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

NEW QUANTITATIVE ASPECTS IN THE FIELD OF PRECISION CALORIMETRY

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Abstract

Different ACTRON calorimeters were used to investigate the alcoholysis of phenyl isocyanate and acetyl chloride, and the reaction of *o*-chloronitrobenzene with alkaline alcohol. An example for a scenario to break off a reaction in a hazardous situation is given.

At least it will be shown, that it is possible to evaluate an interrupted reaction to get the kinetic activation parameters.

Keywords: adiabatic and isoperibolic calorimetry, interrupted reaction, kinetic evaluation, organic reactions

Introduction

Calorimetry is one of the oldest techniques in natural science. It can be applied universally, because all chemical reactions involve heat production. Calorimetric measurements were first reported in the 18th century, and the number of such measurements is still increasing continuously. There have been numerous applications of calorimetry for the kinetic and thermodynamic investigation of chemical reactions and processes. The modern concept of calorimetry includes kinetic aspects such as the rate of heat production, and thermodynamic aspects such as the integrated heat.

Beginning with the simple calorimetric technique, several thermal methods have been developed. All thermal techniques describe the processes in terms of the temperature in the reactor or the heat flow. The course of the reactor temperature during a reaction can be corrected by the equation of TIAN:

$$\frac{dT_R}{dt}=\frac{1}{C_R}\left[-K(T_R-T_U)+\sum_i\frac{d\alpha_i}{dt}\Delta_R H_i\right]$$

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In contrast with calorimetry, thermal analysis is a dynamic method, wereby a change in property of the sample is monitored against time or temperature, while the temperature is changed in a programmed way [1]. In calorimetry, the temperature of the surroundings is predefined, whereby depending on the heat flow between the reactor and the surroundings, adiabatic, isothermal and isoperibolic calorimetry are distinguished.

During a BMBF-supported joint project between the group of Prof. Hugo from the Technical University of Berlin and our own group, different thermal methods were compared as concerns the reaction of phenyl isocyanate with 2-butanol in toluene as solvent. The activation parameters found correspond with the results we derived from a calorimetric investigation.

Experimental

The experiments were carried out in different calorimeters of the ACTRON system [2]. In consequence of the double thermostatization, the apparatus has a high thermal stability of about $\pm 2\cdot 10^{-4}$ K. The working volume of the reactor can be chosen between 8 and 100 ml. The reactor is connected with one, two or three precision burette pumps, for the addition of the final reaction component, a catalyst or a reaction stopper. The addition rate is freely programmable. Optionally, the ACTRON calorimeter can be equipped with two safety pumps in order to stop a reaction quickly and safely in hazardous situations. One of these, the suction pump, empties the reactor content into cold solvent outside the calorimeter, while the other, the pressure pump, rinses the reactor at the same time with cold solvent. At the end of this regime, the reactor is empty after 24 s [3].

The software and parts of the hardware of the ACTRON calorimeter were also used in isoperibolic glass-calorimeters [4]. This calorimeter type is additionally equipped with a tube to allow samples to be taken from the reaction mixture. The samples were quenched immediately and analyzed by HPLC. In this way, it is possible to record the concentration changes of selected reaction components.

Results

During the semibatch alcoholysis of phenyl isocyanate, urethanes are formed. The process is described as a second-order reaction. In organic chemistry, this reaction is used to prove the presence of alcohols.

Figures 1 and 2 show calorimetric curves relating to the alcoholysis of phenyl isocyanate with 2-butanol in toluene as solvent for various starting temperatures and starting concentrations.

The experiments were carried out in semibatch working mode. A solution of phenyl isocyanate as the second reaction component was added at a rate about 0.8 ml min^{-1} to a solution of 2-butanol. To guarantee the complete turnover of the phenyl isocyanate, the alcohol was present in the system in a 2-fold excess. The end of addition is denoted by a straight line. In ACTRON calorimeters, the reactor and the burette pumps are situated in the same thermostatization bath, and differences in temperature between the reactor content and the added components can therefore be neglected.

Figure 1 demonstrates that the reaction rate increases with increasing starting temperature, whilst the experimental curves agree with as concerns the maximum differences in temperature. This proves the good adiabatic conditions in the calorimeter. The reaction rate increases with increasing starting concentration, and the time for complete turnover decreases, as shown in Fig. 2. For the reaction of a 0.25 m solution of phenyl isocyanate, more than 35000 s is needed, whereas for a 1 m solution the reaction is finished after approximately 10000 s.

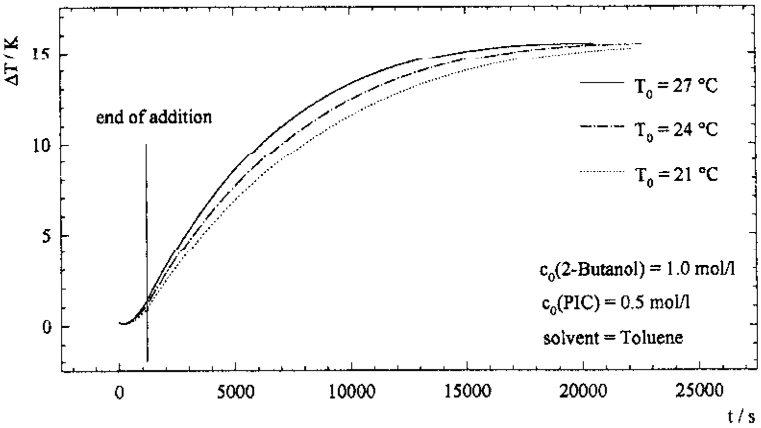

Fig. 1 Influence of the starting temperature on the alcoholysis of phenyl isocyanate with 2-butanol in toluene as solvent

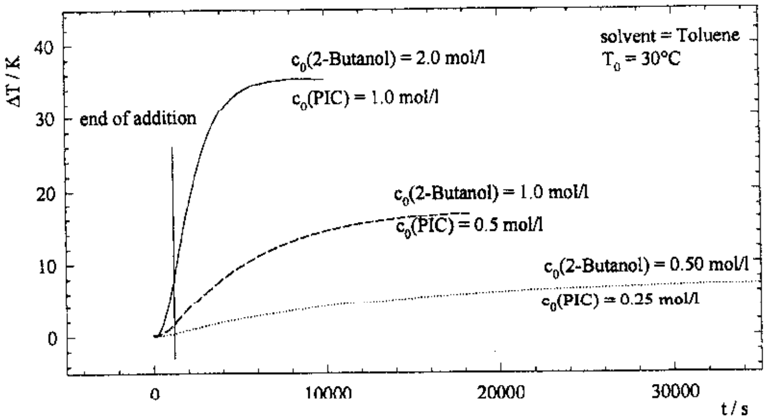

Fig. 2 Influence of the starting concentration on the alcoholysis of phenyl isocyanate with 2-butanol in toluene as solvent

In adiabatic calorimetry, the overall reaction enthalpy is stored in the reactor, i.e. after a suitable calibration it is possible to determine the starting concentrations of reaction components from the maximum differences in temperature. Adiabatic calorimetry can therefore be used to solve analytical questions. For the alcoholysis of phenyl isocyanate with 2-butanol, a linear correlation has been found between the starting concentration and the maximum difference in temperature.

Especially in the case of complex reactions besides the measured temperature, it is useful to involve a second, independently measured data file into the kinetic estimation procedure. This can be the concentration changes in several reaction components. The isoperibolic calorimeter mentioned above was used to analyze the alcoholysis of phenyl isocyanate by taking samples continuously. The resulting temperature–time and concentration–time curves are reported in [5], while the kinetic evaluation with the nonlinear program TA-kin is given in [6].

The same calorimeter type was used to investigate the alcoholysis of acetyl chloride. Figure 3 shows calorimetric curves for the acetylation of several isomeric butanols in acetone as solvent. It is obvious that the reaction rate depends on the molecular structure of the alcohol. Norris and Cortese [7] concluded that the reaction rate increases with increasing distance between a methyl group and the reaction center. For butanolysis, this was manifested. The reaction rate increases from 2-butanol to *n*-butanol.

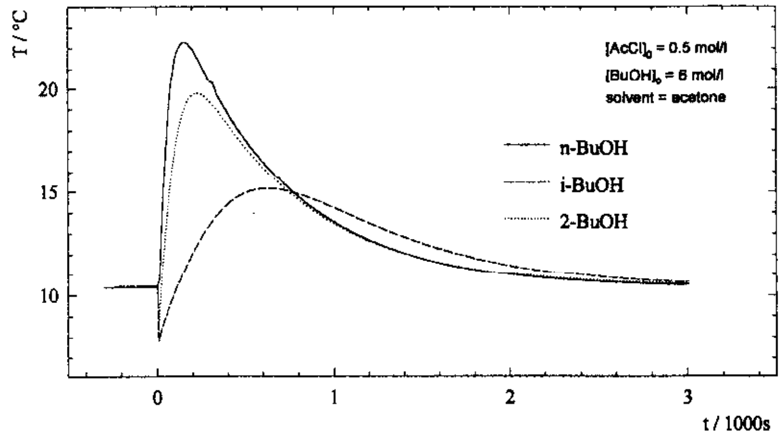

Fig. 3 Influence of the alcohol structure on the acetylation of butanol in acetone as solvent

Alcoholysis with dialcohols was also investigated. Figure 4 presents a comparison of the reactivities of several hexanediols in acetonitrile as solvent. The reactivity increases with increasing number of primary alcohol groups. 1,6-Hexanediol, with two primary alcohol groups, displays the highest reactivity; 2,5-hexanediol reacts distinctly more slowly. As expected, the reactivity of 1,5-hexanediol, with one primary and one secondary alcohol group, lies between those for the other two diols.

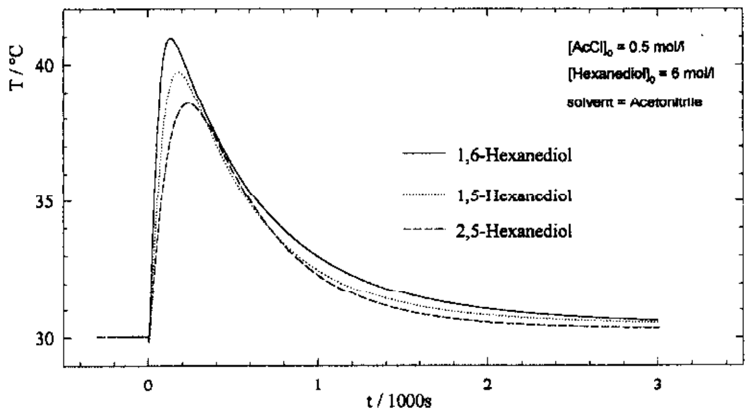

Fig. 4 Influence of the hexanediol structure in acetonitrile as solvent

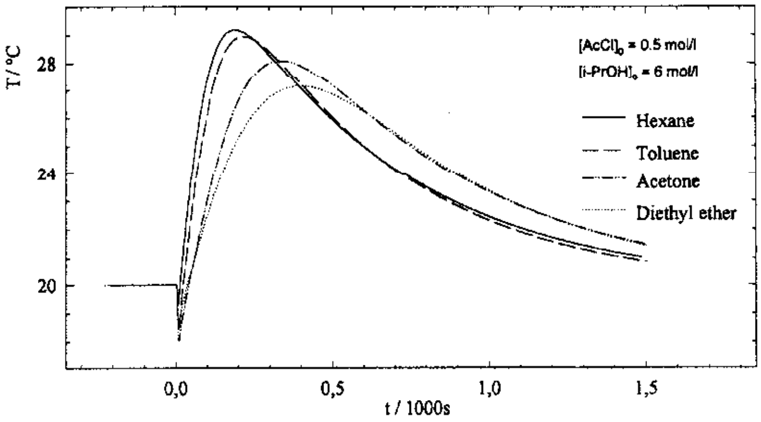

Fig. 5 Influence of the solvent used on the acetylation of *i*-propanol

The reaction rate also depends on the solvent used, as shown in Fig. 5. The calorimetric curves demonstrate that the reactivity is higher in non-polar solvents than in polar solvents. The difference between hexane and toluene is insignificant, whereas the jump in reactivity when acetone is used as solvent is clear.

Safety-scenario investigations

Investigations of chemical safety require information about processes up to the hazardous zone. To prevent damage to an expensive measurement design, scenarios are necessary which lower the reaction rate or stop the reaction completely in hazardous situations. The former can be achieved by adding a reaction stopper.

A reaction can also be stopped by activating the safety pumps of the ACTRON instrument. If the reaction parameters, e.g. the temperature of the reactor or the rate of temperature increase, exceed predefined limits, the computer-controlled pumps are activated automatically.

The reaction of chloronitrobenzene with alkaline alcohol was used to test this scenario. During the induction phase, the chlorine is substituted by an alcohol group; after acceleration of the reaction rate, the exothermic autocatalytic reduction of the nitro group predominates. A kinetic evaluation of this complex reaction system is possible only by considering at least five reaction steps [8].

Figure 6 shows adiabatic calorimetric curves of the reaction of *o*-chloronitrobenzene with sodium hydroxide in *n*-propanol for various starting temperatures. The curves demonstrate that the hazardous potential increases with increasing starting temperature. The reaction course depends very sensitively on changes of the reaction conditions. An increase of the starting temperature from 50 up to 60°C leads to a considerably higher reaction rate. The limiting conditions are exceeded approximately 5200 s earlier; in the event of a starting temperature of 70°C, only 1700 s is needed up to the point of activation of the safety pumps. Indeed, after the limiting values are exceeded, the safety pumps are activated automatically. The temperature in the reactor decreases to a value below the starting temperature in only 12 s, i.e. there is a rapid, substantial fall in the hazardous potential.

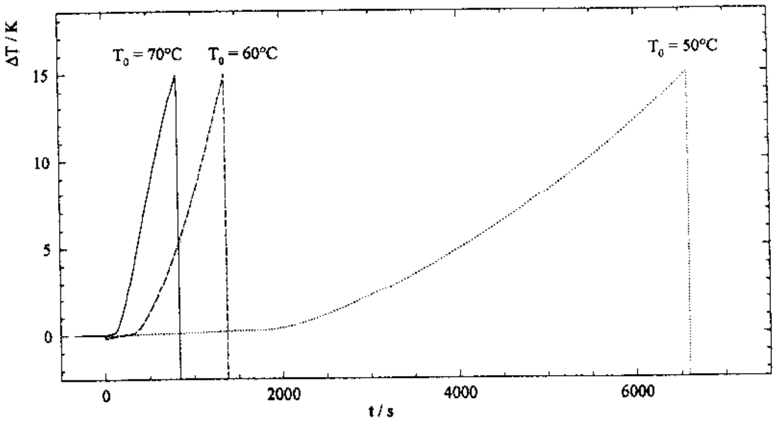

Fig. 6 Influence of the starting temperature on the hazardous potential of the reaction of *o*-chloronitrobenzene with alkaline alcohol; [NaOH]=0.688 mol l^{-1}; [*o*-CNB]=0.408 mol l^{-1}; *n*-propanol; $\Delta T_{r_{max}}$=75°C; r_{max}=3000 mK min^{-1}

The hazardous potential of this reaction also depends on the alcohol used (Fig. 7). For the two *n*-alcohols, the reduction of the nitro group begins earlier, with an accompanying increase in the reactor temperature. For *i*-propanol, the induction phase is longer. After the start of reduction, the temperature increases up to 75°C (ΔT=15 K) in 1000 s. In fact, the reaction with *i*-propanol exceeds the limiting values approximately 10000 s earlier than for *n*-propanol, and 4200 s

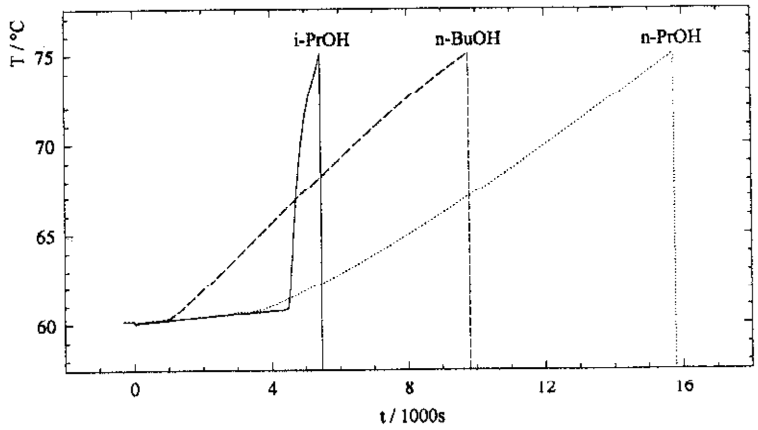

Fig. 7 Influence of the alcohol on the hazardous potential of the reaction of *o*-chloro-nitrobenzene with alkaline alcohol; [NaOH]=0.313 mol l^{-1}; [*o*-CNB]=0.318 mol l^{-1}; $\Delta T_{r_{max}}$=75°C; r_{max}=3000 mK min^{-1}

earlier than for *n*-butanol. This shows that *i*-propanol involves the highest hazardous potential.

Kinetic evaluations

For the kinetic evaluation of all experiments, including those that were broken off, the non-linear software package TA-kin developed by our working group [6] was applied.

As an example, Fig. 8 shows the evaluation of the broken-off reaction of phenyl isocyanate with 2-butanol in toluene as solvent. The experiment was performed with the ACTRON safety calorimeter. The limiting value for the interruption of the reaction was such that the safety pumps were to be activated if the tem-

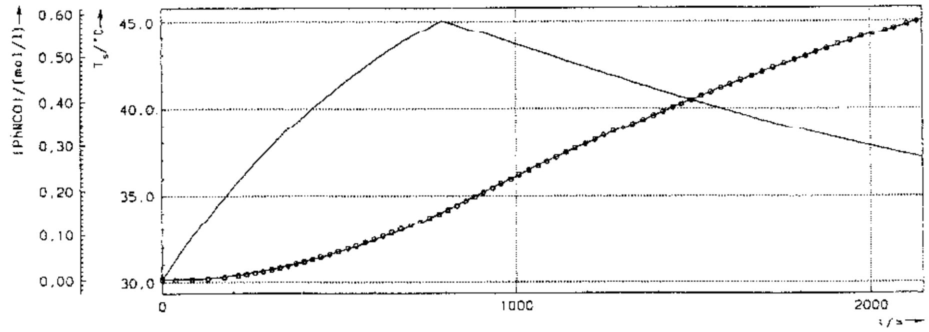

Fig. 8 Kinetic evaluation of an interrupted reaction of phenyl isocyanate with 2-butanol in toluene as solvent

perature of the reactor exceeded 45°C (ΔT=15 K). The reaction was in fact stopped after 2200 s, when about 50% of the phenyl isocyanate remained. The complete turnover would have required approximately 8000 s.

The change in concentration of phenyl isocyanate is characterized by a broken line. This is due to the semibatch mode of addition. The circles represent the measured temperature values, while the full line is the simulated temperature curve obtained by using the estimated activation parameters. The activation energy was estimated to be 39.9 kJ mol^{-1}, and lnk_0 to be 7.8. These values agree with the parameters determined in non-interrupted experiments.

Conclusions

The possibility of stopping reactions by automatic activation of the safety pumps can be utilized to follow processes into the hazardous zone. The data can be recorded beyond the "point of no return". Therefore, the operator can describe the reaction course in hazardous situations by a kinetic evaluation.

By means of a kinetic on-line evaluation during the experiment and a forward simulation, the extrapolated reaction course can be well predicted. From these results, the software can automatically recognize a hazardous situation in the next time region, and activate the safety pumps in time if necessary [5].

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