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EFFECTS OF EXPERIMENTAL VARIABLES ON THE DETERMINATION OF KINETIC PARAMETERS WITH DIFFERENTIAL SCANNING CALORIMETRY. I. CALCULATION PROCEDURES OF OZAWA AND KISSINGER

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ABSTRACT

The effects of sample mass and particle size on the determination of kinetic parameters with the calculation procedures of Ozawa and Kissinger in differential scanning calorimetry were studied with factorial designs. Sodium bicarbonate, three organic hydrates (potassium oxalate hydrate, mercaptopurine hydrate, and sodium citrate dihydrate) and two substances giving solid–solid transformations (potassium nitrate and hexamethylbenzene) were studied. It was found that both sample mass and particle size could influence the values of the kinetic parameters, but the extent of these effects was different for each substance.

The Kissinger procedure did not have practical advantages over the Ozawa method. In some cases it was necessary to use the temperature at half conversion instead of peak temperatures in the Ozawa plotting, because the conversions at peak temperature could vary considerably with heating rates. Sharp and narrow transition peaks were found to lead to extremely high values of activation energy and pre-exponential factor. It is not justified to attribute any physical meaning to such values.

INTRODUCTION

Experimental variables may affect peak characteristics in differential scanning calorimetry (DSC) [1–5]. Kinetic parameters calculated from DSC peaks should, therefore, also be affected by the choice of experimental conditions. Many examples of this are given in the literature [6–10], and it has been stated that there is no one area in thermal analysis so much affected by the operational variables as the determination of kinetic parameters [6].

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In all mathematical procedures to calculate activation energies, the temperature in the sample is assumed to be uniform [7]. However, if the sample is heated, a temperature gradient in the powder bed exists, which broadens the peak. With thermogravimetry it was shown that an increase in heating rate or sample size resulted in a lowering of activation energy [11]. Attempts have been made to make quantitative correlations between kinetic parameters and heating rate and sample size [12]. Particle size (distribution) may also effect the results [10,13]. However, in some instances it was found that the error of the determination is so large that no effects are observed [10].

This series of papers presents the results of a factorial-design study of the effects of heating rate, sample size and particle size (distribution) on the determination of reaction order, activation energy and pre-exponential factor in a number of solid-state reactions. Part I gives the results determined with the calculation methods of Ozawa [14,15] and Kissinger [16]; part II presents the parameters obtained with the method of Freeman and Carroll [17].

EXPERIMENTAL

Materials

As models for solid-state reactions the following substances were used:

(a) sodium bicarbonate ($NaHCO_3$) (Baker Chemicals, The Netherlands), which evolves CO_2 at approximately 156°C;

(b) potassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$) (Baker Chemicals, The Netherlands), which dehydrates at approximately 160°C;

(c) 6-mercaptopurine monohydrate ($C_5H_4N_4S \cdot H_2O$) [Aldrich (Europe)] which dehydrates at approximately 160°C;

(d) sodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot H_2O$) (De Onderlinge Pharmaceutische Groothandel, The Netherlands) which dehydrates at 150–160°C;

(e) potassium nitrate (KNO_3) (Baker Chemicals, The Netherlands), which exhibits a solid–solid transition at 128°C; and

(f) hexamethylbenzene ($C_{12}H_{18}$) [Aldrich (Europe)], which undergoes a solid–solid transition at 110°C.

All substances were of high-purity grade (> 98%). Their (mean) particle sizes are given in Table 1. The fractions were collected by sieving. Sieving of mercaptopurine hydrate was not feasible because of the very small particle size.

Methods

The equipment, a commercial heat-flux DSC apparatus, has been described previously [1]. Weighings were done on an electronic microbalance and were reproducible within 0.040 mg. An Ott planimeter (type 30139) was

TABLE 1

Mean particle sizes of investigated substances (in μm)

Substance	Fractions				
	Comminuted (jet mill)	Small	Medium	Large	Complete size spectrum
Sodium bicarbonate	2–10	18.4	34.2	62.4	43.0
Potassium oxalate H_2O	< 10	90	202	523	314
Mercaptopurine H_2O	5	[a]	[a]	[a]	15.8
Sodium citrate 2 H_2O	4–7	201	368	644	434
Potassium nitrate	2–5	< 160	233	433	337
Hexamethylbenzene	5–10	139	335	> 500	326

[a] Sieving not feasible.

used to determine the areas under the curves. For calorimetric and temperature calibration ultrapure indium (purity > 99.99%) was used. In the Ozawa calculation procedure, the logarithm of the heating rate, β (in K sec^{-1}), is plotted against the reciprocal of the peak temperature, T_p (in K), and the activation energy, E_a (kJ $mole^{-1}$), is calculated from the slope (which corresponds to $-0.4567\ E_a/R$) of the straight line obtained by linear regression [14,15]. In the Kissinger procedure, the slope of the plot of ln (β/T_p^2) vs. $1/T_p$ yields the activation energy [16]. The pre-exponential factors (Z in sec^{-1}) are calculated from the ordinate intersections of the straight lines.

Study design

All tests were carried out in duplicate and in random order. In the studies of the effects of sample mass and heating rate, the following experimental conditions were applied.

Particle size: medium size fraction;
Sample holders with pierced lids;
No reference compound, no dilution;
Stream of flowing nitrogen 24–36 ml min^{-1};
Variables: Heating rate (in K sec^{-1}): 0.04, 0.08, and 0.16; sample mass (mg): 1.0, 2.0, 4.0, 6.0, and 8.0.

In the studies of effects of particle size and heating rate, the following experimental conditions were applied.

Sample mass 1.960–2.040 mg, accurately weighed;
Sample holders with pierced lids;
No reference compound, no dilution;
Stream of flowing nitrogen 24–36 ml min^{-1};

Variables: Heating rate (in K sec^{-1}): 0.01, 0.02, 0.04, 0.08, 0.16 and 0.32; particle size: comminuted, small, medium, large, and complete size spectrum.

RESULTS AND DISCUSSION

In the derivation of the Ozawa procedure it is implicitly assumed that the conversion (α) at the peak temperature (T_p) is constant for any heating rate. As we found this conversion to vary sometimes, we also determined the temperatures at half conversion ($T_{1/2}$) from the conversion curves and used these temperatures in the Ozawa and Kissinger plots. In general, we found that the use of $T_{1/2}$ instead of T_p in the plots only gives straight lines if the conversion at T_p is more than 50% (i.e. if $T_{1/2}$ is found as a point in the descending edge of the peak).

The Kissinger procedure was found to have no practical advantages over the Ozawa method: the activation energy is practically the same, but its coefficient of variation is higher. We showed earlier that the 'shape index', used by Kissinger to determine the reaction order [16], can only be determined with fairly large standard deviations and it depends on the experimental variables [3].

Sodium bicarbonate

The kinetic parameters E_a and ln Z obtained from peak temperatures with the Ozawa method are given in Table 2. The standard deviation of the

TABLE 2

Kinetic parameters obtained from peak temperatures for $NaHCO_3$ using the Ozawa method

Variable	E_a (kJ $mole^{-1}$)	s_E (kJ $mole^{-1}$)	ln Z
Mass (mg)			
1	125.6	2.23	31.68
2	111.0	2.49	27.61
4	99.1	3.70	24.02
6	114.7	5.44	28.54
8	114.8	3.48	28.48
Particle size			
Comminuted	97.1	1.37	24.77
Small	103.3	1.19	25.77
Medium	108.6	1.03	26.86
Large	113.9	2.11	27.90
Complete spectrum	103.7	2.50	25.74

activation energy s_E is also presented. The values from the temperatures at $\alpha = 0.5$ and those calculated with the Kissinger method are practically the same. The mean coefficient of variation (CV) was approximately 3.2% in the experiment with different masses and 1.6% in the case of different particle sizes. Significant effects on E_a of both masses and particle sizes (at $P = 0.01$) were observed. The activation energy for the sample mass of 1 mg is rather high as the differences between peak temperatures at the respective heating rates are smaller than at higher masses. The activation energy for the 4 mg samples is very low. This appears to be due to a very low value of T_p at the lower heating rate of 0.04 K sec^{-1}. If E_a at 4 mg was calculated with only the temperatures at the higher rates, a value of 111.7 kJ $mole^{-1}$ was obtained.

Table 2 shows an increase in E_a and ln Z with increasing particle size. This was to be expected, as the particles are in a less activated state and, therefore, less subject to transformation, as was shown earlier by Huettenrauch [18].

Because of self-insulating effects due to larger thermal resistances, the peak temperatures for the decomposition peaks of larger particles are higher than for smaller particles. Apparently, when the heating rate is increased these self-insulating properties are only partly compensated, which leads to lower differences in heating rates for the larger particles and, therefore, to an increase in the slope of the Ozawa plot.

Potassium oxalate monohydrate

The Ozawa and Kissinger plots with peak temperatures of potassium oxalate dehydration curves gave the results presented in Table 3. The reproducibilities were slightly worse than for sodium bicarbonate and no significant effects were observed. If $T_{1/2}$ was used instead of T_p the values for the kinetic parameters and their standard deviations were approximately the same. No statistically significant effects of particle size or sample mass were observed.

Mercaptopurine hydrate

Activation energies and pre-exponential factors calculated for the mercaptopurine dehydration with Ozawa's method are given in Table 4. The values obtained are much lower than those reported by Niazi [19]. He found activation energies between 211.5 and 264 kJ $mole^{-1}$ with sample masses of 8–9 mg and heating rates of 20, 5 or 2 K min^{-1}. He only compared temperatures at constant conversions. However, we found that at the higher sample masses ($\geqslant 8$ mg) inclusion of peak temperatures at $\beta = 0.16$ K sec^{-1} gave curved Ozawa plots. If the 'best' straight lines out of such curved plots were estimated, E_a values of 210–273 kJ $mole^{-1}$ were obtained (with standard

TABLE 3

Potassium oxalate monohydrate: kinetic parameters obtained from peak temperatures using the methods of Ozawa and Kissinger

Variables	Ozawa		Kissinger	
	E_a (kJ mole^{-1})	ln Z	E_a (kJ mole^{-1})	ln Z
Mass (mg)				
1	91.3	24.16	89.7	23.56
2	86.8	22.29	85.0	21.56
4	92.9	23.76	91.2	23.13
6	96.1	24.33	94.6	23.77
8	89.6	22.14	87.7	21.40
CV (%)	7.8		7.9	
Particle size				
Comminuted	105.3	29.30	104.7	29.06
Small	90.8	23.56	89.2	22.95
Medium	97.1	25.50	95.8	25.02
Large	98.6	26.08	97.5	25.64
Complete spectrum	94.1	24.62	92.7	24.08
CV (%)	4.2		4.2	

TABLE 4

Kinetic parameters for mercaptopurine dehydration obtained using Ozawa's method

Variables	Values with T_p			Values with $T_{1/2}$		
	E_a (kJ mole^{-1})	s_E (kJ mole^{-1})	ln Z	E_a (kJ mole^{-1})	s_E (kJ mole^{-1})	ln Z
Mass (mg)						
1	79.6	8.4	17.25	128.8	11.3	31.44
2	99.2	5.2	22.53	128.6	9.9	31.09
4	119.8	7.3	27.82	130.1	8.3	31.03
6	123.0 [a]	12.5	28.37	137.1	6.0	32.86
8	130.6 [a]	27.5	30.37	138.9	11.6	33.27
Particle size						
Complete spectrum	118.9	2.33	28.04	130.5	1.95	31.62
Comminuted	130.2	2.98	31.28	136.8	5.42	33.76

[a] T_p at heating rate 0.16 K sec^{-1} omitted as inclusion gave curved plots.

deviations of 45–96 kJ mole^{-1}). If calculated with peak temperatures, the activation energy for the complete size spectrum was significantly lower than for the comminuted sample ($P = 0.01$). An explanation may be found by looking at the complete curves, the shapes of which appear to change with

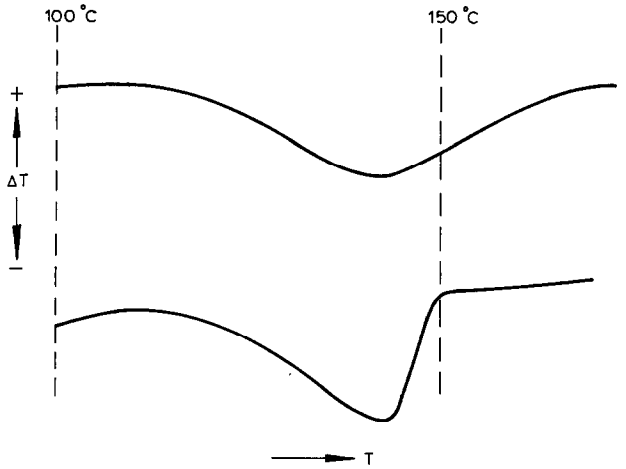

Fig. 1. Peak shapes of mercaptopurine dehydration (low heating rates). Upper curve, complete size spectrum; lower curve, comminuted fraction.

degree of crystallinity (Fig. 1) and heating rate.

At low heating rates the conversion at the peak temperature for the complete size spectrum is approximately 50% whereas at higher rates it is 70%. For the comminuted samples the conversion at the peak temperature remains approximately 75%, independent of heating rate. These differences can also be seen in the reduced-time curves (Fig. 2). It may be stated that nucleation processes lead to relatively low conversions in the initial phase of the reaction. Low conversions in the second part of the reduced-time curves generally indicate that diffusion is then the predominant process. It may therefore be assumed that in the complete-size sample at low rates, diffusion

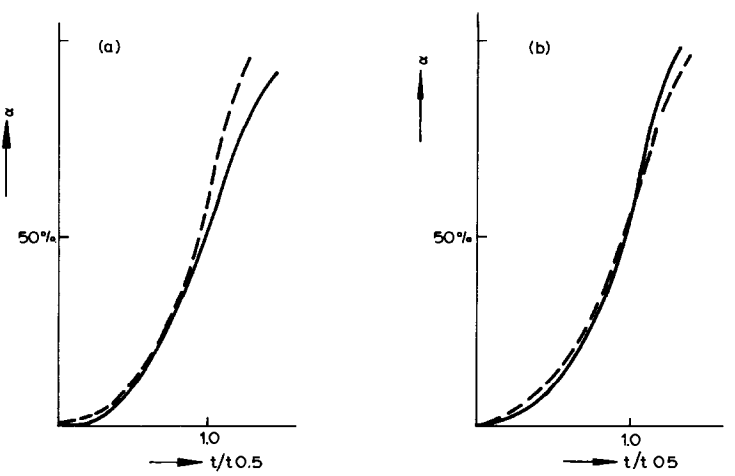

Fig. 2. Reduced time curves for mercaptopurine dehydration. ————, complete size spectrum; - - - - - -, comminuted fraction. Heating rate: (a) 0.01 K sec^{-1}; (b) 0.16 K sec^{-1}.

is a more determining process than nucleation, whereas it is the reverse at high heating rates. Therefore, the conversion at T_p changes with heating rate. For comminuted samples, nucleation is the determining step at any heating rate. It is clear that a change of conversion at T_p with changing heating rate does not allow an Ozawa plot to be drawn, as the assumption of constant conversion in the derivation of the Ozawa method does not apply. If the temperatures at half conversion are used, the activation energies do not differ significantly (Table 4). The same was observed if sample mass instead of particle size was varied.

We may therefore conclude that the Ozawa method with peak temperatures can only be used if we know that the conversions at T_p do not change with changing heating rate. This impairs one of the main advantages of the Ozawa method: its easy use, as only one point of the peak, the peak temperature, has to be determined.

Sodium citrate dihydrate

Table 5 shows that the activation energy for the comminuted fraction is much higher than for the other fractions. This corresponds with a greater standard deviation and is due to the fact that at very low heating rates the comminuted fraction only showed a very small and broad peak, so that the peak temperature could only be determined with large errors. In contrast to what was found with $NaHCO_3$, the large particles of sodium citrate dihydrate had a significantly lower E_a ($P = 0.01$) than the other sizes. At low heating rates the peak temperature is lower for larger than for smaller particles, whereas it becomes increasingly higher at higher heating rates. This means that the temperature differences for large particles are higher, leading to smaller slopes in the Ozawa plot.

TABLE 5

Activation energies with the Ozawa method from peak temperatures of sodium citrate-dihydrate, potassium nitrate and hexamethylbenzene

Particle size	E_a (kJ mole^{-1})		
	Sodium citrate 2 H_2O	KNO_3	Hexamethyl benzene
Comminuted	492	1196	1966
Small	373	2010	1976
Medium	393	2318	1996
Large	298	1600	1507
Complete size spectrum	364	1700	1856
CV (%)	2.6	10.0	10.7

The sharpness of the sodium citrate peaks, in contrast to the broad peaks of the transitions discussed above, indicates that when the temperature of first nucleation is reached, the transition rate accelerates very rapidly, even explosively. This is also shown by the occurrence of negative reaction orders as calculated with the Freeman–Carroll procedure. Once their respective nucleation temperatures are reached the particles react separately and at low heating rates the peak shape is irregular. On the other hand, only a limited number of larger particles have to react to reach 50% conversion. This means that at low heating rates the temperature for this conversion is lower when the particles are larger. However, larger particles also show greater thermal resistance and, consequently, larger thermal lags and greater temperature differences within the powder beds which delay the transition. If the transition times become shorter (i.e. at higher heating rates), these lags and the temperature differences within the bed become greater. The outer sides of the bed are then superheated but the inner parts lag behind in temperature. The higher energy levels of the outer sides of the bed may lead to dissolution of the particles into their released water of hydration and the mean sample temperature needed to reach a 50% conversion becomes higher. This means that the temperature differences between different heating rates are higher for large particles than for smaller ones. Table 5 also shows that the values for the kinetic parameters are very high. This correlates with very sharp peaks which occur over a smaller temperature range than those for the dehydration reactions mentioned above. It can be concluded that the smaller the peaks the higher the activation energies.

Potassium nitrate and hexamethylbenzene

The activation energies for the solid–solid transitions of potassium nitrate and hexamethylbenzene are given in Table 5. Their values were extremely high, and the transition peaks were very narrow and even sharper than for sodium citrate dihydrate. The less perfect comminuted samples of KNO_3 had significantly lower activation energies than the other fractions. The pre-exponential factors were always higher than 10^{100}. The samples with large particles have significantly lower activation energies than the samples with medium-sized particles ($P = 0.05$). Similar reasons as for sodium citrate may account for this behaviour. For hexamethylbenzene no statistically significant effect of particle size was observed.

SUMMARY AND CONCLUSIONS

Factorial experiments were carried out to investigate the effects of sample mass and particle size on kinetic parameters determined with the procedures of Ozawa and Kissinger. We used a commercial heat-flux DSC apparatus

and the following substances: sodium bicarbonate (evolution of CO_2); potassium oxalate monohydrate, 6-mercaptopurine monohydrate and sodium citrate dihydrate (dehydrations), potassium nitrate and hexamethylbenzene (solid–solid transformations).

In general, we found that the use of temperatures at half conversion instead of peak temperatures gave straight lines only if the conversion at the peak temperature was more than 50%. The Kissinger procedure had no practical advantages over the Ozawa method: the activation energy was practically the same but its coefficient of variation was higher. Ozawa plotting for the degradation of sodium bicarbonate gave activation energies of 105–113 kJ $mole^{-1}$ (with coefficients of variation of 1.6–3.2%) and pre-exponential factors of 2.7×10^{10}–5.7×10^{13}.

Significant effects of both sample mass and particle size were observed, which could partly be explained by the more predominant thermal resistances in larger particles. It should be noted, however, that these effects of thermal resistance within the powder bed are only relevant for the Mettler DSC apparatus, in which the sample holder is based on a thermal insulator, so that heat transfer is mainly accomplished through the furnace atmosphere (both by conduction and convection). It is not a priori possible to apply our findings to other types of DSC instruments.

For potassium oxalate monohydrate, no effects of particle size or sample mass were observed.

Ozawa plotting with peak temperatures of mercaptopurine hydrate did not yield 'correct' values, as the conversions at peak temperatures were different for different heating rates. We assume that in complete size spectrum samples nucleation is followed by diffusion as the rate determining step, whereas for comminuted particles nucleation remains the predominant process during the complete decomposition.

The mean activation energy was 384 kJ $mole^{-1}$ (CV 2.6%) for sodium citrate dehydration, 1765 kJ $mole^{-1}$ (CV 10.0%) for potassium nitrate, and 1860 kJ $mole^{-1}$ (CV 10.7%) for hexamethylbenzene. These very high values correlate with the observation that their transition peaks were very sharp and narrow. Large particle samples of sodium citrate dihydrate and potassium nitrate had lower activation energies than samples of the other sieve fractions. For hexamethylbenzene no effect of particle size was observed.

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