Journal of Thermal Analysis, Vol. 37 (1991) 583-596

INFLUENCE OF SAMPLE PARTICLE SIZE AND HEATING RATE ON THE THERMAL DECOMPOSITION OF $K_2C_2O_4$

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(Received March 12, 1990)

The thermal decomposition of $K_2C_2O_4$ in a current of dry nitrogen according to the reaction

$$K_2C_2O_4 \rightarrow K_2CO_3 + CO \qquad (1)$$

is shown to be influenced profoundly by the sample particle size and the heating rate. For finely ground samples, a lower activation energy ($E_a = 255.15 \pm 5$ kJ mol^{-1}) is obtained as compared with the 312.6 ± 6 kJ mol^{-1} observed for crystal chips weighing 30-40 mg. The characteristic temperatures (the reaction start, peak and end temperatures) are markedly reduced by fine grinding. High heating rates tend to separate the thermal decomposition process into two kinetic phases, shown by splitting of the DTG peak. The significance of these observations is discussed, and the results are theoretically accounted for.

The thermogravimetric decomposition of $K_2C_2O_4$ in a current of dry nitrogen according to the reaction:

$$K_2C_2O_4 \rightarrow K_2CO_3 + CO \qquad (1)$$

was undertaken in order to explore the influence of the sample particle size and heating rate. These variables were shown to exert profound effects on the kinetics of (1).

Experimental

Crystal aggregates weighing 30-40 mg and finely ground powders of reagent grade $K_2C_2O_4 \cdot H_2O$ were used. The powders were obtained by

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grinding to paste potassium oxalate crystals and ethyl alcohol in a mortar and subsequently allowing the alcohol to evaporate. The thermal decomposition was carried out on the TG 50 thermal balance of a Mettler TA 3000 thermal analysis system. An atmosphere of dry nitrogen flowing at 100 ml/min was employed throughout.

Results

Behaviour of the powder

The thermogravimetric curve of $K_2C_2O_4 \cdot H_2O$ at a heating rate of 5 deg min^{-1} is shown in Fig. 1. The dehydration of $K_2C_2O_4 \cdot H_2O$ starts at 70^o and is complete at 126^o. The onset temperature of reaction (1), at 467.5^o, agrees well with the predicted value $T_d = 473.6^o$ according to the Kahwa-Mulokozi relation:

$$T_d = 516 - 1.4006\, I_T \qquad \text{(i)}$$

where $I_T = 30.27(\text{kJ mol}^{-1})^{1/2}$ is the value of the ionization potential term [1-3].

The thermogravimetric curves for fine powders of $K_2C_2O_4$ at heating rates between 1 and 5 deg min^{-1} are shown in Fig. 2.

The kinetics of the reaction satisfy the mathematical model of a phase boundary reaction:

$$d\alpha/dt = k(1 - \alpha)^n \qquad \text{(ii)}$$

where k is the rate constant, α is the degree of conversion, and n is the reaction order. This allows derivation of the activation parameters according to the multiple linear equation:

$$\ln (d\alpha/dt) - \ln k_o + E_a(1/-RT + n \ln (1 - \alpha) \qquad \text{(iii)}$$

by the multiple linear regression analysis proposed by Widmann [4], employing the built-in software of the TA 3000 thermal analysis system.

The results summarized in Table 1 give a range of activation energies from 246.41 to 259.67 kJ mol^{-1} with an average of 255.15 ± 5 kJ mol^{-1}. The

Table 1 The kinetic parameters for the thermal decomposition of fine powders of $K_2C_2O_4$. Equation (iii) is the basis of the evaluation

Heating rate β, deg min^{-1}	Sample wt, mg	Kinetic parameters E_a, kJ·mol^{-1}	n	ln K_o	α range of validity of (iii)
1.5	33.228	246.41±10.15	0.24±0.06	29.30±1.56	0.1-0.8
2	32.096	252.06±8.33	0.29±0.05	30.20±1.27	0.1-0.8
3	33.229	252.50±4.90	0.37±0.03	30.23±0.74	0.1-0.8
4	30.148	256.19±3.42	0.45±0.02	30.79±0.51	0.1-0.8
6	35.715	258.20±3.37	0.57±0.02	31.18±0.50	0.1-0.9
8	28.762	258.80±3.60	0.55±0.03	31.27±0.59	0.1-0.8
10	36.738	259.67±4.48	0.61±0.04	31.40±0.66	0.1-0.6
12	29.342	257.35±5.53	0.53±0.05	31.11±0.82	0.1-0.6

Average activation energy E_a = 255.15±5 kJ mol^{-1}

Table 2 The kinetic data and evaluation of the activation energy according to Ozawa for finely powdered $K_2C_2O_4$

Degree of Conversion	Temperature T, K for various heating rates, β							Activation. energy, kJ mol^{-1}
α	1.5	2	2.5	3	4	5	6	
0.1	774.55	779.15	783.65	783.15	793.35	796.65	799.65	257.49
0.2	789.05	794.15	799.15	802.55	808.95	812.65	815.25	260.24
0.3	798.05	803.15	808.65	811.95	818.55	822.65	824.85	254.84
0.4	804.35	809.65	815.15	818.65	825.15	829.65	832.25	256.98
0.5	809.25	814.65	820.65	824.65	830.55	835.15	838.05	260.15
0.6	813.35	818.65	825.15	828.55	835.35	840.65	843.45	252.48
0.7	817.35	822.65	829.15	833.05	840.15	845.15	848.25	243.92
0.8	820.95	826.65	833.15	837.15	837.15	849.65	853.05	243.01

Average activation energy (α = 0.1 to α = 0.7) = 255.03 kJmol^{-1}

reaction order varies from $n = 0.3$ at low heating rates to 0.6 at high heating rates.

The value of the activation energy was confirmed by an alternative evaluation of the data according to the isoconversional method of Ozawa [5], in which the reaction order and the preexponential factor are not as-

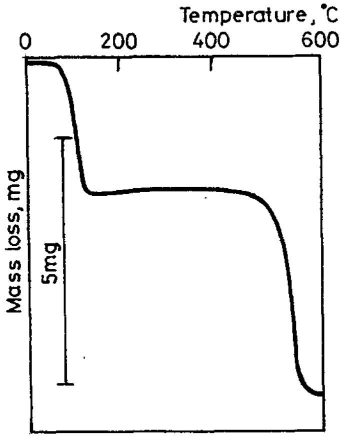


Fig. 1 The TG of $K_2C_2O_4 \cdot H_2O$, heating rate: 5 deg·min^{-1}

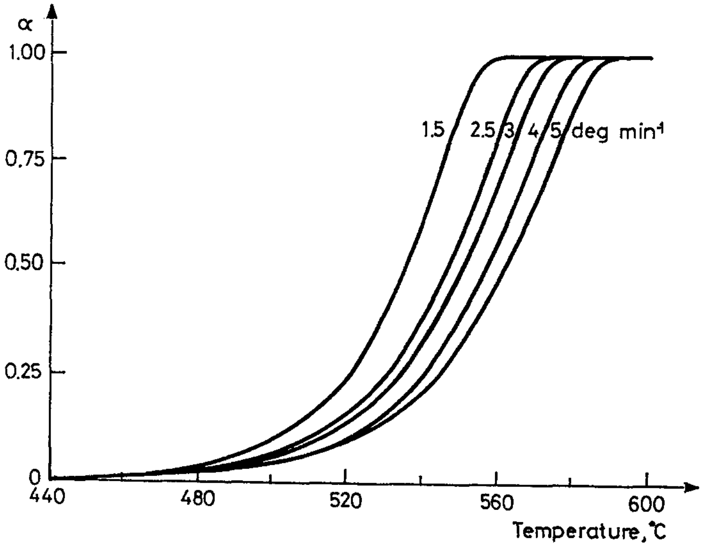


Fig. 2 The temperature displacement of the TG curves for (1) depending on the heating rate from 1 to 5 deg·min^{-1}

sumed. The relevant Ozawa plots and a summary of the results are shown in Fig. 3 and Table 2, respectively.

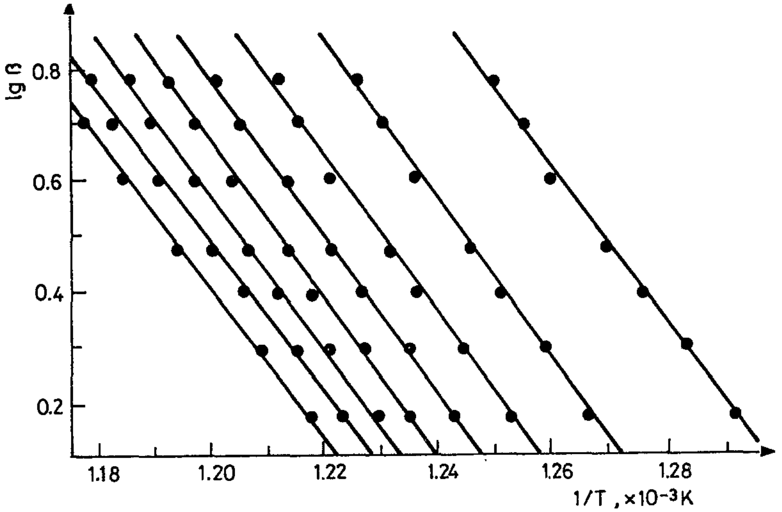


Fig. 3 The Ozawa plots for the thermal decomposition of finely powdered $K_2C_2O_4$ at various heating rates from 1.5 to 6 deg·min^{-1}

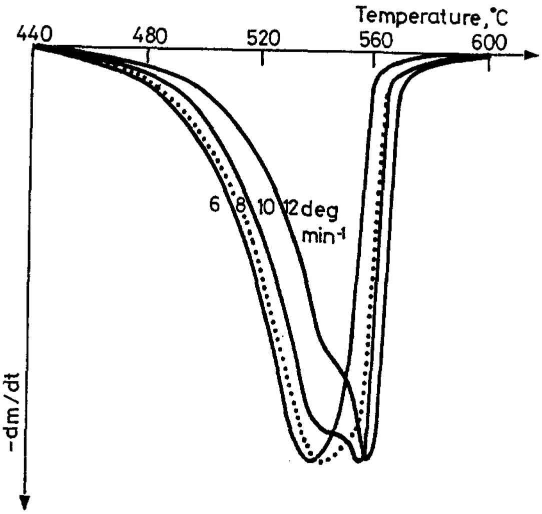


Fig. 4 The DTG curves for (1) showing the complexity of the thermal decomposition process. At high heating rates the powders exhibit the resolution of the peaks to reveal two kinetic phases of the thermal decomposition process

Table 3 The activation energy for the thermal decomposition of crystal chips of 26 - 36 mg weight according to equation (iii)

Heating rate β,	Sample wt,	Kinetic parameters E_a,			α range of
deg.min^{-1}	mg	kJ mol^{-1}	n	ln K_o	validity of (iii)
5	33.099	310.55±3.73	0.66±0.02	38.57±0.55	0.1-0.8
6	35.645	308.72±2.72	0.74±0.01	38.29±0.40	0.1-0.8
8	33.362	312.11±5.25	0.81±0.03	38.74±0.77	0.1-0.8
10	28.685	314.75±9.24	0.78±0.05	39.20±1.34	0.1-0.8
12	26.266	316.96±11.26	0.79±0.09	39.39±1.64	0.1-0.6

Average activation energy: 312.6 kJ mol^{-1}

Table 4 The kinetic data for the thermal decomposition of $K_2C_2O_4$ compact crystals employing the evaluation method according to Ozawa

Degree of conversion α	Temperature T, K for various heating rates β					Activation energy, kJ mol^{-1}
	5	6	8	10	12	
0.1	809.15	811.65	817.55	820.15	825.65	315.9
0.2	822.15	825.45	831.45	834.15	839.45	312.1
0.3	830.15	833.85	840.25	842.65	847.85	309.8
0.4	836.15	839.85	846.65	848.65	854.45	317.2
0.5	841.15	845.25	851.45	854.15	859.85	316.7
0.6	845.65	850.05	856.25	858.65	864.65	315.4
0.7	849.65	854.25	861.05	863.65	869.45	289.3
0.8	854.15	859.05	865.85	868.15	873.0.5	289.0

Average activation energy (α = 0.1 - α = 0.6) = 314.5 kJ mol^{-1}

The kinetic uniformity of the thermal decomposition process appears to be disturbed by high heating rates, as shown by the increasing variance of the kinetic parameters at degrees of conversion greater than α =0.6. The DTG curves (Fig. 4) demonstrate the effect best, showing a deceleration interval at about α = 0.6, because of the subsequent acceleration, this culminates in splitting of the DTG peak. The activation energies from the Ozawa plots are given after the correction proposed by Flynn [6].

Behaviour of compact crystals

The reaction temperatures for compact crystals each weighing between 26 and 36 mg are considerably higher, as shown in Fig. 5, where the TG and DTG curves obtained at a heating rate of 6 deg min^{-1} can be compared for a finely ground sample and a compact crystal weighing 35.64 mg.

The average activation energy obtained according to (iii) for heating rates of from β = 5 deg min^{-1} to 12 deg min^{-1} was 312.6 kJ mol^{-1} (Table 3), in good agreement with the results of the evaluation method according to Ozawa (Table 4 and Fig. 6). The results showed good consistency up to a degree of conversion α<0.7, which is the upper limit before the kinetic parameters for fast heating rates show significant variance.

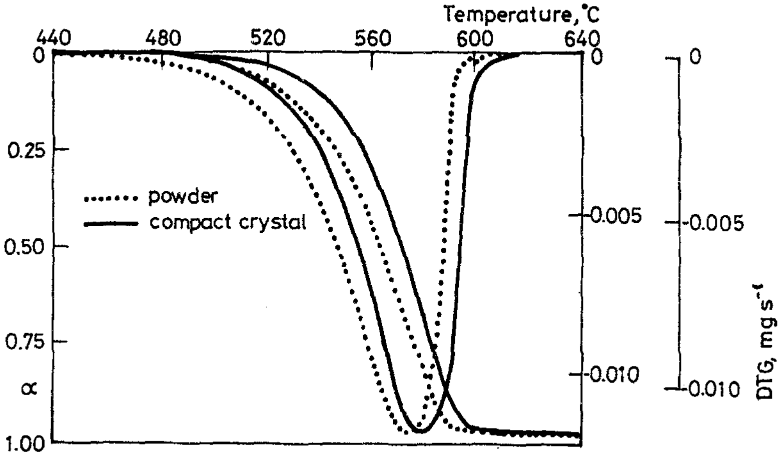


Fig. 5 TG and DTG of powdered $K_2C_2O_4$. . . . . and compact crystal (35.645 mg) —— ; heating rate 6 deg·min^{-1}

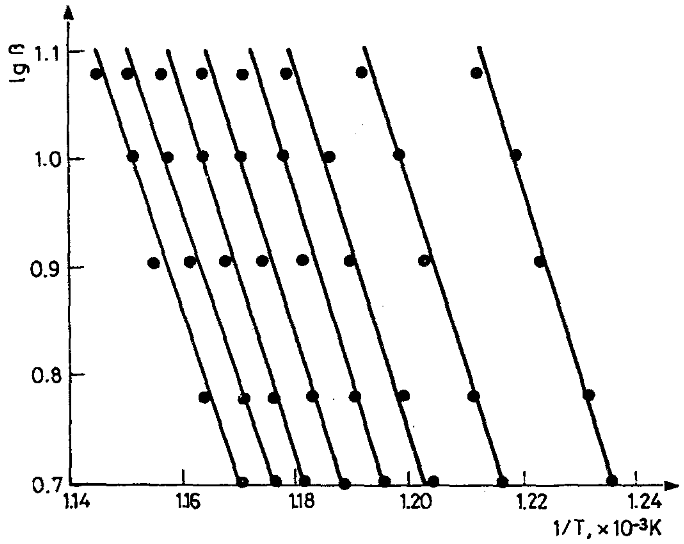


Fig. 6 The Ozawa plots for compact crystals

Discussion

Our mechanistic interpretation of the thermal decomposition of the oxalate is based on the expression [2, 3, 7]

$$E_a = 127 + 1.4853\cdot 10^{-6}(I_T^2 - 9800)^2 \qquad \text{(ii)}$$

where the ionization potential term $I_T = \frac{r_c}{r_i}(\Sigma I)^{1/2}$ is defined by Pauling's covalent radius r_c, the ionic radius r_i in hexacoordination and ΣI, the sum of the ionization potentials of the metal atom. On the basis of (ii), the activation energy of (1) is theoretically predictable.

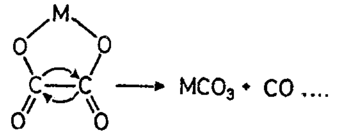
The restriction of the diffusion of a gaseous product from the sample reaction zone is known to influence the thermal decomposition kinetics [8, 9]. When the kinetics is increasingly determined by the rate at which CO diffuses from the reaction zone, the activation energy is no longer predictable according to (ii), and E_a obtained experimentally will be at variance with the value predicted according to (ii). The value of the ionization potential term is I_T = 30.25 (kJ mol^{-1})$^{1/2}$ for potassium, and hence an activation energy E_a = 244.25 kJ mol^{-1} is obtained according to (ii). This agrees reasonably with the experimental values for the powdered samples. We may therefore assume that (1) is diffusion-controlled only in the crystal chips. Indeed, the precision of the activation energy predicted according to (ii) can be increased if we realize that (ii) overestimates the interaction of potassium and oxalate ions. When the correction is made, an activation energy $E_a = 256.09$ kJ mol^{-1} is obtained, in excellent agreement with the experiment.

The cation-oxalate interaction

We previously proposed a mechanism for oxalate thermal decomposition, in which breaking of the C–O bond is considered to be the rate-determining step [3, 7]. Since the multiplicity of the C–O bond decreases with increasing interaction between the metal and oxalate ions, the activation energy will decrease with increasing interaction, to a minimum at $I\frac{2}{r} = 9800$. The activation energy minimum $E_a = 127$ kJ mol^{-1} is the turning point, after which the activation energy starts to increase. The increase in the activation energy suggests an added new factor for the rate-determining step, most probably the breaking of the M–O bond, which, at the prevailing value of the ionization potential term, is now appreciably covalent.

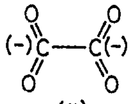
For $Nd_2(C_2O_4)_3$, the activation energy is $E_a = 127$ kJ mol^{-1} ($I\frac{2}{r} \approx 9800$) [3, 7], and hence (I) was proposed as mechanism:

(I)



(2)

For a free oxalate ion (II)



(II)

mechanism (2) can apply with an increased activation energy, since the restraining resonance energy is increased by ½E_R to E_R, i.e. all the C=O bonds of (II) must first be reduced to single bonds. We may assume (I) and (II) to be in vibrational motion, and therefore the activation energies are lowered by the vibrational energy E_ν of the symmetric C–O stretching frequencies.

A general expression for the activation energy in terms of the resonance energy is

$$E_a = E_R - E_i - E_\nu \qquad \text{(iii)}$$

where E_i is the interaction energy. For (I), $E_a = 127 \text{ kJ mol}^{-1}$ (M = Nd) and the interaction energy E_i is

$$E_i\,(I) = 1.4853 \cdot 10^{-6}(0 - 9800)^2 \qquad \text{(iv)}$$

giving $E_i = 142.65 \text{ kJ mol}^{-1}$. The C-O and M-O stretching frequencies are observed in the infrared spectrum at 1320 and 494 cm^{-1}, respectively, for neodymium oxalate [7], giving

$$E_\nu = [\nu(\text{C-O}) + 2\nu(\text{M-O})] = 15.79 + 11.84 = 27.63 \text{ kJ mol}^{-1}.$$

The resonance energy is therefore 297.28 kJ mol^{-1}. It should be noted that E_R is also accessible from the relation

$$E_a(\text{I}) = \tfrac{1}{2}E_R - E_\nu\,(\text{M}-\text{O}) - E_\nu\,(\text{C}-\text{O}) \qquad \text{(v)}$$

Since neodymium oxalate is the reference ($I_T^2 = 9800$ in expression (ii), the expression overestimates the interaction energy E_i for $K_2C_2O_4$ by an amount equal to 11.84 kJ mol^{-1}, the contribution of the M-O vibration, which on correction raises the activation energy $E_a = 244.25 \text{ kJ mol}^{-1}$ calculated according to (ii) to 256.09 kJ mol^{-1} in excellent agreement with the experiment.

Thus, in $K_2C_2O_4$ the interaction is ionic and the contribution from ν(M–O) vanishes. We may use the experimental activation energy $E_a = 255.03 \text{ kJ mol}^{-1}$ for (1) to derive the resonance energy, if we take into consideration the absence of the ν(M–O) contribution. The interaction for $K_2C_2O_4$ is $E_i = 142.65 - 1.4853 \cdot 10^{-6}(I_T^2 - 9800)^2$ for $I_T = 30.27$, giving the uncorrected value of 25.4 kJ mol^{-1}. The corrected value is therefore $25.4 - 11.84 = 13.56 \text{ kJ mol}^{-1}$.

Putting this value in (iii) and the value of $E_\nu = 2E\nu\,(C-O) = 31.33$ kJ mol^{-1} from the stretching frequency of C–O at 1310 cm^{-1}, we obtain $E_R = 299.9$ kJ mol^{-1}, in good agreement with the previously derived value. The value is also in excellent agreement with Pauling's estimate of the resonance energy $\frac{1}{2}E_R = 150.6$ kJ mol^{-1} for a single carboxylate ion [10].

These calculations confirm our mechanism for the thermal decomposition of the oxalate, which, by means of (ii), links the activation energy to the interaction between the metal and oxalate ions [2, 3, 7].

The influence of CO diffusion

Diffusion should limit the reaction rate when the removal of a vapour phase reaction product from the reaction zone in the sample grains is a slow process as compared to the unrestrained reaction rate of the decomposition process at the given temperature. On increase of the thickness to be penetrated by the generated vapour phase, a significant variation in the reaction kinetics should be a good indication of the appearance of a diffusion factor in the reaction kinetics.

The large increase observed in the activation energy for (1) when the fine sample powder is replaced by a compact crystal is therefore attributable to the restricted diffusion of CO, which becomes important in the rate-limiting step. When high heating rates are employed, the observed deceleration phase at about $\alpha = 0.6$ in the DTG curve is therefore explained by the adjustment of the reaction rate to the diffusion rate of CO. Considering the packing geometry of the oxalate ions, the lattice dislocation may be a significant determinant of the nucleation process, by creating the escape routes of CO. The results of the present study show that the kinetic parameters of reaction (1) are consistent with the usual energy barrier model as encountered in homogeneous systems, when the obscuring kinetic processes are contained. There is increasing evidence of the energy barrier model for reactions of condensed phases when a vapour phase is one of the reaction products. Departure from this model can be accounted for by the kinetic factors which influence the diffusion rate of the vapour phase, such as sample weight [11].

The obtained activation energy (255 kJ mol^{-1}) for (1) is in excellent agreement with the value previously obtained from isothermal studies, involving infrared spectroscopy of $K_2C_2O_4$ decomposing in a KBr matrix [12].

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This work was supported by a generous grant from NORAD funds and by the technical assistance of Mr. E. G. Mushi.

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Zusammenfassung – Die thermischer Zersetzung von $K_2C_2O_4$ (entsprechend der Reaktion $K_2C_2O_4 K_2CO_3 + CO$) in einem Strom von trockenem Stickstoff wird durch Partikelgröße und Aufheizgeschwindigkeit wesentlich beeinflußt. Für fein zermahlene Proben wird eine niedrigere Aktivierungsenergie (E_a = 255.15 5 kJ/mol) gefunden als für Kristallchips mit einer Masse von 30-40 mg (E_a = 312.6 6 kJ/mol). Die charakteristischen Temperaturen (für Reaktionsstart, Peak und Endtemperatur) werden durch feines Zermahlen deutlich gesenkt. Große Aufheizgeschwindigkeiten neigen zu einer Separierung der thermischen Zersetzungsprozesse in zwei kinetische Phasen, was durch eine Aufspaltung des DTG-Peaks deutlich wird. Die Bedeutung dieser Beobachtungen wird diskutiert und die Ergebnisse theoretisch erklärt.