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The dimerization of cyclopentadiene – a test reaction for the kinetic analysis of DSC measurements and the performance of a kinetic evaluation program

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Abstract

The formal kinetic description of partially very complex reactions is being increasingly used for the analysis of DSC measurements. Before one begins, one should check with the help of ''kinetic calibration'' whether the available measurement and analysis technique has provided correct results. Only then will the predictions deduced for the reaction behaviour under reaction conditions different to the measurement be meaningful and reliable. Contrary to the situation in the temperature, heat and heat-flow calibrations, there is a shortage of test reactions which are simple, well known and in particular, suitable for the DSC measurement technique. However, this type of test reaction which fulfils the above requirements, has been discovered in the dimerization of cyclopentadiene and a description of the measurement and kinetic analysis follows. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the past, different methods of kinetic evaluation were developed and published in a great number of journals. The activation energy and frequency factor is often estimated on the basis of one single scan or sometimes even on the basis of only a few points of this single scan. Because of the inevitable measuring errors and the distinctive correlation between the frequency factor and the activation energy, the values of both frequency factor and activation energy are often inaccurate and practically useless in the case of complex reactions. In particular, no reliable predictions are possible for conditions that differ from the measuring conditions [1]. Reliable values for the process parameters can now be achieved using modern evaluation methods. One of the main features of these modern methods is that the complete information content of a set of multiple scans measured at different temperatures or heating rates (dynamic or isothermal temperature control), is integrated into the evaluation. Under favourable conditions it is then possible to differentiate between assumed alternative mechanisms. In any event, the practician has a reliable tool to predict the behaviour of reactions under any complex condition [1,2]. The available measurement and evaluation techniques should be checked by means of

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simple reactions for which the mechanism and kinetic parameters are known. This must be carried out before kinetic evaluations of more complex reactions are started. One suitable test reaction is, for example, the *cis–trans* isomerisation of azobenzene [3] which runs strictly as a first-order reaction. A further useful test reaction should be the dimerization of cyclopentadiene (CPD) which is frequently regarded as a simple second-order reaction. There are indications that this Diels–Alder Reaction is actually autocatalyzed [6,7] and also that it reaches a temperature-dependent equilibrium [4]. The kinetic modelling must take these additional aspects into account. At the same time, this means a useful test with regard to the performance of the available analysis tool in the kinetic evaluation of more complex reactions.

Published parameters for dimerization are as follows [4–6]: E_A from 68.4 to 69.9 kJ mol^{-1} and lg(A/s^{-1} l mol^{-1}) from 5.9 to 6.29. For the cracking reaction of dicyclopentadiene (DCPD) running as a first-order reaction, $E_A = 142.2$ kJ mol^{-1} and lg(A/s^{-1}) = 13 are found [4]. The influence of autocatalysis is only discussed at a constant temperature, near room temperature. Howat [6] discovered that an effective rate constant increases by 74% during the reaction at 40°C. Schmid [7] even observed a value of 364% at 25°C. Turnbull [4] determined the value of the reaction heat as being 584.9 ± 19 J g^{-1} at 25°C in an adiabatic calorimeter.

2. Experimental

CPD is produced from commercial DCPD by means of destructive distillation at 150–170°C and atmospheric pressure in an argon stream. This monomer is purified by double distillation at 40°C. The temperature of the distillation receiver should not be higher than −20°C because the dimerization speed is already considerable at room temperature. If no more than 0.5% CPD should be converted into DCPD, then pure CPD can only be stored for a maximum of one day at −20°C.

The DSC measurements are carried out with the following instruments: MDSC 2920 (TA Instruments) and the DSC 2 (Perkin Elmer). The periods of modulation of the MDSC were 60 and 100 s. The modulation amplitudes lay between 0.15 and 1.0 K, depending on the heating rate. As usual, all the instruments were calibrated in the temperature range from −30°C to 250°C concerning base line, temperature (water, indium and tin), heat (indium) and heat flow rate (sapphire). Only the non-isothermal reaction mode was made appropriate for these measurements. The heating rates were varied between 0.25 and 5 K min^{-1}. The temperature range was between 20°C and 165°C. The correction of the original measuring data of the MDSC 2920 with regard to temperature dependence of the heat-flow calibration, the drift of the non-reversing curve and of the disturbances, only occurring at heating rates greater than 2 K min^{-1}, are described elsewhere [2].

The zero-line curvature, overlaying the raw signal of the DSC-2 measurement, was removed according to the Hanitzsch procedure [8]. After each individual measurement, seven isothermal heat-flow levels were recorded between the start and the final temperature. The connection of the seven points by a polynomial of the 5th degree is the zero-line needed for the correction. Afterwards, part of the heat capacity contained in the reaction curves was separated by using the heat capacity functions of both the DCP and DCPD.

3. Results and discussion

Fig. 1 shows the heat capacity functions (|c_p|) of both the first and second measurement obtained with the MDSC 2920 at five different heating rates. For the reaction conditions studied in this work, the complex heat capacity |c_p| is nearly equal to the storage heat

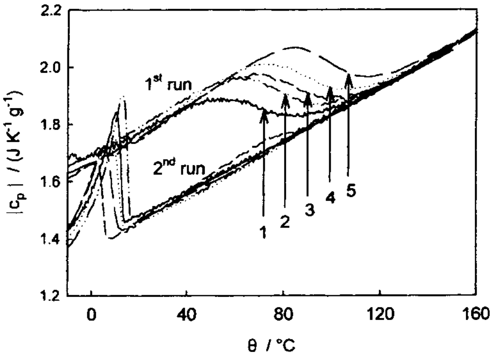

Fig. 1. c_p-functions during 1st and 2nd run, obtained in MDSC 2920 (complex heat capacity |c_p|) heating rates in K min^{-1}: (1) 0.243, (2) 0.487, (3) 0.73, (4) 0.973, (5) 1.947.

capacity c_p. As a result of the transformation of the translational degrees of freedom from the CPD into non- or only slightly excited vibrational degrees of freedom from the DCPD, the heat capacity is decreased during the reaction by approximately $0.29\ \mathrm{J\,K^{-1}\,g^{-1}}$. The temperature dependence of c_p is the same for CPD and DCPD within the accuracy of measurement. The following values were achieved as an average over all measurements.

$$\begin{aligned}\text{CPD}:\ c_p &= 1.6712\,\mathrm{J\,K^{-1}\,g^{-1}}\\ &\quad + 0.004521\,\mathrm{J\,K^{-2}\,g^{-1}}\\ &\quad \cdot T\ (\text{range from 253 to 333 K}),\end{aligned}$$

$$\begin{aligned}\text{DCPD}:\ c_p &= 1.3795\,\mathrm{J\,K^{-1}\,g^{-1}}\\ &\quad + 0.004521\,\mathrm{J\,K^{-2}g^{-1}}\\ &\quad \cdot T\ (\text{range from 298 to 415 K}).\end{aligned}$$

Pure DCPD melts at 32.5°C [4]. The melting temperature decreases by more than 3 K/mol% impurity because of the low melting heat of $2.1\ \mathrm{kJ\,mol^{-1}}$. This explains the melting intervals that were found. The somewhat different melting intervals in repeated measurements (Fig. 1) result from the fact that the DCPD is contaminated to a varying degree with CPD, depending on the final temperature and the heating rate of the first measurement. This is because the rate of the retro-Diels–Alder reaction increases considerably above 150°C.

The measured value of $-596 \pm 15\ \mathrm{J\,g^{-1}}$ for the heat of reaction agrees very well with the value from literature [4]. The kinetic modelling by means of multivariate non-linear regression was carried out using the software "NETZSCH Thermokinetics" (Netzsch Gerätebau GmbH). Three data sets were used for the kinetic analysis: two got with the DSC-2 and one with the MDSC 2920. Every data set always contains eight measurements, each with a different heating rate between 0.25 and 5 K $\mathrm{min^{-1}}$. The model calculations with these three data sets were carried out separately because the present version of "NETZSCH Thermokinetics" only allows eight measurements to be loaded in the same project. After loading in the data and before starting the kinetic evaluation, each measurement is desmeared, smoothed and temperature-corrected with regard to slight sample self-heating [3]. An optimum fit to the measuring data can only be achieved by a model that takes into account the autocatalysis as well as the reverse reaction of DCPD starting at high temperatures.

$$\begin{aligned}-\frac{dc_{\mathrm{CPD}}}{\mathrm{d}t} &= A_1 \exp\left(\frac{-E_{A,1}}{RT}\right)c_{\mathrm{CPD}}^2(1+K_{\mathrm{cat}}c_{\mathrm{DCPD}})\\ &\quad - A_2\exp\left(\frac{-E_{A,2}}{RT}\right)c_{\mathrm{DCPD}}. \qquad (1)\end{aligned}$$

#done#

If the reaction type of the "*n*th-order with autocatalysis" – available in NETZSCH. Thermokinetics – is used for the forward reaction, then two preconditions will be assumed: (a) the activation energy of the autocatalyzed reaction is the same as that of the non-catalyzed parallel reaction; (b) only the pre-exponentials are different. Usually, these are not correct assumptions. Because of the permanent presence of high correlation between the activation energy and the pre-exponential, and also considering the occasional error in the measurements, one accepts that the above is the most practical solution. Of course, one cannot then interpret the parameter K_{cat} which is connected to the above reaction type. Hovat [6] makes an analogue assumption to take into account the autocatalysis for isothermal measurements.

If, in the calculation, the reaction orders n for the forward and back reactions are also optimized, then one obtains values very close to $n_1 = 2$ and $n_2 = 1$, respectively. For this reason, all further calculations have been carried out using $n_1 = 2$ and $n_2 = 1$.

Fig. 2 shows the comparison between measured and calculated curves of the data set measured with the

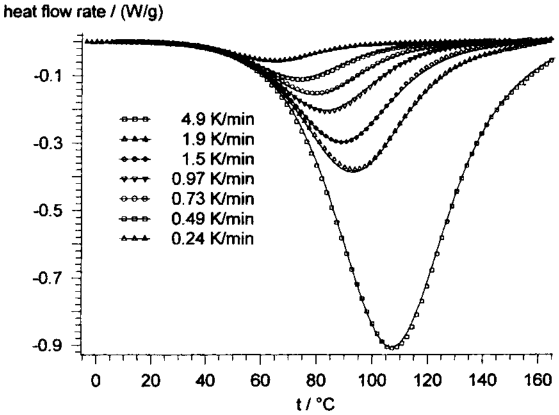

Fig. 2. Comparison between measured (symbols) and calculated (lines) DSC-curves for different heating rates.

Table 1
Results of the kinetic analysis for three different data sets

Parameter	Data set, MDSC 2920	Data set 1, DSC 2C	Data set 2, DSC
$\lg(A_1/\mathrm{s}^{-1}\,\mathrm{l\,mol}^{-1})$	5.973±0.017	5.942±0.03	5.966±0.05
$E_{A,1}/(\mathrm{kJ\,mol}^{-1})$	69.17±0.12	69.01±0.20	69.15±0.29
$\lg(K_{cat}/\mathrm{l\,mol}^{-1})$	0.022±0.0008	0.028±0.0016	0.029±0.0017
$\lg(A_2/\mathrm{s}^{-1})$	12.66±1.6	13.21±0.6	13.23±0.8
$E_{A,2}/(\mathrm{kJ\,mol}^{-1})$	142.1±12.2	142.0±5.5	142.3±7.6
Correlation	0.9998	0.9997	0.9997

MDSC 2920. The fit on the experimental data is perfect. Table 1 summarizes the results of the kinetic optimization based on all three data sets. As NETZSCH Thermokinetics works with degrees of conversion (degrees of reaction) instead of concentrations, two recalculations were necessary to obtain the usual molar quantities.

1. The values of lg A given by the program for the second-order reaction must be divided by the start concentration of CPD. Only then can the pre-exponentials be compared to the literature data. Using the value of density $\varrho_{\mathrm{CPD}} = 0.7968$ g cm^{-3} [6] at 25°C results in a concentration $c_{\mathrm{CPD},0} = 12.073$ mol l^{-1}. The higher density of DCPD ($\varrho_{\mathrm{DCPD}} = 0.9774$ g cm^{-3} at 25°C) leads to a decrease of the reaction volume during the reaction. This effect is not taken into account because it is partially compensated by the unknown expansion of the reacting system when the temperature increases.
2. To convert K_{cat} to values which are consistent with that of Eq. (1) it must be multiplied by the reciprocal concentration of the autocatalytic component ($1/c = M_{\mathrm{DCPD}}/\varrho_{\mathrm{DCPD}} = 0.135$ l mol^{-1}).

The values of the Arrhenius parameters for both reactions (Table 1) were found in exactly at the expected range. Under the assumption that the reaction starts from pure CPD and proceeds to pure DCPD, the values received for K_{cat} indicate an autocatalytic acceleration of the reaction by 140–165%. This acceleration value is in the range found by Hovat [6] and Schmid [7].

It is essential to take the autocatalysis into account in order to achieve a high quality fit of the model to the experimental data. This is clearly demonstrated in Fig. 3. The dashed lines show the modelling of the total reaction as a simple second-order reaction. They differ greatly from the experimental points. Contrary to this the complete model, which also contains the autocatalysis, is practically identical to the experimental points (Fig. 2). For reasons of clarity, Fig. 3 shows only the curves for three heating rates, whereas the calculation was carried out with eight scans. Of course, kinetic parameters calculated with the simple second-order reaction ($\lg(A_1/\mathrm{s}^{-1}\,\mathrm{l\,mol}^{-1}) = 7.48$ and $E_A = 78.6$ kJ mol^{-1}) are erroneous. Ignoring the back reaction of DCPD to CPD has practically no the influence on fit quality and on the results of the forward reaction ($\lg(A_1/\mathrm{s}^{-1}\,\mathrm{l\,mol}^{-1}) = 5.93$, $E_A = 68.9$ kJ mol^{-1}). The reason for this is that the information about the beginning reaction is contained, under the given reaction conditions, in the data points of the last reaction phase. Therefore it is not surprising that the statistical scatter of the activation parameters is clearly more pronounced for the back reaction. Possible slight errors in the baseline drift correction of the DSC curves influence, more or less, only the values of the kinetic parameters of the back reaction. If

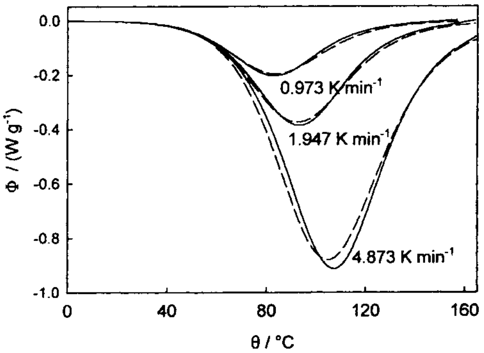

Fig. 3. Calculated DSC-curves, using the Arrhenius parameters of Table 1. Solid lines: complete model with autocatalysis and retro-Diels–Alder reaction (within the line width identical with experimental curves). Dashed lines: ideal second order reaction model.

Table 2
Statistical analysis of the three possible models, using the F-test [1]

Model	F_{exp}	$F_{\mathrm{crit}}(0.05)$
Forward reaction: 2nd order with autocatalysis Reverse reaction: 1st order	1.00	1.07
Without reverse reaction	1.26	1.07
Ideal 2nd order reaction	14.78	1.07

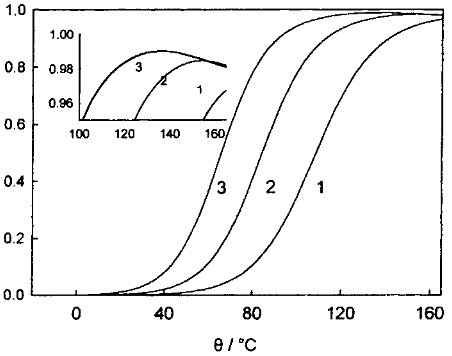

Fig. 4. Degree of reaction vs. temperature at three heating rates: (1) 5 K min^{-1}, (2) 1 K min^{-1}, (3) 0.25 K min^{-1}. Inset scaling up for the higher reaction temperatures.

one evaluates the fit quality achieved with the three models (model 1: second-order reaction including autocatalysis and first-order back reaction, model 2: missing back reaction, model 3: simple second-order reaction), using the F-tests [1] that are well known in the statistics, one sees clearly that model 1 results in a significantly better fit quality than both the other models 2 and 3 (Table 2). The statistical quantity F_{crit} was calculated based on an error probability of 5%. F_{exp} is the quotient of the variances of each model divided by the variance of the best model. If, for a given model, $F_{\mathrm{exp}} > F_{\mathrm{crit}}$ is valid, then this model is significantly less suitable than the best model to describe the data set.

Fig. 4 shows the changes of the degree of reaction calculated for three heating rates using model 1. The inset of this figure shows clearly the temperature range at which, at low heating rates, the rate of the back reaction is greater than that of the forward reaction. Thus, this model calculation additionally confirms the method of preparation of CPD from DCPD by means of destructive distillation.

4. Conclusions

The dimerization of CPD is a suitable test reaction for the kinetic evaluation of DSC curves. The initial substance can be easily obtained from the commercial DCPD. An optimum fit to the experimental data can only be obtained by taking into account the autocatalysis as well as the back reaction of DCPD at higher temperatures. Even in this complicated case, compared with simple nth order reactions, it is possible to achieve reliable values for the process parameters by using modern methods of kinetic analysis and data sets from the measurements with different heating rates. The complete procedure, preparation of the initial substance, DSC measurements and kinetic evaluation, can be realized within 2–3 days. Concerning the cost/performance ratio for practical kinetic studies, this seems to be a reasonable time effort to check the performance of kinetic methods.

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