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# ACTIVATION ENERGY OF THERMAL DECOMPOSITION OF FULLY DEHYDRATED $NdC_2O_4Cl \cdot 3H_2O$ TO NdOCl

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An activation energy $E_a = 195$ kJ mol$^{-1}$ has been determined for the thermal decomposition of $NdC_2O_4Cl$ to NdOCl with simultaneous expulsion of CO and $CO_2$. As compared with the value (127 kJ mol$^{-1}$) predicted by the Kahwa–Mulokozi empirical expression (i)$^+$ for $Ln_2(C_2O_4)_3$ (Ln = light lanthanide), the presence of $Cl^-$ in the coordination polyhedron appreciably raises the activation energy, which is consistent with a corresponding increase in the covalent strength of the Ln-oxalate bond. The same conclusion regarding the strength of this bond is drawn from a study of the infrared spectrum.

Mechanistically, the breaking of the Ln-oxalate bond is suggested to occur in the kinetic rate-determining step.

The thermal decomposition behaviour of the lanthanide oxalates and their derivatives $LnC_2O_4X$ (X = Cl or Br) has been widely investigated [1–37]. The course of the reaction displays pronounced sensitivity to the nature of the bonding, not only with regard to the metal-oxalate interaction, but also as concerns the donor property of X. Those observations are explained in a neat theoretical framework.

The thermal decomposition of oxalate can proceed via three alternative pathways:

$$C_2O_4^{2-} \rightarrow CO_3^{2-} + CO \quad (1)$$

$$C_2O_4^{2-} \rightarrow O^{2-} + CO + CO_2 \quad (2)$$

$$C_2O_4^{2-} \rightarrow 2\,CO_2 + 2\,e \quad (3)$$

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[+] For (i), see text and reference [52].

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(1) and (2) are associated with the oxalates of hard acids in the sense of Pearson [38–39]; the transition from (1) to (2) occurs as the ionic potential of the cation increases. The occurrence of (1) and the decomposition of the product $CO_3^{2-}$ are often separated by only a narrow temperature interval, which decreases rapidly as the ionic potential (charge-radius ratio) of the cation increases. (3) is a redox reaction, usually associated with soft cations. The oxalates of *d* element react variously according to (2) and (3), giving as solid end-product a metal or metal oxide. For the present investigation, (1) and (2) are relevant. (1) occurs when the metal is an alkali metal or alkaline earth metal, excepting Be and Mg [40–55].

Large values of the ionic potential favour (2). There is only a narrow temperature interval between (1) and the decomposition of the carbonate intermediate for the lanthanide oxalates. The intermediate $Ln_2(CO_3)_3$, observed in isothermal decomposition, preferably at the lowest possible temperatures [10], may not be detected at higher temperatures, or when heating is accomplished by rising temperature thermogravimetry. The first carbonate intermediate usually observed is therefore $Ln_2O_2CO_3$ [1–29], suggesting a pronounced overlap of (1) and the decomposition of the carbonate intermediate $Ln_2(CO_3)_3$.

We have been interested in a theoretical framework with which to explain the variable patterns of thermal decomposition of oxalate [31–33]. The position of the lanthanide oxalates in respect of reactions (1) and (2) makes these compounds and their allied derivatives a natural choice for detailed study.

The dependence of the mechanism on the metal-oxalate interaction is unambiguously established from the Kahwa–Mulokozi expression for the activation energy [51–52]:

$$E_a = 127 + 1.4853 \times 10^{-6}[(r_c/r_i)^2\,\Sigma I + 9800]^2 \qquad \text{(i)}$$

where the ionizatoon potential term $I_T = r_c/r_i(\Sigma I)^{\frac{1}{2}}$, defined by Pauling's covalent radius $r_c$, the ionic radius in hexacoordination $r_i$ and the sum of the ionization potentials of the metal atom, provides a superior measure of the metal-oxalate interaction than the ionic potential used in previous studies.

A large value for the ionization potential term not only indicates the strength of the electrostatic interaction, but also gives a measure of the covalent contribution, since the intimate approach of the cation and ligand in the electrostatic model facilitates the overlap of the empty valence orbital on the metal atom with the filled orbital of the donor atom on the ligand.

By making use of the correlation between the activation energies for the thermal decomposition reaction and the values of the ionization potential term $I_T$, the variation of the covalence of $M-X$ in a series of compounds $MX$ with a common ligand $X$ can be established. On the basis of this approach, Ellis and coworkers were able to account for the mechanism of the thermal stabilization of polyacrylamide by metal ions with electron transfer [53].

In the present study, the activation energy of the thermal decomposition of $NdC_2O_4Cl$ is determined. The result (195 kJ $mol^{-1}$) is appreciably higher than the activation energy of the thermal decomposition of $Nd_2(C_2O_4)_3$, indicating that the metal-oxalate bond in $NdC_2O_4Cl$ is more covalent and, by implication, that the covalence of the Nd–Cl bond is negligible.

## Experimental

Crystalline $NdC_2O_4Cl \cdot 3H_2O$ was obtained by gentle evaporation of a solution of neodymium oxalate in concentrated hydrochloric acid [31–33, 54].

Thermogravimetric studies were carried out in a current of dry $N_2$ (25 ml/min) on a Stanton–Redcroft TG 750 thermal balance. The sample mass was kept between 70 and 90 mg for all runs, carried out at heating rates of 1, 2, 3, 5 and 10 deg/min.

The mass and temperature monitored on the potentiometer recorder as mV outputs were also recorded in the "squirrel" meter/logger derive at intervals of 6 seconds. The "squirrel" had a storage capacity sufficient for 4 to 5 TG runs, after which the data were transferred to the computer file for later evaluation.

A complete TG run at 10 deg/min was carried out between room temperature and 800° to show the entire thermal decomposition of $NdC_2O_4Cl \cdot 3H_2O$ to the oxide chloride NdOCl, and thus provide a guide in the choice of the starting temperature for the kinetic study.

## Results and discussion

The TG curve for the thermal decomposition of $NdC_2O_4Cl \cdot 3H_2O$ at a heating rate of 10 deg/min (Fig. 1) is in agreement with previously published data for the compound [30–33].

The dehydration starts at 151° and proceeds to 98.2% at 300°. The retained water is not expelled during 30 minutes of isothermal heating at 300° in a separate run. This observation was very useful for modelling the ideal pretreatment of the samples before undertaking the kinetic TG runs. The residual water hydration (1.8%) was expelled at 370° with the onset of the thermal decomposition of oxalate.

A reduction of the heating rate to 5 deg/min in a separate run did not appreciably affect the temperature (370°) for the expulsion of residual water of hydration. However, lower heating rates markedly lowered the temperature of complete

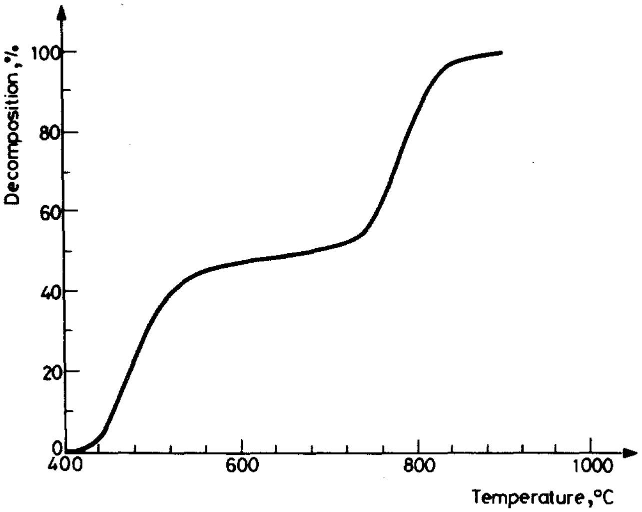

**Fig. 1** Thermal decomposition of $NdC_2O_4Cl\cdot3H_2O$ (73 mg) at a heating rate of 10 deg/min

dehydration and the temperature of thermal decomposition of oxalate, which appears to be triggered by the expulsion of the residual water of hydration. The dehydration was complete at 310° and the thermal decomposition of the oxalate started at 330° when heating rate was set at 1 deg/min after an isothermal heating spell of 20 minutes at 300°. From this observation, we concluded that high heating rates were likely to lead to the overlap of the end phase of the dehydration with the early phase of thermal decomposition of the oxalate. The discrepancy later found for the values of the activation energies at $\alpha<0.1$ and $\alpha>0.2$ seems to justify our fears.

For the evaluation of the kinetic data, the isoconversional method of Ozawa [55, 56] as adopted by Price et al. [57] was applied.

The starting point is the usual Arrhenius type expression for the rate-dependence of the reaction on the temperature:

$$\frac{d\alpha}{dT} = A/\beta \exp(-E/RTf(\alpha) \tag{ii}$$

which, on rearrangement and integration, gives

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = A/\beta \int_{T_0}^{T} \exp(-E/RT)\,dT \tag{iii}$$

On integrating the RHS of (iii) for $E/RT_0 \approx \alpha$ and substituting

$$\int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)}$$

by $g(\alpha)$, we obtain an expression which in the logarithmic form is

$$\log \beta/T^2[1-2!/(E/RT)+3!(E/RT)^2\ldots] = -E/2.303RT+\log AR/E_g(\alpha) \quad \text{(iv)}$$

Reasonable precision of the expression was realised with the asymptotic expansion in $(E/RT)$ to achieve convergence in a computer program based on Newton–Ralpson iteration. The activation energy is then obtained from the plot of $\log \beta_i/T_i^2[1-2!/(E/RT_i\ldots]$ against $1/T_i$ where at a chosen degree of conversion $\alpha_1$, $\beta_i$ and $T_i$ are the respective heating rate and temperature.

The corresponding plots in the original work of Ozawa give $\log \beta_i$ *vs.* $1/T_i$. The activation energy $E_a = 195.28$ kJ mol$^{-1}$ was obtained from the average of the $E_a$ values for $\alpha = 0.2$ to $\alpha = 0.9$.

The value at $\alpha = 0.1$ (Table 1) differs appreciably from the average for the reasons already stated. The corresponding Arrhenius plots are shown in Fig.

**Table 1** Activation energy for thermal decomposition of oxalate in $NdC_2O_4Cl$

| Conversion $\alpha_1$ | Temperatures $T_i$, K, for various heating rates, deg/min 1 | 2 | 3 | 5 | 10 | Activation energy, kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| 0.2 | 691.75 | 703.78 | 720.57 | 727.84 | 740.62 | 178.43 |
| 0.3 | 706.78 | 716.81 | 736.36 | 741.87 | 753.15 | 188.10 |
| 0.4 | 719.32 | 729.34 | 745.38 | 754.41 | 764.43 | 203.21 |
| 0.5 | 729.34 | 736.36 | 758.16 | 761.92 | 773.20 | 202.91 |
| 0.6 | 738.11 | 743.88 | 764.43 | 771.45 | 785.73 | 196.35 |
| 0.7 | 744.38 | 754.40 | 771.95 | 780.72 | 795.76 | 195.57 |
| 0.8 | 755.66 | 764.43 | 781.97 | 793.25 | 804.53 | 203.97 |
| 0.9 | 770.70 | 776.96 | 798.27 | 808.29 | 823.33 | 193.74 |
| 0.1 | 666.68 | 679.97 | 694.76 | 709.29 | 723.83 | 142.90 |

When compared with the activation energy minimum (127 kJ mol$^{-1}$) expected for the oxalates of the very light lanthanides (La to Sm, $I_T = 98.3$ to 107.66), and the experimental value $E_a = 130$ kJ mol$^{-1}$ for $La_2(C_2O_4)_3$ [10] and $Sm_2(C_2O_4)_3$ [28], the result shows an appreciable increase (60 kJ mol$^{-1}$), which must be attributed to the presence of $Cl^-$ in the coordination polyhedron. Apparently, the chloride is weakly coordinated (compared with the oxalate), which enhances the electrophilicity of the metal atom with respect to the coordinative interaction with the oxalate. The net result is an increase in the effective value of the ionization potential term $I_T$ applicable in (i). The implicit variable oxalate bonding has been confirmed by the X-ray structures of $Ln_2(C_2O_4)_3 \cdot 10H_2O$ [58–60] and $LaC_2O_4Cl \cdot 3H_2O$ [61].

Since the oxalates of the light lanthanides are at the minimum of the curve $E_a$ *vs.* $I_T^2$ (i.e. $I_T^2 \sim 9800$) [52], a weakly coordinating ligand $X$ in $LnC_2O_4X$ promotes a

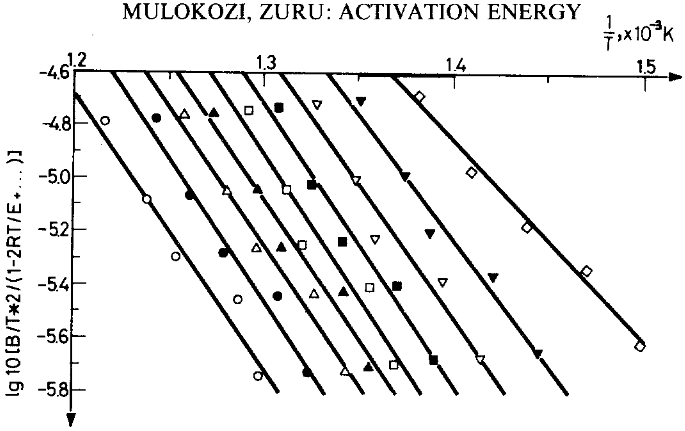

**Fig. 2** Arrhenius plots for evaluation of kinetic measurements on $NdC_2O_4Cl$ according to the isoconversional method

stronger Ln-oxalate coordinate bond and an increase in the activation energy implies that the breaking of the Ln-oxalate bond is significant in the rate-determining step. Reciprocally, a strongly coordinating ligand $X$ will effect the weakening of the Ln-oxalate bond, giving an increasingly ionic bond for which C—O becomes stronger; hence, its breaking in the rate-determining step raises the activation energy.

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**Zusammenfassung** — Für die thermische Zersetzung von $NdC_2O_4Cl$ zu NdOCl, bei der gleichzeitig CO und $CO_2$ freigesetzt wird, wurde eine Aktivierungsenergie $E_a = 195$ kJ/mol bestimmt. Verglichen mit dem durch die empirische Kahwa–Mulokozi-Beziehung für $Ln_2(C_2O_4)_3$ (mit Ln = leichtes Lanthanid) vorhergesagtem Wert (ca. 127 kJ/mol) hebt die Gegenwart von $Cl^-$ im Koordinationspolyeder die Aktivierungsenergie merklich an, was mit dem damit verbundenen Ansteigen des kovalenten Charakters der Ln–Oxalat-Bindung in Einklang gebracht werden kann. Die gleiche Schlußfolgerung für die Bindungsstärke dieser Bindung ergibt sich aus einer Untersuchung der IR-Spektren. Die Spaltung der Ln–Oxalat-Bindung scheint also während des reaktionsgeschwindigkeitsbestimmenden Schrittes zu geschehen.

**Резюме** — Для реакции термического разложения $NdC_2O_4Cl$, протекающей с образованием NdOCl и выделением одновременно CO и $CO_2$, была определена энергия активации $E_a$ равная 195 кдж·моль$^{-1}$. По сравнению со значением 127 кдж·моль$^{-1}$, установленным на основе эмпирического выражения Кава–Мулокози для $Ln_2(C_2O_4)_3$ (Ln–легкий лантаноид), наличие хлорид иона в координационном многограннике заметно повышает энергию активации, что согласуется с соответствующим увеличением ковалентности связи лантаноид–оксалат. Аналогичное заключение о прочности этой связы было выведено на основе ИК спектров. Предложено, что стадией, определяющей скорость реакции, является разрыв связи лантаноид–оксалат.