.41 m) with 2-butanol (2.82 m) in toluene as solvent was chosen. This is a second-order reaction with a simple mechanism [6,7]. Fig. 6 shows the calorimetric curves of the break-off reaction. The reaction was carried out in semi-batch mode. As the second component, the solution of phenyl isocyanate in toluene was added at a
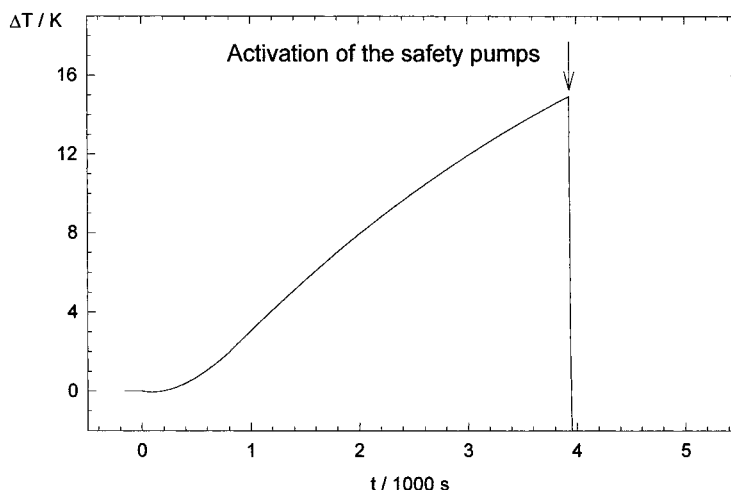
Fig. 6. Calorimetric curve of the break-off reaction of phenylisocyanate with 2-butanol in toluene; $[PIC]_0 = 1.41$ mol/l; $[2\text{-BuOH}]_0 = 2.82$ mol/l. Break-off conditions: maximum temperature 45°C; maximum temperature increase 3000 mK/min.

rate of ca. 0.8 ml/min. The second component was added during 12.5 min; the end of addition is marked by a straight line. The reaction was started at 30°C. The limiting value of the reactor temperature was defined at 45°C, i.e. 15 K over the starting temperature. The safety pumps were activated 3900 s after the start of the reaction by turning on the burette pump. At this point, the turnover was ca. 50%. The turnover would be complete after 10,000 s [7].

The data of the first part of the reaction were evaluated by the convenient software-package TA-kin v3.3 [8]. TA-kin was developed in Greifswald and based on non-linear procedures to estimate the thermodynamic and kinetic reaction parameters. Fig. 7 shows results of the evaluation of alcoholysis of phenyl isocyanate by TA-kin. Thereby, the points represent the measured data and the steady line the fitted curve. The other curve characterizes the course of concentration of phenyl isocyanate. The course clearly shows the semi-batch mode of addition; the peak of the curve characterizes the end of addition. The activation energy of ca. 40.0 kJ/mol, the fre-
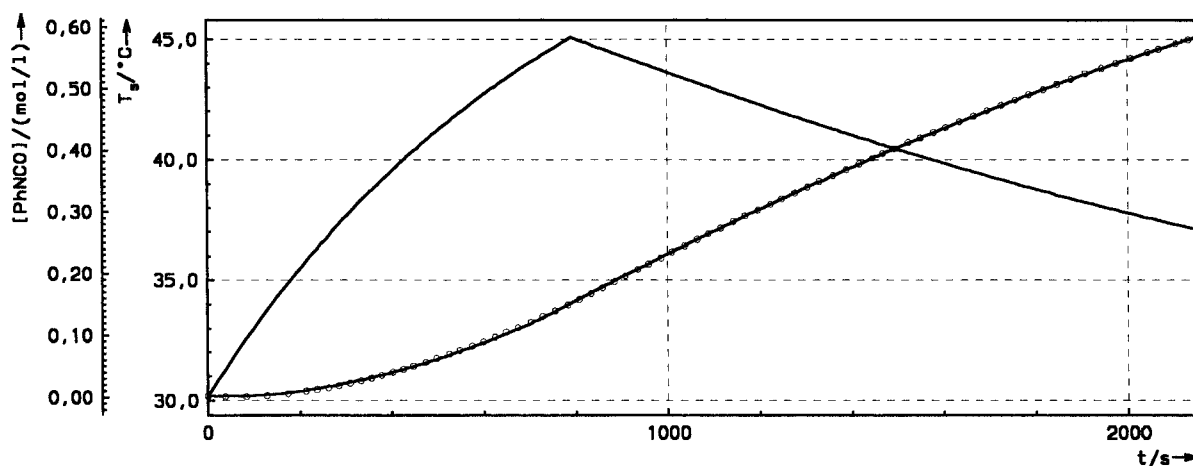

Fig. 7. Results of the kinetic evaluation of the first part of the reaction of phenylisocyanate with 2-butanol in toluene by TA-kin.

quency factor ln k_0=7.8 and a reaction enthalpy of ca. −74.3 kJ/mol correspond with the parameters given in literature [6].

3. Conclusions

The results show that calorimetric investigation of hazardous reactions, till the point-of-no-return, are practicable. If the temperature of the reactor or else the temperature reaches predefined limiting values, the reaction can be stopped quickly and safely by automatic activation of the safety pumps. The recorded files of the break-off reaction can be evaluated by the software package TA-kin.

Activation of the safety pumps by crossing limiting values describes a static working mode. If the evaluating program, even during the reaction, determines the activation parameters, it becomes possible to activate the safety pumps only in a hazardous situation. The evaluating program can recognize a change in the mechanism of the reaction, e.g. an autocatalytic reaction step, and, if necessary, stop the reaction by a microelectronic switch. Developments in this direction may help us by precision calorimetry, to adjust controlling software and intelligent evaluation software for optimizing chemical reaction management, including safer production [9].

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