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REACTION CALORIMETRY FOR THE DEVELOPMENT OF CHEMICAL REACTIONS

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SUMMARY

A new reaction calorimeter is described that has been developed to study chemical reaction processes on a laboratory scale. It provides precise measurements of kinetic and thermal data, of heat transfer data, as well as of the physical properties of the reaction product. The reaction calorimeter is applied successfully in the development of chemical processes, in the evaluation of hazards and risks of chemical synthesis.

Working principles and evaluation are described using the example of the nitration of benzaldehyde.

INTRODUCTION

Chemical reactions are accompanied by the release or the adsorption of energy in the form heat. This HEAT OF REACTION is a definite and reproducible characteristic of a given chemical change. Also, chemical reactions occur at widely differing rates of speed, depending on reaction, partners, temperatures, pressures etc. The characteristic time variation of the reaction rate is referred to as REACTION KINETICS.

The measurement of reaction heat and of reaction kinetics is a fundamental part of the experimental development of the chemical manufacturing process. Data derived from such measurements are used directly to scale-up the reaction process or to assess potential hazards risks.

THE REACTION CALORIMETER SYSTEM METTLER RC1/RD10

Wide practical experience (refs. 1 - 3) has lead to the development of the RC1/RD10 System which consists basically of the following three elements:

- Reactor-/Thermostat unit RC1
- Dosing Controller RD10
- Operating unit (IBM-PC/XT)

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Reactor-/Thermostat unit RC1

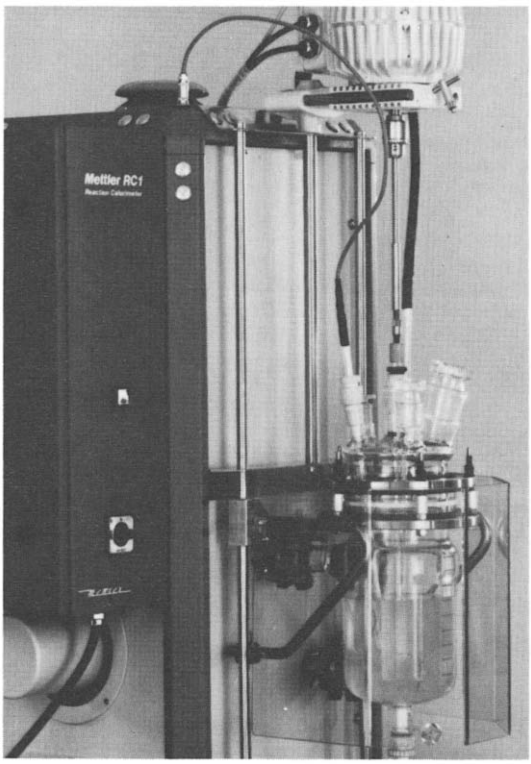

Fig. 1: METTLER Reaction Calorimeter RC1

The standard reactor type is a glass reactor for volumes of 0.5 to 2 l with norm fittings in the cover to allow for convenient dosing or the insertion of measuring sensors. A speed controlled stirrer motor allows the use of various different stirrer types.

The powerful thermostat unit is particularly rapid and is capable of controlling the reactor temperature accurately by adjusting the temperature of the heat transfer medium (Silicon oil) in the jacket of the reactor.
The operating modes Tr (Reactor temperature) isothermal, ramp, or adiabatic and Tj (Jacket temperature) isothermal are possible in the range from -20 to 200°C.

Dosing Controller RD10

This controller allows the accurate and controlled dosing of reaction partners into the reactor (example in fig. 3).

By configuring the measuring inputs (e.g. weight, pressure, pH, temperature) with the standardised outputs (power, voltage, frequency) and by addressing the corresponding software modules, a multitude of user-defined operations may be carried out:

- accurate dosing of liquids, gasses and solids
- pH control, pressure control
- installation of user-defined PID controller

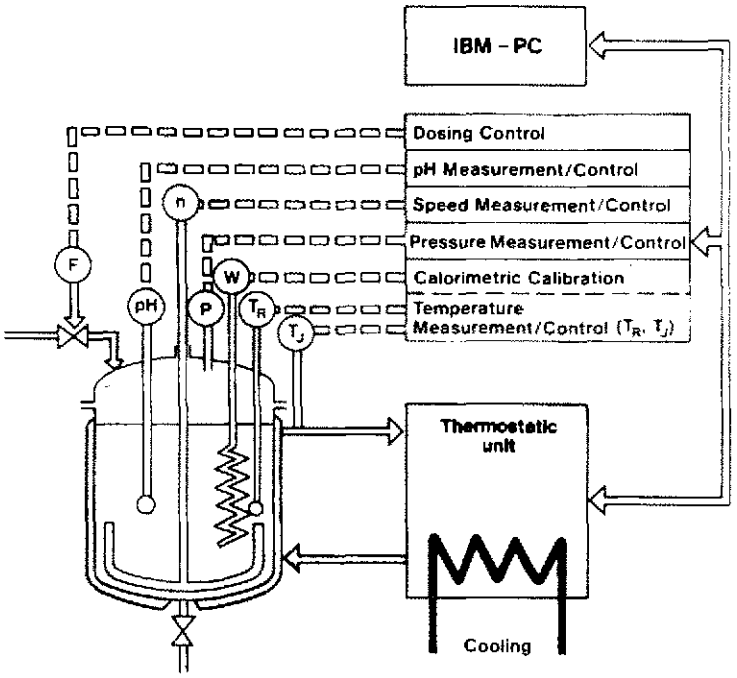

Fig. 2. Schematic of Dosing Controller RD10

Operating Unit IBM-PC/XT

The RC1/RD10 is operated through a personal computer IBM-PC/XT. An advanced menu technique software makes the system extremely userfriendly. A multitasking realtime operating system allows to do simultaneously:

- Check the plausibility of parameters input by operator
- Transfer of set values and safety related parameters to RC1/RD10
- Display and store data measured by RC1/RD10
- Print-out of measuring data as curves (on-line) on a multicolor matrix printer

Manual (interactive input of all set values and automatic operation (preprogrammed sequences) are possible. The change from one operating mode to the other is possible at all times.

CALORIMETRIC MEASURING PRINCIPLE AND EVALUATION OF DATA

The calorimetric principle of the RC1 is based on the following system specific features:

- extremely rapid and accurate adjustment of the jacket temperature to the required value
- continuous measurement of the temperature difference between reaction content (Tr) and heat transfer medium in the jacket (Tj)

The heatflow between the reaction mixture and the reactor jacket is given by the temperature difference over the reactor wall (Tr-Tj) and the heat transfer coefficient (U . A):

$$qflow = U \cdot A \, (Tr - Tj) \qquad (1)$$

U . A is determined during the experiment at repeated intervals with an electrical heater immersed in the reactor. As the heater power qc is known, the heat transfer coefficient U can be calculated. Typical values for qflow for the standard reactor are around $\pm$ 400W.

The actual heat generation rates qr of chemical reactions can be derived from the following equation:

$$qr = qflow - qc + qacc + qdos + qloss + qadd \qquad (2)$$

qr:	heat generation rate by chemical reaction
qflow:	heatflow through glass wall reactor - jacket
qc:	power of calibration heater
qacc:	heat accumulation in the reactor
qdos:	correction of heatflow due to the addition of reaction partner (dosing)
qloss:	heatloss to the environment
qadd:	correction term (proportional to user-defined measuring units)

The user can, therefore, choose the terms that are required for the calculation of the heatflow qr.

The evaluation of the experiment and the creation of curve plots is supported by a high-resolution graphics display. This allows an easy determination of integration and baseline limits for the calculation of the reaction heats.

PRACTICAL APPLICATION OF REACTION CALORIMETRY

Nitration of Benzaldehyde

The scope was to evaluate the nitration of benzaldehyde with respect to the reaction process and to potential hazards. Previous studies in a DSC microcalorimeter (METTLER TA3000) (4) has shown strong exothermal sidereactions at temperature above 50°C with the occurrence of heat heat production rates up to 500 W/kg.

The experiment with the RC1/RD10 is shown on Fig. 4. Benzaldehyde has been pumped into the reactor previously filled with nitrating acid mixture. Already the shape of the heatflow curve is enormously informative:

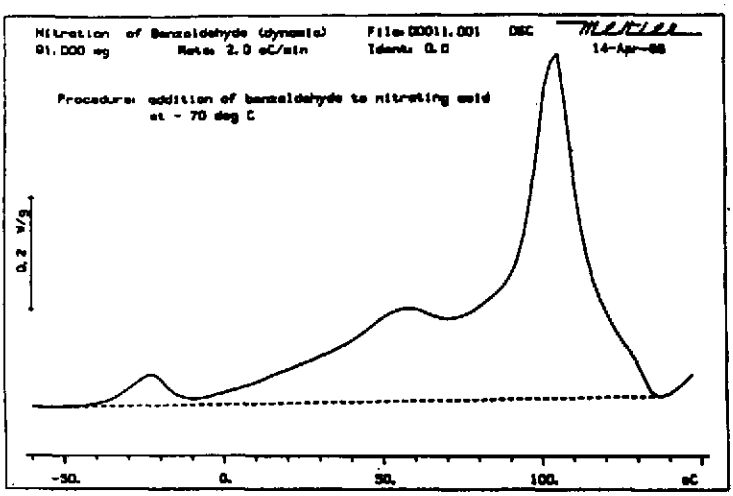

Fig. 3 DSC curve of the nitration of Benzaldehyde

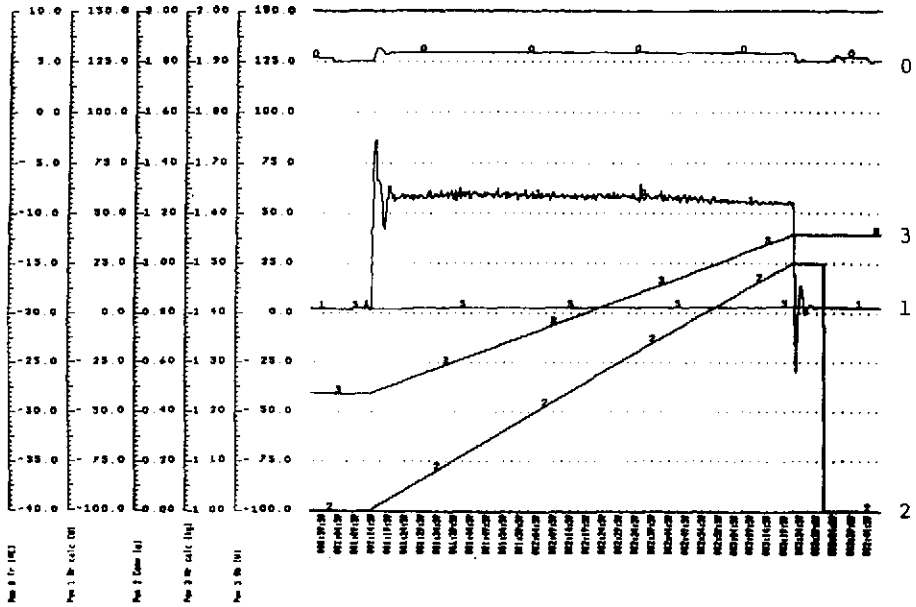

Fig. 4: Example of experiment with RC1
0 = Tr (Reactor Temp.), 1 = Qr (Heat Generation Rate),
2 = Conv (Conversion), 3 = Mr (Reaction Mass)

The reaction runs under perfectly dosing-controlled conditions, it starts immediately and can be terminated by simply stopping the dosing. The accumulation of unreacted aldehydes does not take place.

The quantitative evaluation provides a series of valuable additional information:

- the maximum heatflow (scale-up parameter)
- the heat of reaction by integration of the heatflow curve
- the maximum adiabatic temperature rise (derived from heatflow and the specific heat of the reaction mixture)
- partial integrals of the heatflow curve as a function of the reaction time ("Conversion"). This is the basis for subsequent kinetic calculations
- specific heat cp of the actual reaction mixture

METTLER RC1 EVALUATION 31-Jul-86 16:01

NITRATION OF BENZALDEHYDE
2nd test

bg
evaluation of 1st step: nitration

TYPE OF STORED VALUES

Values		min	max	Time Start	Time End
Tr [°C]	:	-0.52	43.87	0:00:00	8:01:36
dTr/dt [K/s]	:	-0.12	1.12	0:00:00	8:01:36
Qc [W]	:	0.00	23.71	0:00:00	8:01:36
B1 [kg]	:	0.00	0.32	0:00:00	8:01:36
B2 [kg]	:	0.00	0.54	0:00:00	8:01:36
Ta [°C]	:	-10.54	37.95	0:00:00	8:01:36
deltaT [°C]	:	-21.85	27.78	0:00:00	8:01:36
Experiment Duration :				0:00:00	8:01:36

HEAT OF REACTIONS

Pos	Reaction Limits from	to	Integral [kJ]	Mass mr [kg]	Cp [J/kg K]	Adiabatic T-rise [°C]
1	1:12:14	3:32:05	424.453	1.557	1575.9	172.941

BASELINES

Pos	Reaction Limits from	to	Warnings	Type
1	1:12:14	3:32:05	0	integral

Warnings:
0 : None
1 : Less than 5 measured values for regression on one side.
2 : Baseline limit in bad zone (RR fully interfering with other action).
3 : Too many iterations for integral baseline determination.

EVALUATION PARAMETERS and HEAT FLOW COMPUTATION PARAMETERS

Qr is calculated using the terms :

Qr = Qflow + Qaccu + Qdos + Qloss

Settling Time : 400 s Regression Range : 180 s

Heat Loss constant (alpha) : 0.1 W/K Ambient temperature : 25.2 °C

Fig.5 Example of Evaluation Print-out of Mettler RC1

General Application within the Chemical Reaction Technique (3)

The qualitative and quantitative information that can be gained with the RC1/RD10 while running the experiment is of great importance for the efficient determination of the optimal reaction design. The influence of process variables such as catalyst concentration, temperature, stirring speed, and dosing procedure to the reaction rate can be followed directly and under realistic near process conditions through the heatflow curve.

The subsequent detailed evaluation of the measured data provide the accurate information of MATERIAL DATA, REACTION DATA, and TRANSPORT DATA that are of importance to the optimization and mastering of the reaction.

Material data:
- specific heat
- heat of mixing
- solubility data

Reaction data:
- temperature - time diagram
- actual heat generation rate
- overall heat generation rate
- heat of reaction
- adiabatic reaction process

Transport data:
- qualitative information on rate limiting steps in the reaction process
- quantitative determination of heat transfer coefficients of the operation vessel according to the modified Wilson-method

With the introduction of reaction calorimetry to the study of chemical reaction processes, the user has a valuable tool at his disposal, will provide him with answers to a better understanding of the process as such and its associated hazard risks. Improvements in quality, yield, and energy balance are an immediate result.

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