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

THE *CIS-TRANS* ISOMERIZATION OF AZOBENZENE IN THE MOLTEN STATE

A useful test reaction for the kinetic evaluation of DSC measurements

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Abstract

Contrary to the situation in the field of temperature, heat and heat flow rate calibration, so far no generally accepted and easily practicable chemical reaction exists with regard to a kinetic evaluation. A possible reaction would be the well-known first-order *cis-trans* isomerization of subcooled liquid azobenzene. Surprisingly, the evaluation of measurements performed with a power compensated calorimeter yields activation parameters, which are dependent on the heating rate. The desmearing of the curves does not produce any improvements. However, constant activation parameters are obtained, if a small self-heating of the sample during the exothermic reaction is taken into account.

Keywords: azobenzene, DSC, kinetics

Introduction

The DSC method is a very effective technique for the kinetic investigation of reactions in the homogeneous liquid phase. Software packages allow the fast and convenient evaluation of both isothermal and non-isothermal measurements. The concept of the activation parameters, although originally developed to describe the temperature dependence of reactions in the gas phase, is generally accepted also for liquid phase reactions. Meanwhile, also reactions with a very complicated mechanism can be approximated by a mathematical model, which includes several consecutive and/or competitive steps. As a rule, such a formal

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description of the reaction is completely sufficient for the practitioner, but circumspection is advisable with regard to a physical interpretation of the model parameters. On the other hand, the true aim of a kinetic analysis is an evaluation of the correct reaction mechanism. This means that the sequence of all, or better of all *important*, elementary steps is known. Contrary to the situation in the past decades, it is no longer necessary to find an analytical solution of the system of differential equations. The activation parameters of all steps can be determined by numerical optimization without any approximations, using the technique of multivariate (nonlinear) regression. In any case and independent of the objective, a well-known reaction should be used to test the individual calorimeter, the sample preparation technique and the evaluation procedure.

Cammenga has suggested the first-order *cis-trans* isomerization of azobenzene in the liquid phase as suitable test reaction. Using isothermal spectrophotometric measurements [1], he obtained the following activation parameters: $\ln A=27.6$ and $E_A=103.4$ kJ mol^{-1}. An advantage of this test reaction is the complete absence of any side reactions, the yield of *trans*-azobenzene is 100%. DSC investigations in a heat-flux calorimeter by the same author [1, 2] and unpublished results of Sarge and Cammenga [3] verify these parameters. Independent of the heating rate, E_A has been found to be 103.5 kJ mol^{-1} by multiple linear regression. *Cammenga's conclusion [2]: "The reaction and its data may thus be* used as a kinetic reference." Somewhat surprisingly, measurements with a power-compensated DSC 2 (Perkin-Elmer) resulted in heating rate dependent activation parameters, if the heating rates exceeded 5 K min^{-1}. This result was found, although the original runs were desmeared and corrected to zero heating rate. Of course, comparable with purity determinations, the most favourable measuring conditions are low sample masses (1–3 mg) and slow heating rates (1– 2 K min^{-1}). But slow heating rates are very time consuming and low masses may result in unfavourable signal-to-noise ratios. Therefore, it was our objective to develop a procedure for the treatment of the raw data, which gives the correct activation parameters also for higher sample masses (up to 10 mg) and faster heating rates (up to 40 K min^{-1}).

Experimental

DSC measurements were performed at six different heating rates between 1 and 40 K min^{-1}. The apparatus was a Perkin-Elmer DSC 2, modified by an equipment for program control and data sampling (ifa GmbH Ulm, Germany). Temperature, heat and heat flow rate calibration were controlled weekly as usual. To avoid a partial light-induced *cis-trans* isomerization, the initial substance was filled into sample pans for volatile samples in a dark room, using low-intensity red light. Fortunately, due to the fact that the isomerization strictly follows first-order kinetics, a partial conversion during this period would only influence the measured isomerization heat and by no means the activation parameters. The samples were stored up to the DSC measurement at –20°C. Typical sample masses were between 4 and 6 mg, but we have investigated also heavier samples up to 12 mg.

Our measuring procedure was as follows:

1. *Cis*-azobenzene is solid at room temperature. To obtain it as subcooled melt, the samples were heated rapidly (20 K min^{-1}) to the maximum of the melting peak (about 72°C). Then, the samples were cooled as quickly as possible to 35°C, the starting temperature for all kinetic measurements.

2. All runs were made in the so-called C_p-mode. Every measurement consists of a short isothermal at T_{start} (1–2 min), a heating up period and another short isothermal at T_{final}.

3. Usually, a linear zero line is drawn between the heat flow rates at T_{start} and T_{final}. According to Hanitzsch [4], the reliability of the measurement is improved, if the subsequent cooling to the start temperature is interrupted six or eight times to get several isothermal heat flow rate levels. From the heat flow rates of the initial, end and intermediate isothermals a polynomial can be calculated, which describes the generally existing curvature of the temperature dependence of the isothermals. If the curvature of the instrumental zero line is really unchanged during all necessary measurements, this step can be neglected.

4. The switch-on and the switch-off behaviour of the scanning mode (heating rate 20 K min^{-1}) is recorded within the temperature range of the measurement.

5–7. The steps 2 to 4 are repeated after the substance has been removed from the sample side.The reference side remains unchanged.

The treatment of the raw data includes:

– Subtraction of the (possibly curved and differing from run to run) instrumental zerolines. The zeroline corrected reaction curves (I) and baselines (II) are obtained as the differences of the curves from the steps 2 and 3 and the steps 5 and 6, respectively.

– Then, the subtraction of the baseline (II) from the measurement gives a curve, which still includes the contributions of the heat capacities of substance and sample pan in addition to the heat flow rates due to the chemical reaction.

– The next operation is the subtraction of the two curves from the steps 4 and 7. By differentiation of the resulting curve the apparatus function (Green's function) can be derived. Schawe [8] has shown that the apparatus function extracted from the baseline corrected heat flow curve is more valid than that obtained from a single sample run (step 4).

Now, the desmearing and the calculation of the self-heating of the sample (sample pan) can be carried out. Two another corrections are required before the kinetic evaluation.

– The contribution of the sample pan (Al as a rule) is easily removed, using corresponding temperature-dependent polynomials. We have used:

$$C_p/\mathrm{J\,K^{-1}mol^{-1}} = 20.6516 + 0.0124076\,T/\mathrm{K}.$$

– There are several possibilities to remove the heat capacity contribution of the sample from the measured signal [7]. The simplest correction may be realized by a linear connection of the points, where the reaction starts and finishes. In the case of the *cis-trans* isomerization this is a completely sufficient approximation. An estimation of the possible error follows from published heat capacities for solid *cis-* and *trans*-azobenzene [5, 6] and from our measurements with liquid *cis-* and *trans*-azobenzene. Unfortunately, subcooled liquid *cis* azobenzene crystallizes below 305 K. Therefore, the temperature range before the reaction starts is very small and allows only a rough estimation of the heat capacity function. But similar to the heat capacities of the solid forms, the heat capacities of the liquid forms differ by approximtely 0.05 J $\mathrm{K^{-1}g^{-1}}$, nearly independent of the temperature. Then, the maximum errors by neglecting this fact are about 0.2, 0.5 and 0.1% at 5, 50 and 95% conversion. The scatter of the activation parameters, resulting from successive measurements with the same experimental conditions, is more pronounced than the scatter resulting from the uncertainties in constructing the baseline for an individual run. We have verified this by determining the activation parameters for two runs with heating rates of 10 and 20 K $\mathrm{min^{-1}}$ respectively.

Results and discussion

Table 1 shows the measuring conditions and the obtained reaction heats. Cammenga *et al.* [1, 2] have found $\Delta_{iso}H^{o}_{298}$=–48.2 kJ $\mathrm{mol^{-1}}$ or –264.5 J $\mathrm{g^{-1}}$. The

Table 1 Experimental conditions and reaction heats for the cis-trans isomerization of azobenzene; T_{start} was 308 K for all runs

β/K $\mathrm{min^{-1}}$	m/mg	T_{final}/K	ΔH_{iso}/J $\mathrm{g^{-1}}$
1	8.15	393	–244.7
1	5.84	393	–252.0
1	8.91	393	–245.1
2	6.88	408	–247.3
2	6.62	408	–260.3
5	7.28	428	–255.8
5	7.60	428	–256.6
10	5.28	438	–252.0
10	4.56	438	–256.8
20	5.55	453	–258.9
20	5.26	453	–257.2
40	5.56	468	–258.2

isomerization heats found in our measurements are very close to this value. In other words, the conversion during the preliminary melting of *cis*-azobenzene and the subsequent quenching to the start temperature for the kinetic measurements was very small. Three procedures were tested for the kinetic evaluation:

1. The simplest correction of the individual runs would be the shift of the curves (the extrapolation to a zero heating rate) according to:

$$T_{\mathrm{true}} = T_{\mathrm{m}} - \text{time lag}\,\frac{\beta}{60} \qquad (1)$$

where T_{true} is the corrected and T_{m} the measured temperature; β is the heating rate in K min^{-1}. The value for the time lag (6.2 s) follows from both the heating rate dependence of the melting peak of *trans*-azobenzene and the evaluation of the apparatus function (see below). If only this correction is made, the activation parameters (Table 2) are clearly dependent on the heating rate.

Table 2 Activation parameters of the *cis-trans* isomerization of azobenzene, using different corrections of the raw data

Heating rate/ K min^{-1}		Corrected to β = 0		Corrected to β = 0 and desmeared		Corrected to β = 0, desmeared and temperature corrected	
		lg$A$/s^{-1}	E_A/kJ mol^{-1}	lg$A$/s^{-1}	E_A/kJ mol^{-1}	lg$A$/s^{-1}	E_A/kJ mol^{-1}
1		12.03	102.4	12.02	102.3	11.98	102.0
	*	12.26	103.6	12.22	103.3	12.19	103.1
		12.49	105.2	12.42	104.7	12.40	104.5
2	*	12.39	104.8	12.41	105.0	12.35	104.6
		12.43	105.4	12.34	105.0	12.47	105.4
5	*	12.12	102.9	12.14	103.1	12.02	102.3
		12.53	106.0	12.48	105.7	12.33	104.7
10	*	12.35	104.8	12.37	104.9	12.22	104.0
	*	12.55	106.2	12.53	106.1	12.38	105.1
20	*	12.81	108.2	12.94	109.2	12.53	105.9
	*	12.77	108.5	12.85	108.5	12.50	105.5
40	*	13.34	112.2	13.23	111.4	12.21	104.3

*Values selected for non-linear regression program

2. Next, we have investigated, whether the so-called "smearing" is responsible for the apparent heating rate dependence of the activation parameters. Because the transport of heat needs time, the measured heat flow rate differs from the true heat production of the sample. The extent of the smearing depends on the heating rate, the sample mass and the thermal resistances in the sample/calo-

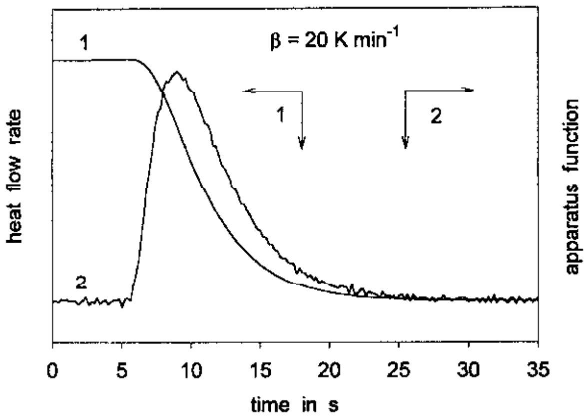

Fig. 1 Apparatus function (2) of liquid *trans*-azobenzene at 400 K, obtained by differentiation of the switch-off behaviour from the scanning to the isothermal region (1)

rimeter system. If the apparatus function is known, the true heat production can be calculated by various mathematical procedures. We have used a combination of the methods suggested by Schawe *et al.* [8–11], Löblich [12, 13] and Ulbrich [14]. As mentioned above and described in detail by Schawe, we have obtained the apparatus function from the switch-on/switch-off behaviour of the liquid *trans*-azobenzene (Fig. 1). Löblich [12] describes the apparatus function by two exponential functions. But this model with two time constants is not able to describe the clearly distinctive inflection point on the leading edge (Fig. 1). To improve the fit, at least a third time constant is required. Therefore, we have used a fit with four serial low passes (four additive coupled exponential functions). The four time constants of this model and an additional dead time are obtained by nonlinear regression. The dead time takes into consideration that the origin of the apparatus function is somewhat shifted with respect to the time "0" (the time at which the scanning mode is switched on or off). Typical values for subcooled liquid *trans*-azobenzene are: dead time=0.2 s, τ_1=2.5–3.5 s, τ_2=1.0–1.5 s, τ_3=0.5–0.75 s and τ_4=0.5–0.75 s. Extensive investigations have shown that the sum of these constants – on average 6.2 s – is always equal to the total time lag, necessary for the heating rate correction of thermal events.

$$\text{time lag} = \text{dead time} + \tau_1 + \tau_2 + \tau_3 + \tau_4 \qquad (2)$$

Furthermore, we have found that for substances with low thermal conductivity the largest time constant τ_1 corresponds well to the sum of the two time constants, which are needed to describe the descending section of a first-order transition peak. Therefore, we split up the total time lag into two contributions. The largest time constant τ_1 is used for the desmearing (deconvolution), the same average value of 3.0 s being used for all curves. If a second order Tian equation [12, 14] is used for the desmearing, the best results (desmeared peak as triangle, no oscillations of the steep descending side of the triangle) for substances with high thermal conductivity would be obtained by splitting this time in the approximate ratio 4:1 (2.4 and 0.6 s). Desmearing peaks of substances with low thermal conductivity, such a splitting doesn't yield any improvement. A simple first order Tian equation is sufficient. Obviously the remaining part of the total time lag (dead time $+\tau_2+\tau_3+\tau_4$) is caused by electronic factors of the DSC 2. It is used for a shift of the curves as described in point 1.

The kinetic results which are obtained by this procedure are within the error limits the same as those with the simple correction 1. The reason for this becomes obvious from Fig. 2. Even at the greatest heating rates, the changes of the experimental heat flows are relatively small. Therefore, the desmearing produces only a shift of the original curve and hardly any change in the peak shape.

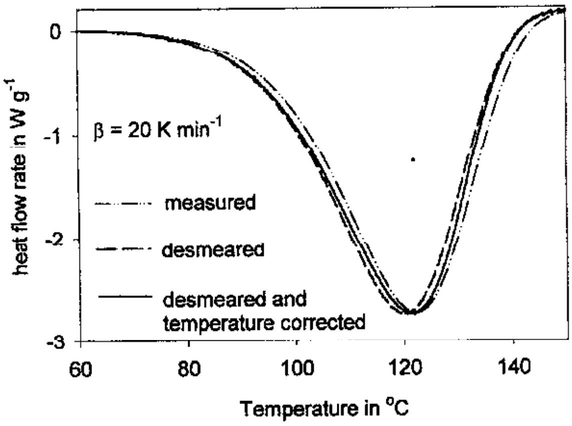

Fig. 2 Measured, desmeared and additional temperature corrected curve for the *cis-trans* isomerization of azobenzene

3. The deconvolution does not take into account a possible temperature difference between sample and recorded temperature. For instance, the correct desmearing of a melting peak results in a triangle, but the sample temperature is constant for the duration of the phase transition [7]. Investigating exothermal reactions of samples with lower thermal conductivity, we encounter more complicated conditions and the correction of the sample temperature is not so simple. We have used the following procedure as surely rough approximation: The quasi-adiabatic self-heating of the sample – compared to the program temperature – is calculated for a sufficient small time interval according to:

$$\Delta T_1 = \frac{-\mathrm{d}Q}{\mathrm{d}t}\frac{\Delta t}{C_p} \tag{3}$$

where C_p is the overall heat capacity from sample and sample pan. The temperature difference ΔT_1 relaxes with the overall time constant τ_1 of sample and sample pan. As already mentioned, τ_1 ranges from 2.5 to 3.5 s. According to $R_{th}=\tau_1/C_{p,\,total}$ ($C_{p,\,total}$ is the sum of the contributions of sample pan and substance, typical values: 35 37 mJ K^{-1} at our experimental conditions), the effective thermal resistances are then between 70 and 100 K s J^{-1}. This is consistent with R_{th}=82 K s J^{-1}, as determined from the leading edge of the melting peak of *trans*-azobenzene. We have made our calculations with an average τ_1 of 3.0 s:

$$\Delta T_2 = \Delta T_1 \exp\left(-\frac{\Delta t}{\tau_1}\right) \tag{4}$$

If $\Delta T_2<\Delta T_1$, is valid, the remaining temperature difference is added to the ΔT_1 of the next time interval. That is, we assume the validity of the superposition principle. The result of this correction is in addition to the curve shift a slight change of the peak shape, as shown in Fig. 2 for the heating rate of 20 K min^{-1}. Another possibility to demonstrate the results of these calculations is chosen in Fig. 3 for three heating rates (5, 10 at 20 K min^{-1}). The difference between sample and program temperature is plotted against the program temperature. Of course, the steady state temperature difference before and after the isomerization results from the total time lag of 6.2 s.

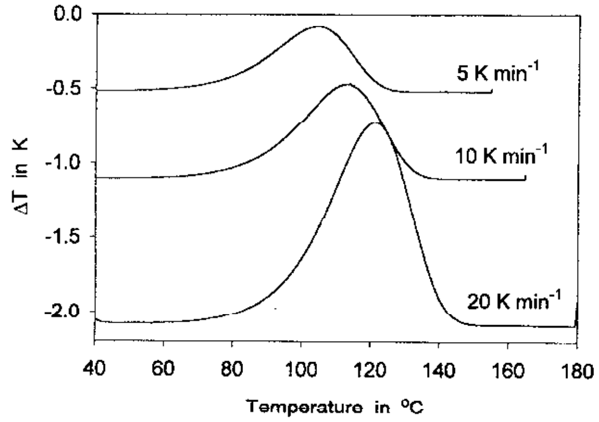

Fig. 3 Difference between sample and program temperatures, caused by the self-heating of the sample during the exothermal reaction

After this correction, the clearly distinctive heating rate dependence of the activation parameters disappears, as shown in the last column of Table 2. Finally, we have used the program for the multivariate non-linear regression (Netzsch-Gerätebau GmbH) to sum up several measurements in one analysis. Since the maximum number of curves is eight at present, we have selected the curves marked by an asterisk in Table 2. Figure 4 shows the comparison between measured and calculated curves, the mean activation parameters are as follows:

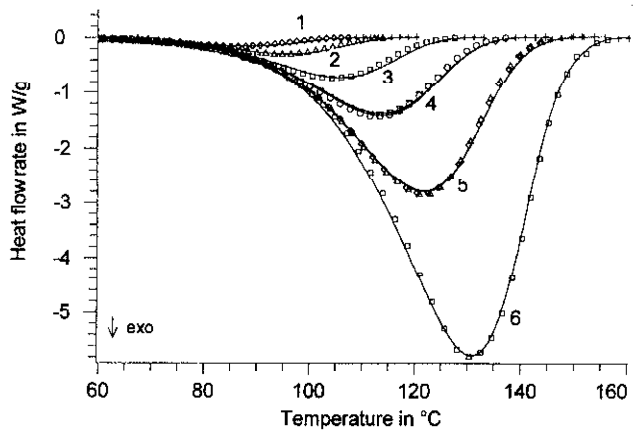

Fig. 4 Evaluation by multivariate nonlinear regression; discrete points: experimental curves, solid lines: regression curves; 1–6: 1, 2, 5, 10, 20 and 40 K min^{-1}, respectively

$$\lg A = 11.98 \pm 0.1;\ E_A = (102.5 \pm 0.8)\ \text{kJ mol}^{-1}$$

(Other possible combinations of eight curves yield almost the same results.)

If the data sets of Sarge [3] are evaluated by multivariate regression, the results ($\lg A$=12.08±0.1; E_A=(102.5±1) kJ mol^{-1}) agree very well with our values. Therefore, we think that the concept of the calculation of true sample temperatures in power compensated calorimeters (taking into account all weak points of the simplified model) is a reasonable approximation to obtain reliable kinetic parameters.

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