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A simple method for determining activation energies of organic reactions from DSC curves[1]

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Abstract

An approximate formula for a rapid and simple estimation of activation energies from DSC curves is given and applied to various homogeneous reactions. The results obtained are compared with the approximate values of the Duswalt method and with the results by the mathematically more demanding method of Borchardt and Daniels (additional application of multiple linear regression). In this connection the efficiency of the new approximation method is demonstrated. © 1998 Elsevier Science B.V.

Keywords: Activation energy; DSC; Kinetics; Non-isothermal analysis

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1. Introduction

Chemists, involved in making preparations, hitherto made only little use of the methods of thermal analysis, compared to other established analytical techniques. The reason for this is not the unavailability of instrumentation, but the poor familiarity of many chemists with the procedures necessary for measurement and evaluation.

The various known methods enable the determination of many important data with little expenditure and with sample masses of only a few milligrams [1,2]. For example, the calculation of kinetic parameters from thermoanalytical measurements (e.g. DSC measurements) for simple reactions is no problem. Many methods are available for the evaluation:

- direct methods (e.g. Borchardt and Daniels [3]),
- integral methods (e.g. Coats and Redfern [4]) and
- differential methods (e.g. Freeman and Carroll [5]).

Besides, there are different approximation methods, which only make use of special points of the peak, e.g. peak maxima or points of inflection (see Refs. [6,7]). Exact results, however, are only obtained by evaluations including all data points and making use of non-linear regression analysis [8], which employs the mathematical model without any transformations, e.g. linearization.

For most applications (e.g. kinetics), efficient and validated software is becoming only gradually available, these evaluation methods remain inaccessible to those, who do not want to implement them on their own. Thus, we like to introduce here a simple method

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to determine the activation energy of homogeneous reactions in the liquid phase from the measured curve of a differential scanning calorimeter (DSC).

2. Methods

An approximate value for the activation energy E_A may be obtained without great mathematical manipulation (Eq. (2)), from the following Eq. (1) which has been developed from numerical methods [9] and is based on the fact that the $\alpha(t)$ curves of homogeneous reactions are almost independent of the reaction order x for small values of α:

$$E_A \approx \frac{\mathrm{R}T^2}{\alpha}\frac{1}{\beta}\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{\mathrm{R}T^2}{\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}T} \tag{1}$$

where T is the temperature, at which the reaction rate is ca. 0.4 times the maximum rate, $\mathrm{d}\alpha/\mathrm{d}t$ the rate of conversion at this temperature T (and constant heating rate β), α the degree of conversion, up to temperature T, and R the universal gas constant ($=8.3141\ \mathrm{J\,K^{-1}\,mol^{-1}}$).

To evaluate the activation energy by means of Eq. (1), one needs only three parameters, which are determined according to Fig. 1:

1. the temperature T, at which the reaction rate is ca. 40% of the maximum reaction rate at temperature $T_{\max}$ (here, the deviations due to certain simplifications compensate to the greatest extent in model reactions);
2. the value of $\mathrm{d}\alpha/\mathrm{d}T$ at this temperature, which is proportional to the signal height (difference between measured curve and interpolated baseline); and
3. the degree of conversion α at this temperature, which is represented by the partial peak area.

Another simple method to estimate the activation energy was reported by Duswalt [7]:

$$E_\mathrm{A} \approx \mathrm{R}\ln 2\frac{\overline{T}^2}{\Delta T_\mathrm{d}} \tag{2}$$

here, ΔT_d is the temperature interval around the average temperature $\overline{T}$, within which the rate of conversion has doubled (Fig. 2). With respect to its derivation, this approximation should apply only to first-order reactions.

Following Borchardt and Daniels [3], the rate constant k as a function of temperature T and, thus, the frequency factor k_∞ and E_A can be calculated from Eq. (3):

$$k(T) \equiv \frac{(\mathrm{d}\alpha/\mathrm{d}t)}{c_0^{x-1}(1-\alpha)^x} = k_\infty \exp\left(-E_\mathrm{A}/\mathrm{R}T\right) \tag{3}$$

here, c_0 is the initial concentration of the reactant and x the reaction order.

In this method, the kinetic parameters are obtained by evaluation of all data. Plotting Eq. (3) as an Arrhenius plot by varying the reaction order, x, leads to the optimal x.

By application of MLR (multiple linear regression) the reaction parameters k_∞ and E_A and x can be

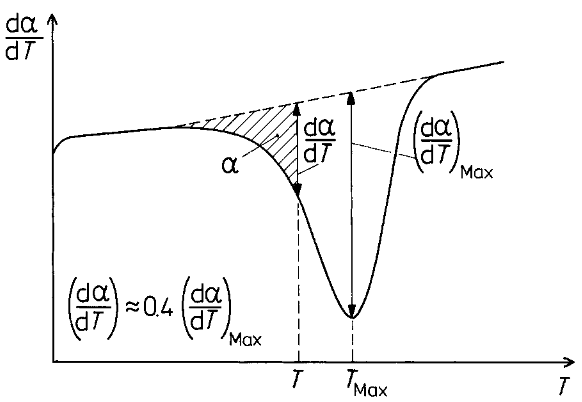


Fig. 1. Determination of parameters from a DSC curve necessary for approximation Eq. (1).

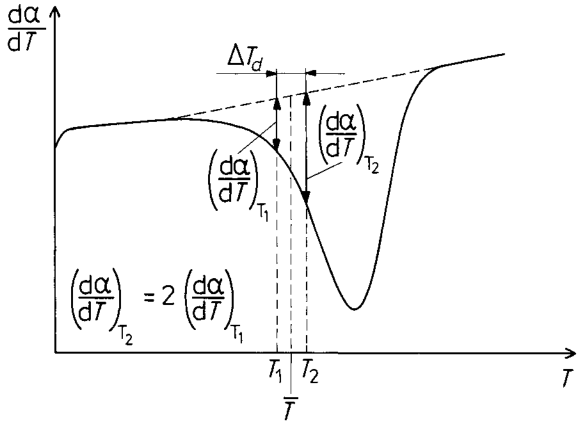


Fig. 2. Duswalt method to estimate the activation energy from a DSC curve.

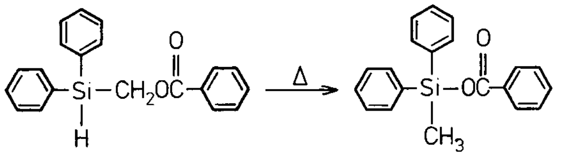
obtained simultaneously [1]. In this work, the MLR is only used to confirm the supposed reaction order.

Prior to the kinetic evaluation of the data, the already described algorithm [1,10] was applied.

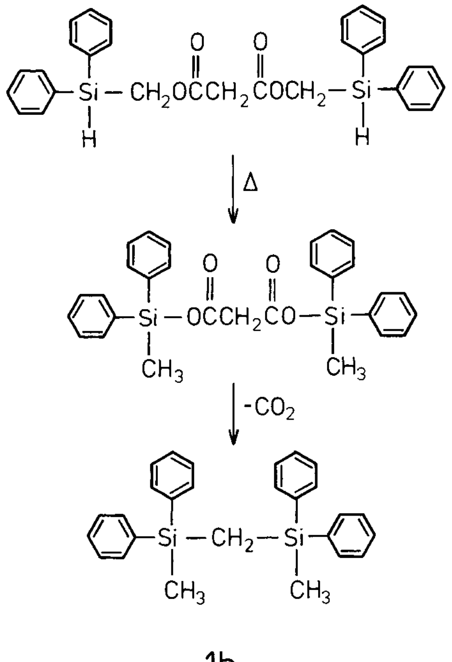
3. Experimental

To compare the validity of Eqs. (1) and (2) with the Borchardt and Daniels method, the following reactions were investigated:

1. The thermally induced single or double rearrangement, respectively, of an organosilicon ester (a) (benzoyloxymethyl)diphenylsilane [11] and (b) malonic acid bis[(diphenylsilyl)methyl]ester [12]):

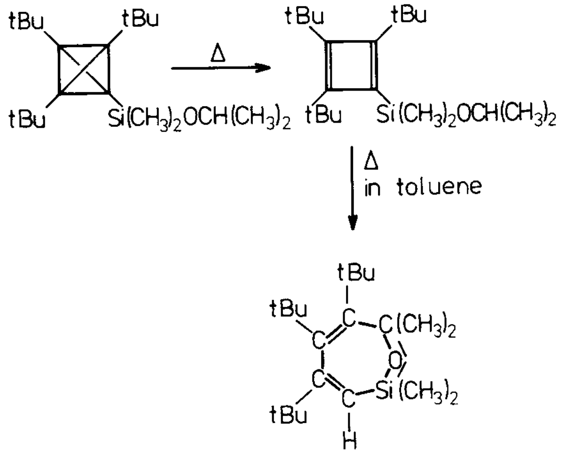


1a

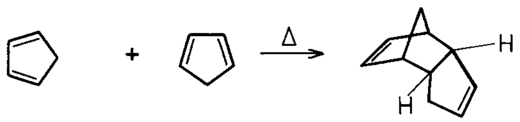


1b

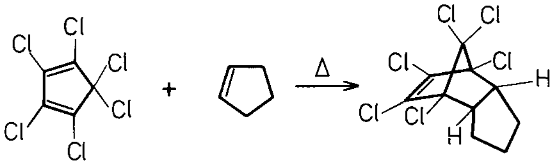
2. The rearrangement with ring expansion of tri-*tert*-butyl(isopropoxydimethylsilyl)tetrahedrane leading to the oxasilepine in a 0.40 molar solution in toluene [13]:



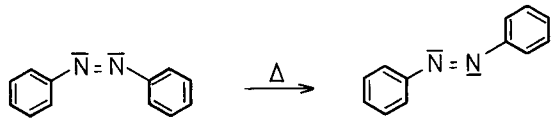
3. As an example of a Diels–Alder reaction, the dimerization of cyclopentadiene (from dicyclopentadiene by cracked distillation at 170°C, repeated distillation for purification while the receiving flask was cooled in an ice bath) in 1,4-dioxan (spectroscopically pure, shaken with NaOH, refluxed for 1 h over sodium, freshly distilled):



4. the Diels–Alder-reaction with inverse electron demand of hexachlorocyclopentadiene (freshly distilled) with cyclopentene (freshly distilled) in solution. The hexachlorocyclopentadiene was used in excess and simultaneously served as solvent, thus the reaction was carried out as pseudo-first order:



5. The thermal *cis→trans* isomerization of azobenzene (recrystallized from petroleum ether) in the melt [14]:



The DSC curves were recorded by a power-compensating microcalorimeter Biflux MCB (Thermanalyse, France) or a heat-flux calorimeter Heraeus TA 500 (Heraeus, Germany). The heating rates applied were in the 0.1–1.0 K min^{-1} range. The amount of substance was chosen between 10 and 40 mg. Sealed glass ampoules were used as sample holders for the MCB and aluminium crucibles for the Heraeus instrument, respectively. As a reference, usually a totally reacted sample and in a few cases an empty sample holder were used.

4. Results and discussion

In Table 1 (for an individual DSC curve of each reaction) the values for the activation energy, as calculated according to Eq. (1), are compared with the values by the Duswalt approximation. Listed as “reference” are the results we determined by the Borchardt and Daniels evaluation of the same calorimetric curves (the variation around the listed value lies within 2% for independent measurements of a definite reaction) and some values taken from the literature. The latter had been determined by isothermal, spectrometric measurements at different temperatures.

As shown in Table 1, the differences between the activation energy according to Eq. (1) and the values obtained by evaluation of all data (i.e. the full curve, Borchardt and Daniels) lies within 4% (with the exception of reaction 1b). The values obtained by the Duswalt approximation, on the other hand, are strongly dependent on the region chosen for evaluation. Using for T_2 (compare Fig. 2) the temperature, at which the reaction rate is ca. 0.4 times the maximum rate (compare Fig. 1) results in values for E_A which correspond quite well with the data gained by the Borchardt and Daniels method. These values are listed in Table 1. If the temperature region chosen for evaluation is shifted towards the peak maximum the results obtained by the Duswalt method differ significantly in some cases as shown in Table 2 for the *cis-trans* isomerization of azobenzene (reaction 5).

Eq. (1) thus seems to be a reasonable and reliable approximate formula for the estimation of activation energies from DSC curves. It is also often applicable to the approximate determination of the activation energy of such reactions, where several reaction peaks

Table 1
Activation energy: comparison of different calculation methods; x – reaction order, (1) – pseudo-first order

No.	Reaction	x	This work Eq. (1) E_A kJ mol^{-1}	Duswalt Eq. (2) E_A kJ mol^{-1}	Borchardt and Daniels E_A kJ mol^{-1}	Reference data from literature E_A kJ mol^{-1}
1	Rearrangement of organosilicon esters					
	(a) single (1a)	1	115.0	132.7	113.1	
	(b) double (1b)	1	98.8	100.2	107.3	
2	Rearrangement of tetrahedrane derivative	1	193.7	157.6	187.8	
3	Diels–Alder-reaction dimerization of cyclopentadiene	2	70.4	72.0	72.4	72.4[15] 72.4[16]
4	Diels–Alder-reaction hexachlorocyclopentadiene/ cyclopentene	(1)	72.8	65.4	72.7	
5	*cis→trans* isomerization of azobenzene	1	99.2	94.3	102.3	109.0[17] 103.4 [18]

Table 2
The Duswalt method: dependence of the activation energy calculated for reaction 5 on the region of the DSC curve chosen for evaluation; T_{Max}=360.6 K

Temperature region chosen for evaluation	E_A kJ mol^{-1}
337.3–344.4 K	94.3
344.4–354.4 K	70.3
346.1–360.6 K	49.6

overlap, where decomposition of reactants takes place at the later stage or when the end of the reaction is not discernible due to an uncertain baseline construction.

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References

[1] W. Hemminger, H.K. Cammenga, Methoden der Thermischen Analyse (Anleitungen für die chemische Laboratoriumspraxis Band XXIV), Springer, Berlin und Heidelberg, 1989.
[2] H.K. Cammenga, M. Epple, Angew. Chem. 107 (1995) 1284; and Angew. Chem. Int. Ed. Engl. 34 (1995) 1171.
[3] H.J. Borchardt, F. Daniels, J. Amer. Chem. Soc. 79 (1957) 41.
[4] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[5] E.S. Freeman, B. Carroll, J. Phys. Chem. 62 (1958) 394.
[6] H.E. Kissinger, J. Res. Natl. Bur. Stand. 57 (1956) 217; Anal. Chem. 29 (1957) 1702.
[7] A.A. Duswalt, Thermochim. Acta 8 (1974) 57.
[8] E. Koch, Angew. Chem. 95 (1983) 185.
[9] Ya.A. Belikhmaer, V.A. Bir, Termicheskii Analiz i Fazovye Ravnovesiya (Thermal Analysis and Phase Equilibria) (1982) 6, in Russian.
[10] S. Sarge, Ph.D. Thesis, Technical University of Braunschweig, 1988.
[11] R. Tacke, F. Wiesenberger, B. Becker, R. Rohr-Aehle, P.B. Schneider, U. Ulbrich, S.M. Sarge, H.K. Cammenga, T. Koslowski, W. von Niessen, Chem. Ber. 125 (1992) 591.
[12] F. Wiesenberger, Ph.D. Thesis, University of Karlsruhe (TH), 1991.
[13] G. Maier, R. Wolf, H.-O. Kalinowski, R. Boese, Chem. Ber. 127 (1994) 191.
[14] H.K. Cammenga, S.M. Sarge, S. Eligehausen, Solid State Ionics 32/33 (1989) 625.
[15] A. Wassermann, Diels–Alder Reactions, Organic Background and Physico-chemical Aspects, Elsevier Publishing Company, Amsterdam, London, New York, 1965.
[16] J. Sauer, H. Wiest, A. Mielert, Chem. Ber. 97 (1964) 3183.
[17] G.S. Hartley, J. Chem. Soc. (1938) 633.
[18] E. Wolf, H.K. Cammenga, Z. Phys. Chem. (Frankfurt/Main) 107 (1977) 21.