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DTA EQUIPMENT FOR INVESTIGATIONS OF LIQUID-PHASE REACTIONS

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An exact kinetic evaluation is practicable in homogeneous systems if no gradients of concentration or temperature appear. With permanent stirring, the measurement of the real difference temperature and absolute temperature at a suitable heating rate allows the application of liquid-phase DTA in the range between 170 and 380 K. For the examination of air — and moisture-sensitive substance too, equipment has been developed, that operates under inert conditions.

After the application of differential thermal analysis (DTA) to solid-phase reactions the possibility now exists for this dynamic method to be used for investigations of chemical reactions in solution [1 – 3].

Description of the DTA apparatus

The main conception is based on a metallic heating system block. Figure 1 shows a scheme of the arrangement. The measuring cell consists of a cylindrical steel vessel with a PTFE tube (10) for the investigation of aggressive substances too. The chamber is closed by a special seal (15) and can be evacuated or filled with inert gas in repeating steps. A thermocouple (18), a lockable filling device (19) and safety pipe (16) are led through the seal.

Additionally the reaction cell contains an electrical calibrating heater. For one investigation 10 to 15 ml solution is used. The constant equilibration of temperature and concentration is guaranteed by a stirrer (11) rotating at, 120 r.p.m., which in the upper part is protected by inert gas against invading air (17). The components are added by means of a gas-tight syringe. The medium of heating and cooling is a metallic block of octagonal cross-section consisting of aluminium (6/7).

To limit heat flow to or from the outside, the block is surrounded by three heat shields (4). Cooling is achieved with liquid nitrogen in the milled fins of the block. Finally, liquid nitrogen vaporizes in a cavity (12) under the block and streams up through the channels (7). In the same channels a heating wire (8) is built, insulated by ceramic tubes. Temperature control is performed through copper-constantan thermocouples near the cells. In the range 180 – 300 K the thermocouple response is approximately a linear function of temperature. For the measurement of abso-

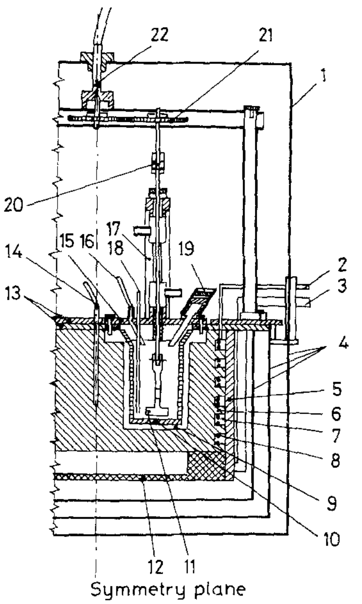

Fig. 1. Scheme of DTA-equipment

lute temperature and temperature difference nickel/chromium-constantan thermocouples with higher EMF are used. The difference thermo-EMF is amplified and measured by compensation.

Determination of coefficients

The quantitative evaluation of chemical reactions requires a knowledge of the non-reactive parameters. Heat capacity C_p, heat transfer coefficient K and cooling constant B depend on the apparative arrangement, the reaction system investigated

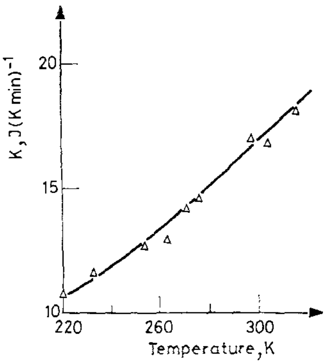

Fig. 2. Temperature dependence of K for mixture of toluene/tetrahydrofurane

and the temperature. The heat capacity of the measuring or reference cell consists of the value for the blank chamber and the solution. C_p is proportional to the volume of solution. Often the temperature-dependence of the solution heat capacity is linear. The heat transfer coefficient contains the heat conductivity of the reaction solution, the measuring cell and the aluminium block.

The temperature function of K is non-linear and can be described by a quadratic function (Fig. 2). K is determined by electrical calibration. The best way to find B is to record the cooling curve after electrical heating. From Newton's law $\Delta T = \Delta T_0 \exp(-Bt)$ one gets B by plotting ln ΔT agaist t. The cooling constant can be described by a quadratic temperature function too.

Experimental conditions and accuracy

For quantitative evaluation homogeneous conditions are to be presumed. Problems of solubility occur for reactions which take place in lower temperature ranges. Phase conversions or precipitation reactions must be excluded.

Therefore, the solvent must have sufficient dissolving power at low temperature too and side-reactions are not allowed. The choice of heating rate depends on the reaction rate. For liquid-phase reactions, heating rates of 1–5 K/min are most favourable. For a sure kinetic evaluation of exothermic reactions with 300 kJ mole^{-1}, concentrations of about 10^{-2} mole l^{-1} are required. Energy turnovers in the range of $1-10^3$ J min^{-1} can be investigated. The error in the activation energy of chemical reactions is about 3–5%, as in the case of the pre-exponential factor, whereas the error in the reaction enthalpy may be 7–10%.

Aminolysis of benzenesulfochloride

An example for this dynamic method is given in the reaction between aniline and benzenesulfochloride [4]. Figure 3 shows the DTA curve and the turnover curve of this reaction. The characteristic of the reaction is represented in the starting and main part which extends to behind the ΔT maximum of the DTA peak. The

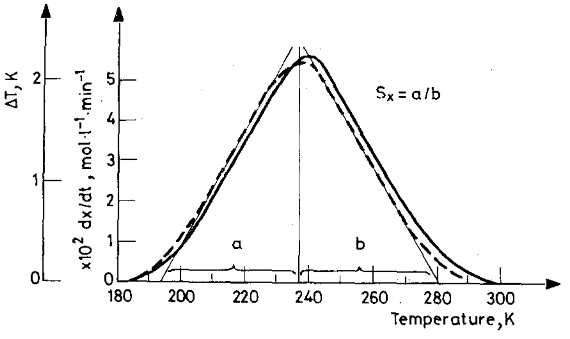

Fig. 3. DTA- and dx/dt-curve (dashed) of the sulfamide formation

decreasing curve part is determined increasingly by the cooling constant and is not suitable for the kinetic evaluation of the activation parameters.

By means of the form factor S_x, which is defined as the ratio of the tangents of the turnover curve at the first and second inflection points, it is possible to determine the reaction order. In the thermodynamic and kinetic evaluation of this reaction, we obtain the following results by the method of Borchardt and Daniels [1] (see Table 1).

Further examples are given in the reaction of aluminiumtriethyl with aliphatic and aromatic alcohols in solution [6].

Table 1

Thermodynamic and kinetic parameters of the reaction of aniline with benzenesulfochloride compared with lit. [5] for second order

	Enthalpy change, kJ/mole	Activation energy, kJ/mole	Pre-exponential factor log k
	-83.4 ± 3.2	36.6 ± 0.5	7.76 ± 0.1
lit.	–	39.3	7.14

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Zusammenfassung — Eine exakte kinetische Auswertung kann in homogenen Systemen durchgeführt werden, wenn keine Konzentrations- oder Temperaturgradienten erscheinen. Unter ständigem Rühren gestattet die Messung der wahren Temperaturdifferenz und der absoluten Temperatur bei einer entsprechenden Aufheizgeschwindigkeit den Einsatz der Flüssigphasen-DTA im Bereich zwischen 170 und 380 K. Für die Untersuchung von luft- und feuchtigkeitempfindlichen Substanzen wurde ebenfalls ein Gerät entwickelt, das unter inerten Bedingungen arbeitet.

Резюме — Точная оценка кинетических параметров практически выполнима в гомогенных системах, где не происходит градиента концентрации или температуры. При постоянном перемешивании системы измерения действительной температурной разницы и обсолютной температуры в условиях приемлемой скорости нагрева, позволяют применение жидкофазной ДТА в области температур 170—380 К. Для исследования чувствительных к воздуху и влаге веществ, разработана аппаратура, действующая в инертных условиях.