

ACTIVATION ENERGY OF THERMAL DECOMPOSITION OF $\text{LaC}_2\text{O}_4\text{Br}$

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The activation energy of the thermal decomposition of finely ground $\text{LaC}_2\text{O}_4\text{Br}$ was determined according to the method of Ozawa as $E_a = 203.83 \text{ kJ mol}^{-1}$. As compared to the value for the parent oxalate $\text{La}_2(\text{C}_2\text{O}_4)_3$ ($E_a = 130 \text{ kJ/mol}$), this value is higher by about 70 kJ/mol, which is consistent with the increased interaction between the metal and oxalate ions. The substitution of Br by Cl does not affect the decomposition kinetics profoundly.

Introduction

We previously studied the kinetics of thermal decomposition of $\text{NdC}_2\text{O}_4\text{Cl}$ [1] and $\text{SmC}_2\text{O}_4\text{Cl}$ [2]. The present investigation was intended to study the effect of substitution of Cl by Br. The results show that the substitution does not have a profound effect, which is consistent with the almost identical thermal decomposition characteristics of $\text{LnC}_2\text{O}_4\text{Cl}$ and $\text{LnC}_2\text{O}_4\text{Br}$ [3-5].

Experimental

Crystalline lanthanum oxalato bromide trihydrate ($\text{LaC}_2\text{O}_4\text{Br} \cdot 3\text{H}_2\text{O}$) was obtained by mixing stoichiometric amounts of lanthanum oxide (La_2O_3) and oxalic acid dissolved separately in concentrated hydrogen bromide solution. The mixture was heated gently until crystals of $\text{LaC}_2\text{O}_4\text{Br} \cdot 3\text{H}_2\text{O}$ appeared. On cooling, the bulk of the crystalline product was obtained. The colourless crystals were isolated by suction, and finally dried in an oven at $100^\circ\text{--}120^\circ\text{C}$.

The thermal decomposition studies were carried out in a current of dry nitrogen between 22° and 600°C in a Mettler TG 50 thermal balance at heat-

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ing rates of 0.5, 0.75, 1, 1.5, 2, 3, 4, 5, 6, 8 and 10 deg/min. Finely ground powder samples weighing 30–35 mg were used for all runs.

Results and discussion

The TG curve for fine powder of $\text{LaC}_2\text{O}_4\text{Br}\cdot 3\text{H}_2\text{O}$ at a heating rate of 10 deg min^{-1} is shown in Fig. 1. The dehydration starts near 160° and is complete at 350°C. Typical TG and DTG curves of $\text{LaC}_2\text{O}_4\text{Br}$ are shown in Figs 2 and 3. The experimental results are summarized in Table 1.

The kinetic data on $\text{LaC}_2\text{O}_4\text{Br}$ were evaluated according to Ozawa's method [6], employing the logarithmic expression

$$\log \beta_i + \frac{0.4567(E/R)}{T_i} = \text{constant}$$

where β_i and T_i are the heating rate and temperature, respectively, and R is the gas constant.

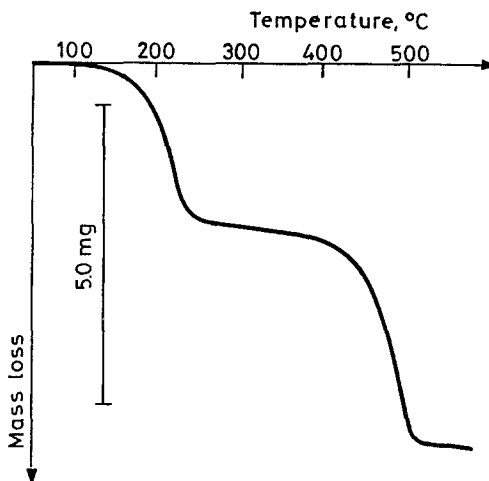


Fig. 1 The TG of $\text{LaC}_2\text{O}_4\text{Br}\cdot 3\text{H}_2\text{O}$ at the heating rate of 10 deg $\cdot \text{min}^{-1}$

Plots of $\log \beta_i$ against $1/T_i$ for selected values of degrees of conversion, α , produced straight lines (Fig. 4), from which the activation energies, E_a (Table 1), were obtained. The value at $\alpha = 0.1$ deviates appreciably from the average. This behaviour was also observed for the oxalato chlorides [1, 2] and is to be expected from the shape of the DTG curve. We now believe the effect

Table 1 The kinetic data and the activation energy according to Ozawa for the oxalate thermal decomposition $\text{La}_2\text{O}_4\text{Br}$

Degree of conversion, α_1	Temperature, T_i/K for various heating rates ($\text{deg} \cdot \text{min}^{-1}$) in nitrogen										Activation energy / $\text{kJ} \cdot \text{mol}^{-1}$	
	0.5	0.75	1	1.5	2	3	4	5	6	8		10
0.1	631.35	640.15	647.85	653.15	660.05	670.95	675.55	680.65	684.15	689.65	694.25	
0.2	656.05	664.45	672.15	677.45	683.05	691.55	695.95	700.65	704.55	709.65	713.75	201.347
0.3	667.35	675.75	682.95	688.25	693.55	702.45	707.35	712.15	715.35	720.85	725.25	200.42
0.4	675.45	683.85	691.55	696.35	702.05	710.55	715.75	720.15	724.35	729.65	734.25	204.17
0.5	683.55	691.45	699.55	704.05	709.55	718.55	723.55	728.65	732.15	738.45	742.75	204.17
0.6	691.15	699.15	707.75	711.65	717.55	726.25	731.35	736.15	740.55	746.45	750.75	204.17
0.7	697.95	705.85	714.45	718.85	724.55	733.45	738.55	743.65	747.75	753.65	758.25	206.1
0.8	704.65	712.65	720.75	725.15	731.05	739.75	745.15	750.65	754.95	761.65	766.25	206.1
0.9	711.85	719.35	727.55	732.35	738.05	746.95	752.95	758.15	762.75	769.65	774.75	204.17

average activation energy ($\alpha = 0.2$ to $\alpha = 0.9$) = $203.83 \text{ kJ} \cdot \text{mol}^{-1}$

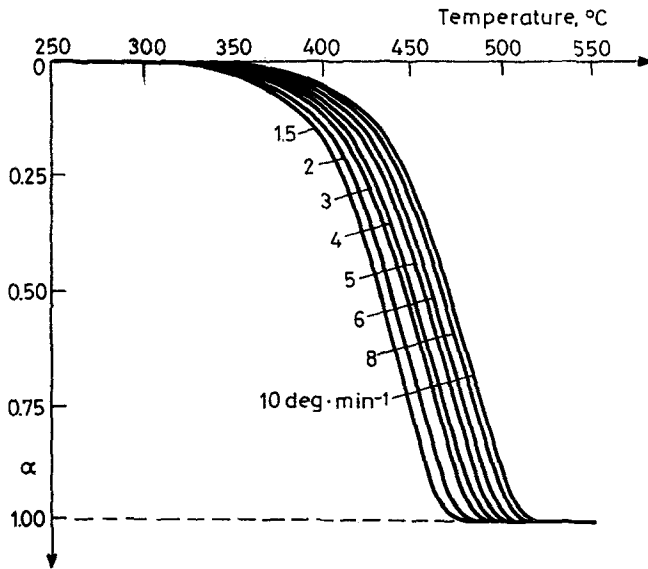


Fig. 2 The temperature displacement of the TG curves depending on the heating rate from 1 to 10 $\text{deg}\cdot\text{min}^{-1}$

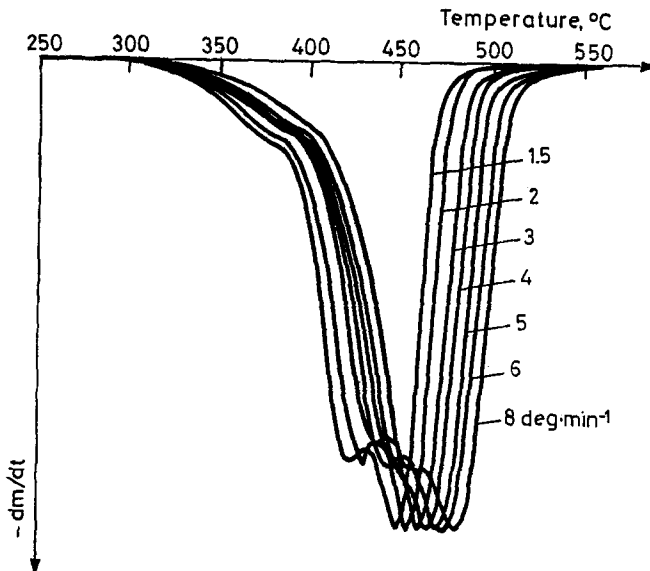


Fig. 3 The DTG of powdered $\text{LaC}_2\text{O}_4\text{Br}$ at the heating rate from 1 to 8 $\text{deg}\cdot\text{min}^{-1}$

to be a result of a mechanistic transition. Potassium oxalate shows this behaviour too [7].

As in our previous study on the kinetics of decomposition of $\text{NdC}_2\text{O}_4\text{Cl}$ [1] and $\text{SmC}_2\text{O}_4\text{Cl}$ [2], the results of the present investigation fit well into the general theoretical framework [8, 9] relating the thermal decomposition behaviour to the nature of the bonding.

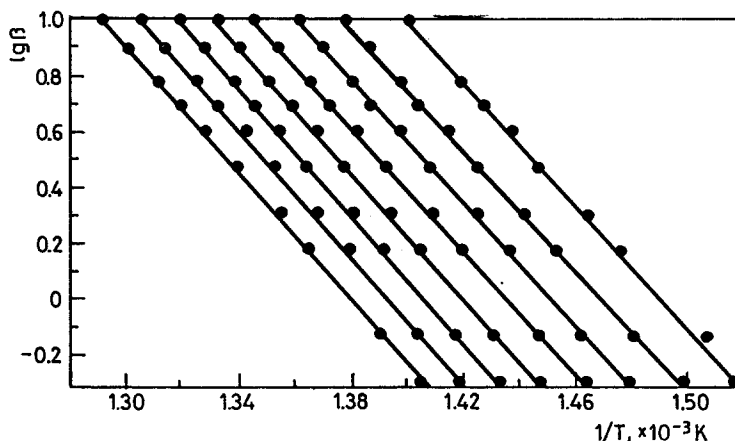


Fig. 4 The Ozawa plots for the thermal decomposition of finely powdered $\text{LaC}_2\text{O}_4\text{Br}$ at various heating rates from 0.5 to 10 $\text{deg}\cdot\text{min}^{-1}$

The increase in the activation energy from 130 kJ mol^{-1} [10] to 203.83 kJ mol^{-1} when the oxalate in $\text{La}_2(\text{C}_2\text{O}_4)_3$ is partially substituted by bromide to give $\text{LaC}_2\text{O}_4\text{Br}$ is explained by the increase in the covalent interaction between the metal and the oxalate ion. Since the halide ion is a weak nucleophile, the oxalate ion experiences almost the full charge of the cation α [1, 2]. The effective charge experienced by a decomposing oxalate is increased by a factor of approximately 3/2. Calculations on $\text{NdC}_2\text{O}_4\text{Cl}$ [1] and $\text{SmC}_2\text{O}_4\text{Cl}$ [2] support this conclusion.

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Zusammenfassung — Gemäß der Methode von Ozawa wurde die Aktivierungsenergie der thermischen Zersetzung von fein zermahlenem $\text{LaC}_2\text{O}_4\text{Br}$ mit $E_a = 208.83 \text{ kJ/mol}$ bestimmt. Beim Vergleich mit dem entsprechenden Wert für die Mutterverbindung $\text{La}_2(\text{C}_2\text{O}_4)_3$ ($E_a = 130 \text{ kJ/mol}$) erweist sich dieser Wert um etwa 70 kJ/mol höher, was mit der verstärkten Wechselwirkung zwischen Metall- und Oxalationen übereinstimmt. Der Ersatz von Br durch Cl hat keinen tiefgreifenden Einfluß auf die Kinetik der Zersetzung.